Nonlinear responses of particulate nitrate to NOx emission controls in the megalopolises of China

Mengmeng Li1, Zihan Zhang1, Quan Yao2, Tijian Wang1, Min Xie1, Shu Li1, Bingliang Zhuang1, and Yong Han3

1School of Atmospheric Sciences, Nanjing University, Nanjing 210023, China
2Statistical Bureau of Qingjiangpu District, Huaian 223001, China
3Guangdong Province Key Laboratory for Climate Change and Natural Disaster Studies, School of Atmospheric Sciences, Sun Yat-Sen University, Guangzhou 510000, China

Correspondence: Mengmeng Li (mengmengli2015@nju.edu.cn)

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Abstract. Nitrate is an increasingly important component of fine particulate matter (PM2.5) in Chinese cities. The production of nitrate is not only related to the abundance of its precursor, but it is also supported by the atmospheric photochemical oxidants, raising a new challenge for the current emission control actions in China. This paper uses comprehensive measurements and a regional meteorology–chemistry model with optimized mechanisms to establish the nonlinear responses between particulate nitrate and the emission controls of nitrogen oxides (NOx) in the megalopolises of China. Nitrate is an essential component of PM2.5 in eastern China, accounting for 9.4 %–15.5 % and 11.5 %–32.1 % of the PM2.5 mass for the warm and cold seasons. The hypothetical NOx emission reduction scenarios (−10 % to −80 %) during summer–autumn result in almost linearly lower PM2.5 by −2.2 % in Beijing–Tianjin–Hebei (BTH) and −2.9 % in Yangtze River Delta (YRD) per 10 % reduction of NOx emissions, whereas they lead to a rather complicated response of PM components in winter. Wintertime nitrate is found to increase by +4.1 % in BTH and +5.1 % in YRD per 10 % reduction of NOx emissions, with nearly unchanged nitric acid (HNO3) and higher dinitrogen pentoxide (N2O5) intermediate products produced from the increased atmospheric oxidant levels. An inflexion point appears at 30 %–50 % NOx emission reduction, and a further reduction in NOx emissions is predicted to cause −10.5 % reduction of nitrate for BTH and −7.7 % for YRD per 10 % reduction of NOx emissions. In addition, the 2012–2016 NOx control strategy actually leads to no changes or even increases of nitrate in some areas (8.8 % in BTH and 14.4 % in YRD) during winter. Our results also emphasize that ammonia (NH3) and volatile organic compounds (VOCs) are effective in controlling nitrate pollution, whereas decreasing the sulfur dioxide (SO2) and NOx emissions may have counterintuitive effects on nitrate aerosols. This paper helps understand the nonlinear aerosol and photochemistry feedbacks and defines the effectiveness of proposed mitigations for the increasingly serious nitrate pollution in China.

1 Introduction

Secondary inorganic aerosols (SIAs), including sulfate (SO42−), nitrate (NO3−) and ammonium (NH4+), account for 30 %–60 % of the total fine particulate matter (PM2.5) mass during haze events in China (R. J. Huang et al., 2014; Zhao et al., 2013). Since the enactment of the Air Pollution Prevention and Control Action Plan in 2013, the Chinese government has taken drastic measures to reduce the emissions of sulfur dioxide (SO2), nitrogen oxides (NOx) and primary PM2.5, leading to significant decreases in sulfate and overall PM2.5 concentrations in cities (Silver et al., 2018; Li et al., 2021a; J. D. Wang et al., 2017). Meanwhile, the nitrogen/sulfur (N/S) ratio in PM2.5 increased significantly, and nitrate became the main component of PM2.5 (16 %–45 %) during haze episodes, despite a more than 20 % reduction in the concentrations of its precursor NOx (Shao et al., 2018; Wen et al., 2018; Zhai et al., 2019). The increasingly serious nitrate pollution has emerged to be the new emphasis of air pollution controls in China.
Nitrate formation involves complex multiphase chemical reactions. In the daytime, nitrogen dioxide (NO$_2$) reacts with the hydroxyl radical (OH) to produce nitric acid (HNO$_3$). With excess ammonium (NH$_3$), low temperature and insufficient sulfuric acid, this reaction can proceed quickly and produce high ammonium nitrate (Seinfeld and Pandis, 2006). In the nighttime, however, high-concentration NO$_2$ reacts with ozone (O$_3$) to produce the nitrate radical (NO$_3^-$) and dinitrogen pentoxide (N$_2$O$_5$). The heterogeneous hydrolysis of N$_2$O$_5$ on wet particles is the main pathway for nocturnal nitrate formation (56%–97%) (He et al., 2018; Pathak et al., 2011; Xue et al., 2014).

Nitrate chemistry is not only related to the abundance of its precursor NO$_x$, but it is also supported by the atmospheric oxidants and that in the VOC-limited regime the decrease of HNO$_3$ production due to the NO$_x$ emission control might be offset by the increase of OH. Nguyen and Dabdub (2002) calculated the detailed isopleth between nitrate and NO$_x$ emissions; they found that the reduction of NO$_x$ emissions resulted in a decrease of nitrate in the NO$_x$-limited regime, and an increase of nitrate under extreme conditions in the VOC-limited regime. Despite that, the single-site box model results could not distinguish the regional differences among chemical regimes; the basic hypotheses in box models to predict nitrate formation are also unreasonable in the real atmosphere.

