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Summertime fine particulate nitrate pollution in the North China Plain: Increasing trends, formation mechanisms, and implications for control policy

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Abstract

10   Nitrate aerosol composes a significant fraction of fine particles and plays a key role in regional air quality and climate. To obtain a holistic understanding of the nitrate pollution and its formation mechanisms over the North China Plain (NCP) – the most industrialized and polluted region in northern China, intensive field observations were conducted at three sites during summertime in 2014-2015. The measurement sites include the downtown and

15   downwind of Ji'nan, the capital city of Shandong Province, as well as the peak of NCP – Mt. Tai (1534 m a.s.l.), and hence cover representative urban, rural and remote areas of the region. Elevated nitrate concentrations were observed at all three sites despite distinct temporal and spatial variations. The nitrate/$PM_{2.5}$ and nitrate/sulfate ratios have significantly increased in Ji'nan (2005-2015) and at Mt. Tai (from 2007 to 2014), indicating the worsening situation of

20   regional nitrate pollution. A multi-phase chemical box model (RACM/CAPRAM) was deployed and constrained by observations to elucidate the nitrate formation mechanisms. The principal formation route is the partitioning of gaseous HNO_3 to aerosol phase at daytime, whilst the nocturnal nitrate formation is dominated by the heterogeneous hydrolysis of N_2O_5. The daytime nitrate production in the NCP region is mainly limited by the availability of NO_2

25   and to a lesser extent O_3 and NH_3, and the nighttime formation is controlled by both NO_2 and O_3. NH_3 prompts significantly the nitrate formation at daytime but plays a slightly negative role in the nighttime. Our analyses suggest that controlling NO_X and O_3 is an efficient way at

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the moment to mitigate nitrate pollution in the NCP region, where NH_3 is usually in excess in summer. This study provides observational evidence of rising trend of nitrate aerosol as well as scientific support for formulating effective control strategies for regional haze in China.

1. Introduction

5   Atmospheric particles are vital players in tropospheric chemistry, regional air pollution, and climate change. High concentrations of fine particles (i.e., $PM_{2.5}$) can reduce visibility (Xu and Penner, 2012), deteriorate air quality (Huang et al., 2014), and are harmful to human health (Xie et al., 2016). They play an essential role in the Earth's radiation balance and hence affect the climate change, directly by scattering and absorbing the incoming solar

10 radiation (IPCC, 2013) and indirectly by modifying the cloud properties (Ding et al., 2013; Fukushima et al., 2016). Aerosol particles can also serve as a medium for reactive gases to undergo heterogeneous and aqueous phase reactions (Chang et al., 2011). Understanding the chemical compositions and sources of atmospheric particles is crucial for quantifying their environmental consequences.

15   Nitrate (NO_3^-) is a principal chemical component of atmospheric fine particles. It is an oxidation product of nitrogen oxides ($NO_X=NO+NO_2$) in the ambient atmosphere. At daytime, the oxidation of NO_2 by the hydroxyl radical (OH) produces gaseous nitric acid (HNO_3), which then reacts with ammonia (NH_3) or other alkaline compounds to form nitrate aerosol (Calvert and Stockwell, 1983). The partitioning of HNO_3 between gas and aerosol phases is

20 dependent on ambient temperature, humidity and the abundances of alkaline species (Wang et al., 2009a; Yao and Zhang, 2012). In dark conditions, the reactions of NO_2 with O_3 produce nitrate radical (NO_3) and then dinitrogen pentoxide (N_2O_5), the latter of which can undergo hydrolysis reactions on wet aerosol surfaces to form nitrate aerosol (Pathak et al., 2009 and 2011). These two chemical processes have been recognized as the major sink pathways of

25 nitrogen oxides in the troposphere (Liu et al., 2013). There are also some other formation routes of fine nitrate such as the aqueous transformation of the NO_3 radicals (Hallquist et al., 1999). Obviously, the ambient formation of nitrate aerosol highly depends on the chemical mix of NO_X, O_3 and NH_3. In particular, NH_3 plays a very important and complicated role in the fine particulate nitrate formation. At daytime, the presence of NH_3 can prompt the

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partitioning of gaseous HNO_3 into the aerosol phase and thus may enhance the nitrate formation in fine particles, whilst at night high levels of NH_3 might decrease the aerosol acidity and restrict the hydrolysis reactions of N_2O_5. To date the detailed relationship between nitrate formation and the chemical mix of NO_x, O_3 and NH_3 is still relatively poorly

5   understood.

China has been suffering from severe haze pollution as a result of its fast urbanization and industrialization processes in the past decades. The North China Plain (NCP), covering the Beijing-Tianjin-Hebei area and surrounding Shandong and Henan provinces, is the most polluted region with the highest annual concentrations of $PM_{2.5}$ in China

10 (http://www.cnemc.cn/kqzlzkbgyb2092938.jhtml). Previous air pollution control in China primarily focused on the reduction of anthropogenic emissions of sulfur dioxide (SO_2), given the dominant contributions of sulfate (SO_4^{2-}) to the $PM_{2.5}$ and acid depositions (Hao et al., 2000 and 2007). In the last decade, about 75% reduction of SO_2 emissions in China has successfully resulted in decreases in the ambient levels of both SO_2 and aerosol SO_4^{2-} in

15 fast-developing regions including the NCP (Wang et al., 2013; Li et al., 2017). In comparison, several recent observational studies have indicated the severity of fine nitrate aerosol pollution, and nitrate may even play a dominant role in the summertime haze in the NCP region (Wen et al., 2015; Li et al., 2018). A recent modeling study has predicted a significant increase of aerosol nitrate along with the decrease of sulfate during 2006-2015 over eastern

20 China (Wang et al., 2013). To the best of our knowledge, nevertheless, there is still no observational evidence for the increase of nitrate aerosol in northern China, and apparently long-term measurements are much valuable for better understanding the trend, current situation and formation mechanisms of nitrate pollution in China.

To achieve a better understanding of the summertime nitrate pollution and its formation

25 mechanism in the NCP region, four phases of intensive observations were conducted at three different sites covering urban, rural and mountainous areas in 2014 and 2015. The spatial distribution and temporal variation of nitrate aerosol pollution were examined. The data were combined with previous measurements to derive the trends of nitrate/$PM_{2.5}$ and nitrate/sulfate, confirming the significant increase of regional nitrate pollution in 2005-2015. A multi-phase

chemical box model, constrained by in-situ observations, was then deployed to unravel the formation mechanisms of fine particulate nitrate. The impacts of NO_2, O_3 and NH_3 on the regional nitrate formation were finally quantified. Overall, the present study provides the first piece of the observational evidence for the increasing trend of nitrate aerosol, and also has

5   important implications for the future control of regional haze pollution in northern China.

