https://doi.org/10.5194/acp-2021-330
Preprint. Discussion started: 4 June 2021

Atmospheric Chemistry and Physics Discussions

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

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Abstract

Nitrate is an increasingly important component of fine particulate matter ($PM_{2.5}$) in Chinese cities. The production of nitrate is not only related to the abundance of its precursor, but also supported by atmospheric photochemical oxidants. The control of nitrogen oxides (NO_x) emissions may thereby lead to nonlinear changes of nitrate concentrations, raising a new challenge to 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 NO_x emission controls in the megalopolises of China. Nitrate is an essential component of $PM_{2.5}$ in eastern China, accounting for 9.4–15.5% and 11.5–32.1% of the $PM_{2.5}$ mass for the warm and cold seasons. The hypothetical NO_x emission reduction scenarios (−10%~−80%) during summer-autumn result in almost linearly lower $PM_{2.5}$ by −2.65% in Beijing-Tianjin-Hebei (BTH) and −2.79% in Yangtze River Delta (YRD) per 10% cut of NO_x emissions, whereas they increase the oxidant levels and lead to a rather complicated response of PM components in winter. Wintertime nitrate is found to increase by 4.28% in BTH and 4.60% in YRD, with higher dinitrogen pentoxide (N_2O_5) intermediate products produced from

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increased ozone introduced by lower NO_x emissions. An inflexion point appears at 40–50% NO_x emission reduction, and a further cut in NO_x emission is predicted to cause −8.74% reduction of nitrate for BTH and −10.59% for YRD per 10% cut of NO_x emissions. In addition, the 2012–2016 NO_x control strategy actually leads to no change or even increase of nitrate in some areas (8.82% in BTH and 14.41% in YRD) during winter. 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.

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1 Introduction

Secondary inorganic aerosols (SIA), including sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) account for 30–60% of the total fine particulate matter ($PM_{2.5}$) mass during haze events in China (Huang et al., 2014a; Zhao et al., 2013). Since the enactment of the Air Pollution Action Plan in 2013, the Chinese government has taken drastic measures to reduce the emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x) and primary $PM_{2.5}$, leading to significant decreases in sulfate and overall $PM_{2.5}$ concentrations in cities (Silver et al., 2018; Li et al., 2021a; Wang et al., 2017). Meanwhile, the nitrogen/sulfur (N/S) ratio in $PM_{2.5}$ increased significantly and nitrate had been the main component of $PM_{2.5}$ (16–45%) during haze episodes, despite a more than 20% reduction in the concentrations of its precursor NO_x (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 hydroxyl radical (OH) to produce nitric acid (HNO_3). With excess ammonium (NH_3), low temperature and insufficient sulphuric 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_2O_5). The heterogeneous hydrolysis of N_2O_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 also supported by atmospheric oxidants (OH and O_3) produced from the photochemical reactions of NO_x and volatile organic compounds (VOC_s) (Meng et al.,

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1997). Using a box model, some studies have determined that the relationship between particulate nitrate and NO_x emissions is nonlinear depending on the ozone chemical sensitivity regime (Pun and Seigneur, 2001; Nguyen and Dabdub, 2002). Pun and Seigneur (2001) showed that the daytime HNO_3 production was more sensitive to the concentration of 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 a detailed isopleth between nitrate and NO_x emission; they found that the reduction of NO_x emission 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 production, e.g., stagnant atmosphere or fixed NO_2/NO_y ratio, are also unreasonable in the real atmosphere.

As an important precursor for both fine particles and ozone, the strict control of NO_x emission has started in China since the 12th Five-Year Plan (Zheng et al., 2018). A confounding factor is that, for most cities in China, the production of O_3 is usually limited by VOC_s (Liu et al., 2010). The control of NO_x emission has therefore resulted in an increase of O_3 concentrations in recent years (Li et al., 2021a; Li et al., 2019a; Kalsoom et al., 2021), implying complex impacts on nitrate formation. Some simulations thought 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) suggested that the NO_x emission

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reduction in China could result in an increase of nitrate in winter through increased photochemical oxidants and nocturnal N_2O_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. Sect. 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. (2002) to simulate the 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; Li et al., 2017), and optimizing the SIA formation pathways enhanced by mineral aerosols (Li et al., 2019b; Huang et al., 2014b).

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-hour model cycle, with the first 12

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hours discarded as spin-up time and model outputs of each model cycle to provide chemical initial conditions for the subsequent overlapping 84-hour simulation. The 6-hour, 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 further updated the land cover type and vegetation data in WRF mesoscale model with the latest land surface parameters derived from Moderate Resolution Imaging Spectroradiometer (Li et al., 2014; Li et al., 2017).

The atmospheric chemistry is simulated using the Carbon Bond Mechanism version Z (CBMZ) (Zaveri and Peters, 1999) gas-phase chemistry module coupled with a 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 model accounts for the gas-phases oxidation of SO_2 and NO_2, and aqueous-phase oxidation of SO_2 by hydrogen peroxide (H_2O_2) and O_3 in cloud. We have also optimized the SIA formation pathways by including the aqueous SO_2 oxidation catalyzed by mineral ions and heterogeneous uptake of SO_2, NO_2, NO_3, N_2O_5 and HNO_3 on mineral aerosols in the MOSAIC aerosol module (Li et al., 2019b; Huang et al., 2014b).

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).

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Biogenic emissions are calculated online using the Model of Emissions of Gases and Aerosols from Nature (Guenther et al., 2006).

A series of WRF-Chem simulations are 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. Simulation N0 is the same as the base case B0, but it only considers the NO_2+OH gas-phase oxidation pathway for the production of nitrate aerosol. The B0 and N0 simulations are designed to distinguish the formation mechanisms for the high concentrations of nitrate aerosols during the warm and cold seasons. A group of sensitivity scenarios (C1~C8) are designed with the perturbed anthropogenic NO_x emissions in China cut by 10%, 20%...and 80%, respectively. The differences between B0 and C1~C8 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 emission of NO_x in China set to the 2012 level to show the impacts of 2012–2016 NO_x control strategy on particulate pollution.