As an important precursor for both fine particles and ozone, strict control of NO$_x$ emissions has started in China since the 12th Five-Year Plan was established (Zheng et al., 2018). A confounding factor is that, for most cities in China, the production of O$_3$ is usually limited by VOCs (Xie et al., 2014; Dong et al., 2014; Liu et al., 2010). The control of NO$_x$ emissions has therefore resulted in an increase of surface O$_3$ concentrations in recent years (Li et al., 2021a; K. Li et al., 2019; Kalsoom et al., 2021), implying complex impacts on nitrate formation. Li et al. (2021a) and Liu and Wang (2020) examined the influencing factors on the surface O$_3$ trends in China from 2013 to 2017 using regional chemical models. They highlighted that the control of NO$_x$ emissions explained 11%–35% of the increased O$_3$ due to the nonlinear NO$_x$–VOC–O$_3$ chemistry and that for most regions the magnitudes could be comparable to those resulting from the meteorological influences and aerosol effects. Some simulations suggested that the NO$_x$ emission increase in 2005–2012 resulted in an increase of nitrate by 3.4% yr$^{-1}$ in eastern China (Geng et al., 2017; Wang et al., 2013), and the following NO$_x$ emission control resulted in a decrease of nitrate by 3%–14% (Wang et al., 2014). Recent evidence from field observations (Fu et al., 2020) and numerical simulations (Dong et al., 2014), however, has suggested that the NO$_x$ emission reduction in China could result in an increase of nitrate in winter through increased photochemical oxidants and nocturnal N$_2$O$_5$ chemistry but a decrease in other seasons. In the next 5–10 years, SO$_2$ emissions might level off in China, while NO$_x$ emissions will become stringently controlled to ensure further air quality improvements (Zheng et al., 2018).

Accurately understanding the nonlinear aerosol and photochemistry feedbacks is crucial to resolve the emerging nitrate pollution and to establish reasonable air pollution control strategies in China.

To address this issue, we use comprehensive measurements and a regional meteorology–chemistry model combined with hypothetical NO$_x$ emission scenarios to establish the nonlinear response relationships between particulate nitrate and NO$_x$ emission controls in the megalopolises of China. The model configurations, numerical designs and observational data are presented in Sect. 2. Section 3 discusses the results. Finally, a summary is presented in Sect. 4.

2 Materials and methods

2.1 Model setup and experimental designs

This study uses the Weather Research and Forecasting-Chemistry (WRF-Chem) model version 4.1 developed by Grell et al. (2005) to simulate the regional meteorology and atmospheric chemistry. The mesoscale meteorology and air quality simulations of WRF-Chem have been improved in terms of incorporating the satellite-derived land surface parameters (Li et al., 2014, 2017) and optimizing the SIA formation pathways enhanced by mineral aerosols (M. M. Li et al., 2019; X. Huang et al., 2014).

The modeling domain covers two main megalopolises of China and its adjacent areas – the Beijing–Tianjin–Hebei (BTH) region and the Yangtze River Delta (YRD) region (Fig. 1). The modeling framework is configured with 81 × 86 grid cells at 25 km horizontal resolution. The model is run with an 84 h model cycle, with the first 12 h discarded as spin-up time and model outputs of each model cycle to provide chemical initial conditions for the subsequent overlapping 84 h simulation. The 6 h, 1° × 1° National Centers for Environmental Prediction Final (NCEP/FNL) analysis fields are regularly input for the model initial and lateral boundary meteorological conditions.

The model physical configurations include the YSU boundary layer scheme (Noh et al., 2003), the RRTMG radiation scheme (Iacono et al., 2008), the Noah land surface scheme (Ek et al., 2003) and the Lin microphysics scheme (Lin et al., 1983). We have updated the land cover type and vegetation data in the WRF mesoscale model with the latest land surface parameters derived from the Moderate Res-
The atmospheric chemistry is simulated using the Carbon Bond Mechanism version Z (CBMZ) (Zaveri and Peters, 1999) gas-phase chemistry module coupled with the four-bin sectional Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri et al., 2008). The aqueous-phase chemistry is based on the Carnegie Mellon University (CMU) scheme including 50 species and more than 100 reactions (Fahey and Pandis, 2001). Formation of SIA in the default WRF-Chem model accounts for the gas-phase oxidation of SO$_2$ and NO$_2$ and aqueous-phase oxidation of SO$_2$ by hydrogen peroxide (H$_2$O$_2$) and O$_3$ in cloud. We have optimized the SIA formation pathways by including the aqueous SO$_2$ oxidation catalyzed by mineral ions and heterogeneous uptakes of SO$_2$, NO$_2$, NO$_3$, N$_2$O$_5$ and HNO$_3$ on mineral aerosols in the MOSAIC aerosol module (M. M. Li et al., 2019; X. Huang et al., 2014).

Anthropogenic emissions are adopted from the 2016 Multi-resolution Emission Inventory for China (MEIC) and the 2010 MIX-Asia emission inventory for regions outside of mainland China developed by Tsinghua University (http://meicmodel.org, last access: December 2020). Biogenic emissions are calculated online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006).

A series of WRF-Chem simulations is designed, as summarized in Table 1. In the baseline simulation (denoted as the B0 scenario), the anthropogenic emissions in China remain unchanged at the usual levels in 2016. Simulation N0 is the same as B0, but it only considers the gas-phase oxidation production of HNO$_3$ (NO$_2$ + OH $\rightarrow$ HNO$_3$) and its subsequent partitioning to the aerosol phase of nitrate in WRF-Chem. The B0 and N0 simulations are combined to distinguish the contributions of gas-phase oxidation and heterogeneous pathways (i.e., uptakes of N$_2$O$_5$, NO$_3$ and NO$_2$) for the formation of nitrate aerosols during the warm and cold seasons. A group of sensitivity scenarios ($C_{NO_x-N}$ ($N = 10\%$, $20\%$, $..., $ and $80\%$)) are designed with the perturbed anthropogenic NO$_x$ emissions in China reduced by $10\%$, $20\%$, $..., $ and $80\%$, respectively. The differences between B0 and $C_{NO_x-N}$ simulations are calculated to illustrate the responses of particulate pollution in China’s megacities to the NO$_x$ emission reduction scenarios. Another simulation (E1) is designed with the anthropogenic emissions of NO$_x$ in China set to the 2012 levels to show the impacts of 2012–2016 NO$_x$ control strategy on particulate pollution. Additionally, in order to evaluate the effectiveness of multi-pollutant cooperative controls, three series of simulations ($C_{SO_2-N}$, $C_{NH_3-N}$ and $C_{VOCs-N}$, $N = 20\%$, $40\%$, $60\%$ and $80\%$) are also supplemented with the anthropogenic emissions of SO$_2$, NH$_3$ and VOCs in China reduced by $20\%$, $40\%$, $60\%$ and $80\%$, respectively. The differences between B0 and $C_{NO_x-N}$/$C_{SO_2-N}$/$C_{NH_3-N}$/$C_{VOCs-N}$ simulations are calculated to illustrate the responses of nitrate pollution in China’s megacities to the multi-pollutant cooperative controls.
Table 1. The emission scenarios in WRF-Chem numerical experiments.