2. Materials and methods

2.1. Study sites

To better understand the regional-scale nitrate pollution and formation processes, four phases of intensive field campaigns were conducted at three sites in the central part of North

10   China Plain in the summers of 2014-2015. Considering that southerly/southeasterly winds generally prevail in summertime, the three study sites were carefully selected to lie on a southeast-northwest transect (see Figure 1), and to represent typical urban, rural and remote atmospheres of the region.

The urban site (36.67 °N, 117.06 °E, ~50 m above sea level (a.s.l.)) was located in the

15   downtown area of Ji'nan, the capital city of Shandong province accommodating more than 7 million inhabitants, ~1.7 million automobiles and many factories. Ji'nan is one of the largest cities in the central NCP, and has been frequently ranked among the last ten key cities of China in terms of air quality (http://www.cnemc.cn/kqzlzkbgyb2092938.jhtml). The site is built on the rooftop of a six-floor building in the Central Campus of Shandong University,

20   which is situated in the residential and commercial areas. Details of this site have been provided in our previous publications (Gao et al., 2011; Wang et al., 2015). Two intensive campaigns took place during 5th-17th May 2014 and 23rd August - 21st September 2015, respectively. In addition, measurements of aerosol ionic components have been made previously at this site in selected years since 2005 (Yang et al., 2007 and 2012; Gao et al.,

25   2011; Zhu et al., 2015).

The rural site (36.87 °N, 116.57 °E, ~23 m a.s.l.) was set up at the Chinese Academy of Sciences Comprehensive Station in Yucheng. Although Yucheng belongs to Dezhou city, it serves as a satellite town of Ji'nan due to the closer distance. The measurement site is located

about 50 km northwest (normally downwind in summer) of downtown Ji'nan (Fig. 1), and thus can be regarded as a receptor site of urban pollution. The instruments were housed in a temperature controlled container that was placed in an open cropland with few anthropogenic emissions nearby (Wen et al., 2015; Zhu et al., 2016). A six-week campaign was carried out

5   here from 2nd June to 16th July 2014.

The remote site (36.26 °N, 117.11 °E, 1465 m a.s.l.) was installed at the summit of Mt. Tai. Mt. Tai is the highest mountain over the North China Plain (with a peak of 1534 m a.s.l.), and has been frequently used as the sampling platform to investigate regional air pollution (e.g., Gao et al., 2005; Sun et al., 2016). The station was set up in a hotel to the north of mountain

10   peak with a little lower elevation. It is located approximately 15 km north of Tai'an city (with a population of 5.6 million) and 40 km south of urban Ji'nan (Fig. 1). Detailed description of this site can be found elsewhere (Guo et al., 2012; Shen et al., 2012). In the present study, the measurements were conducted from 23rd July to 27th August 2014. Previous data collected at Mt. Tai in summer 2007 are also analyzed to examine the long-term change in the regional

15   nitrate pollution (Zhou et al., 2010).

2.2. Measurement techniques

A Monitor for AeRosols and GAses (*MARGA, ADI20801, Applikon-ECN, Netherlands*) was deployed in the present study to measure continuously, at a time resolution of 1-hour, inorganic water soluble ions (i.e., NO_3^-, SO_4^{2+}, NH_4^+, etc.) in $PM_{2.5}$ together with acid and

20   alkaline gases (i.e., HNO_3, NH_3, etc.). The target gases and ions are collected and dissolved by a Wet Rotating Denuder (WRD) and a Steam Jet Aerosol Collector (SJAC), respectively (Brink et al., 2009). The dissolved components are then analyzed by a cationic and an anionic ion chromatography with eluent solutions of methane sulfonic acid (308 mg L^{-1}) and $NaHCO_3$ (672 mg L^{-1})-Na_2CO_3 (742 mg L^{-1}). An internal standard solution of LiBr (4 mg L^{-1})

25   was added automatically into the collected sample solutions to calibrate the detection in each analytic process. Multi-point calibration was performed before and after the field campaigns to examine the sensitivity of the detectors. The detection limits were evaluated as 0.05, 0.04 and 0.05 μg m^{-3} for particulate NO_3^-, SO_4^{2-} and NH_4^+, and 0.01, 0.01 and 0.07 ppbv for gaseous HNO_3, SO_2 and NH_3, respectively.

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To achieve a detailed analysis of nitrate formation processes, a large suite of ancillary measurements were concurrently made during the field studies. $PM_{2.5}$ mass concentrations were in-situ quantified by a SHARP monitor (*Model 5030, Thermo Scientific, USA*); particle size and counts in the range of 5-10000 nm were monitored by a wide-range particle

5   spectrometer (*WPS; Model 1000XP, MSP Corporation, USA*); NO and NO_2 by a chemiluminescence instrument equipped with an internal molybdenum oxide (MoO) catalytic converter (*Model 42C, Thermo Electron Corporation, USA*); O_3 by an ultraviolet absorption analyzer (*Model 49C, Thermo Electron Corporation, USA*); CO by a non-dispersive infrared analyzer (*Model 300EU, API, USA*); SO_2 by an ultraviolet fluorescence analyzer (*Model 43C,*

10   *Thermo Electron Corporation, USA*); meteorological parameters including temperature, relative humidity (RH) and wind sectors by commercial automatic weather stations. All of these techniques have been well qualified and widely applied in many previous studies, to which detailed information can be referred (Gao et al., 2011; Wang et al., 2012; Xue et al., 2014).

15   **2.3.   Multi-phase chemical box model**

A zero-dimensional chemical box model was configured to simulate the in-situ formation of fine nitrate aerosol. It couples the regional atmospheric chemistry mechanism version 2 (RACM2) and the chemical aqueous phase radical mechanism version 2.4 (CAPRAM 2.4) to account for the gas- and aqueous-phase atmospheric chemistry (Goliff et al., 2013; Herrmann

20   et al., 2000 and 2005). The gas-aqueous phase transfer processes were adopted from the resistance scheme of Schwartz (1986). There are 34 chemical reactions in the model to represent the nitrate formation (see Table S1), which can be categorized into three major formation pathways, namely, partitioning of gaseous HNO_3 to the aerosol phase, hydrolysis reactions of N_2O_5, and aqueous-phase reactions of the NO_3 radicals. This model has been

25   utilized to simulate the nighttime nitrate formation in Beijing and Shanghai (Pathak et al., 2011).