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

2.2 Weather and air pollutants data

Surface meteorological observations at 186 land-based automatic stations in China (Fig. 1) are collected for model meteorological validation, including hourly

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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 pollutants data at the national air quality monitoring network and regional supersites of China (Fig. 1) are used for model chemical validation. Six routine air pollutants including particulate matter with aerodynamic diameter less than 10 μm (PM_{10}), $PM_{2.5}$, SO_2, NO_2, carbon monoxide (CO) and O_3 are monitored and reported hourly by Chinese National Environmental Monitoring Center (CNEMC) network (available at http://websearch.mep.gov.cn/). This nationwide monitoring network includes 1597 sites covering 454 cities in mainland China, as shown in Fig. 1.

Additionally, four comprehensive atmospheric environment supersites in YRD including Dianshanhu (DSH; 31.1ºN, 121.0°E), Pudong (PD; 31.2º N, 121.5°E), Nanjing (NJ; 32.1ºN, 118.8°E) and Hangzhou (HZ; 30.3ºN, 120.2°E) measured the mass concentrations of $PM_{2.5}$, 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_2, NO_2, CO and O_3) during the CAPUM-YRD campaign. 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

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WRF simulation and is attributed to the influence of the boundary layer parameterization on the weather forecast (Bhati 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 faithfully captures the spatial and seasonal patterns of observed surface $PM_{2.5}$, SO_2, NO_2 and O_3 levels in both seasons (Fig. 2). Both simulations and observations display high air pollutant concentrations in the vicinity of North China Plain (NCP) and eastern China, but with higher O_3 levels in the warm seasons and oppositely higher $PM_{2.5}$ and other gaseous pollutants in winter. The model statistical evaluations show a MB of −3.66, −1.14, 4.7 and 18.32 μg m^{-3}, and 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 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 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 component of $PM_{2.5}$, reasonable representation of SIA is imperative to $PM_{2.5}$ 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

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model also captures the large change of S/N ratios from the warm to cold seasons, that vary from 2.4 in Period I to 0.6 in Period II. Our previous work (Li et al., 2019) has confirmed that the optimized aqueous and heterogeneous SIA formation pathways in WRF-Chem significantly reduce the model biases by 41.38% for sulfate and 44.55% for nitrate during the CAPUM-YRD campaign of 2016. Recent studies highlighted that the remaining SIA simulation biases may be attributed to the missing aqueous oxidation of SO_2 by NO_2 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 $PM_{2.5}$, SO_2, NO_2 and daily-maximum O_3 in China's routine air quality monitoring network are 36.88, 17.65, 28.53 and 237.45 μg m^{-3} for Period I, and 91.59, 41.45, 53.01 and 125.62 μg m^{-3} for Period II. The $PM_{2.5}$, SO_2 and NO_2 concentrations show obvious increases by 148.35%, 134.84% and 85.80% during winter. The maximum $PM_{2.5}$ concentration recorded in the winter period could be more than 600 μg m^{-3}, which is the highest value ever recorded in 2016 and leads 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 Fig. 4–5. Organic matter (OM) is obtained by multiplying the OC concentrations by a factor of 1.6, accounting for the hydrogen and oxygen in organic compounds. The measured SIA concentrations

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exhibit 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 48.6% and 56.9% of the total $PM_{2.5}$ mass concentrations, and become the dominant components of $PM_{2.5}$ in the two periods. The ratios 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 higher proportion of nitrate in $PM_{2.5}$ than that of sulfate during winter, with a sulfur/nitrogen (S/N) ratio of 0.64, 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 Clean Air Action Plan in 2013, the $PM_{2.5}$ components had 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, indicating enhanced secondary oxidation formation. Figure 6 illustrates the contributions of each formation pathway for the high concentrations of nitrate 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 60.19% for BTH and 91.71% for YRD in Period I and 75.14% for BTH and 85.94% for YRD in Period II, heterogeneous hydrolysis of N_2O_5 and other reactive nitrogen gases contributed to the remaining nitrate particularly in BTH with high aerosol loading. These results are in line with previous assessments (Alexander et al., 2009; Wen et al., 2018; Sun et al.,

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2018), which reported that the global tropospheric nitrate burden is dominated by nitrate formation via NO_2+OH (76%), followed by N_2O_5 hydrolysis (18%).

3.3 Nonlinear responses of $PM_{2.5}$ to NO_x emissions and their policy implication

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 (−10%~−80%) to assess the responses of $PM_{2.5}$ mass concentrations to NO_x emissions in two megalopolises 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 in winter. To better quantify their effectiveness, we define the NO_x emission control efficiency (β), denoting the percentage change of $PM_{2.5}$ or its components concentrations in response to successive 10% cut of NO_x emission. In Period I (Aug–Sep), the $PM_{2.5}$-NO_x responses are closer to a linear function, reflecting a stronger sensitivity to 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 β values of −2.65% in BTH and −2.79% in YRD. However, the $PM_{2.5}$-NO_x emission responses in Period II (Nov–Dec) display strong nonlinearity and are analogous to a bell-shaped distribution for both regions. The NO_x emission reduction within the first 50% would even increase surface mean $PM_{2.5}$ concentrations by +1.33% in BTH, and this β value increases to +1.42% in YRD with the first 40% NO_x emission reduction. Subsequently, the $PM_{2.5}$ responses shift towards a similar linear pattern, with a β value of −3.47% in BTH and −3.89% in YRD.