<table>
<thead>
<tr>
<th>Simulation scenarios</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>Base simulation under the 2016 emission conditions.</td>
</tr>
<tr>
<td>C_{NO_3-N} (N = 10%, 20%, \ldots and 80%)</td>
<td>Same as B0, but anthropogenic NO\textsubscript{3} emissions are reduced by 10%, 20%, \ldots and 80%, respectively, relative to the usual levels in 2016.</td>
</tr>
<tr>
<td>C_{SO_2-N} (N = 20%, 40%, 60% and 80%)</td>
<td>Same as B0, but anthropogenic SO\textsubscript{2} emissions are reduced by 20%, 40%, 60% and 80%, respectively, relative to the usual levels in 2016.</td>
</tr>
<tr>
<td>C_{NH_3-N} (N = 20%, 40%, 60% and 80%)</td>
<td>Same as B0, but anthropogenic NH\textsubscript{3} emissions are reduced by 20%, 40%, 60% and 80%, respectively, relative to the usual levels in 2016.</td>
</tr>
<tr>
<td>C_{VOCs-N} (N = 20%, 40%, 60% and 80%)</td>
<td>Same as B0, but anthropogenic VOC emissions are reduced by 20%, 40%, 60% and 80%, respectively, relative to the usual levels in 2016.</td>
</tr>
<tr>
<td>NO</td>
<td>Same as B0, but it only considers the NO\textsubscript{2} + OH gas-phase oxidation pathway for the production of nitrate aerosol.</td>
</tr>
<tr>
<td>E1</td>
<td>Same as B0, but anthropogenic NO\textsubscript{2} emissions are replaced using the MEIC inventory in 2012.</td>
</tr>
</tbody>
</table>

For all simulation scenarios, two month-long periods during the Campaign on Air Pollution and Urban Meteorology in Yangtze River Delta (CAPUM-YRD) – 15 August to 16 September (Period I) and 24 November to 26 December (Period II) in 2016 – are simulated to represent the warm and cold seasons, respectively (Shu et al., 2019). The complete simulation consists of 13 84 h model cycles, with the first 6 d as a spin-up for chemistry and the remaining model outputs for analysis.

2.2 Weather and air pollutant data

Surface meteorological observations at 186 land-based automatic stations across China (Fig. 1) are collected for model meteorological validation, including hourly data of 2 m air temperature, 2 m relative humidity and 10 m wind speed. These data are archived at the U.S. National Climatic Data Center (NCDC) (Smith et al., 2011).

Air pollutant data at the national air quality monitoring network and regional supersites of China (Fig. 1) are used for model chemical validation. This nationwide monitoring network contains 1597 sites covering 454 cities in mainland China, as shown in Fig. 1. Six routine air pollutants including PM\textsubscript{2.5}, particulate matter with aerodynamic diameter less than 10 μm (PM\textsubscript{10}), SO\textsubscript{2}, NO\textsubscript{2}, carbon monoxide (CO) and O\textsubscript{3} are monitored and reported hourly by the Chinese National Environmental Monitoring Center (CNEMC) network (available at http://www.cnemc.cn, last access: December 2020).

Additionally, four comprehensive atmospheric environment supersites in YRD including Dianshanhu (DSH; 31.1°N, 121.0°E), Pudong (PD; 31.2°N, 121.5°E), Nanjing (NJ; 32.1°N, 118.8°E) and Hangzhou (HZ; 30.3°N, 120.2°E) measured the mass concentrations of PM\textsubscript{2.5}, water-soluble ions (sulfate, nitrate, ammonium, sodium, chloride, potassium, calcium and magnesium), carbonaceous aerosols (elemental carbon (EC) and organic carbon (OC)) and gaseous pollutants (SO\textsubscript{2}, NO\textsubscript{2}, CO and O\textsubscript{3}) during the CAPUM-YRD. Details for the methods and data at the four supersites are described in Shu et al. (2019).

3 Results and discussions

3.1 Model weather and chemical validation

Model evaluations indicate that the WRF-Chem model is able to simulate the weather and atmospheric pollution characteristics in China. The simulated magnitudes of surface temperature by WRF-Chem in general agree with actual observations, with a correlation efficient (R) of 0.89 and 0.94 and a normalized mean bias (NMB) of −0.55 % and −0.80 %, respectively, in Period I and Period II (Table 2). Underestimation of relative humidity (−5.65 % in Period I and −6.56 % in Period II) is common in the WRF simulation, and it might be attributed to the influence of the boundary layer parameterization on the weather forecast (Bhatti and Mohan, 2018; Gomez-Navarro et al., 2015). Clear overestimation of wind speed (23.72 % in Period I and 40.64 % in Period II) might be because of the unresolved topography in WRF (Jimenez et al., 2013; Li et al., 2014).

