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-PM1), 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-PM1. 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 PM2.5. Our results provide useful information for air quality improvement strategies in Beijing during Spring.

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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., 2014). 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...
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; 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 evaporation 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 particles (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

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):

$$
\frac{b_{ap}(\lambda_1)}{b_{ap}(\lambda_2)} = \left( \frac{\lambda_1}{\lambda_2} \right)^{-5AC}
$$

(1)
where, $\lambda_1$ is 670 nm, $\lambda_2$ is 550 nm, $b_{ap}$ (Mm$^{-1}$) is the aerosol absorption coefficient, $b_{sp}$ (Mm$^{-1}$) is the aerosol scattering coefficient; a scattering Angstrom coefficient (SAC) of 1.2 was used (Pereira et al., 2011), and an absorption Angstrom coefficient (AAC) of 1.3, determined using a seven-wavelength aethalometer (Model AE-31, Magee, USA), was used for the absorption scale (Liu et al., 2009).

2. Results and discussion

2.1. General description of HEs

2.1.1. Mass concentration

Fig. 1 shows temporal variations in the mass concentrations of NR-PM$_1$ and PM$_{2.5}$, together with meteorological conditions during the measurement period. The HE was formed after a precipitation event that occurred on April 16, and it then lasted more than a week until April 24. The average (±SD) mass concentrations of NR-PM$_1$ were (82.8 ± 34.3) $\mu$g/m$^3$. Average mass concentrations of PM$_{2.5}$ were (98.7 ± 50.6) $\mu$g/m$^3$, which is almost three times the National Ambient Air Quality Standards (NAAQS) of the U.S. Environmental Protection Agency (EPA) (35 $\mu$g/m$^3$, 24 hr average), and approximately 1.3 times that of the second grade of China NAAQS (75 $\mu$g/m$^3$, 24 hr average). The average ratio of NR-PM$_1$/PM$_{2.5}$ was 0.84 during the HE, indicating that submicron particles dominated the total mass of fine particles. In addition, meteorological conditions were stagnant; low-speed winds (~0.6 m/sec) were dominant from the south and RH was high (>60%). The stagnant dispersal conditions were exacerbated by a low-pressure system, the front of which persisted around Beijing during the HE (Fig. S1). As a result, the mass concentration of PM$_{2.5}$ remained consistently high throughout the HE until meteorological conditions underwent a significant change on April 24. The back trajectories seen in Fig. 1f show that air masses were predominantly from the south and southeast of Beijing. Gray haze clouds over the north China plain, including Beijing, can be seen on the Moderate Resolution Imaging Spectroradiometer (MODIS) true color composite image taken on April 22, indicating that the haze was formed on a regional scale (Fig. 1g).

2.1.2. Submicron aerosol composition

Fig. 2 shows a time series of the mass concentration and mass fractions of NR-PM$_1$ species (Org, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and Chl) throughout the entire study period. Secondary inorganic aerosols (SIA = NO$_3^-$ + NH$_4^+$ + SO$_4^{2-}$) dominated NR-PM$_1$ during the HE, and on average accounted for 66.5% of the total NR-PM$_1$ mass. The SIA was elevated by a factor of 11–fold compared to that observed during the clean period — April 25 (Table 1). In comparison, organics contributed 31% of NR-PM$_1$ during the HE, with OOA, which is a surrogate of secondary OA, accounting for 79% of OA. These results suggest that the HE was primarily caused by secondary formation. The enhanced roles of secondary species during HEs have previously been observed at various sites in eastern China (Huang et al., 2012a; Li et al., 2011; Sun et al., 2006; Tan et al., 2009; Wang et al., 2006a). However, the event in this study differs from that of previous studies because nitrates were the most abundant secondary species, contributing 32.2% of NR-PM$_1$ on average. This amount is much higher than levels observed in summer (16%–25%) (Sun et al., 2010, 2012) and winter (14%–16%) (Sun et al., 2013a; Zhang et al., 2014), which indicates that nitrates played a leading role in the formation of the HE in Spring. As shown in Fig. 2, the contribution of nitrates can reach up to 42% during an HE. Furthermore, higher contributions of nitrates to Particulate Matter (PM) in spring than in other seasons have been observed by Zhang et al. (2013). The formation of nitrates will be discussed in detail in the following section.