The distinct forms of $PM_{2.5}$-NO_x emission responses in the warm and cold seasons are determined by the changing features of SIA concentrations in response to

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NO_x controls (Fig. 8–9) under the seasonal ozone chemical sensitivity regimes. The photochemical indicator of $\Delta[O_3]_{NOx}/\Delta[O_3]_{VOCs}$ 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_s emission reduction (Fig. S1). The results indicate a strong VOC-limited ozone chemistry across China during winter, while either VOC-limited regime over a large portion of NCP and eastern China or NO_x-limited regime in northern and western China during summer-autumn, as also indicated from previous studies (Xie et al., 2014; Dong et al., 2014; Liu et al., 2010). We find larger O_3 and OH productions under lower NO_x emission conditions in both seasons, particularly in Period II (Nov–Dec) with an increase rate of 28.51% and 36.92% in BTH and 34.36% and 33.6% in YRD per 10% cut of NO_x emission than the base case (Fig. 8–9(b, d)). The SIA formation chemistry is highly limited by atmospheric oxidants produced from the NO_x-VOC_s-O_3 photochemical cycles. The nonlinear O_3-NO_x responses indicate a rather complicated aerosol and photochemistry feedback in megacities.

3.3.2 Nonlinear responses of particulate nitrate to NO_x emissions

The SIA formation chemistry is basically driven by atmospheric oxidants levels, and a reduction of NO_x emission may have counter-intuitive effects on SIA components by controlling atmospheric oxidants levels. The calculated SIA components for each emission scenario in both months show that sulfate has minor changes with reducing NO_x emissions but nitrate and ammonium aerosols can be substantially decreased/increased (Fig. 8–9).

Response of sulfate to the NO_x emissions is more predictable and determined by the changes of atmospheric oxidant levels since that the conversion of SO_2 to sulfate is mainly driven by OH in the gas-phase and by dissolved H_2O_2 or O_3 in the presence

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of fog or cloud. In Period I (Aug–Sep), the sulfate-NO_x response follows a bell-shaped distribution as that of O_3-NO_x response curve, with a fitted curve in Eq. 1. The surface sulfate concentrations has minor changes by −6.69%~+2.33% in BTH and by −9.55%~+3.47% in YRD under the −10~−80% NO_x emission reduction scenarios.

$$[SO_4^{2-}]=-2.45\Delta E_{NOx}^2-2.15\Delta E_{NOx}+5.90 \text{ in BTH} \quad \text{(Eq. 1)}$$

$$[SO_4^{2-}]=-2.26\Delta E_{NOx}^2-1.31\Delta E_{NOx}+6.65 \text{ in YRD}$$

where $[SO_4^{2-}]$ is the surface mean concentration of sulfate (μg m^{-3}); ΔE_{NOx} is the percentage change of NO_x emission (%).

As expected, the production of nitrate reflects a strong sensitivity to NO_x and it decreases linearly with the NO_x emission control, with a β value of −10.89% in BTH and −11.39% in YRD, which further leads to a decrease of ammonium concentrations by −4.10% in BTH and −4.73% in YRD. The formation of nitrate involves the NO_2+OH→HNO_3 gas-phase oxidation and the heterogeneous hydrolysis of N_2O_5. The strong sensibility of particulate nitrate in response to NO_x decrease can be explained by its synchronously suppressive production of intermediate products HNO_3 and N_2O_5. For example, when the NO_x emission is cut by 20%, the surface NO_2 concentration in BTH drops by 21.96% but O_3 increases slightly by 2.56% due to greater VOC availability in warm season, leading to substantial reductions in the surface HNO_3 (−16.72%) and N_2O_5 (−8.94%) concentrations.

In Period II (Nov–Dec), we find opposite results with bell-shaped distributions for nitrate-NO_x response (Eq. 2) and ammonium-NO_x response (Eq. 3), and linearly increasing sulfate concentrations (β=+1.34% in BTH and +2.29% in YRD) in the VOC-poor environment, leading to small $PM_{2.5}$ changes in winter. Such nonlinear nitrate-NO_x emission responses can be explained by the derived excess oxidants as we gradually reduce NO_x emissions in each scenario. It is noted that in winter the nitrate-

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NO_x response is determined by the production of N_2O_5 intermediate product, which is more sensitive to the concentration of atmospheric oxidants under low NO_x emission reduction conditions. The significant increase of surface O_3 in each NO_x emission scenario leads to an enhancement of N_2O_5 level from 10% to more than 100%, which is produced from the $NO_2 \xrightarrow{O_3} NO_3 \xrightarrow{NO_2} N_2O_5$ chemical reaction and is a crucial intermediate product for nitrate formation. 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 (β=+4.28% in BTH and +4.60% in YRD) with higher N_2O_5 produced from the increased ozone introduced by attenuated titration. An inflexion point appears at the 40–50% NO_x emission reduction scenario, and a further reduction in NO_x emission is predicted to cause −8.74% and −6.18% reductions of particulate nitrate and ammonium for BTH, and −10.59% and −8.17% for YRD.

$$[NO_3^-]=-34.54\Delta E_{NOx}^2-30.66\Delta E_{NOx}+10.52 \text{ in BTH} \quad \text{(Eq. 2)}$$

$$[NO_3^-]=-36.53\Delta E_{NOx}^2-26.94\Delta E_{NOx}+9.70 \text{ in YRD}$$

$$[NH_4^+]=-9.12\Delta E_{NOx}^2-8.73\Delta E_{NOx}+5.40 \text{ in BTH} \quad \text{(Eq. 3)}$$

$$[NH_4^+]=-10.55\Delta E_{NOx}^2-8.36\Delta E_{NOx}+4.58 \text{ in YRD}$$

where $[NO_3^-]$ and $[NH_4^+]$ are the surface mean concentrations (μg m^{-3}) of nitrate and ammonium, respectively.

These results reveal that the increase in atmospheric oxidants in response to NO_x control can offset the decreasing precursor 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). Our results provide insights for developing mitigation strategies for the ubiquitous secondary aerosols in winter haze of China.

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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_x emissions set to the levels of 2012 in E1.

