Short communication

# Redefining the importance of nitrate during haze pollution to help optimize an emission control strategy

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## HIGHLIGHTS

- Nitrate is enriched more rapidly than organics during haze episode.
- Nitrate plays an important role in the haze formation and development.
- Control measures targeting nitrogen oxides are a priority.

## GRAPHICAL ABSTRACT
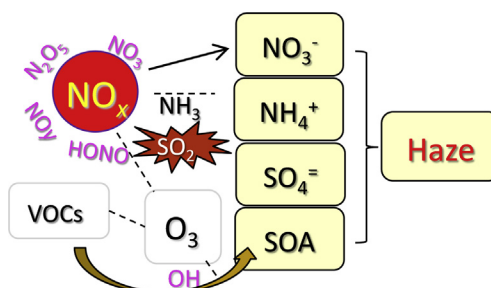
## ABSTRACT

Nitrate salts represent a major component of fine mode aerosols, which play an important role in air pollution worldwide. Based on on-line and off-line aerosol measurements in urban Beijing for both clean and haze conditions, we demonstrate that the absolute and relative concentrations of nitrate increased with visibility degradation (relative humidity), whereas the variations of organics tracked the patterns of mixing-layer height and temperature. We propose that the increase in the relative contribution of nitrate to $PM_1$ observed during the early stages of haze pollution was due to new particle formation, whereas the nitrate formed in $PM_{1-2.5}$ during the latter stages was due to heterogeneous formation and hygroscopic growth. The increasing trend of nitrate (and also sulfate and ammonium) but decreasing trends of organics during haze development, together with the increase of the $NO_2/SO_2$ molar ratio with increasing proximity to downtown Beijing and with visibility degradation, provide further evidence that controlling $NO_x$ emissions should be a priority for improving air quality in mega cities. Additional large-scale investigation is required to adequately characterize the regional features of $NO_x$-induced haze pollution in China. Such studies may provide insight into the formation of critical nuclei or the subsequent growth of freshly nucleated particles and advance our understanding of the role of nitrate in new particle formation.

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## 1. Introduction

Haze pollution caused by particulate matter suspended in the air remains a major environmental issue because of its substantial

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impacts on climate, air quality, and human health. Previous publications have reported that large fractions of both organic and inorganic matter contribute to $PM_{2.5}$ (aerodynamic diameter less than 2.5 μm) and induce severe haze pollution in urban China. A recent study regarding haze pollution in Beijing proposed two distinct aerosol formation processes, nucleation and growth, with minor contributions from primary emissions and regional particle transport (Guo et al., 2014). However, it remains unclear which species are nucleating and which species are condensed onto these new particles in the early stages of growth. It is widely recognized that the mitigation of VOC, $NH_3$, $SO_2$ and $NO_x$ precursors aids in reducing $PM_{2.5}$, the key factor in visibility degradation. However, it is impractical to control all precursors at the same time, especially VOCs, when the geographical locations and emission strengths remain unclear in China. Thus, control strategies for these various precursors remain critical challenges. Moreover, it is necessary to target species having well-constrained sources, such as $SO_2$ and $NO_x$. This concept is well-supported by the recent finding that the reductions in anthropogenic $SO_2$ and $NO_x$ emissions can considerably reduce the secondary organic aerosols burden and hence consequently the submicron particulate matter ($PM_1$) in the southeastern US during the summer (Xu et al., 2015). Although such relationships have not been established in Beijing, the reduction of anthropogenic emissions of $SO_2$ and $NO_x$ can improve visibility due to the major contribution of sulfate and nitrate in fine particles (Zhang et al., 2015).

In addition, field and laboratory studies have shown that $NO_x$ acts as a catalyst and can promote the conversion of $SO_2$ to sulfate on the surfaces of mineral oxides (He et al., 2014; Wang et al., 2014). Moreover, the formed nitrate species can enhance the hygroscopicity of mineral oxides (Ma et al., 2010) and the uptake of liquid water, which accelerates $SO_2$ and $NO_x$ gas–liquid–solid reactions and further increases the hygroscopicity of the particles. These findings suggest that $NO_x$ reduction might represent a positive feedback mechanism that reduces the conversion of primary gas pollutants into secondary aerosols.