There was also a significant increase in sulfate during the HE (12.4 ± 5.7 $\mu$g/m$^3$) compared to the clean period (0.4 ± 0.1 $\mu$g/m$^3$), which could be related to the higher oxidation ratio of SO$_2$. The average sulfur oxidation ratio (SOR) was 0.19 ± 0.08 during the HE (Table 1), which was within the range of 0.16–0.29 in North China Plain HE (Zhao et al., 2013), and is almost 10 times higher than levels observed during the clean period (0.02 ± 0.01). The increased level of SOR indicates enhanced secondary formation during the HE. The conversion of SO$_2$ to sulfate is likely due to the aqueous-phase processing associated with increased RH. In this study, the high RH during the HE was a favorable factor for the aqueous-phase oxidation of SO$_2$. As illustrated by previous study, aqueous-phase processing, mostly fog processing, could contribute more than 50% of sulfate production at high RH in Beijing (Sun et al., 2013b). The variations of SOR and RH are presented in Fig. S2. Similar to that observed in Sun et al. (2013b), SOR shows a rapid increase accompanied with RH increasing. The SOR varied from 0.05 at RH < ~40% to 0.2 at RH = ~60%. In particular, the SOR was greatly increased with the highest value close to 0.4 when RH = ~80%, indicating that a large fraction of SO$_2$ had been oxidized via aqueous-phase processing.

The mass ratio of NO$_3^-$/SO$_4^{2-}$ in the present study was 2.2 ± 0.8, which is significantly higher than values observed in 2006 (0.64) (Wang et al., 2006b) and 1999–2000 (0.43) (Yao et al., 2002; Ye et al., 2003). The higher ratio of NO$_3^-$/SO$_4^{2-}$ further demonstrates the significant role of nitrates in haze formation during Spring.

2.2. Investigation of evolutionary processes and sources of HE

2.2.1. Evolutionary process and sources of nitrates

As discussed in the above section, nitrate concentrations in NR-PM$_1$ species exhibited the highest levels during the HE, accounting for an average of 32.2% of the NR-PM$_1$ mass. The contribution of nitrates was elevated from ~3% in the clean period to ~42% at high mass loadings of NR-PM$_1$ during the HE, demonstrating the fastest increase of all species. In this section, we therefore focus on the formation and evolution of nitrates during this HE, the results of which could be used for the formulation of air quality control strategies in Beijing during spring. To adequately demonstrate nitrate formation, the HE was segregated into three sub-episodes, i.e., HE$_1$, HE$_2$, and HE$_3$ (Fig. 3), according to the growth and dissipation of concentrations. A detailed time period for each sub-episode is shown in Table S1.

The higher contribution of nitrates could have been related to the high oxidation rates of NO$_2$. Previous studies have indicated that the nitrogen oxidation ratio (NOR), NOR = nNO$_3^-$/(nNO$_2^+$ + nNO$_2^-$) (where n refers to the molar concentration) can
Fig. 1 – Time series of meteorological parameters and particulate concentrations observed during the study period (April 15–26, 2012) in Beijing. (a) Wind speed and wind direction, (b) precipitation and pressure, (c) relative humidity and temperature, (d) visibility, (e) hourly particulate concentrations of NR-PM$_1$ and PM$_{2.5}$, (f) 48-hr air mass backward trajectories during haze episode (HE) (the starting altitude was 100 m and the start time was 00:00 Universal Time Coordinated (UTC) (=Beijing Standard Time — 8 hr) for each day), (g) Moderate Resolution Imaging Spectroradiometer (MODIS) true color composite images at around 10:30 Local Standard Time (LST) April 22, 2012 (Terra: bright white pixels are clouds and bluish-white pixels are haze (Engel-Cox et al., 2004)). NOAA: national oceanic and atmospheric administration, GDAS: Global Data Assimilation System.
be used to estimate the degree of secondary nitrogen formation (Sun et al., 2006; Wang et al., 2006a). In this respect, the entire time series of NOR is shown in Fig. 3a, where the average value of NOR is shown to be 0.23 ± 0.06 and 0.24 ± 0.06 during HEa and HEc, respectively, which is approximately 23 times higher than that during the clean period (0.01 ± 0.01). It is known that the formation of nitrates by NO2 is mainly driven by three different processes: daytime photochemical production (R1), gas-particle partitioning (R2), and nighttime heterogeneous reactions (R3–R5), as follows:

$$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 (\text{g}) + \text{M} \quad \text{(R1)}$$

$$\text{HNO}_3 (\text{g}) + \text{NH}_3 (\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3 (\text{s}) \quad \text{(R2)}$$

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R3)}$$

$$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(R4)}$$

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{aq}) \rightarrow 2\text{HNO}_3 \quad \text{(R5)}$$

The NO3− concentration during HEa and HEc reached peaks in the early morning and/or around noon, and it seems that the evolution of NO3− was separated into two stages, i.e., from midnight to around 3:00–4:00, and from around 5:00–6:00 to noon. However, when nitrate peaks occurred at around noon (~5:00–6:00 to noon), the high concentration of NO3− appeared to be closely linked to high levels of O3 and NO2 (Fig. 2), which are two key precursors in the formation of nitrate particles. It is therefore very likely that the NO3− plume was due to rapid photochemical production from reactions of NO2 and OH, and that nitrate particles were then formed under the condition of an adequate precursor (NO2) and strong solar radiation (Guo et al., 2014) (R1). In addition, the relatively high RH (58.6%) would also have facilitated the partitioning of HNO3 to nitrate particles (R2). Furthermore, the relatively low temperature would have delayed the evaporative loss of ammonium nitrate to gas-phase HNO3 and NH3.

However, when nitrate peaks occurred at midnight (i.e., 18, 21 and 22 April), the increase in NO3− was approximately associated with a synchronous increase in NO2 and a corresponding decrease in O3. The considerably high levels of NO2 and O3 facilitated the formation of NO3 radicals and dinitrogen pentoxide ((R3)–(R5)), and hence the heterogeneous formation of HNO3 under high RH conditions. Results from a previous study correspond with this observation, Pathak et al. (2009) analyzed sulfates, nitrates, and ammonium in PM2.5 in four cities in China, and concluded that the nitrate was most probably formed via the heterogeneous hydrolysis process of

Fig. 2 – Time series of (a) mass concentrations, and (b) mass fraction of NR-PM1 species as measured by ACSM. Pie charts show average chemical compositions of NR-PM1 during the HE and during a clean period (April 25). HOA: hydrocarbon-like organic aerosol, OOA: oxygenated organic aerosol; ACSM: Aerodyne Aerosol Chemical Speciation Monitor; HE: haze episode.
N₂O₅ on the surface of moist and acidic aerosols in Beijing and Shanghai, particularly during humid and hazy weather. Meanwhile, a time lag between the peak concentrations of nitrate and its oxidants was observed, indicating that chemical production time is existed from gas-phase precursors to particle-phase nitrate. Previous studies about nitrate mostly based on filter measures; the low time resolution limited the exploring of lag-time phenomena between nitrate and oxidants, to the knowledge of us, few studies have discussions on this, but a lag-time of the peak concentrations between the secondary OA and its precursors was observed in the precious research (Fu and Kawamura, 2011).

The nitrate concentration during HEb was (26.0 ± 6.8) μg/m³, which is as high as that during HEa (27.1 ± 9.4 μg/m³), but dissimilar to amounts during HEa and HEc. Values of NOR were 0.19 ± 0.03, which is only ~80% of those in HEa and HEc (0.23 ± 0.06 in HEa and 0.24 ± 0.05 in HEc). The low levels of NOR illustrate that a relatively low chemical formation of nitrates occurred during HEb compared with that during HEa and HEc. In addition, weak solar radiation was observed in HEb (Guo et al., 2014), corresponding to a low concentration of ozone (1.6 ± 1.6 ppb in HEb, which was nearly ~10% that determined during HEa and HEc. Solar radiation directly affects the rate of photochemical production; therefore, the formation of nitrates through photochemical production was inhibited in HEb.