The model simulations (Fig. 10) suggest that reducing China's NO_x emissions alone from 2012 to 2016 leads to an average −24.93%~−8.62% decrease of NO_x concentrations in the surface layer. As previously pointed out, the 2012–2016 NO_x emission control measures lead to increased O_3 and OH levels in winter, which offset the effectiveness of NO_x emission reduction in alleviating winter nitrate. No obvious declines in the winter nitrate levels are observed and even increase in some areas (+8.82% in BTH and 14.41% in YRD; Fig. S2–S3). As shown, the largest $PM_{2.5}$ responses shift towards the southern Hebei and central China provinces, where the wintertime $PM_{2.5}$ concentrations are particularly high in this region. The substantial emission changes from 2012 to 2016 lower the $PM_{2.5}$ air pollution by up to −1.84% in BTH and −3.52% in YRD for Period I and oppositely increase $PM_{2.5}$ by 2.36% in BTH and 4.67% in YRD for Period II. The past NO_x emission control strategy leads to increased atmospheric oxidant levels and deteriorate particulate pollution in winter due to the nonlinear photochemistry and aerosol chemical feedbacks, without regard to the other control measures. This conclusion is also supported by evidence from the recent field observations (Fu et al., 2020).

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4 Conclusions

Recent air pollution actions have significantly lowered the $PM_{2.5}$ levels in China via controlling emissions of SO_2 and NO_x, but raised a new question of how effective NO_x emission controls can be on the mitigation of emerging nitrate and ozone air pollution. We use comprehensive measurements and a regional meteorology-chemistry model with optimized mechanisms to establish the nonlinear responses between particulate nitrate and NO_x emission controls in the megalopolises of China.

Nitrate is an essential component of $PM_{2.5}$ in eastern China, accounting for 9.4–15.5% and 11.5–32.1% of the total $PM_{2.5}$ mass for the warm and cold seasons, respectively. We find that the efficiency of $PM_{2.5}$ reduction is highly sensitive to NO_x emission and it varies in different seasons depending on the ozone chemical regimes. The reduction of NO_x emissions during summer-autumn results in almost linearly lower $PM_{2.5}$ by −2.65% in BTH and −2.79% in YRD per 10% cut of NO_x emissions, whereas it increases the atmospheric oxidant levels (28.51% and 36.92% for O_3 and OH in BTH and 34.36% and 33.6% in YRD) and leads to a rather complicated response of the PM components in winter. Nitrate is found to increase (β=+4.28% in BTH and +4.60% in YRD) in winter with higher N_2O_5 intermediate produced from the increased ozone introduced by attenuated titration, despite the nearly unchanged or slightly decreased HNO_3 concentrations in response to NO_x control. An inflexion point appears at 40–50% NO_x emission reduction, and a further reduction of NO_x emission is predicted to cause −8.74% reductions of particulate nitrate for BTH and −10.59% for YRD. In addition, the 2012–2016 NO_x emission control strategy leads to −24.93%~−8.62% decrease of surface NO_x, and no change or even increase of wintertime nitrate in BTH (+8.82%) and YRD (14.41%).

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Our results emphasize that future $PM_{2.5}$ pollution mitigation strategies should also focus on reducing the key oxidants involved in secondary aerosol production. VOC_s, which is not a direct precursor for SIA, is effective in SIA controls due to their influence on atmospheric oxidation cycles (Tsimpidi et al., 2008; Womack et al., 2019; Nguyen and Dabdub, 2002). Womack et al. (2019) evaluated the impacts of traditional ozone mitigation strategies on ammonium nitrate production in the Salt Lake Valley, USA. They found that the ammonium nitrate aerosol pollution is responsive to VOC_s control and not initially responsive to NO_x control. Tsimpidi et al. (2008) also showed that the reduction of VOC_s emissions caused a marginal increase of $PM_{2.5}$ during summer in eastern United States, whereas it resulted in a decrease of oxidant levels and 5–20% reduction of both inorganic and organic $PM_{2.5}$ components during winter. Larger and synchronized NO_x and VOC_s emissions reductions are required to overcome the adverse effects of nonlinear photochemistry and aerosol chemical feedbacks.

Atmospheric NH_3 also acts as a critical neutralizing species for SIA production and efficient haze mitigation (Liu et al., 2019). Atmospheric chemistry modeling indicated that controlling NH_3 emission would significantly reduce the population-weighted $PM_{2.5}$ concentration by 6.2–21% with 60–100% NH_3 reductions in January, implying the need to consider NH_3 emission controls when designing the $PM_{2.5}$ pollution mitigation strategies (Wen et al., 2021). China's anthropogenic emissions are estimated to decrease by 62% for SO_2 and 17% for NO_x over 2010–2017, while NH_3 emissions slightly increased by 1% (Zheng et al., 2018). The recent “Three-year Action Plan Fighting for a Blue Sky” calls for agricultural NH_3 emission controls but without a specific reduction target. Such emission changes would emphasize the need to jointly consider multi-pollutants emissions controls for mitigating SIA air pollution.

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Author contribution

Mengmeng Li developed the model code, designed the numerical experiments, and wrote the original draft. Zihan Zhang carried out the numerical experiments. Shu Li and Bingliang Zhuang validated and analyzed the model results. Tijian Wang and Min Xie reviewed and revised the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgement

This study is funded by the National Natural Science Foundation of China (41975153, 42077192 and 41775056), the National Key Basic Research Development Program of China (2019YFC0214603, 2020YFA0607802), and the Emory University-Nanjing University Collaborative Research Grant.

Data availability statement

The WRF-Chem model version 4.1 is available at http://www2.mmm.ucar.edu/wrf/users/downloads.html. The NCEP FNL data are accessible at the National Center for Atmospheric Research (NCAR) Research Data Archive (RDA; http://rda.ucar.edu/datasets/ds083.2/). The MEIC anthropogenic emission inventories are available at www.meicmodel.org, and for more information, please contact Q. Zhang (qiangzhang@tsinghua.edu.cn). The surface weather data are accessible at the Integrated Surface Database (https://www.ncdc.noaa.gov/isd/data-access). The surface air pollutants and aerosol species data are provided by Chinese National Environmental Monitoring Center (http://www.cnemc.cn/en/) and archived at https://doi.org/10.6084/m9.figshare.12818807.v1.