The model calculation requires a large number of variables and parameters, including: 1) gas phase concentrations of NO, NO_2, O_3, SO_2, HCl, HNO_2, HNO_3, NH_3, CO and VOCs, etc.; 2) particulate (or aqueous) phase concentrations of NO_3^-, SO_4^{2-}, Cl^-, HSO_4^-, NH_4^+, H^+, OH^-,

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etc.; 3) other auxiliary parameters such as temperature, RH, pressure, mixing layer height, particle radius, and aerosol water content, etc. Most of the above parameters were in-situ observed during our intensive measurement campaigns, and the data available were directly used to constrain the model. The particle radius was calculated from the measured aerosol

5   number and size distribution with an assumption that all particles were spherical. Aerosol H^+, OH^-, HSO_4^-, and water content were simulated by a thermodynamic model (E-AIM; http://www.aim.env.uea.ac.uk/aim/aim.php) based on the measured aerosol chemistry data (Clegg et al., 1998; Zhang et al., 2000). The VOC measurements were not made in the present study, and we used the average data previously collected at the same sites during

10   summertime for approximation (Zhu et al., 2016 and 2017; note that the VOC data in Ji'nan were just taken in 2017 and not yet published). Sensitivity studies showed that the nitrate formation was insensitive to the input VOC concentrations. The boundary layer height, which affects the dry deposition of various constituents, was estimated by the Nozaki method (Nozaki, 1973).

15   The simulation was conducted for selected nighttime or daytime nitrate formation cases. The starting time and simulation periods depended on the individual cases. The output data included particulate nitrate concentrations and reaction rates of the major formation pathways. In addition, a number of sensitivity simulations were performed to examine the relationships between nitrate formation and its precursors (see Sections 3.3 and 3.4).

20 **3.   Results and discussions**

3.1.   Temporal and spatial variations

Table 1 summarizes the statistics of the aerosol chemical properties and meteorological parameters measured at three study sites. It clearly shows the spatial distribution of regional aerosol pollution though elevated levels of $PM_{2.5}$ and major ions were observed at all three

25   sites. The highest $PM_{2.5}$ levels were recorded at the receptor rural site (Yucheng; 97.9±53.0 µg m^{-3}), followed by the urban (Ji'nan; 68.4±41.7 and 59.3±31.8 µg m^{-3}) and mountain sites (Mt. Tai; 50.2±31.7 µg m^{-3}). Nitrate shows a similar gradient with average concentrations ranging from 6.0±4.6 µg m^{-3} at Mt. Tai to 13.6±10.3 µg m^{-3} at Yucheng. In comparison, SO_4^{2-} shows a slightly different pattern with the lowest levels found in urban Ji'nan (12.2±7.5 and

12.7±7.9 µg m^{-3}), then Mt. Tai (14.7±8.9 µg m^{-3}) and Yucheng (23.6±13.4 µg m^{-3}). For NO_2, an anthropogenic emission indicator and a major precursor of NO_3^-, the highest mixing ratios were determined in urban Ji'nan, followed by Yucheng and Mt. Tai. The nitrate oxidation ratio (NOR), defined as the molar ratio of NO_3^- to NO_3^-+NO_X, shows an opposite pattern with

5   the lowest values in Ji'nan (0.11±0.07 and 0.16±0.08) and highest levels at Mt. Tai (0.39±0.20). This indicates the different extent of chemical processing of air masses in different types of areas. The above regional gradients of air pollution are mainly owing to the spatial distribution of anthropogenic emissions and different chemical aging of air masses.

Table 1 also illustrates some homogeneity of the regional aerosol pollution and chemistry

10   in the NCP region. First, secondary inorganic ions (i.e., SO_4^{2-}, NO_3^- and NH_4^+) accounted for on average 41%-56% of $PM_{2.5}$ at three sites, indicating their dominant roles in the aerosol composition and regional haze. Second, NO_3^- alone presented an important fraction of fine particles, and the NO_3^-/$PM_{2.5}$ ratios were nearly uniform over the region, with average values of 11%-14% at all three sites. Based on field measurements in January 2013, Huang (2014)

15   also reported that NO_3^- accounted for 12%, 14% and 13% of $PM_{2.5}$ in Beijing, Shanghai and Guangzhou, with a smaller ratio (7%) recorded in a western city (Xi'an). This elucidates the significance of nitrate aerosol in the haze pollution over the eastern China. At the surface sites (i.e., Ji'nan and Yucheng) in the present study, the molar concentrations of NO_3^- were even comparable to SO_4^{2-}, with mean NO_3^-/SO_4^{2-} ratios of 0.93-1.04. In comparison, the

20   NO_3^-/SO_4^{2-} ratio was relatively lower (0.62±0.33) at Mt. Tai, which should be due to the longer lifetime of sulfate aerosol and frequent transport of plant plumes to the mountain site (Wang et al., 2017). Finally, NH_4^+ was generally in excess in $PM_{2.5}$. The average excess NH_4^+ (excess NH_4^+=18*([NH_4^+]-1.5*[SO_4^{2-}]-[NO_3^-])) were calculated in the range of 1.4-5.2 µg m^{-3} at our three study sites. This highlights the NH_3-rich chemical environment of the NCP

25   region, and the abundant NH_3 may significantly affect the formation of nitrate aerosol (see Section 3.4).

Figure 2 clearly shows the distinct diurnal variation patterns of NO_3^- and NO_2 at the three different types of sites. In urban Ji'nan, NO_3^- showed a maximum level in the early morning (8:00 local time; LT) with a secondary peak in the afternoon (15:00 LT). At Yucheng, the

average diurnal profile displays a continuous nitrate formation process throughout the nighttime with a NO_3^- increase of 16.9 µg m^{-3}, followed by a sharp decrease during daytime with a trough in the late afternoon (16:00 LT). The nighttime NO_3^- levels were higher than the daytime concentrations at Ji'nan and Yucheng, owing to the dilution within the uplifted

5   planetary boundary layer (PBL) and thermal decomposition in high temperature conditions at daytime. An opposite diurnal profile was observed at Mt. Tai, which showed an NO_3^- increase throughout the daytime and high concentrations remaining in the early evening. The daytime increase was due to the development of the PBL and the mountain-valley breeze, both of which could carry the boundary layer pollution aloft, and the elevated evening levels should

10   be ascribed to the regional transport of polluted plumes to the mountain top (Sun et al., 2016). Overall, NO_2 showed similar diurnal variations with NO_3^-, and the NO_3^- concentration peaks generally lagged behind NO_2, suggesting the role of NO_2 in the nitrate formation as a precursor. Inspection of diurnal variations day by day also revealed frequent nitrate formation at all three sites during nighttime and also at daytime (especially at Mt. Tai). We then selected

15   a dozen of nitrate formation cases for detailed modeling analyses in Section 3.3.