The predicted concentrations of routine air pollutants also accurately capture the spatial and seasonal patterns of observed surface PM\textsubscript{2.5}, SO\textsubscript{2}, NO\textsubscript{2} and O\textsubscript{3} levels in both seasons (Fig. 2). Both simulations and observations display high air pollutant concentrations in the vicinity of the North China Plain (NCP) and eastern China but with higher O\textsubscript{3} levels in the warm season and oppositely higher PM\textsubscript{2.5} and other gaseous pollutant concentrations in winter. The model...
Table 2. Statistical evaluations of the model meteorological performance.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Obs</th>
<th>Sim</th>
<th>$R^a$</th>
<th>MB</th>
<th>NMB</th>
<th>ME</th>
<th>RMSE $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period I (15 Aug to 16 Sep)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ($^\circ$C)</td>
<td>24.04</td>
<td>23.91</td>
<td>0.89</td>
<td>-0.13</td>
<td>-9.92%</td>
<td>1.98</td>
<td>2.63</td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>70.89</td>
<td>66.88</td>
<td>0.78</td>
<td>-4.01</td>
<td>-6.46%</td>
<td>11.17</td>
<td>14.67</td>
</tr>
<tr>
<td>Wind speed (m s$^{-1}$)</td>
<td>2.46</td>
<td>3.04</td>
<td>0.50</td>
<td>0.58</td>
<td>23.72%</td>
<td>1.38</td>
<td>1.83</td>
</tr>
<tr>
<td>Period II (24 Nov to 26 Dec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ($^\circ$C)</td>
<td>3.43</td>
<td>3.40</td>
<td>0.94</td>
<td>-0.03</td>
<td>-0.80%</td>
<td>2.18</td>
<td>2.83</td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>69.85</td>
<td>65.27</td>
<td>0.63</td>
<td>-4.58</td>
<td>-6.56%</td>
<td>13.51</td>
<td>17.88</td>
</tr>
<tr>
<td>Wind speed (m s$^{-1}$)</td>
<td>2.61</td>
<td>3.66</td>
<td>0.55</td>
<td>1.06</td>
<td>40.64%</td>
<td>1.70</td>
<td>2.23</td>
</tr>
</tbody>
</table>

$^a$ $R$: correlation coefficient; MB: mean bias; NMB: normalized mean bias; ME: mean error; RMSE: root mean square error.

Table 3. Statistical evaluations of the model chemical performance.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Obs</th>
<th>Sim</th>
<th>MB</th>
<th>NMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>36.88</td>
<td>33.22</td>
<td>-3.66</td>
<td>-9.92%</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>17.65</td>
<td>16.51</td>
<td>-1.14</td>
<td>-6.46%</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>28.53</td>
<td>33.23</td>
<td>4.70</td>
<td>16.47%</td>
</tr>
<tr>
<td>Daily-maximum O$_3$</td>
<td>237.45</td>
<td>255.77</td>
<td>18.32</td>
<td>7.72%</td>
</tr>
<tr>
<td>Period II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>31.05</td>
<td>64.28</td>
<td>-27.31</td>
<td>-29.82%</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>9.92</td>
<td>29.82</td>
<td>20.90</td>
<td>28.11%</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>11.65</td>
<td>27.31</td>
<td>16.65</td>
<td>22.20%</td>
</tr>
<tr>
<td>Daily-maximum O$_3$</td>
<td>119.2</td>
<td>255.77</td>
<td>136.57</td>
<td>31.05%</td>
</tr>
</tbody>
</table>

statistical evaluations show a mean bias (MB) of −3.66, −1.14, 4.70 and 18.32 µg m$^{-3}$ and a NMB of −9.92, −6.46, 16.47 and 7.72 % for PM$_{2.5}$, SO$_2$, NO$_2$ and O$_3$ in Period I and a relatively larger MB of −27.31, −11.65, 1.27 and −39.01 µg m$^{-3}$ and a NMB of −29.82, −28.11, 2.40 and −31.05 % in Period II, respectively (Table 3). The uncertainty in emissions data, the absence of secondary organic aerosol in MOSAIC aerosol chemistry or the simulated wind errors (Table 2) may be responsible for the larger atmospheric chemical biases in winter, which has been extensively discussed in some studies (Zhao et al., 2016; Li et al., 2021a).

As the most important components of PM$_{2.5}$, reasonable representation of SIA is imperative to the PM$_{2.5}$ simulation. Evaluations with measurements of PM$_{2.5}$ components at the four supersites of eastern China show that the model performs reasonably in simulating the seasonal variations and proportions of aerosol species in PM$_{2.5}$, but it is biased low by 10%–40% in simulating the magnitudes of SIA concentrations (Fig. 3). The model underestimation is −1.8, −2.2 and −2.2 µg m$^{-3}$ for sulfate, nitrate and ammonium, respectively, in Period I and −2.6, −4.3 and −3.4 µg m$^{-3}$ in Period II. The model also captures the large change of N/S ratio from the warm to cold seasons, that increases from 0.4 in Period I to 1.6 in Period II. Our previous work (Li et al., 2019) has confirmed that the consideration of the optimized aqueous and heterogeneous SIA formation pathways in WRF-Chem significantly reduces the model biases by 41.4% for sulfate and 44.6% for nitrate during the CAPUM-YRD of 2016. Recent studies highlighted that the remaining SIA simulation biases may be attributed to the missing aqueous oxidation of SO$_2$ by NO$_x$ on alkaline aerosols under humid conditions (Wang et al., 2016; Cheng et al., 2016).

3.2 Air pollution and aerosol composition characteristics

Chemical composition analyses of major gaseous and particulate air pollutants suggest large seasonal variations of air pollution characteristics in China (Fig. 2). Mainly emitted from combustion sources, atmospheric pollutants accumulate in the densely industrialized and populated megalopolises of China, with a hotspot along Beijing, Hebei, Shandong and their adjacent cities frequently exceeding China’s National Ambient Air Quality Standards. The average concentrations of surface PM$_{2.5}$, SO$_2$, NO$_2$ and daily-maximum O$_3$ in China’s routine air quality monitoring network are 33.8, 15.8, 26.5 and 223.2 µg m$^{-3}$ for Period I and 80.2, 34.7, 47.7 and 131.4 µg m$^{-3}$ for Period II. The surface PM$_{2.5}$, SO$_2$ and NO$_2$ concentrations show obvious increases by 137.6%, 119.2% and 80.2% during winter compared to those of the summer–autumn period (Period I). The maximum surface PM$_{2.5}$ concentration recorded in the winter period was more than 600 µg m$^{-3}$, which is the highest value ever recorded in 2016 and led to the “orange” air quality alert.