The flat pattern of the NO₃/CO (Fig. 3) illustrates that nitrate concentration correlates well with the primary combustion tracer of CO. Compared to HEa and HEc, NO₃/CO variations in HEb have a different pattern, indicating that there were different sources during HEb compared to during the two other HE sub-periods. It is considered likely that the formation of high-nitrate concentration was partly contributed by the transport of haze from southeast of Beijing, in addition to that contributed by heterogeneous formation. Transportation is further discussed in detail in Section 2.2.2.

2.2.2. Vertical profiles of aerosol properties

Fig. 4a shows the time-height cross section of aerosol properties obtained from Lidar measurements during this study. The high extinction peaks (e.g., 18:00 on April 18, and 12:00 and 18:00 on April 23) seen in Lidar observations are consistent with those obtained with ground measurements (Fig. 1e). In addition, the aerosol extinction coefficient exhibited a strong vertical gradient from the ground to the upper layer, although the pollution was mainly concentrated in the boundary layer (~1 km).

Three periods were selected to investigate the vertical characteristics of aerosol properties and meteorological conditions: during HEa at 20:00 on April 17 and 20:00 on April 18, and during HEc at 20:00 on April 21. The average profile of the extinction coefficient (Fig. 4b1, b3) shows a steep decrease from 2.25–3.25/km near the ground to ~0.1/km above 1.3 km. Aerosol particles were mainly concentrated below ~1 km during HEa and HEc, and the maximum aerosol loading was located at around 200–400 m in the Lidar observation range. The vertical distributions of RH and temperature observed by radiosonde during HEa and HEc are shown in Fig. 4c. Observations show that temperature and RH inversions occurred at about 800 m on April 17 and 21 (Fig. 4c), which strengthened and descended gradually to around 600 m during the night of April 18 (Fig. 4c). The vertical distributions of potential temperature, RH, and aerosol indicate a planetary Boundary Layer (PBL) height of less than 1000 m during the HE. It is considered that the shallow PBL height would limit the diffusion of pollutant in the vertical direction, but would favor the accumulation of pollutants. There were no obvious
changes in the wind pattern until the end of these two sub-episodes. A weak horizontal wind limited the horizontal dispersion of pollutants, thereby leading to high concentrations of aerosol particles. Therefore, the stagnant boundary structure was one of the main factors in the haze formation during HEa and HEc.

Unlike during HEa and HEc, the haze pollution episode in HEb was controlled by a high-pressure system associated with southeasterly winds. This type of synoptic weather is favorable for the transport of air pollution to Beijing from the south. Correspondingly, a layer with high aerosol loading between ~800 and 1000 m was observed at around 11:00 on April 19 (Fig. 4a). Between April 19 and 20, both the strong southeasterly wind and subsidence of an air mass throughout the whole vertical direction (Fig. 4a) resulted in a rapid increase in pollutant concentrations in Beijing. Vertical profiles of the extinction coefficient (Fig. 4b2) indicate that ground pollutants during April 19–20 (HEb) were mainly transported in haze from the southern parts of Beijing. Transport at an altitude of ~700–1000 m lasted for at least 12 hr and then disappeared at around 00:00 on April 20. These results also well explain the higher concentration of nitrates transported from the south of Beijing during HEb.