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Table 1. The emission scenarios in WRF-Chem numerical experiments

Simulation scenarios	Descriptions
B0	Base simulation under the 2016 emission conditions.
N0	Same as B0, but only consider the gas-phase oxidation pathway for the production of nitrate aerosol.
C_N (N=1/2/…/8)	Same as B0, but anthropogenic NO_x emissions are reduced by 10%, 20%...80%, respectively, relative to the usual levels in 2016.
E1	Same as B0, but anthropogenic NO_x emissions are replaced using the MEIC inventory in 2012.

Table 2. Statistical evaluations of the model meteorological performance

Variable	Obs	Sim	R [a]	MB [a]	NMB [a]	ME [a]	RMSE [a]
Period I (15 August to 16 September)							
Temperature (°C)	24.04	23.91	0.89	−0.13	−0.55%	1.98	2.63
Humidity (%)	70.89	66.88	0.78	−4.01	−5.65%	11.07	14.67
Wind speed (m s^{-1})	2.46	3.04	0.50	0.58	23.72%	1.38	1.83
Period II (24 November to 26 December)							
Temperature (°C)	3.43	3.40	0.94	−0.03	−0.80%	2.18	2.83
Humidity (%)	69.85	65.27	0.63	−4.58	−6.56%	13.51	17.88
Wind speed (m s^{-1})	2.61	3.66	0.55	1.06	40.64%	1.70	2.23

[a] R: correlation efficient; MB: mean bias; NMB: normalized mean bias; ME: mean error; RMSE: root mean square error.

Table 3. Statistical evaluations of the model chemical performance

Variable	Obs	Sim	MB	NMB	Obs	Sim	MB	NMB
	Period I				Period II			
$PM_{2.5}$	36.88	33.22	−3.66	−9.92%	91.59	64.28	−27.31	−29.82%
SO_2	17.65	16.51	−1.14	−6.46%	41.45	29.80	−11.65	−28.11%
NO_2	28.53	33.23	4.70	16.47%	53.01	54.28	1.27	2.40%
Daily-maximum O_3	237.45	255.77	18.32	7.72%	125.62	86.61	−39.01	−31.05%

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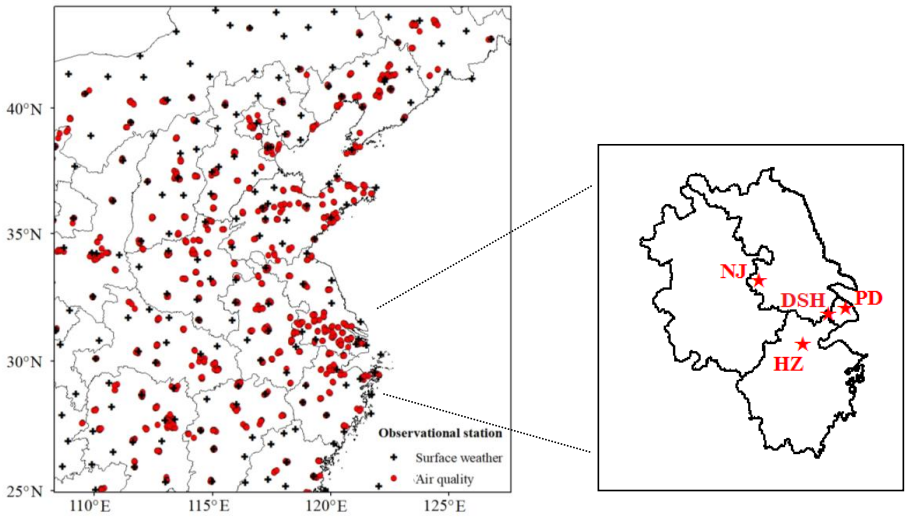

Fig. 1. WRF-Chem domain configuration and observational stations. Black crosses: surface weather stations; Red dots: CNEMC routine air quality monitoring stations; Red stars: surface supersites in YRD.

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Atmospheric Chemistry and Physics Discussions

