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NO_x promotion of SO₂ conversion to sulfate: An important mechanism for the occurrence of heavy haze during winter in Beijing^{*}

Jinzhu Ma ^{a, b, c, 1}, Biwu Chu ^{a, b, c, 1}, Jun Liu ^{a, d}, Yongchun Liu ^{a, b, c}, Hongxing Zhang ^e, Hong He ^{a, b, c, *}

^a State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

^d College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

^e Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

In this study, concentrations of NO_x, SO₂, O₃ 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 SO₂ 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 SO₂⁴⁻, NH₄⁺, NO₃⁻ and organic aerosol were positively related to the conversion of SO₂ to sulfate. At the same time, we found that NO₂ can promote the formation of NH₄⁺ 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.

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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 μ g/m³) occurred in the Beijing-Tianjin-Hebei regions in January 2013. Therein, Beijing's PM_{2.5} concentration exceeded the Second Grade National Standard (75 μ g/m³) and the First Grade National Standard (35 μ g/m³) of China for 22 days and 27 days, respectively (He et al., 2014). The air

* Corresponding author. State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.



quality in Beijing exceeded the safety standard of the World Health Organization (WHO) (10 μ g/m³) for nearly the whole month.

nitrogen oxides (NO_x) and sulfur dioxide (SO₂) 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 SO₄²⁻, NO₃ and NH⁴ 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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^{*} This paper has been recommended for acceptance by Charles Wong.

E-mail address: honghe@rcees.ac.cn (H. He).

 $^{^{1}\,}$ These authors contributed equally to this work and should be considered as co-first authors.

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 PM2.5 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 SO₂ 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, H₂O₂, O₃ 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 NO₂ and SO₂ on the surface of Al₂O₃, CaO, ZnO, TiO₂, MgO, and a-Fe₂O₃, and thus the conversion of SO₂ to sulfate is promoted by the coexistence of NO_x (Liu et al., 2012; Ma et al., 2008). Further analysis indicates that O₂ is the key oxidizing agent during the reaction, while NO_x and mineral oxides act as catalysts to promote the activation of O₂ (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 NO₂ and SO₂ 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 SO₂ to sulfate in Beijing during 2015 using surface measurements in the real atmosphere. PAM experiments further confirmed that the formation of sulfate from SO₂ 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⁻¹at 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 $\times \ 10^{-3} \ s^{-1}$ and $9.18 \times 10^{-4} \text{ s}^{-1}$ 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, NH₃, SO₂ and NO₂, with a sum about 1.6 L min⁻¹. The concentrations of SO₂ and NH₃ were 66 ppb and 230 ppb, respectively. The concentrations of NO₂ were controlled at 35, 80 or 160 ppb, for clean day simulation. The concentrations of NO₂ 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



(a) PAM (or bypass) reactor



(b) Experimental system

Fig. 1. The PAM flow reactor (a) and the experimental system (b).

similar to the ambient. By using a mass flow controller before the exhaust pump, the ambient air was continuously added so that the total air flow of the reactor was fixed at 6.3 L min⁻¹. The Reynolds number were less than 100, therefore the flow in the reactor was laminar. The residence time of gas and aerosol was 120 s at the used flow rate. Both the outlets of the PAM flow reactors were connected to a three-way electromagnetic valve, which switched the gas between the two reactors. Aerosol particles, gases, temperature, and relative humidity (RH) were sampled after the electromagnetic valve. In this study, the temperature and relative humidity (RH) of the reactor was well controlled and was 24 ± 0.2 °C and 30 ± 1.7 %, respectively. The chemical composition of aerosols was measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Incorporated, USA).

 O_3 was generated by irradiating purified air in a custom-made chamber with 185 nm UV light (GPH 150T5L/4 & GPH 287T5L/4, UV-TEC Electronics Co., LTD). OH and HO₂ radicals generated by an external O_3 generator decomposed before they reached the reactor chamber. Different concentrations of O_3 were generated by switching on different numbers of UV lamps.

To evaluate the concentration of OH radical and the ambient

exposure time (T_a) in the reactor, a flow of methanol was added to the reactor. T_a was calculated by Equation (1):

$$T_{a} = \frac{\ln \frac{C_{CH_{3}OH,0}}{C_{CH_{3}OH,1}}}{k_{CH_{3}OH+OH} \times C_{OH,air}}$$
(1)

where $C_{\text{CH}_3\text{OH},0}$ and $C_{\text{CH}_3\text{OH},1}$, represents the concentrations of methanol after the bypass reactor and the PAM reactor, respectively, while $k_{\text{CH}_3\text{OH}+\text{OH}}$ and $C_{\text{OH},\text{air}}$ are the rate constant for the reaction between methanol and OH radical, and the concentration of OH radical under typical atmospheric conditions $(1.0 \times 10^6 \text{ molecule/cm}^3)$, respectively.