The further analyses of PM$_{2.5}$ mass concentrations, major PM$_{2.5}$ components and gases at the four supersites in YRD are presented in Figs. 4–5. Organic matter (OM) is obtained by multiplying the OC concentrations by a factor of 1.6, mainly accounting for the hydrogen and oxygen masses in OM. The measured SIA concentrations exhibit...
Figure 2. Spatial patterns of the surface average PM$_{2.5}$, NO$_2$, SO$_2$ and daily-maximum O$_3$ concentrations in Period I (a) and Period II (b) from the WRF-Chem modeling (shaded contours) and routine air quality observations (dots).
Figure 3. Comparisons of surface PM$_{2.5}$ components from WRF-Chem simulations and observations in Period I (a) and Period II (b) at the four supersites in YRD.

Figure 4. Observed aerosol composition and gaseous pollutant concentrations at the four supersites during Period I.

high levels, with average values of 18.8 µg m$^{-3}$ for Period I and 37.1 µg m$^{-3}$ for Period II. The three SIA components together account for 32.3%–57.4% (48.6% on average) and 27.7%–70.9% (56.9% on average) of the total PM$_{2.5}$ mass concentrations and become the primary components of PM$_{2.5}$ in the two periods. The proportions of sulfate, nitrate and ammonium in total PM$_{2.5}$ range from 13.5%–28.9%, 9.4%–15.5% and 9.4%–14.9% at the four supersites for Period I and 9.2%–20.3%, 11.5%–32.1% and 7.0%–19.8% for Period II, respectively. The strikingly higher proportion

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of nitrate than that of sulfate in PM$_{2.5}$ during winter, with a N/S ratio of 1.6, is in accordance with recent observations during other winter haze periods in China (Shao et al., 2018; Zhang et al., 2018; Zhang et al., 2019). They emphasized that since the enactment of the Clean Air Action Plan in 2013, the PM$_{2.5}$ components have changed clearly, with decreasing contributions from coal combustion.

The high proportions of sulfate and nitrate in PM$_{2.5}$ could be related to the high oxidation rates of SO$_2$ and NO$_2$. The observed average values of sulfur oxidation ratio (SOR = [SO$_4^{2-}$]/([SO$_4^{2-}$] + [SO$_2$])) and nitrogen oxidation ratio (NOR = [NO$_3^-$]/([NO$_3^-$] + [NO$_2$])) are 0.41 and 0.13 in Period I and 0.33 and 0.21 in Period II. In contrast, the observed SOR is generally higher in summer–autumn than winter, opposite to that of NOR, indicating the enhanced formation of nitrate in winter. Shu et al. (2019) also noted similar seasonal distinctions for SOR and NOR in YRD. They attributed the weakened conversion from NO$_2$ to nitrate in summer to the volatility and evaporative loss of nitrate (Sun et al., 2012). The sharp increase of particles and moderate ambient humidity in winter also benefits the heterogeneous formation of SIA, leading to high NOR and SOR (Wang et al., 2012).

Figure 6 illustrates the contributions of gas-phase oxidation and heterogeneous reactions for the nitrate production calculated from B0 and E0 simulations. It is shown that on a daily basis the gas-phase oxidation production of HNO$_3$ and its subsequent partitioning to the aerosol phase is the principal formation route for particulate nitrate, with the average contributions of 60.2 % for BTH and 91.7 % for YRD in Period I and 75.1 % for BTH and 85.9 % for YRD in Period II. The heterogeneous hydrolyses of N$_2$O$_5$ and other nitrogenous gases (calculated as the model differences between B0 and N0 simulations) contribute to the remaining nitrate, particularly in BTH with high aerosol loading. These calculated results (60.2 %–91.7 % for NO$_2$ + OH oxidation and 8.3 %–39.8 % for heterogeneous pathways) are in line with previous assessments in China and globally. Alexander et al. (2009) reported that the global tropospheric nitrate burden is dominated by NO$_2$ + OH (76 %), followed by N$_2$O$_5$ hydrolysis.
In Period I (August–September), the PM$_{2.5}$–NO$_x$ responses are closer to a linear function, reflecting a stronger sensitivity to the NO$_x$ emission changes in the warm season. The surface PM$_{2.5}$ concentrations decrease almost linearly as we gradually reduce NO$_x$ emissions in China, with the average $\beta$ values of $-2.2\%$ in BTH and $-2.9\%$ in YRD. However, the PM$_{2.5}$–NO$_x$ emission responses in Period II (November–December) display strong nonlinearity and are analogous to a quadratic parabola distribution for both regions. The NO$_x$ emission reductions within the first 50% would even increase surface PM$_{2.5}$ concentrations by $+1.2\%$ averagely in BTH, and this $\beta$ value increases to $+1.8\%$ in YRD with the first 40% reductions of NO$_x$ emissions. Subsequently, the PM$_{2.5}$ responses shift towards a similar linear pattern, with an average $\beta$ value of $-2.5\%$ in BTH and $-4.0\%$ in YRD.

The distinct forms of PM$_{2.5}$–NO$_x$ emission responses for the warm and cold seasons are determined by the seasonal ozone chemical sensitivity regimes. The photochemical indicator of $\Delta$[O$_3$/NO$_x$/VOC] with a critical value of 1.0 is used to investigate the season-varying ozone sensitivity in China, which is calculated as the ratio of ozone concentration changes under 20% NO$_x$ emission reduction to that under 20% VOC emission reduction (Fig. S1 in the Supplement). The results indicate a strong VOC-limited ozone chemistry across China during winter while either a VOC-limited regime over a large portion of the NCP and eastern China or a NO$_x$-limited regime in northern and western China during summer-autumn, as also indicated by previous studies (Xie et al., 2014; Dong et al., 2014; Liu et al., 2010). We find larger O$_3$ and OH production under the NO$_x$ emission reduction conditions in both seasons (Figs. 8 and 9), particularly in Period II (November–December), with an average increase rate of $+14.7\%$ and $+18.5\%$ in BTH and $+25.2\%$ and $+23.1\%$ in YRD per 10% reduction of NO$_x$ emissions. The SIA formation chemistry is highly limited by atmospheric oxidants produced from the NO$_x$–VOC–O$_3$ photochemical cycles. The nonlinear O$_3$–NO$_x$ responses indicate a rather complicated aerosol and photochemistry feedback in megacities.