3.2. Trend over 2005-2015

Figure 3 shows the increasing trends of NO_3^- in $PM_{2.5}$ in the past decade over the NCP region. Intensive measurements of aerosol ionic species have been made by our group in urban Ji'nan in selected years since 2005 (Yang et al., 2007 and 2012; Gao et al., 2011; Zhu

20   et al., 2015) and at Mt. Tai in 2007 (Zhou et al., 2010), and these previous data were combined with the more recent observations in the present study to derive the decadal trends. To eliminate the interference of inter-annual variation of weather condition on the absolute concentrations, we focused on the ratios of $NO_3^-/PM_{2.5}$ and NO_3^-/SO_4^{2-} for the trend analysis. In urban Ji'nan, the fraction of NO_3^- in $PM_{2.5}$ has increased at a rate of 0.9% per year over

25   2005-2015 ($p<0.01$). A similar increasing rate (0.7% per year) was also derived at Mt. Tai from 2007 to 2014, affirming the significant increase of fine particulate nitrate over the region. At the same time, the SO_4^{2-} in $PM_{2.5}$ has significantly declined in urban Ji'nan (0.7% per year) and at Mt. Tai (1.3% per year; figures not shown), as a result of the strict control of SO_2 emissions in China. As a consequence, the molar ratio of NO_3^-/SO_4^{2-} has increased at a

rate of 0.09 per year in Ji'nan during 2005-2015 ($p<0.01$) and 0.05 per year at Mt. Tai from 2007 to 2014 (Fig. 3b).

Our observations directly evidence the significant increase of summertime nitrate aerosol in the NCP region along with a decrease of sulfate in the last decade. The comparable

5   contributions of NO_3^- and SO_4^{2-} to $PM_{2.5}$ suggest the gradual shift of the secondary inorganic aerosol type from SO_4^{2-}-dominant to NO_3^--and-SO_4^{2-}-dominant. A recent modeling study also predicted an increase of nitrate with a decrease of sulfate from 2006 to 2015 over the entire eastern China (Wang et al., 2013). A more recent observational study at two sites (Beijing and Xinxiang) in the NCP region indicated the important contributions of nitrate in PM_1 and its

10   driving role in the summertime haze pollution (Li et al., 2018). Overall, nitrate has been playing a more and more important role in the haze pollution in northern China. In recent years, the strict anti-pollution measures implemented by the central government have led to a significant reduction in $PM_{2.5}$ in the NCP (http://www.cnemc.cn/kqzlzkbgyb2092938.jhtml). Nitrate and its precursors should be the next major target for the future control of regional

15   haze pollution in China.

3.3. Nitrate formation mechanisms

Multi-phase chemical modeling was then conducted for typical nitrate formation events to understand the formation mechanisms of fine particulate nitrate at three study sites. The selected cases met the following criteria: 1) the nitrate formation (accumulation) process

20   should last for a considerable time period (i.e., at least three hours); 2) the meteorological conditions were stable without wet depositions. A total of 21 nitrate formation events were finally sorted out, including 10 daytime cases (3, 3 and 4 in Ji'nan, Yucheng and Mt. Tai) and 11 nighttime ones (3, 5 and 3 in Ji'nan, Yucheng and Mt. Tai). Details of these selected cases are provided in the supplement (see Table S2).

25   Figure 4 compares the model-simulated versus observed nitrate enhancements for the daytime cases, and also presents the contributions of the major nitrate formation pathways. Generally, the model reproduced well the observed nitrate formation, with a strong positive correlation between simulations and observations (with reduced major axis (RMA) slope of 0.92 and r^2 of 0.63). The partitioning of HNO_3 gas to the particulate phase was clearly the

predominant daytime formation pathway of nitrate aerosol, with average contributions of 96%, 95% and 94% at the urban, rural and mountain sites, respectively. Hydrolysis of N_2O_5 contributed to the remaining (4-6%), and the aqueous-phase reactions of NO_3 radicals was negligible.

5   The modeling results for the nighttime cases are shown in Figure 5. The model also worked reasonably well for the simulation of nitrate formation at night, as indicated by the strong positive correlation between the simulated and observed NO_3^- enhancements with a RMA slope of 1.42 and r^2 of 0.86. The hydrolysis reaction of N_2O_5 turned over to be the overwhelming formation pathway at nighttime, with mean contributions of 94%, 98% and 91%

10   at the urban, rural and mountain sites, respectively. Other processes such as the HNO_3 partitioning and aqueous reactions of NO_3 radicals were minor routes.

Obviously, the budgets of nitrate formation were almost the same among the three sites. This indicates the regional homogeneity of formation mechanism of fine nitrate aerosol over the NCP region. The formation of HNO_3 and its subsequent partitioning to the aerosol phase

15   is the principal formation route at daytime, while the hydrolysis reactions of N_2O_5 on the particles play a dominant role during the night. This is in line with the current understanding that the oxidation of NO_2 by OH forming HNO_3 and heterogeneous reactions of N_2O_5 present the major NO_X sinks during the daytime and nighttime, respectively (Liu et al., 2013). According to the above identified major formation pathways, the nitrate formation can be

20   influenced by the availability of NO_x, O_3 and NH_3. NO_X are direct precursors of nitrate formation. O_3 is a major oxidant and supplier of OH radicals at daytime, and is also a precursor of N_2O_5 at night. NH_3 may prompt the partitioning of HNO_3 to the aerosols, and alter the aerosol acidity that affects not only the partitioning of HNO_3 but also the uptake of N_2O_5.

25   Therefore, we further examined the dependence of nitrate formation to NO_2, O_3 and NH_3 at the three sites by sensitivity analyses. Sensitivity modeling calculations were conducted by adjusting the concentrations of the target species (NO_2 or O_3 or NH_3) by X times (i.e., 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.2 and 1.5), and the other settings remained unchanged with the base simulations. The difference in the simulated NO_3^- concentrations between base and sensitivity

runs should reflect the impact of the change in the target species on the nitrate formation. The sensitivity modeling results for the daytime cases are documented in Figure 6. Similar results were derived from the three different study areas. At daytime, the nitrate formation was the most sensitive to NO_2, a necessary precursor of NO_3^- aerosol. It was also sensitive to a lesser

5   extent to O_3, which is a major OH source and thus affects the gaseous HNO_3 formation. An interesting finding was the dependence of nitrate formation to the abundance of NH_3. Adjusting (neither increasing nor decreasing) the currently measured NH_3 concentrations by up to 50% would not lead to significant changes in the model-simulated NO_3^-, whilst further reduction of NH_3 (c.a., more than 50%-80%) would result in a significant decrease of NO_3^-.