3. Results and discussion

By analysis of the annual data of the three sites in 2015, we found that the extreme haze episode occurred during 25 Nov. - 3 Dec. (Fig. S2). Previous results suggested the stagnant meteorological conditions was likely the primary external factor driving the formation of the severe haze episode (Sun et al., 2016). The

temporal variations of the meteorological parameters at DX, ZWY and STZX station during 25 Nov. - 3 Dec. are shown in Fig. S3. Compared to a clean day, the characteristics of the surface meteorological parameters during a severe haze episode in Beijing were as follows: relatively weak pressure (1017–1021 hPa for a haze episode and 1019–1026 hPa for a clean period), higher temperature ($-1 \sim 0 \,^{\circ}$ C for a haze episode and $-5.3 \sim -1.8 \,^{\circ}$ C for a clean period), higher relative humidity (65–82% for a haze episode and 36–45% for a clean period), and a weak wind (0.4 m s⁻¹ for a haze episode and 1.6 m s⁻¹ for a clean period). This relatively stable synoptic condition limited the dispersion of air pollutants and led to an increase in the pollutant concentrations. Meanwhile, the relatively high RH favored hygroscopic growth of ambient particles and heterogeneous reactions of gaseous precursors (Wang et al., 2012; Zhao et al., 2013).

Fig. 2 shows the variation of $PM_{2.5}$, O_3 , SO_2 , and NO_x concentrations in DX, ZWY, and STZX monitoring stations during 25 Nov. -3 Dec. The averaged $PM_{2.5}$ mass concentrations in DX, ZWY and STZX were 193, 224 and 220 μ g m⁻³, respectively, during the most severe days, 27 Nov-1 Dec. The PM_{2.5} mass concentration had a very large variation, and the maximum hourly PM2.5 mass concentrations in DX, ZWY and STZX were 480, 490 and 430 μg m⁻³, respectively. The concentrations of gaseous pollutants also showed large variations. The concentrations of O₃ were lower than 10 ppb probably because of the titration by freshly emitted NO at these stations during the haze episode. These results indicates that the photochemical reaction was insignificant and O3 was not the important oxidant. The concentration of PM2.5 and NOx were observed to have synchronous variations, that is when the concentration of PM_{2.5} was high, the concentration of NO_x was also high. On the other hand, the peak value of SO₂ concentration was earlier than the peak value of PM2.5 concentration, which indicates that NO_x may have promoted the formation of $PM_{2.5}$ for the occurrence of heavy haze during winter in Beijing.

In order to confirm that NO_x promotes the conversion of SO_2 to sulfate, the concentration of sulfate in $PM_{2.5}$ was measured and compared with the variation trends of gas pollutants, which is shown in Fig. 3. The concentration of sulfate tracked $PM_{2.5}$ well. The

sulfate concentration was high when the concentration of O₃ was low and the concentration of NO_x was high, and vice versa, which indicated that the photochemical activity had an insufficient effect on the gas-phase conversion of SO₂ to sulfate in haze episodes. In addition, as shown in Fig. 3, in the stage of the accumulation of pollutants under static stability conditions (11/25-11/27), NO_x, SO₂, sulfate and PM_{2.5} all increased; and in the stage of pollutant removal process with the north wind (11/31-12/3), NO_x, SO₂, sulfate and PM_{2.5} all decreased. While in the stage of the haze formation (11/28-11/30), with the increase of NO_x concentration, the concentration of SO₂ decreased, resulted in a high increase of sulfate and PM_{2.5}. These data definitely confirm our previous laboratory simulation and observation study. NO_x reduced the environmental capacity for SO_2 , so that high concentrations of NO_x promoted the oxidation of SO₂ to sulfate. It is obvious that the high concentration of NO_x in the Beijing city was mainly from the emission of vehicles. These results confirmed that NO_x promotes the conversion of SO₂ to sulfate in the heavy haze occurrence in winter in Beijing.

