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NO_x promotion of SO_2 conversion to sulfate: An important mechanism for the occurrence of heavy haze during winter in Beijing☆

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ABSTRACT

In this study, concentrations of NO_x, SO_2, O_3 and fine particles ($PM_{2.5}$) were measured at three monitoring stations in Beijing during 2015. For extreme haze episodes during 25 Nov. - 3 Dec. 2015, observation data confirmed that high concentrations of NO_x promoted the conversion of SO_2 to sulfate. Annual data confirmed that this is an important mechanism for the occurrence of heavy haze during winter in Beijing. Furthermore, in situ perturbation experiments in a potential aerosol mass (PAM) reactor were carried out at Shengtaizhongxin (STZX) station during both clean and polluted days. The concentrations of SO_4^{2-}, NH_4^+, NO_3^- and organic aerosol were positively related to the concentration of added NO_2. These results provide definitive evidence that NO_2 can promote the conversion of SO_2 to sulfate. At the same time, we found that NO_2 can promote the formation of NH_4^+ and organic compounds in the aerosols. Our results illustrate that strengthened controls of nitrogen oxides is a key step in reducing the fine particles level in China.

1. Introduction

Haze in China has been increasing in frequency of occurrence as well as in the area of the affected region due to the dramatic increase in the amount of energy consumption in the past 20–30 years, especially in eastern and southwestern China (Chang et al., 2009; Che et al., 2008). For example, five severe haze episodes (concentrations of $PM_{2.5}$ greater than 300 μg/m^3) occurred in the Beijing-Tianjin-Hebei regions in January 2013. Therein, Beijing's $PM_{2.5}$ concentration exceeded the Second Grade National Standard (75 μg/m^3) and the First Grade National Standard (35 μg/m^3) of China for 22 days and 27 days, respectively (He et al., 2014). The air quality in Beijing exceeded the safety standard of the World Health Organization (WHO) (10 μg/m^3) for nearly the whole month.

Extensive studies have been conducted in recent years to investigate the formation mechanisms of severe haze pollution in China. Gustafsson et al. (2009) pointed out that the emission of carbonaceous aerosol from the combustion of biomass and fossil fuel was the main reason for haze formation in South Asia. Based on the observations of $PM_{2.5}$ in representative Chinese megacities, Yang et al. (2011) indicated that “complex atmospheric pollution” and secondary aerosols were the main reasons for the haze in China. For the typical haze pollution episode in the early autumn of Beijing in 2013, field observation found that the contribution of secondary PM formation from volatile organic compounds (VOCs), nitrogen oxides (NO_x) and sulfur dioxide (SO_2) was more significant than primary emissions and regional transport of PM (Guo et al., 2014). Zhang et al. (2011) analyzed the water-soluble inorganic ions of $PM_{2.5}$ in Xi'an from March 2006 to March 2007; they found that SO_4^{2-}, NO_3^- and NH_4^+ were the major pollutant ions in autumn and winter haze events. Secondary inorganic aerosols (sulfate, nitrate, and ammonium, defined as SNA) accounted for about 30–50%

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of the $PM_{2.5}$ mass during the haze pollution in early 2013 in Beijing (Ji et al., 2014; Tian et al., 2014). The enhancement ratio (defined as the mean concentrations during the haze divided by those during the clean period) was 4.2 for SNA and 5.4 for sulfate during the haze; when scaled to total $PM_{2.5}$ mass, sulfate had the largest increase from 15% (clean period) to 28% (haze period) in 2013 (Wang et al., 2014). However, the contribution of SNA to $PM_{2.5}$ was only 6% in Beijing in winter of 2009 (Zhang et al., 2013). Consequently, the increased proportion of SNA enhances the hygroscopicity of particle and accelerates the formation of haze. All of the above results show that secondary aerosols and particularly secondary inorganic aerosols make important contributions to the formation of haze in China. Several studies have found a faster increase in sulfate than in nitrate during the haze, and that this is strongly associated with high concentrations of NO_x (He et al., 2014; Sun et al., 2016; Wang et al., 2013; Xie et al., 2015).

When the heterogeneous uptake of SO_2 on deliquesced aerosols under high RH conditions was added to the nested-grid GEOS-Chem model, sulfate concentrations and sulfate fraction in $PM_{2.5}$ were simulated better in January 2013 over North China (Wang et al., 2014). Zheng et al. (2015) also captured the magnitude and temporal variation of sulfate and nitrate for both clean days and polluted haze days during January 2013 by adding nine heterogeneous chemistry reactions for nitrate, sulfate, H_2O_2, O_3 and OH to the WRF-CMAQ model. However, these corrections yet cannot fully explain the model's discrepancy for sulfate. The observed high peak concentrations of sulfate could not be reproduced in the air quality models (Zheng et al., 2015). Therefore, there are still missing chemical formation mechanisms of sulfate which can reconcile the model results with observed sulfate during the haze period (Wang et al., 2014).