10   This indicates that NH_3 plays an important role in the nitrate formation, but it is now highly in excess in the NCP region so that the nitrate formation is somewhat insensitive to NH_3.

Figure 7 presents the dependence of nitrate formation to NO_2, O_3 and NH_3 for the nighttime cases. Again, the results obtained from the three study sites were similar. Nitrate formation was very sensitive to both of NO_2 and O_3. Adjusting the abundances of NO_2 or O_3

15   would lead to almost a linear response in the model-simulated nitrate formation. As discussed above, the nocturnal nitrate formation was mainly controlled by the hydrolysis reactions of N_2O_5, which is the product of the reactions of NO_2 with O_3. In comparison, nitrate formation was not sensitive to NH_3 at all three sites. Furthermore, large reductions of NH_3 (c.a. >60% at Yucheng and >90% in Ji'nan) would give a slight increase of the NO_3^- aerosol formation.

20   This should be due to the increase of aerosol acidity by reducing the NH_3 levels. Indeed, the acidic aerosol particles have potentials to prompt the hydrolysis reactions of N_2O_5 (Pathak et al., 2009 and 2011).

3.4.   Implications for control policy

The above analyses revealed the important roles of NO_2 and O_3 in the nitrate formation

25   at three different types of areas. Although NH_3 can facilitate the partitioning of HNO_3 to the aerosol phase, it seems that the summertime nitrate formation is less sensitive to NH_3 due to the NH_3-rich environments in the NCP region. To achieve a comprehensive understanding of the effect of NH_3 on nitrate formation, a large set of theoretical simulations were designed with varying initial concentrations of NO_2 and NH_3. The multi-phase chemical box model

was initialized by a typical pollution and meteorological condition in the NCP region (see Table S3 for the detailed modeling setup), and was run to simulate the daytime nitrate formation from 8:00 to 19:00 LT. The initial concentrations of NO_2 and NH_3 were set to vary in wide ranges of 0-200 ppbv and 0-40 ppbv, to cover a variety of real atmospheric conditions.

5   The dependence of the model-simulated nitrate increment (ΔNO_3^-) to the pair of NO_2 and NH_3 can be established.

Figure 8 shows the contour plot of the model-simulated daytime ΔNO_3^- as a function of NO_2 and NH_3 concentrations. Several interesting aspects are noteworthy from the figure. First, NH_3 indeed plays a very important role in prompting the nitrate formation. A relatively small

10   amount of NH_3 could significantly enhance the nitrate formation efficiency of NO_X. For example, formation of 25 $\mu g\ m^{-3}$ of NO_3^- would consume 116 ppbv of NO_2 in the absence of NH_3, but only need 16 ppbv of NO_2 in the presence of 10 ppbv of NH_3. Second, at high NH_3 conditions (e.g., the right panel of the figure), the nitrate formation becomes to be insensitive to NH_3. Nitrate formation is mainly limited by NO_2 when NH_3 is in excess. Third, the nitrate

15   formation regimes can be classified into three types, namely, "NO_X-limited at NH_3-deficient condition", "NH_3-controlled", and "NO_X-limited at NH_3-rich condition", according to the concentration ratios of NO_2 and NH_3. Identification of the nitrate formation regime is a fundamental step towards the formulation of science-based control policy of nitrate pollution.

Similarly, we also performed theoretical simulations to examine the detailed dependence

20   of nocturnal nitrate formation to both NO_2 and O_3. The detailed model configuration is given in Table S4. The initial concentrations of NO_2 and O_3 were set to vary in the range of 0-80 ppbv to represent various nocturnal environments. The contour plot is shown in Figure 9. It clearly shows the three categories of nighttime nitrate formation regimes, i.e., "NO_X-limited" under high O_3 and low NO_2 conditions, "O_3-limited" at low O_3 and high NO_2 conditions, and

25   "mixed-limited" by both NO_X and O_3. The ambient pollution conditions measured at the three study sites in the present study were generally lie in the mixed-limited regime. Effective control measures could be established based upon the diagnosis of the nitrate formation regimes.

Our findings have important implications for the control policy of regional aerosol

pollution. Our observations demonstrate the increasing trend and serious situation of nitrate pollution over the NCP region. Given the decline of sulfate and primary particles in the recent decade (Wang et al., 2013), nitrate should be a major target for the future control of haze pollution in China. The observation-based modeling analyses in this study suggest that the

5 summertime nitrate formation in the NCP region is mainly controlled by NO_X and O_3 (particularly in nighttime). Recent studies have also confirmed the increasing trends of surface O_3 levels in the past decades in several major fast-developing regions of eastern China (Ding et al., 2008; Xu et al., 2008; Wang et al., 2009b; Xue et al., 2014; Sun et al., 2016). Therefore, further reduction of anthropogenic NO_X emissions and mitigation of

10 regional O_3 pollution should be an efficient way to alleviate the nitrate-driven haze pollution in China. NH_3 also plays a very important role in the nitrate aerosol formation, as a relatively small amount could efficiently prompt the HNO_3-to-NO_3^- partitioning and nitrate formation. However, the summertime nitrate formation seems to be less sensitive to NH_3 in the NCP region, where ambient NH_3 is generally in excess. Indeed, the available field observations of

15 ambient NH_3 confirmed the widespread NH_3-excess chemical environments in polluted regions of northern China in summer (Meng et al., 2018 and references therein). Thus, it looks like that cutting down the NO_X emissions should be more efficient for the current control of nitrate pollution in the NH_3-rich environments. Nevertheless, reduction of NH_3 emissions is still very important for the future aerosol pollution control in North China from a

20 long-term perspective, in light of the fact that the nitrate formation would be largely restricted at NH_3-poor conditions (see Fig 8).