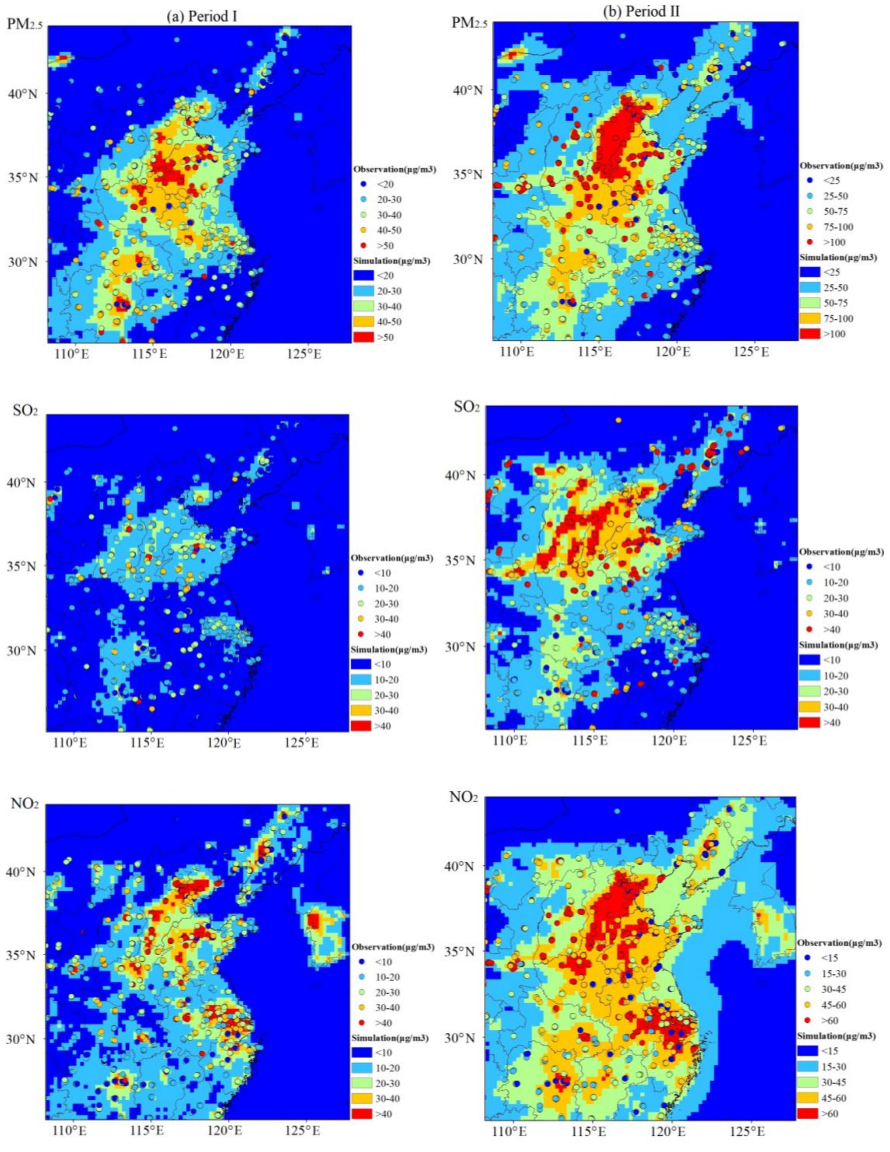

Fig. 2. Spatial patterns of the surface average $PM_{2.5}$, NO_2, SO_2 and daily-maximum O_3 concentrations in Period I (left panels) and Period II (right panels) from the WRF-Chem modeling (shaded contours) and routine air quality observations (dots).

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Atmospheric Chemistry and Physics Discussions

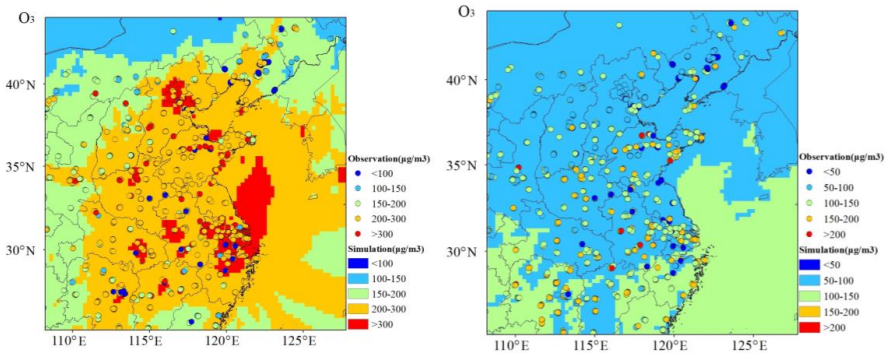

Fig. 2. Continued.

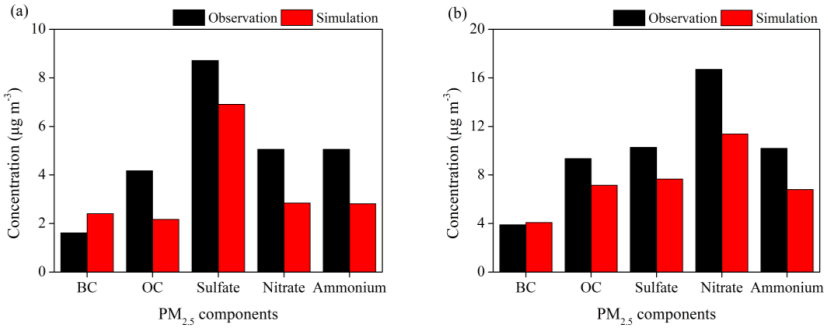

Fig. 3. Comparisons of surface $PM_{2.5}$ components from WRF-Chem simulations and observations in Period I (a) and Period II (b) at the four supersites in YRD.

https://doi.org/10.5194/acp-2021-330
Preprint. Discussion started: 4 June 2021

Atmospheric Chemistry and Physics Discussions

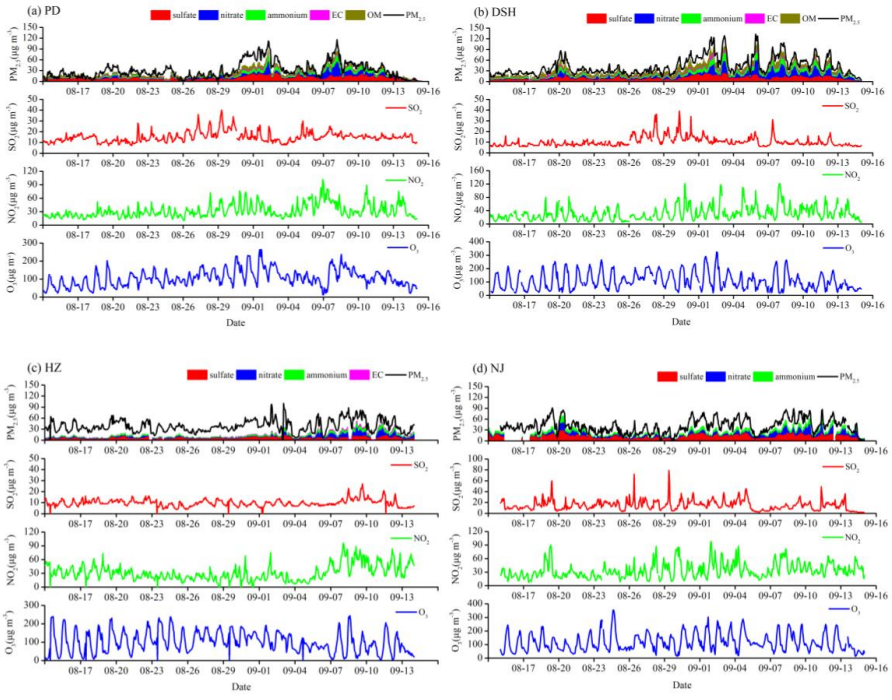

Fig. 4. Observed aerosol composition and gaseous pollutants concentrations at the four supersites during Period I.