To understand the role of heterogeneous reactions in the formation of sulfate, the relationships of SO₂, NO_x and O₃ with sulfate were analyzed and shown in Fig. 4. The value of p < 0.05 implies a significant correlation between sulfate and NO₂, SO₂ or O₃. Sulfate concentration showed a stronger correlation with NO_x ($r^2 = 0.74$) suggested that NO_x may play a key role in sulfate formation. It is important to point out that many factors affect the oxidation of SO₂, for example the pH of particles (Shi et al., 2017), gas-phase reaction of stabilized Criegee Intermediates (Berndt et al., 2014) and so on. Therefore, in order to eliminate the influence of other factors, we carried out PAM experiments under controlled conditions to demonstrate the effect of NO_x on SO₂ oxidation. A negative correlation was found between sulfate and O₃, indicating that gas-phase oxidation of SO₂ by OH radicals produced form O₃ was most likely negligible during this haze episode.

In order to confirm that NO_x promotes the conversion of SO_2 to sulfate is a prevailing mechanism during winter in Beijing, Fig. 5 shows the correlation analysis results of gaseous pollutants and $PM_{2.5}$ concentrations at STZX station over the heating season (1 Jan. –15 Mar. and 15 Nov. –31 Dec.). Good correlations with $PM_{2.5}$



Fig. 2. Variation trends of PM_{2.5}, O₃, SO₂, and NO_x concentrations at DX, ZWY, and STZX stations during 25 November - 3 December.



Fig. 3. Variation trends of PM_{2.5}, sulfate, SO₂, and NO_x at DX, ZWY and STZX stations during 25 November - 3 December.



Fig. 4. Scatter plots of sulfate vs. SO₂, sulfate vs. NO_x, and sulfate vs. O₃ during 25 November - 3 December.

were observed for NO₂ and NO_x ($r^2 > 0.5$ for these two species) for all data in heating season 2015, while for SO₂ and CO the correlation became weaker. On the other hand, weak correlations with PM_{2.5} were observed for all four species ($r^2 < 0.3$) in the non-heating season (Fig. S4). Considering the concentration of sulfate tracked PM_{2.5} well, the good correlations between PM_{2.5} and NO_x (NO₂) meaning a good correlations between sulfate and NO_x (NO₂). In addition, with the increase of NO_x during haze conditions, sulfate was the largest increase composition of PM_{2.5}. This means that NO_x promotion of SO₂ conversion to sulfate is an important mechanism in the heavy haze occurrence during winter in Beijing. The data in other two stations confirmed the above mechanism (Figs. S5–8).

The PAM experiments were carried out on 8th Jan in 2017 at STZX station. The meteorological conditions of that day were

relatively stable, and the PM_{2.5} concentration was relatively low, which might be in favor of high formation potential of secondary aerosol. The average temperature during this period was about 5.2 °C, ranging from 4.4 °C to 6.1 °C. The average RH was about 24.4%, ranging from 23.4% to 24.7% and inversely related to the temperature. However, since the air was sampled to the flow reactor, for which the temperature was controlled by circulating water, the temperature in the flow reactor was stabilized at about 24 °C, consistent with the operating temperature of the analysis instruments. The higher temperature in the reactor than ambient condition was also in favor of maintaining enough water vapor to generate high concentrations of OH radicals. The relative humidity was stabilized at about 30% with a humid zero air flow added to the flow reactor. The wind direction in this period was northwest, and



Fig. 5. Hourly PM2.5 mass concentration plotted against concentration of individual species at STZX stations in heating season (1.1-3.15 and 11.15-12.31).

the average wind speed was about 2.2 m s⁻¹, ranging from 1.2 m s⁻¹ to 3.1 m s⁻¹. These data indicate that the meteorological conditions were relatively stable during the experiment.

During the experiment, 66 ppb SO₂ and 230 ppb NH₃ was continuously added to the reactor. In order to investigate the influence of NO₂ on the formation of particles, 160, 80 and 35 ppb NO₂ were introduced during the experiment, and labeled as "Period I", "Period II" and "Period III", respectively. The ambient exposure time (T_a) in "Period I", "Period II" and "Period III" was calculated to be 2.3 ± 0.2d, 2.4 ± 0.3d and 3.5 ± 0.1d, respectively. The time variation of NO₂, SO₂, CO, SO₄²⁻, NH₄, NO₃ and Org concentrations during the experimental periods were shown in Fig. 6 and Fig. 7. When the gas flowed through the bypass reactor, the concentrations of SO₄²⁻, NH₄, NO₃ and Org were less that 6 µg m⁻³. When the gas flow was

switched to the PAM reactor, the concentrations of NO₂ and SO₂ dropped and SO₄⁻⁷, NH₄⁺, NO₃⁻ and Org were formed. It can be seen from Fig. 7 that the concentrations of SO₄²⁻⁷, NH₄⁺, NO₃⁻ and Org decreased with decreasing NO₂.