4.   Conclusions

We report recent field measurements of fine particulate nitrate chemistry at three urban, rural and mountain sites in the NCP region. Serious aerosol pollution was observed at all sites,

25 with nitrate accounting for on average 11%-14% of the $PM_{2.5}$. Distinct temporal and spatial distributions of nitrate pollution were found at different sites. The $NO_3^-/PM_{2.5}$ and NO_3^-/SO_4^{2-} ratios have increased significantly in urban Ji'nan over 2005-2015 and at Mt. Tai from 2007 to 2014, highlighting the worsening situation of nitrate pollution in the region. Fine nitrate aerosol was primarily formed via the production of HNO_3 followed by its partitioning to the

aerosol phase at daytime, and by the hydrolysis reactions of N_2O_5 on particles during the night. The daytime nitrate formation was mainly controlled by NO_2 and to a lesser extent to O_3 and NH_3, and the nocturnal formation was controlled by both NO_2 and O_3. NH_3 plays a vital role in the nitrate formation by prompting the partitioning of HNO_3 to particles. A small

5 amount of NH_3 can significantly enhance the efficiency of nitrate formation from NO_X. Given the highly NH_3-excess condition, the summertime nitrate formation was relatively less sensitive to NH_3 in the NCP region. We recommend that further reduction of anthropogenic emissions of NO_X should be the most efficient pathway for the current control of nitrate aerosol, whilst control of regional ozone pollution and NH_3 emissions is very important for

10 the future haze pollution control in China. We note that the present study was only confined to the summer conditions, and the chemical mix of NO_2, O_3 and NH_3 should be different in the wintertime. It would be expected that NH_3 plays a more important role in the nitrate formation in winter when the NO_X concentrations are higher with relatively lower levels of O_3 and NH_3. Further studies are urgently needed to better understand the formation regimes

15 of nitrate aerosol in winter, when the haze pollution is more serious in China.

Acknowledgements

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Table 1. Statistics (average ± standard deviation) of the measured aerosol chemical properties and meteorological conditions in urban Ji'nan, rural Yucheng, and Mt. Tai

Site	Jinan (Urban)	Jinan (Urban)	Yucheng (Rural)	Mt. Tai (Mountain)
Period	May 2014	Aug-Sep 2015	Jun-Jul 2014	Jul-Aug 2014
NO_3^- ($\mu g\ m^{-3}$)	8.8±8.2	7.4±5.1	13.6±10.3	6.0±4.6
SO_4^{2-} ($\mu g\ m^{-3}$)	12.2±7.5	12.7±7.9	23.6±13.4	14.7±8.9
NH_4^+ ($\mu g\ m^{-3}$)	6.8±5.3	11.1±8.2	11.9±7.7	7.3±5.0
$PM_{2.5}$ ($\mu g\ m^{-3}$)	68.4±41.7	59.3±31.8	97.9±53.0	50.2±31.7
$NO_3^-/PM_{2.5}$	0.12±0.06	0.14±0.07	0.14±0.07	0.11±0.05
$[NO_3^-]/[SO_4^{2-}]$	1.04±0.46	0.98±0.49	0.93±0.53	0.62±0.33
NO_2 (ppb)	20.5±9.0	14.1±4.5	16.6±10.7	3.0±2.3
NOR [a]	0.11±0.07	0.16±0.08	0.24±0.13	0.39±0.20
Excess NH_4^+ ($\mu g\ m^{-3}$)[b]	2.6±2.9	5.2±6.4	1.5±2.6	1.4±1.9
T (°C)	22.2±4.2	23.6±3.4	25.4±4.7	18.0±2.7
RH (%)	38.8±19.7	66.0±21.0	70.3±19.8	86.9±12.8

[a] NOR (Nitrate Oxidation Ratio) = $[NO_3^-]/([NO_3^-]+[NO_x])$;

[b] Excess NH_4^+ = $([NH_4^+]-1.5*[SO_4^{2-}]-[NO_3^-])*18$;

5   Note that $[NO_3^-]$, $[NO_x]$, $[NH_4^+]$ and $[SO_4^{2-}]$ are molar concentrations of NO_3^-, NO_x, NH_4^+ and SO_4^{2-}, respectively.
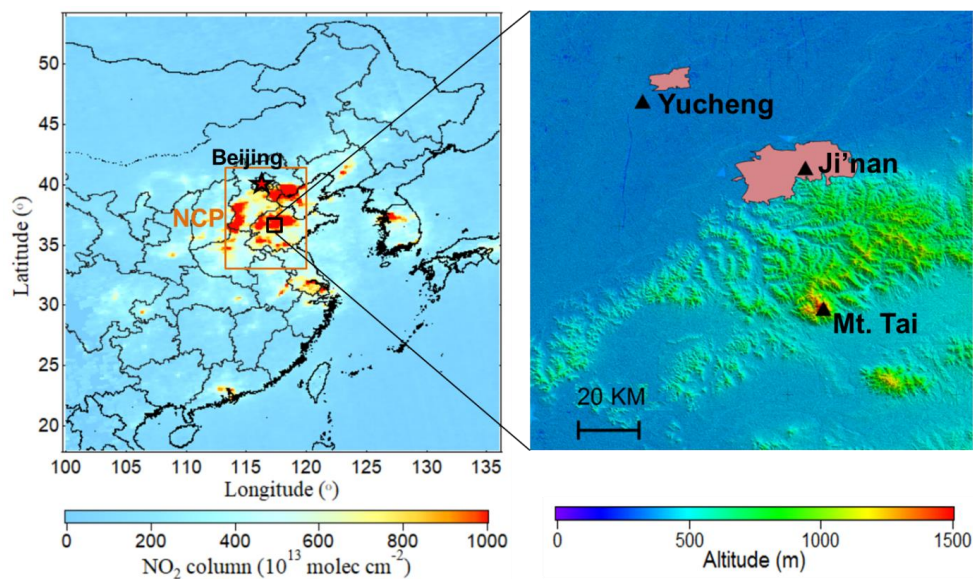
Figure 1. Map showing the study region and three measurement sites. The left map is color-coded with the OMI-retrieved tropospheric NO_2 column density in July 2014, and the right map is color-coded with the topographic height (the pink regions denote urban areas).