Our previous research has confirmed a synergistic effect between NO_2 and SO_2 on the surface of Al_2O_3, CaO, ZnO, TiO_2, MgO, and a-Fe_2O_3, and thus the conversion of SO_2 to sulfate is promoted by the coexistence of NO_x (Liu et al., 2012; Ma et al., 2008). Further analysis indicates that O_2 is the key oxidizing agent during the reaction, while NO_x and mineral oxides act as catalysts to promote the activation of O_2 (Liu et al., 2012; Ma et al., 2008). Field observations found the enhanced sulfate formation by nitrogen dioxide at Beijing (Wang et al., 2013) and Nanjing (Xie et al., 2015), China. Mineral dust is an important composition of fine particles (about 20% of the mass) (Huang et al., 2017; Zheng et al., 2005), so the synergistic effect between NO_2 and SO_2 can occur on the surface of fine mode particles.

In this study, we provide a comprehensive insight into NO_x promotion of the conversion of SO_2 to sulfate in Beijing during 2015 using surface measurements in the real atmosphere. PAM experiments further confirmed that the formation of sulfate from SO_2 is promoted by the coexistence of NO_x.

2. Experiments

2.1. Measurement site

The locations of the air quality observation stations, which were constructed by the Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, in Beijing, were shown in Fig. S1 and Table 1. The sites include Daxing (DX), Zhiwuyuan (ZWY), and Shengtaizhongxin (STZX). These sites represent a suburb in the southeast of Beijing, an urban district of Beijing, and a suburb in the northwest of Beijing, respectively. All the air quality observation stations were set up according to the United States Environmental Protection Agency method designation (US EPA, 2007).

2.2. Instruments

Concentrations of NO_x, SO_2, and O_3 were measured using a commercial NO-NO_2-NO_x chemiluminescence analyzer (Model 42i), a pulsed fluorescence SO_2 analyzer (Model 43i) and an ozone analyzer (Model 49i) instruments form Thermo-Fisher Scientific, respectively. $PM_{2.5}$ were measured using a Tapered Element Oscillating Microbalance (Model 1400A, R&P). The operation of the instruments and scheduled quality control procedures have been described in detail previously (He et al., 2014).

$PM_{2.5}$ filter sample collection was performed from 25 November to 3 December 2015. $PM_{2.5}$ samples were collected onto PTFE filters at a flow rate of 15.75, 15.6 and 1.6 L min^{-1}at Daxing (DX), Zhiwuyuan (ZWY), and Shengtaizhongxin (STZX) for 24 h, respectively. After sampling, all filter samples were sealed in an aluminum foil bag individually and stored in a freezer under -20 °C prior to analysis. The $PM_{2.5}$ filter samples were analyzed for sulfate by an ion chromatography (IC).

2.3. Potential aerosol mass (PAM) flow reactor

The PAM flow reactor was designed according to Kang et al. (2007). Two PAM flow reactors were used in this work. Each PAM flow reactor is a cylinder made of steel coated with Teflon FEP film (0.5 mm thick). Fig. 1(a) shows the structure of the PAM flow reactor. The length of the reactor is 50 cm and the diameter is 20 cm, thus the volume is about 15 L. In order to make the sample well-mixed before reaction, a 30 cm length mixing tube (i.d. 6 cm) is placed in front of the reactor. Four 254 nm UV lamps (ZW20S26W, Beijing Lighting Research Institute) are mounted in the wall of the reactor. The light intensity measured as the photolysis rate of NO_2 to NO (k_1) is 3.67×10^{-3} s^{-1} and 9.18×10^{-4} s^{-1} for simulation of clean and polluted days. During the experiment, lamps were on for the PAM reactor and no lamps were on for the bypass reactor. The temperature were controlled by circulating water and zero air flowed continuously through the out jacket and the houses of the lamps, respectively. The temperature and the relative humidity (RH) were measured near the outlet of the reactors.

As shown in Fig. 1(b), seven gas flows enter the reactor, including three flows of zero air carrying ozone, water, and methanol respectively, and the other four flows are ambient air, NH_3, SO_2 and NO_2, with a sum about 1.6 L min^{-1}. The concentrations of SO_2 and NH_3 were 66 ppb and 230 ppb, respectively. The concentrations of NO_2 were controlled at 35, 80 or 160 ppb, for clean day simulation. The concentrations of NO_2 were controlled at 117, 161 or 243 ppb, for polluted day simulation. The gas concentrations are

Table 1
Locations and characteristics of monitoring stations selected for the study.

Site	Abbreviation	Site characteristics	Latitude	Longitude
Daxing	DX	Suburb	116°41′42″E	39°39′14″N
Zhiwuyuan	ZWY	Urban	116°25′40°E	39°52′22″N
Shengtaizhongxin	STZX	Suburb	116°20′15″E	40°0′26″N