https://doi.org/10.5194/acp-2021-330
Preprint. Discussion started: 4 June 2021

Atmospheric Chemistry and Physics Discussions

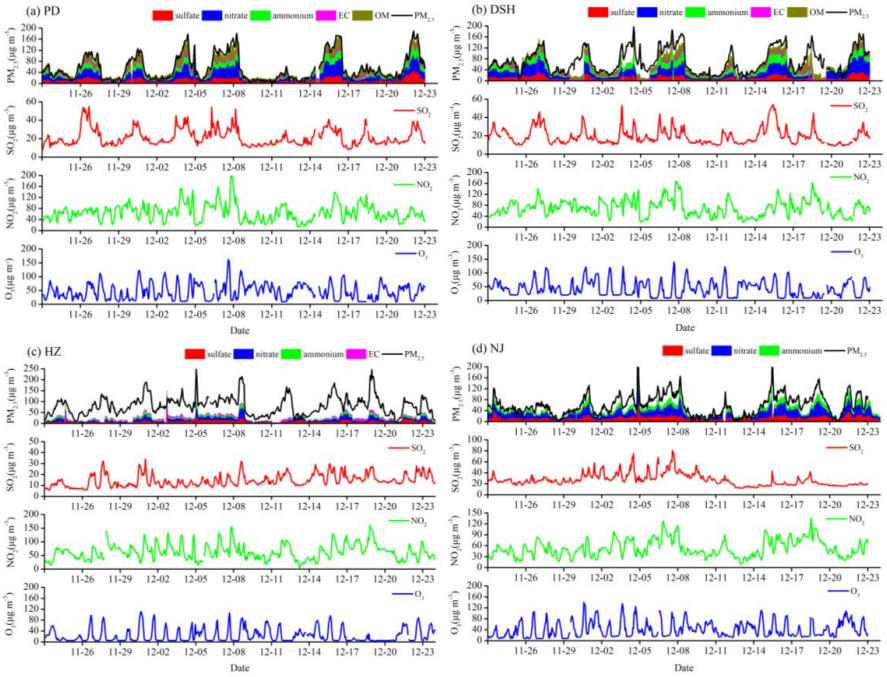

Fig. 5. Same as Fig. 3, but for Period II.

https://doi.org/10.5194/acp-2021-330
Preprint. Discussion started: 4 June 2021

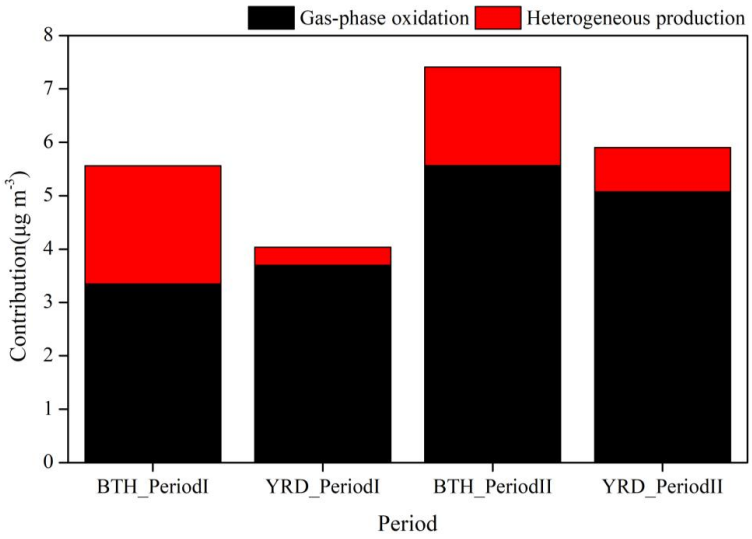

Fig. 6. Contributions of gas-phase oxidation and heterogeneous production to the surface nitrate concentrations for the BTH and YRD regions in two seasons.

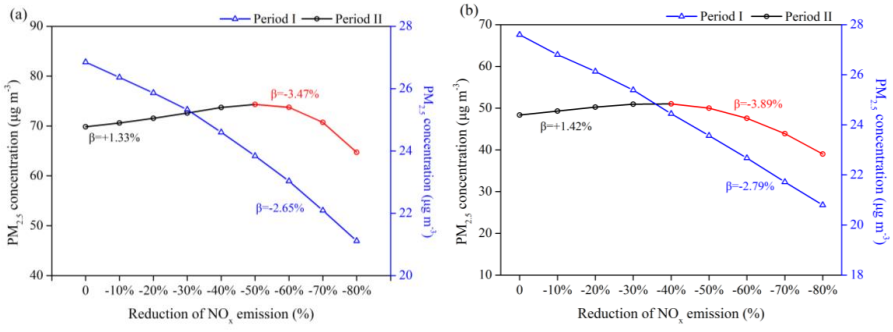

Fig. 7. Responses of surface $PM_{2.5}$ concentrations to the NO_x emission reduction scenarios in (a) BTH and (b) YRD. The calculated NO_x emission control efficiency (β) is also marked in the figure.