$SO_2$ emissions in China began to decrease after 2006 primarily due to the widespread application of flue-gas desulfurization devices in power plants in response to a new policy implemented by the Chinese government (Lu et al., 2010; Zhang et al., 2012b). The benefit of $SO_2$ reduction in China has been offset due to an increase in $NO_x$ emissions by power plants and vehicles (Wang et al., 2013; Zhang et al., 2012a). As a result, measured nitrate to sulfate ratios in Beijing are higher than those reported a decade ago, coinciding with the increasing trend in $NO_x$ (Cheng et al., 2015). Thus, an effective strategy to control $PM_{2.5}$ and haze pollution over North China should emphasize the future control of $NO_x$ emissions. In this paper, we present an extensive data set for urban Beijing observed in October 2014 that indicates the important role of nitrate in haze pollution.

## 2. Experimental details

Measurements were performed at an urban site located at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58′N, 116°22′E). The site is situated between the 3rd and 4th ring roads (Fig. 1) and approximately 1 km from the 3rd ring road, 200 m west of G6 Highway (which runs north-south) and 50 m south of Beitucheng West Road (which runs east-west). A suite of state-of-the-art instruments was deployed to simultaneously measure aerosol mass concentrations and chemical compositions. Mass concentrations of $PM_{10}$ and $PM_{2.5}$ were measured using a tapered element oscillating microbalance (TEOM 1405-DF, Thermo Scientific, USA) with a filter dynamic measurement system (FDMS), which is designed to measure mass concentration of

ambient particulate matter consisting of both non-volatile and semi-volatile species. Mass concentrations for $PM_1$ was also measured with a TEOM (TEOM 1405, Thermo Scientific, USA), the system of which was heated to 50 °C; thus, some semivolatile compounds were lost. The size-resolved submicron aerosol composition was measured with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (Aerodyne Research, Inc., USA), following procedures described elsewhere (DeCarlo et al., 2006; Zhang et al., 2014). In addition, black carbon (BC) in $PM_1$ was measured using a multi-angle absorption photometer (MAAP, model 5012, Thermo Electron Cooperation). The organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ were measured with a thermal optical transmission OC/EC analyzer (RT-4, Sunset Laboratory Inc. USA).

To investigate particle compositions, a medium-volume sampler (TH-150A, 100 L min$^{-1}$) was used to collect $PM_{2.5}$ over a period of 12 h onto quartz filters (precombustion at 800 °C for 2 h). A quarter of each quartz filter was cut and extracted using 25 ml of deionized water (Millipore, 18.2 MΩ) and an ultrasonic bath at room temperature for 30 min. The extraction liquid was filtered using 0.22 μm filters and subsequently analyzed to determine the $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ concentrations with an ion chromatograph (DIONEX, ICS-90, USA). Another quarter of each quartz filter was used to examine OC and EC loaded on the samples with a thermal/optical carbon aerosol analyzer (DRI Model 2001A, Desert Research Institute, USA), according to a previously described method (Tian et al., 2014). A multiplication factor of 1.4 (organic matter-OM/OC) has typically been used to convert OC to OM (Offenberg and Baker, 2000).

Meteorological parameters, including temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD), were observed using an automatic meteorological observation instrument (Milos520, Vaisala, Finland). An eye-safe LIDAR ceilometer (Vaisala CL51) was also operated at a wavelength of 910 nm to detect the boundary layer structure. This instrument was necessary because atmospheric layering and mixing-layer height (MLH), in addition to wind speed and direction, can influence the exchange processes of ground level emissions (Schäfer et al., 2012).

The concentrations of $SO_2$ and $NO_2$ in Beijing were monitored at 35 stations by Municipal Environmental Protection Bureau (MEP, http://zx.bjmemc.com.cn/). The temporal variations of hourly concentrations of $SO_2$ and $NO_2$ at Aoyuncun site from MEP (2 km NE to the IAP site) were consistent with the measurements in our study (Fig. S1).

## 3. Results and discussion

### 3.1. Characterization of particulate matter pollution and meteorology

As shown in Fig. 2, the daily concentrations of $PM_{2.5}$ in Beijing ranged from 3 to 276 μg m$^{-3}$, with a mean of 93 μg m$^{-3}$ during October 2014. There were 15 days during which $PM_{2.5}$ concentrations exceeded the Chinese National Ambient Air Quality Standard (GB3095-2012, Grade II) of 75 μg m$^{-3}$. This number increased to 23 days when compared with the U.S. EPA standard (daily average value of 35 μg m$^{-3}$). Several severe haze pollution episodes with a well-defined periodic cycle of 4–8 days were clearly observed during the sampling campaign. These typical cycles are of representative of the haze pollution in Beijing (Guo et al., 2014).

To focus our analysis on haze pollution, the 31 days observed were divided into five disjoint groups by city-average visual range, and the particle chemistry data were averaged within each visibility group. These five groups were defined as follows: clean conditions (with visibility exceeding 10 km; hereafter $VIS_{>10}$,