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Evolutionary processes and sources of high-nitrate haze episodes over Beijing, Spring

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ABSTRACT

Rare and consecutive high-nitrate haze pollution episodes were observed in Beijing in spring 2012. We present detailed characterization of the sources and evolutionary mechanisms of this haze pollution, and focus on an episode that occurred between 15 and 26 April. Submicron aerosol species were found to be substantially elevated during haze episodes, and nitrates showed the largest increase and occupation (average: 32.2%) in non-refractory submicron particles (NR-PM_1), which did not occur in other seasons as previously reported. The haze episode (HE) was divided into three sub-episodes, HEa, HEb, and HEc. During HEa and HEc, a shallow boundary layer, stagnant meteorological conditions, and high humidity favored the formation of high-nitrate concentrations, which were mainly produced by three different processes — daytime photochemical production, gas-particle partitioning, and nighttime heterogeneous reactions — and the decline in visibility was mainly induced by NR-PM_1. However, unlike HEa and HEc, during HEb, the contribution of high nitrates was partly from the transport of haze from the southeast of Beijing — the transport pathway was observed at ~800–1000 m by aerosol Lidar — and the decline in visibility during HEb was primarily caused by $PM_{2.5}$. Our results provide useful information for air quality improvement strategies in Beijing during Spring.

Introduction

China is currently facing tremendous challenges with respect to air quality because of substantial increases in anthropogenic emissions associated with rapid industrialization, motorization, and urbanization (Chan and Yao, 2008). Haze pollution has become of interest to the public, government, and atmospheric scientists in China. Haze not only reduces visibility and affects transportation but also exerts detrimental effects on human health. The number of patients with respiratory and cardiovascular diseases increases significantly during haze episodes (HEs) (Zhang et al., 2014b). There is an increase in participation in outdoor activities after the cold winter season and people are more likely to be exposed to the polluted atmosphere during Spring. Therefore, gaining an understanding of the sources, formation mechanisms, and evolutionary processes of haze pollution in spring is of top priority in the development of effective environmental protection policies and making accurate assessments of health and climate impacts.

Owing to growing concern about the effects of haze pollution, extensive studies have been conducted in recent years to investigate the sources and formation mechanism of haze in

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China (An et al., 2007; Huang et al., 2012b; Li et al., 2010; Liu et al., 2013, 2016; Ma et al., 2010; Sun et al., 2006; Tao et al., 2012). However, most previous studies have been conducted in the Summer, Autumn or Winter (Han et al., 2015; Huang et al., 2012a; Q16 Li et al., 2010; Sun et al., 2012, 2013a, 2013b; Zhao et al., 2013), while studies focusing on spring are limited. It is acknowledged that the aerosol composition and processing, and boundary layer characteristics are significantly different between seasons, owing to differing meteorological conditions and source emissions. Moreover, despite previous efforts made to characterize spring haze pollution (Shen et al., 2016), its sources and evolutionary processes have not yet been fully clarified.

Haze pollution often evolves rapidly and dynamically in the atmosphere, and involves complex processes such as direct emissions, secondary formation, aging and mixing, and fog processing. The chemical, physical, and optical properties of aerosol particles may change significantly in a few hours. However, previous studies based on filter measurements are limited by either low time resolution from hours to days or sampling artifacts, such as evaporative loss (Sun et al., 2014). In our work, an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) is employed, which is unique in its ability to provide non-refractory submicron aerosol (NR-PM_1) species (organics, sulfates, nitrates, ammonium, and chlorides) in real time with a high time resolution ranging from seconds to minutes (Ng et al., 2011).

In this study, we employ various high temporal resolution instruments to investigate and comprehensively characterize the sources and evolutionary mechanisms of a rare and lengthy high-nitrate haze pollution episode that occurred in Beijing from April 15 to 26, 2012. The formation mechanisms of the largest increase and occupation species, nitrates, are investigated in detail and the sources of haze pollution, *e.g.*, local sources *versus* regional transport, are elucidated. In particular, the relationship between chemical evolution of the submicron aerosol composition, boundary layer meteorological parameters, and visibility is estimated in detail.