### 3.3 Nonlinear responses of nitrate to NO$_x$ emissions and their policy implications

#### 3.3.1 PM$_{2.5}$–NO$_x$ and O$_3$–NO$_x$ responses in the warm and cold seasons

NO$_x$ is key in atmospheric chemistry and serves as an important precursor for both ozone and secondary aerosols. We conduct a series of simulations with perturbed NO$_x$ emissions to assess the responses of PM$_{2.5}$ mass concentrations to NO$_x$ emissions in two megapolarises of China (Fig. 7). The WRF-Chem simulation results show that the responses of surface PM$_{2.5}$ concentrations to NO$_x$ emissions vary in different seasons and display strong nonlinear behavior in winter. To better quantify their effectiveness, we define the NO$_x$ emission control efficiency ($\beta$), which denotes the percentage changes of surface PM$_{2.5}$ or its component concentrations in response to the successive 10% reduction of NO$_x$ emissions.

### 3.3.2 Nonlinear responses of particulate nitrate to NO$_x$ emissions

The SIA formation is basically driven by the atmospheric oxidant levels, and a reduction of NO$_x$ emissions may have counterintuitive effects on SIA components by controlling the atmospheric oxidant levels. The calculated SIA components for each emission scenario in both months show that the surface nitrate aerosols can be substantially decreased/increased with reducing NO$_x$ emissions, but the sulfate and ammonium concentrations have moderately smaller changes (Figs. 8–10).

Response of sulfate to the NO$_x$ emissions is more predictable and determined by the changes of atmospheric ox-
Figure 7. Responses of surface PM$_{2.5}$ concentrations to the NO$_x$ emission reduction scenarios in (a) BTH and (b) YRD. The calculated NO$_x$ emission control efficiency ($\beta$) is also marked in the figure.

Figure 8. Responses of the surface concentrations of SIA components and key atmospheric trace gases (NO$_2$, O$_3$, OH, HNO$_3$ and NO$_3$) to the NO$_x$ emission reduction scenarios in (a, b) BTH and (c, d) YRD during Period I.

Ident levels since the conversion of SO$_2$ to sulfate is partly driven by OH in the gas phase and by dissolved H$_2$O$_2$ or O$_3$ in the presence of fog or cloud. In Period I (August–September), the sulfate–NO$_x$ response follows a gradual quadratic parabola distribution as that of O$_3$–NO$_x$ and OH–NO$_x$ response curves (Figs. 8 and 10), with a fitted function in Eq. (1). The $\beta$ values for surface sulfate change by $-0.7\%$–$+1.2\%$ in BTH and $-1.5\%$–$+0.2\%$ in YRD under
each NO$_x$ emission reduction scenario.

$$[\text{SO}_4^{2-}] = -2.4\Delta E_{\text{NO}_x}^{2} - 1.7\Delta E_{\text{NO}_x} + 6.1 \quad \text{in BTH (} R^2 = 0.93 \text{)}$$

$$[\text{SO}_4^{2-}] = -2.3\Delta E_{\text{NO}_x}^{2} - 0.9\Delta E_{\text{NO}_x} + 6.8 \quad \text{in YRD (} R^2 = 0.99 \text{),}$$

where $[\text{SO}_4^{2-}]$ is the surface mean concentration of sulfate ($\mu g m^{-3}$), and $\Delta E_{\text{NO}_x}$ is the percentage change of NO$_x$ emissions ($\%$).

As expected, the production of nitrate reflects a strong sensitivity to NO$_x$, and it decreases linearly with the NO$_x$ emission control, with an average $\beta$ value of $-10.2\%$ in BTH and $-11.5\%$ in YRD, which further leads to a decrease of ammonium concentrations by $-3.3\%$ in BTH and $-4.3\%$ in YRD (Figs. 8 and 10). The formation of nitrate mainly involves the NO$_2$ + OH $\rightarrow$ HNO$_3$ gas-phase oxidation and the heterogeneous hydrolysis of N$_2$O$_5$ and other nitrogenous gases. The strong sensibility of particulate nitrate in response to the NO$_x$ emission decreases can be explained by the synchronously suppressive production of its intermediate products HNO$_3$ and N$_2$O$_5$. For example, when the NO$_x$ emission is reduced by 20 $\%$, the surface NO$_2$ concentration in BTH drops by 20.0 $\%$, but the surface O$_3$ and OH concentrations increase slightly by 2.6 $\%$ and 5.3 $\%$ due to the reduction of NO+O$_3$ titration reaction and the greater VOC availability in the warm season, leading to substantial reductions in surface HNO$_3$ ($-16.7\%$) and N$_2$O$_5$ ($-8.9\%$) concentrations.

$$[\text{NO}_3^-] = -34.5\Delta E_{\text{NO}_x}^{2} - 23.8\Delta E_{\text{NO}_x} + 13.2 \quad \text{in BTH (} R^2 = 0.84 \text{)}$$

$$[\text{NO}_3^-] = -36.5\Delta E_{\text{NO}_x}^{2} - 19.6\Delta E_{\text{NO}_x} + 12.0 \quad \text{in YRD (} R^2 = 0.99 \text{)}$$

$$[\text{NH}_4^+] = -9.1\Delta E_{\text{NO}_x}^{2} - 6.9\Delta E_{\text{NO}_x} + 6.2 \quad \text{in BTH (} R^2 = 0.78 \text{)}$$

$$[\text{NH}_4^+] = -10.5\Delta E_{\text{NO}_x}^{2} - 6.2\Delta E_{\text{NO}_x} + 5.3 \quad \text{in YRD (} R^2 = 0.98 \text{),}$$

where $[\text{NO}_3^-]$ and $[\text{NH}_4^+]$ are the surface mean concentrations ($\mu g m^{-3}$) of nitrate and ammonium, respectively.