2.2.3. Major sources for visibility decline
Visibility degradation caused by light extinction by aerosol particles is closely related to air pollution (Molnár et al., 2008). Fig. 5 shows the time series of aerosol components and optical properties (including $\alpha_{\text{ext}}$, $\alpha_{\text{sp}}$, and $\alpha_{\text{ap}}$) and single scattering albedo (SSA). Similar to the PM concentration, values of $\alpha_{\text{sp}}$ and $\alpha_{\text{ap}}$ gradually increased during the three consecutive stages of the HE, i.e., April 17–18, 19–20, and 21–24, and they varied considerably in accordance with the meteorological conditions. All three parameters increased gradually from April 16 and then remained at relatively high levels until April 24. The HE was interrupted by two precipitation events on April 18 and 20, when optical properties showed dramatic decreases due to scavenging of aerosol species. The average values of $\alpha_{\text{sp}}$ and $\alpha_{\text{ap}}$ during the HE were 714.3 and 33.9/Mm$^{-1}$ respectively; the average value of $\alpha_{\text{sp}}$ during the HE ($742$/Mm$^{-1}$) was close to that observed during a pollution episode in spring at Wuqing (a suburban site located between Beijing and Tianjin) (Ma et al., 2011), but it was significantly higher than that observed at a rural background site (201/Mm$^{-1}$) at Shangdianzi, to the northwest of Beijing (Zhao et al., 2011). The average SSA value during the HE was 0.95 ± 0.02, which was within the range of 0.85–0.95 retrieved through Aerosol Robotic Network (AERONET) for the northern hemisphere (Dubovik et al., 2002), and was similar to the value of 0.93 obtained at Lin’an in November 1999 (Xu et al., 2002) and 0.95 at Yulin (Xu et al., 2004). However, it was higher than the value (0.81) reported at an urban site in Beijing (Bergin et al., 2001), and slightly higher than the value (0.85) used in climate modeling simulations for China and India (Menon et al., 2002).

To further interpret the major sources for the decline in visibility during each of the HE sub-episodes, the correlations
between extinction coefficients and NR-PM$_1$ and PM$_{2.5}$ during the three sub-haze episodes are shown in Fig. 5c and d. The extinction coefficients present stronger correlations with NR-PM$_1$ than with PM$_{2.5}$ during HEa and HEc ($r^2 = 0.93$ and 0.85, respectively), but much weaker correlations with HEb ($r^2 = 0.12$ for NR-PM$_1$, $r^2 = 0.87$ of PM$_{2.5}$). Although the results suggest that the decline of visibility was primarily caused by NR-PM$_1$ during HEa and HEc, which is consistent with a previous study that suggested that PM$_1$ contributes to over 80% of the total light extinction in Beijing (Bergin et al., 2001; Garland et al., 2008), it is considered that during HEb the decline in visibility could be more closely related to the larger particles (2.5 $\mu$m). All the above observations are consistent with the results delivered in Sections 2.2.1 and 2.2.2. Compared to HEa and HEc, the haze in HEb was caused by transportation of particles from the southern part of Beijing.

3. Conclusions

This study comprehensively characterizes the chemical and optical evolution and sources of haze pollution that occurred in Beijing in April 2012. Three sub-episodes of haze were observed between April 15 and 26, in which the overall average concentrations of NR-PM$_1$ and PM$_{2.5}$ were $(82.8 \pm 34.3)$ and $(98.7 \pm 50.6)$ $\mu$g/m$^3$, respectively. All submicron aerosol species were substantially elevated during sub-episodes, and nitrates presented the largest increase and occupation (average: 32.2%) in NR-PM$_1$. However, this observation was made using online equipment, and such levels differ from those obtained during other seasons and in previous studies.

In sub-episodes of haze HEa and HEc, a shallow boundary layer height (~800 m maximum PBLH), stagnant meteorological conditions (<1 m/sec), and high humidity (58.6% on average) 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. Meanwhile, the relatively low temperature inhibited the evaporative loss of ammonium nitrate particles. However, in contrast to the occurrence in HEa and HEc, the high levels of nitrates during HEb were partly contributed by the transport of haze from southeast Beijing; the transport pathway was observed at ~800–1000 m by aerosol Lidar.
An analysis of the major sources of visibility decline in each haze sub-episode illustrates that the haze was produced by local chemical formations in HEa and HEC, and the visibility decline was mainly induced by PM1; and during the regional contribution haze (HEb), the visibility decline was primarily caused by PM$_{2.5}$. It is considered that the results presented here will be useful in the development of air quality improvement strategies during spring in Beijing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.04.024.

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