1. Experimental

1.1. Sampling site

Field measurements were carried out from April 15 to 26, 2012, at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58′28″N, 116°22′16″E), which is located between the north 3rd and 4th ring roads in Beijing. The sampling site is located on the roof of a second-story building (~8 m high). All aerosol and gaseous species, including NR-PM_1 species, $PM_{2.5}$, NO, NO_2, NO_y, O_3, SO_2, CO, and aerosol extinction coefficients were measured at this site. In addition, meteorological variables, including temperature, relative humidity (RH), wind speed, and wind direction, were obtained from the meteorological tower (325 m) at IAP.

1.2. Aerosol and gaseous species measurements

Q17 NR-PM_1 species (including organics, sulfates, nitrates, ammonium, and chlorides) were measured *in situ* with an ACSM (Ng et al., 2011). The aerosol sampling setup and ACSM operations in this study were the same as those in Sun et al. (2012). Following the procedures described in Ulbrich et al. (2009), the positive matrix factorization (PMF) was performed using the PMF2.exe algorithm (v4.2) in robust mode (Paatero and Tapper, 1994) to obtain the ACSM organic aerosol (OA) mass spectra. PMF2 solutions were then evaluated with an Igor Pro-based PMF Evaluation Tool (PET, V 2.04) (Ulbrich et al., 2009) following the procedures detailed in Zhang et al. (2011). A two-factor solution that included a hydrocarbon-like OA (HOA) and an oxygenated OA (OOA) with *f*peak = 0 was chosen in this study. A detailed ACSM data analysis of Beijing aerosol data can be found in Sun et al. (2013a).

$PM_{2.5}$ mass was simultaneously measured using a tapered element oscillating microbalance (TEOM series 1400a, Thermo Scientific, USA), and the collocated gaseous species (including CO, SO_2, NO_2, NO/NO_y, and O_3) were measured using various gas analyzers obtained from Thermo Scientific.

1.3. Lidar observation

A dual-wavelength depolarization Lidar (Model: L2S-SM), developed by the National Institute for Environmental Studies (NIES), was operated during this field campaign. The Lidar was continuously operated at 15-min intervals at a height resolution of 30 m, setting a boundary condition at 3 km, and the measured extinction coefficients and depolarization ratio at a wavelength of 532 nm. Detailed information related to the Lidar can be found in Yang et al. (2010). The Fernald inversion method (Fernald, 1984) was used to derive the extinction coefficient with the Lidar ratio (extinction-to-backscatter ratio) set to 50 sr (Liu et al., 2002) in the inversion process.

1.4. Aerosol optical properties

Optical properties of aerosol particles (scattering and absorption) were measured at Beijing Normal University (BNU), a site located approximately 3 km to the southwest of the IAP. The sampling site is located on the roof of a six-floor building (~20 m above ground level). The light scattering coefficient of dry particles, b_{sp} (dry), at a wavelength of 532 nm was measured by an Ecotech (Australia) M9003 integrating nephelometer (Liu et al., 2008). A processor-controlled heating system was used to dry aerosol particles in the sampling line (RH < ~30%). The nephelometer was routinely calibrated by zero and span checks, and the truncation error was corrected (Liu et al., 2008).

A multi-angle absorption photometer (MAAP) (Petzold and Schönlinner, 2004) was operated at an incident light wavelength of 670 nm on the principle of light attenuation due to absorption by aerosols deposited on the quartz fiber filter. The aerosol absorption coefficient, b_{ap}, was then calculated by converting the mass concentration of black carbon (BC) to b_{ap} using a mass absorption efficiency of 6.6 m^2/g, as suggested by the manufacturer.

The scattering and absorption coefficients were scaled to values at the wavelength of 550 nm using a power-law wavelength dependence of aerosol optical properties, as given in Eqs. (1) and (2):

$$\frac{b_{sp}(\lambda_1)}{b_{sp}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-SAC} \quad (1)$$

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