24
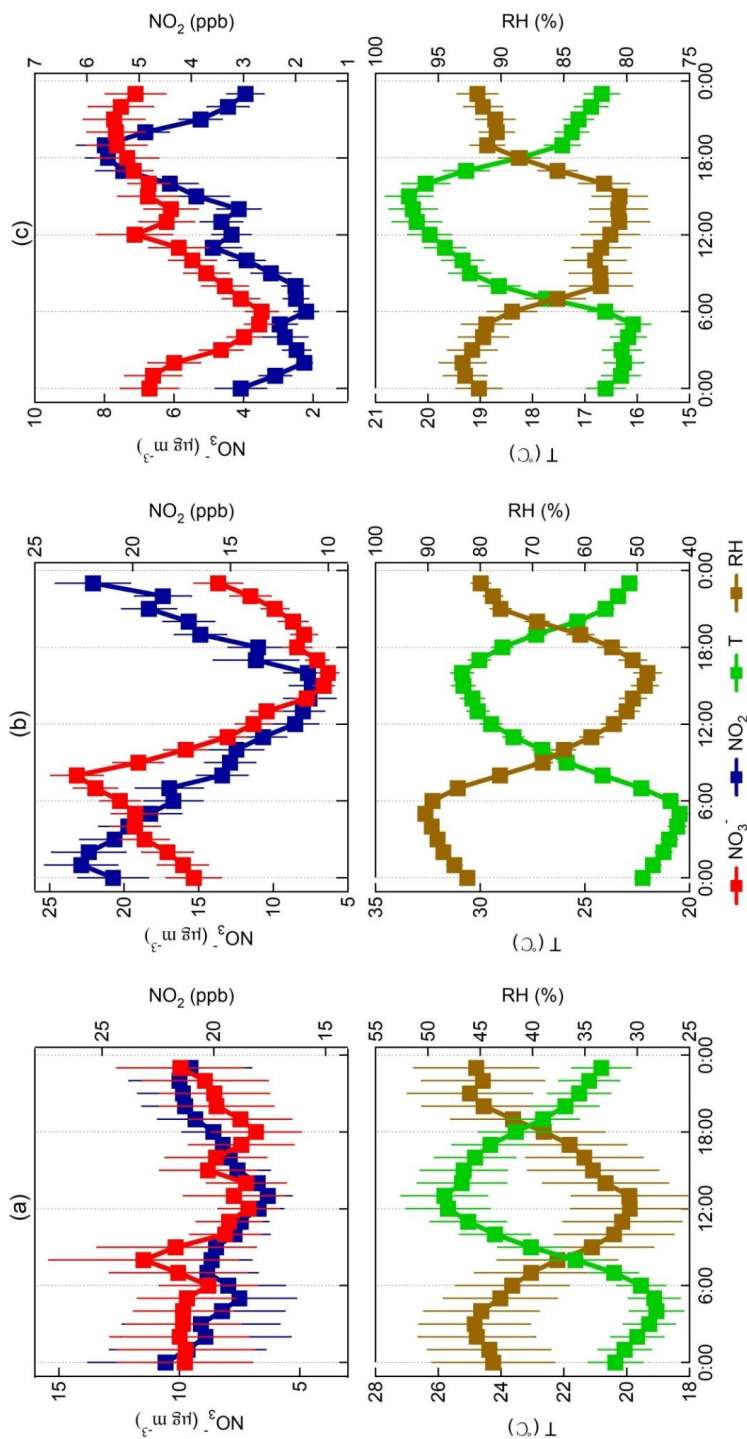
Figure 2. Average diurnal variations of fine particulate NO_3^-, NO_2 and meteorological conditions in (a) urban Ji'nan, (b) rural Yucheng, and (c) Mt. Tai. Error bars stand for the standard errors of the measurements.

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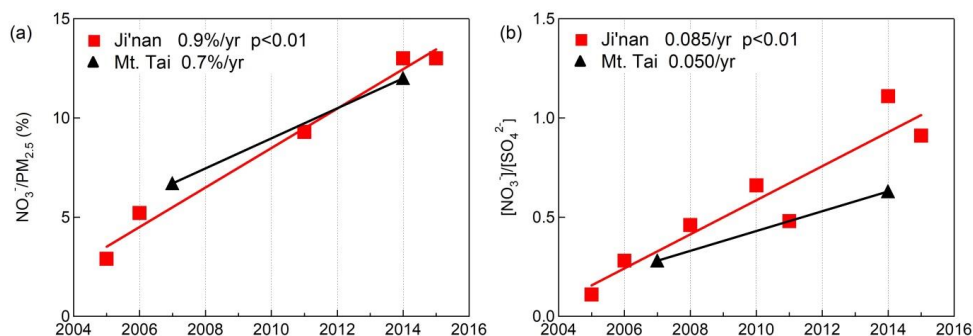
Figure 3. Long-term trends of (a) mass ratio of $NO_3^-/PM_{2.5}$ and (b) molar ratio of NO_3^-/SO_4^{2-} in urban Ji'nan and at Mt. Tai in summertime from 2005 to 2015. The fitted lines are derived from the least square linear regression analysis, with the slopes and p values (95% confidence intervals) denoted.
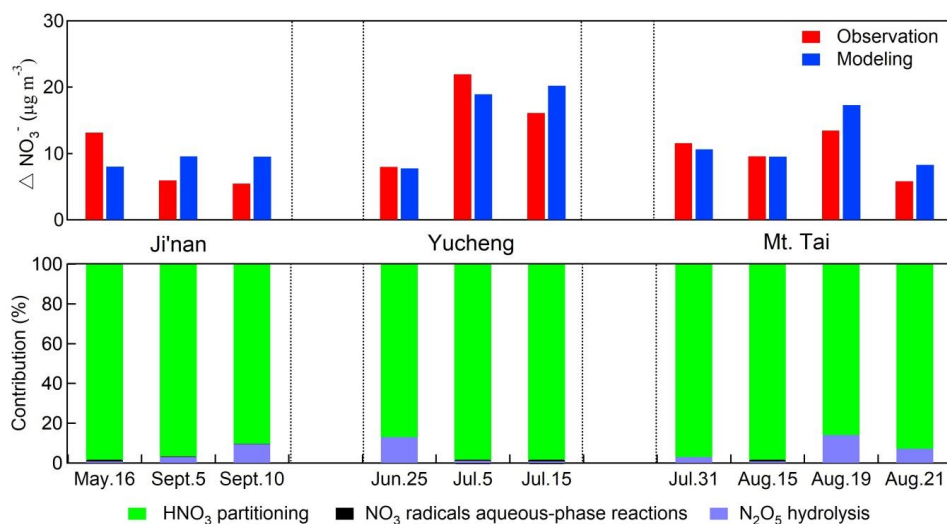