In Period II (November–December), we find opposite results, with quadratic parabola distributions for the nitrate–NO$_x$ response (Eq. 2) and the ammonium–NO$_x$ response (Eq. 3) but linearly increasing sulfate concentrations (average $\beta$ values of $+2.0\%$ in BTH and $+2.6\%$ in YRD; Figs. 9 and 10), leading to small PM$_{2.5}$ changes in winter. Such nonlinear nitrate–NO$_x$ responses can be explained by the substantially increased oxidants as we gradually reduce NO$_x$ emissions in each scenario. It is noted that in winter the nitrate–NO$_x$ response highly depends on the production of N$_2$O$_5$, which is produced from the NO$_2$ $\rightarrow$ N$_2$O$_5$ $\rightarrow$ N$_2$O$_5$ chemical reactions and is a crucial intermediate product for nitrate formation. Under the low NO$_x$ emission reduc-

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**Figure 9.** Same as Fig. 8 but for Period II.
tion conditions, the production of N$_2$O$_5$ is more sensitive to the atmospheric oxidant concentrations. The significant increases of surface O$_3$ in each NO$_x$ emission scenario in the VOC-poor environment (Fig. 9b and d) lead to an enhancement of N$_2$O$_5$ levels from 10% to more than 100%. In spite of the HNO$_3$ concentration remaining nearly unchanged or decreasing slightly by less than 5% in response to NO$_x$ control, nitrate is found to increase (average $\beta$ values of $+4.1\%$ in BTH and $+5.1\%$ in YRD), with higher N$_2$O$_5$ produced from the increased ozone introduced by attenuated titration. An inflexion point appears at the 30%–50% NO$_x$ emission reduction scenario, and a further reduction in NO$_x$ emissions is predicted to cause $-10.5\%$ and $-5.3\%$ reductions of surface particulate nitrate and ammonium for BTH and $-7.7\%$ and $-7.4\%$ for YRD.

These results reveal that the increase in atmospheric oxidants in response to NO$_x$ emission control can offset the decreasing precursors concentrations and further enhance the formation of secondary nitrate, as recently found during the COVID-19 pandemic (Huang et al., 2020; Li et al., 2021b).

3.3.3 Impacts of 2012–2016 NO$_x$ control strategy on particulate pollution

During the 12th Five-Year Plan period (2011–2015), a series of end-of-pipe pollutant controls (e.g., selective catalytic reduction techniques) were carried out for power, industry and transportation sectors. These measures effectively controlled the national NO$_x$ emissions by 22.8% from 2012 to 2016 (MEIC v1.3) in China. To quantify the effects of recent NO$_x$ control measures on the levels of photochemical oxidants and...
particulate nitrate, we conduct an additional simulation with NO\textsubscript{x} emissions set to the levels of 2012 in E1.

The model simulations (Fig. 11) suggest that reducing China’s NO\textsubscript{x} emissions alone from 2012 to 2016 leads to an average $-24.9\%$ to $-8.6\%$ decrease of NO\textsubscript{x} concentrations in the surface layer. As previously pointed out, the 2012–2016 NO\textsubscript{x} emission control measures led to increased O\textsubscript{3} and OH levels in winter, which offset the effectiveness of NO\textsubscript{x} emission reduction in alleviating winter nitrate. No obvious declines in the winter nitrate levels are observed and even increases in some areas $(+8.8\%$ in BTH and $14.4\%$ in YRD; Figs. S2 and S3 in the Supplement). As shown, the largest PM\textsubscript{2.5} responses shift towards the southern Hebei and central China provinces, where the wintertime PM\textsubscript{2.5} concentrations are particularly high. The substantial emission changes from 2012 to 2016 lower the PM\textsubscript{2.5} air pollution by up to $-1.8\%$ in BTH and $-3.5\%$ in YRD for Period I and oppositely increase the surface PM\textsubscript{2.5} by $2.4\%$ in BTH and $4.7\%$ in YRD for Period II. The past NO\textsubscript{x} emission control strategy leads to increased atmospheric oxidant levels and deteriorated particulate pollution in winter due to the nonlinear photochemistry and aerosol chemical feedbacks, without regard of the other emission control measures. This conclusion is also supported by evidence from the recent field observations (Fu et al., 2020).

### 3.3.4 Responses of particulate nitrate to multi-pollutant cooperative controls

In order to evaluate the effectiveness of multi-pollutant cooperative controls in China, three series of additional simulations ($C_{\text{SO}_2\text{N}}, C_{\text{NH}_3\text{N}}$ and $C_{\text{VOCs}-\text{N}}$) are also designed to show the responses of nitrate and PM\textsubscript{2.5} to the emission controls of NO\textsubscript{x}, SO\textsubscript{2}, NH\textsubscript{3} and VOCs, respectively. The results (Fig. 12) show that atmospheric NH\textsubscript{3} and VOCs are effective in controlling the particulate nitrate pollution for both seasons, whereas decreasing the SO\textsubscript{2} and NO\textsubscript{x} emissions may have counterintuitive effects on the concentration levels of nitrate aerosols.

Atmospheric NH\textsubscript{3} acts as a critical neutralizing species for SIA production and efficient haze mitigation (Liu et al., 2019). According to the WRF-Chem simulation, reduction of NH\textsubscript{3} emissions may be effective in reducing the nitrate component, with an average $\beta$ value of $-10.0\%$ in BTH and $-10.3\%$ in YRD for Period I and $-8.3\%$ in BTH and $-11.5\%$ in YRD for Period II, primarily by suppressing the ammonium nitrate formation. Quantitatively, a $10\%$ reduction in NH\textsubscript{3} emissions can alleviate the PM\textsubscript{2.5} pollution by $-2.7\%$ during summer–autumn and $-3.2\%$ during winter in the two Chinese megacities. Atmospheric chemistry modeling by Wen et al. (2021) also indicated that controlling NH\textsubscript{3} emissions in Beijing would significantly reduce the population-weighted PM\textsubscript{2.5} concentrations by $6.2\%$–$21\%$, with $60\%$–$100\%$ NH\textsubscript{3} reductions in January, implying the need to consider NH\textsubscript{3} emission controls when designing the PM\textsubscript{2.5} pollution mitigation strategies.