https://doi.org/10.5194/acp-2021-330
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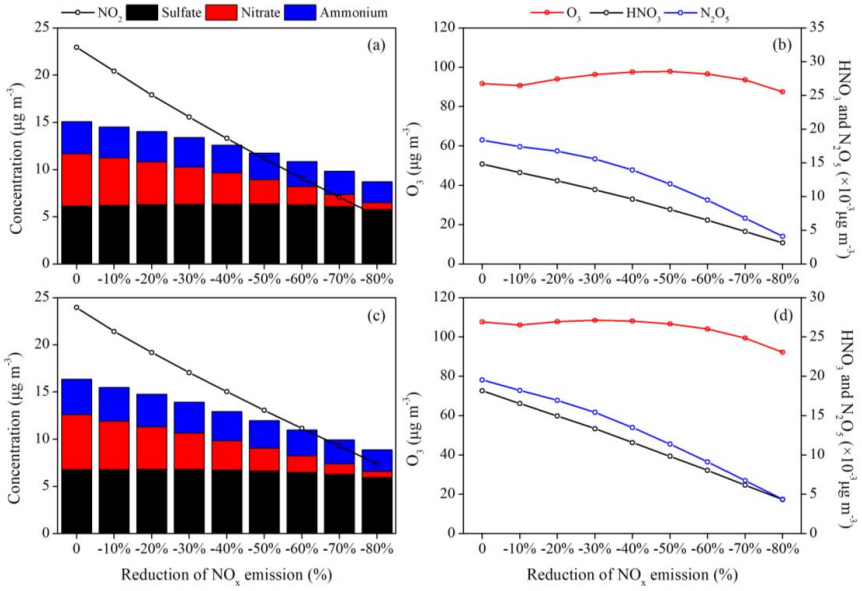

Fig. 8. Responses of the concentrations of surface SIA and key atmospheric trace gases (NO_2, O_3, HNO_3 and NO_3) to the NO_x emission reduction scenarios in (a, b) BTH and (c, d) YRD during Period I.

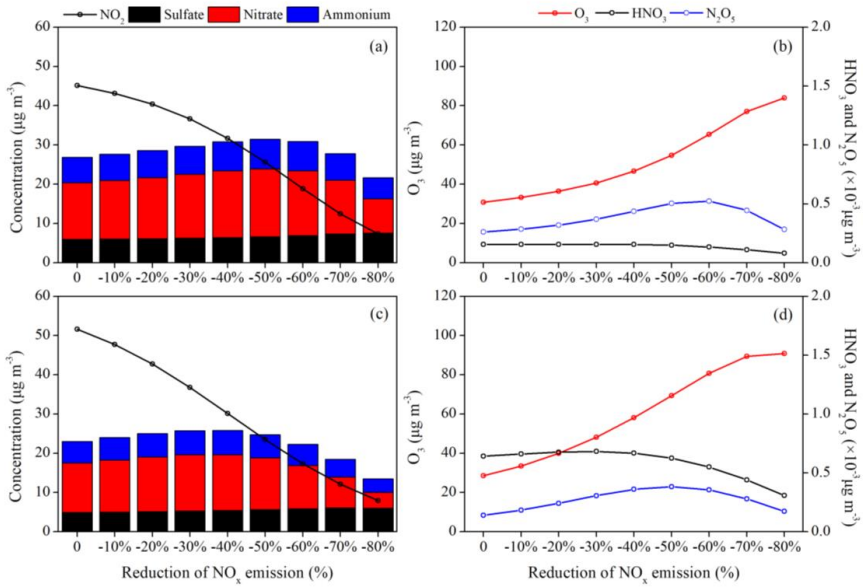

Fig. 9. Same as Fig. 7, but for Period II.

https://doi.org/10.5194/acp-2021-330
Preprint. Discussion started: 4 June 2021

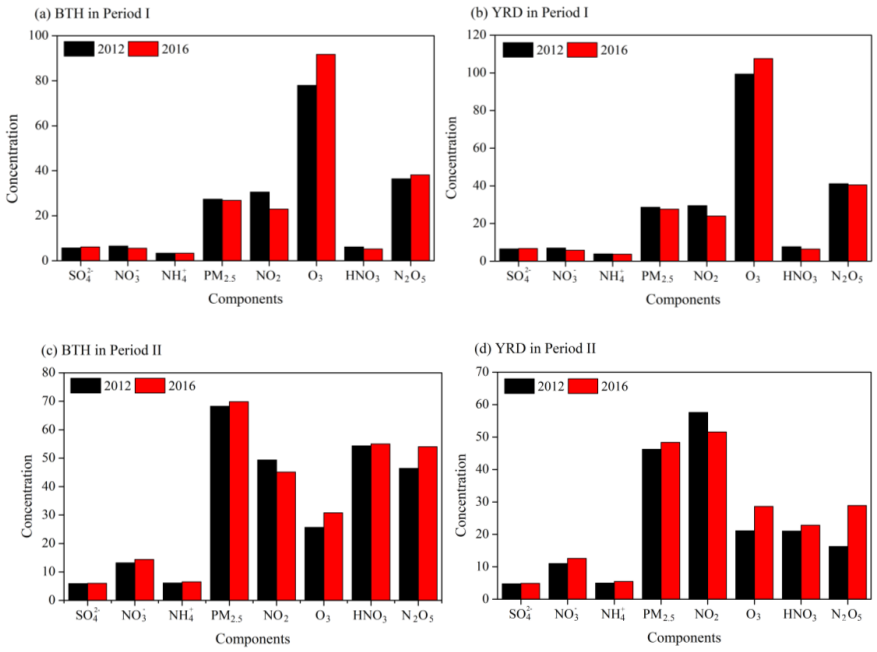

Fig. 10. Changes in the concentrations of surface $PM_{2.5}$, SIA components and key atmospheric trace (NO_2, O_3, HNO_3 and N_2O_5) due to the 2012–2016 NO_x emission reductions in China estimated as the differences between the base simulation and E1 scenario. The units are ppt for HNO_3 and N_2O_5, and μg m^{-3} for other chemical species.