Figure 4. Comparison of the model-simulated versus observed nitrate enhancement (upper panel) as well as the contributions from the major three formation pathways (lower panel) for the daytime cases in urban Ji'nan, rural Yucheng and Mt. Tai.
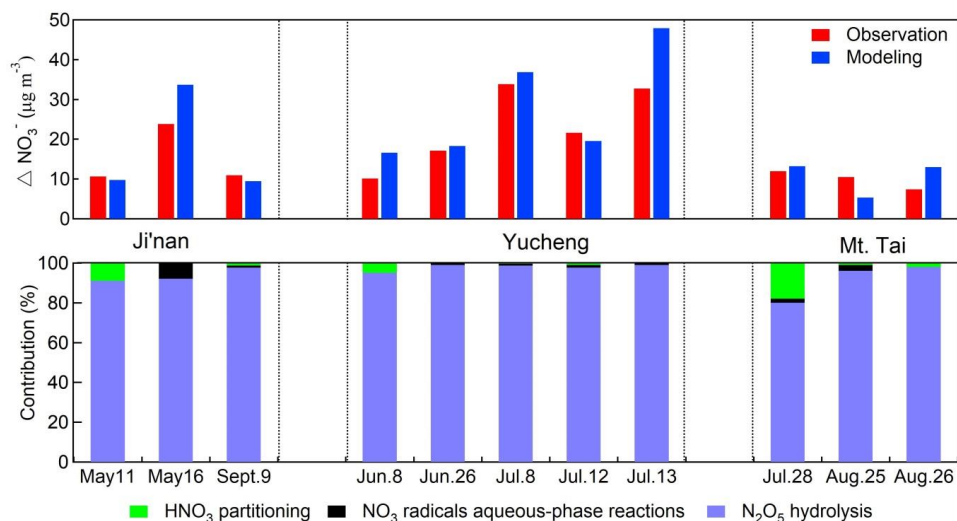
**Figure 5.** The same as Figure 4 but for the selected nocturnal nitrate formation cases.
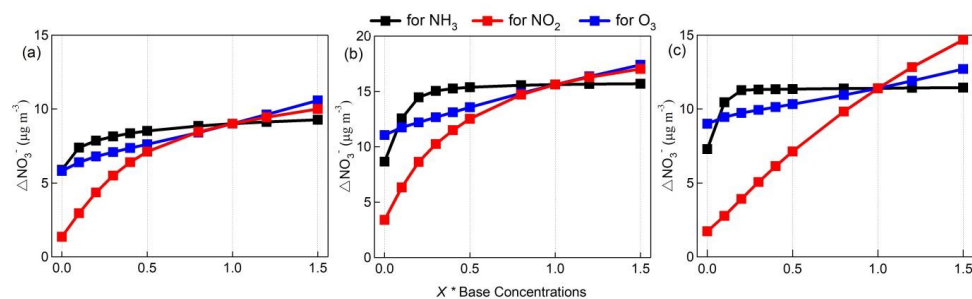
Figure 6. Model-simulated daytime average NO_3^- enhancements as a function of the X times of the base concentrations of NH_3, NO_2 and O_3 in (a) urban Ji'nan, (b) rural Yucheng and (c) Mt. Tai. The results are the average of sensitivity analyses for all selected daytime cases.
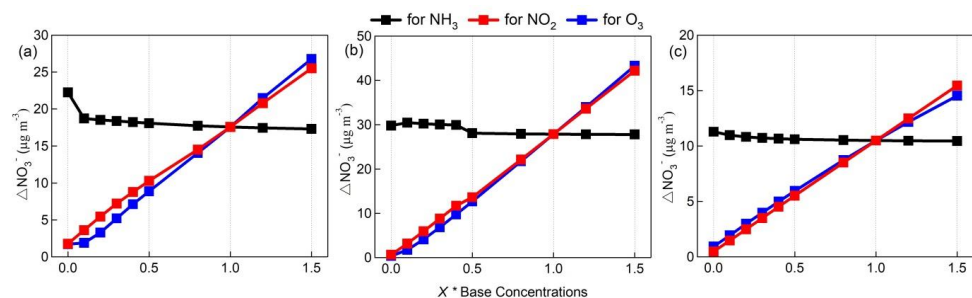
Figure 7. The same as Figure 6 but for the nocturnal nitrate formation cases.
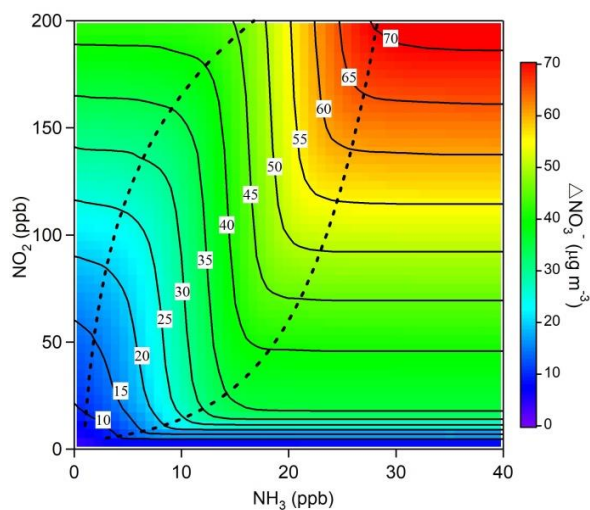
Figure 8. Contour plot of the model-simulated daytime NO_3^- formation as a function of the initial concentrations of NO_2 (0-200 ppbv) and NH_3 (0-40 ppbv).
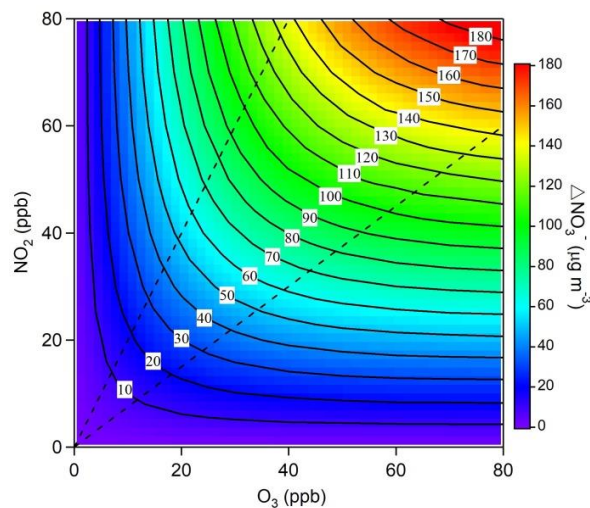
Figure 9. Contour plot of the model-simulated nighttime NO_3^- formation as a function of the initial concentrations of NO_2 (0-80 ppbv) and O_3 (0-80 ppbv).