VOCs, which are not a direct precursor for SIA, are effective in SIA controls due to their influences on the atmospheric oxidation cycles (Tsimpidi et al., 2008; Womack et al., 2019; Nguyen and Dabdub, 2002). Our results suggest that decreasing VOC emissions per $10\%$ would suppress the oxidation formation of nitrate and decrease the nitrate concentrations by $-2.5\%$ in BTH and $-1.7\%$ in YRD for Period I and $-5.0\%$ in BTH and $-6.3\%$ in YRD for Period II. The reduction of VOC emissions would result in a decrease of PM\textsubscript{2.5} by $-0.7\%$ during summer–autumn and $-1.8\%$ during winter in the two megacities. Tsimpidi et al. (2008) also showed that the reduction of VOC emissions caused a marginal increase of PM\textsubscript{2.5} during summer in the eastern United States, whereas it resulted in a decrease of atmospheric oxidant levels and $5\%$–$20\%$ reduction of both inorganic and organic PM\textsubscript{2.5} components during winter. Larger and synchronized NO\textsubscript{x} and VOC emission controls are required to overcome the adverse effects of nonlinear photochemistry and aerosol chemical feedbacks.

The SO\textsubscript{2} emission reduction, although effective in reducing sulfate and PM\textsubscript{2.5}, is not successful in regulating the nitrate pollution due to the chemical competition in nitrate and sulfate formations (Geng et al., 2017; Wang et al., 2013). Changes in nitrate concentration are linearly associated with the SO\textsubscript{2} emission reductions, with the average $\beta$ values of $2.9\%$ during summer–autumn and $1.3\%$ during winter. Decreasing SO\textsubscript{2} emissions is less effective (a $\beta$ value of $-0.7\%$) in mitigating the wintertime haze pollution because the benefit of SO\textsubscript{2} reduction is partly offset by the significant increase of nitrate, demonstrating the critical role of multi-pollutant cooperative controls. Lei et al. (2013) evaluated the impacts of SO\textsubscript{2} control strategies on nitrate and sulfate production in the United States and also found that the competition for bases in nitrate and sulfate formation significantly affects the nitrate concentrations.

Our results emphasize that future nitrate and PM\textsubscript{2.5} pollution mitigation strategies should focus on reducing the chemical precursors and key atmospheric oxidants involved in the production of secondary aerosols. The recent “Three-Year Action Plan for Winning the Blue Sky Defense Battle” calls for stringent emission controls of NO\textsubscript{x}, SO\textsubscript{2}, VOCs and NH\textsubscript{3} but without specific reduction targets. Such emission changes would emphasize the need to jointly consider multi-pollutant emission controls for mitigating haze air pollution.

### 4 Conclusions

Recent air pollution actions have significantly lowered the PM\textsubscript{2.5} levels in China via controlling emissions of SO\textsubscript{2} and NO\textsubscript{x} but raised a new question of how effective the NO\textsubscript{x} emission controls can be in the mitigation of emerging nitrate and ozone air pollution. We use comprehensive mea-

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Figure 11. Changes in the concentrations of surface PM$_{2.5}$, SIA components and key atmospheric trace (NO$_2$, O$_3$, HNO$_3$ and N$_2$O$_5$) due to the 2012–2016 NO$_x$ emission reductions in China, estimated as the differences between the base simulation and the E1 scenario. The units are parts per trillion (ppt) for HNO$_3$ and N$_2$O$_5$ and micrograms per cubic meter ($\mu$g m$^{-3}$) for other chemical species.

Figure 12. Responses of the surface nitrate (upper panels) and PM$_{2.5}$ (bottom panels) concentrations to the emission reduction scenarios of NO$_x$, SO$_2$, NH$_3$ and VOCs during Period I (a, b) and Period II (c, d).
measurements and a regional meteorology–chemistry model with optimized mechanisms to establish the nonlinear responses between particulate nitrate and NO\textsubscript{x} emission controls in the megalopolises of China.

Nitrate is an essential component of PM\textsubscript{2.5} in eastern China, accounting for 9.4\%–15.5\% and 11.5\%–32.1\% of the total PM\textsubscript{2.5} mass for the warm and cold seasons, respectively. We find that the efficiency of PM\textsubscript{2.5} reduction is highly sensitive to NO\textsubscript{x} emissions, and it varies in different seasons depending on the ozone chemical regimes. The reduction of NO\textsubscript{x} emissions results in almost linearly lower PM\textsubscript{2.5} by −2.2\% in BTH and −2.9\% in YRD per 10\% reduction of NO\textsubscript{x} emissions during summer–autumn, whereas it increases the atmospheric oxidant levels and leads to a rather complicated response of the PM components in winter. Nitrate is found to increase (average β values of +4.1\% in BTH and +5.1\% in YRD) in winter with higher N\textsubscript{2}O\textsubscript{5} intermediate produced from the increased ozone introduced by attenuated titration, despite the nearly unchanged or slightly decreased HNO\textsubscript{3} concentrations in response to NO\textsubscript{x} control. An inflexion point appears at 30\%–50\% NO\textsubscript{x} emission reduction, and a further reduction of NO\textsubscript{x} emissions is predicted to cause −10.5\% reductions of particulate nitrate for BTH and −7.7\% for YRD. In addition, the 2012–2016 NO\textsubscript{x} emission control strategy leads to −24.9\% to −8.6\% decreases of surface NO\textsubscript{x} concentrations and no changes or even increases of wintertime nitrate in BTH (+8.8\%) and YRD (14.4\%). Our results also emphasize that atmospheric NH\textsubscript{3} and VOCs are effective in controlling the particulate nitrate pollution, whereas decreasing the SO\textsubscript{2} and NO\textsubscript{x} emissions may have counterintuitive effects on nitrate aerosols. These results provide insights for developing mitigation strategies for the ubiquitous nitrate aerosols in the winter haze of China.

Author contributions. ML developed the model code, designed the numerical experiments and wrote the original draft. ZZ carried out the numerical experiments. QY provided and analyzed some of the data. MX, SL and BZ validated and analyzed the model results. TW and YH reviewed and revised the manuscript.

Competing interests. The contact author has declared that neither they nor their co-authors have any competing interests.

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