The correlation between SO_4^{2-} , NO_3^- , NH_4^+ and Org concentrations and the concentration of NO_2 is given in Fig. 8. The concentrations of SO_4^{2-} , NH_4^+ , NO_3^- and Org were positively related to the concentration of NO_2 . Because of the variation in the concentration of OH, which was sensitive to the RH of the ambient air, the ambient exposure time of "Period III" was one day longer than "Period I" and "Period II". If the ambient exposure time is consistent, the promotion effect of NO_2 will be more obvious. 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



Fig. 6. Time variation of NO₂, SO₂ and CO concentrations during experimental periods.



Fig. 7. Time variation of $SO_4^{2-},\,NH_4^+,\,NO_3^-$ and Org concentrations during experimental periods.



Fig. 8. Variation of SO₄²⁻, NO₃⁻, NH₄⁺ and Org concentrations with the concentration of NO₂.

aerosols. This is because NO₂ could be a significant oxidant under high NH₃ and NO₂ concentrations (Huang et al., 2014; Pandis and Seinfeld, 1989). Because the emission of NH₃ in the north China plain is high (Huang et al., 2014), NO_x promoting the conversion of SO₂ to sulfate and NH₃ neutralizing sulfate would further promote the growth of particulate matter, and would be an important mechanism in the formation of heavy haze in this region. It is generally believed that the yield of secondary organic aerosol (SOA) decreases as the NO_x level increases (Ng et al., 2007; Xu et al. 2014, 2015). The reversal of the NO_x dependence of SOA formation for our experiments may be due to the formation of relatively lowvolatility organic nitrates (Chu et al., 2016; Ng et al., 2007; Presto et al., 2005). The m/z = 30 (mainly NO) and m/z = 46 (mainly NO₂) fragments in organic compounds increased with increasing NO₂ concentration (Fig. S9), indicating an increase in organic nitrate. Li et al. (2015) proposed that NO at sub-ppb level enhances ·OH formation increasing HO_2 · and RO_2 · and therefore promotes SOA formation. In this study, NO is at sub-ppb level, increasing the amount of NO₂ will increase the amount of NO, which is from the photolysis of NO₂, and promote SOA formation. These results indicate that NO_x has a very important role in the formation of particles under the air pollutant conditions of China.

Due to the dimming effect, haze limits the availability of light. In order to simulate the sulfur oxidation during haze, PAM experiments with weak light intensity ($k_1 = 9.18 \times 10^{-4} \text{ s}^{-1}$) were also performed (Fig. S10). It can be seen that NO₂ can promote the conversion of SO₂ to sulfate even under weak light intensity conditions in haze days.

Our previous research indicates that O_2 is the key oxidizing agent during that NO_x promote the oxidation of SO_2 to sulfate, while NO_x and mineral oxides act as catalysts to promote the activation of O_2 (Liu et al., 2012; Ma et al., 2008). Here we present a schematic diagram of the reaction mechanism. NO is oxidized to NO_2 by oxygen and SO_2 is oxidized to SO_4^{2-} by NO_2 , which is reduced to NO on the surface of mineral dust (see Fig. 9).



Fig. 9. Reaction mechanism for the SO_2 oxidized by NO_x on the mineral dust.

4. Conclusions

According to the field observation at three monitoring stations in Beijing during 2015, we found that a high concentration of NO_x promoting the conversion of SO₂ to sulfate is an important mechanism in the heavy haze occurrence in winter. The correlation analysis results for gaseous pollutants and PM_{2.5} concentrations indicate that NO_x is correlated to haze occurrence in heating season in Beijing, suggesting that NO_x play a key role in the explosive growth of PM_{2.5}. The concentrations of SO_4^{2-} , NH_4^+ , NO_3^- and Orgwere increased with the increasing of NO₂, which was confirmed by the in situ perturbation experiments in a potential aerosol mass (PAM) reactor carried out on 8th January in 2017 at STZX station. The field observation and PAM experiments results confirmed that NO₂ can promote the conversion of SO₂ to sulfate. At the same time, we found that NO₂ 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 level of fine particles in China.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.10.103.

Competing financial interests

The authors declare no competing financial interests.

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