

Reply to the comments of Anonymous Referee #3

[Atmospheric Chemistry and Physics, MS ID: acp-2021-730]

Title: The formation and mitigation of nitrate pollution: Comparison between urban and suburban environments

General Remarks:

The authors investigated the formation processes of nitrate in both urban and suburban areas using local chemical and meteorological measurements in southern China and a chemical box model. They found that reducing nitrate is essential for reducing the occurrence of aerosol pollution since the higher ratios of nitrate/sulfate occurred during the polluted periods. They further explored the relevant key factors in nitrate chemistry and concluded that it is necessary to integrate emission controls on NO_x and VOCs to have a comprehensive mitigation of nitrate pollution over different environments. This is an interesting and valuable study. I recommend publishing it in ACP after the authors make the following major modifications.

Reply: We thank the reviewer for the comments. These comments are valuable and very helpful for revising and improving our paper, as well as the important guiding significance to our study. We reviewed these comments carefully and made necessary revisions according to the reviewer's comments. Our Replies to the comments are itemized below in blue color.

Major comments:

1. It may be worth adding one more simulation at the GIG station with a similar methodology adopted at the HeShen, i.e., allowing ground measured chemical fields to evolve freely. There are two advantages to this approach: 1). Such a simulation provides a clean comparison between GIG and HeShan for their chemical evolution in NBL and RL, and such a comparison is key for this study. 2). The evaluation of this new simulation against their conducted GIG simulation (i.e., using the observed tower-level

data) targets the end nitrate products directly, not only at a couple of important tracers as shown in Fig S6.

Reply: We thank the reviewer's suggestion. Actually, the simulation suggested by the reviewer which treated the GIG site with a similar methodology at the Heshan site, allowing the ground measured chemical fields to evolve freely, has been already included in the original manuscript (original Fig.S6). These results were presented in **Fig.S11** in the revised manuscript as follows. The simulated results of trace gases (NO_2 , NO_x , O_3 and O_x) agreed well with the observed data at the 488m Canton Tower site. Based on the reliability of the test simulation, we modeled the residual layer chemistry at the Heshan site.

1) The simulated comparison about nitrate production rate from N_2O_5 uptake between GIG and Heshan with the same methodology is shown in the following Fig. R4 (a, b), indicating the chemical evolution in the nocturnal layer and residual layer. The nitrate production rate from N_2O_5 uptake in the residual layer was significantly higher than that in the nocturnal layer at the GIG site, suggesting active nocturnal chemistry in the residual layer. It was consistent with the analysis in the manuscript which suggested the importance of the nitrate production from N_2O_5 uptake in the residual layer at the GIG site. At the Heshan site, the nitrate production rate from N_2O_5 uptake in the residual layer was comparable with that in the nocturnal layer, with no significant difference between the two layers.

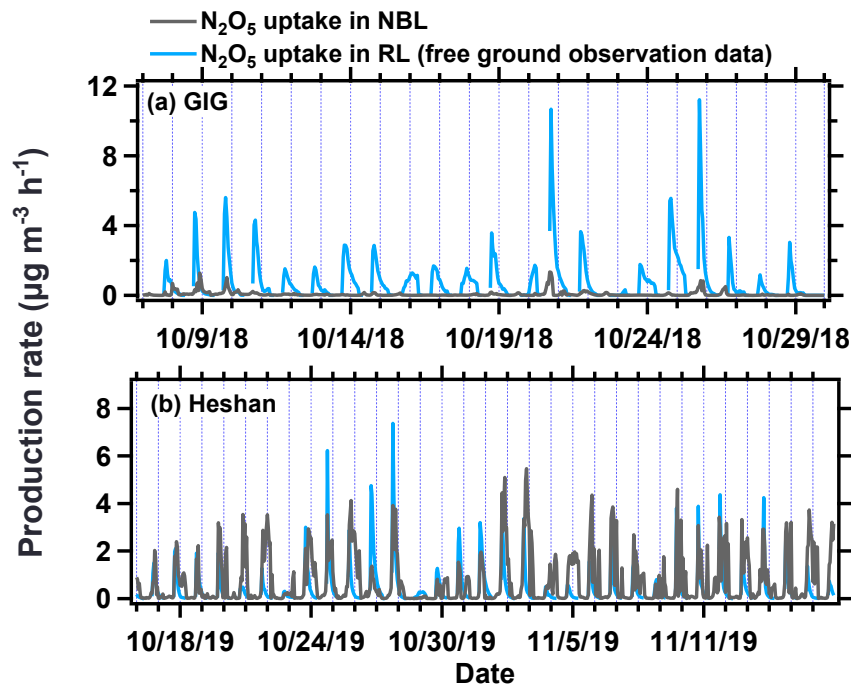


Figure.R4 Time series of simulated nitrate production rate from N_2O_5 uptake in the nocturnal layer and residual layer at the GIG and Heshan site with the same methodology, which adopted ground observation data as the initial input in the residual layer.

2) We have added the modeled nitrate and nitrate production rate from N_2O_5 uptake with the observation from the GIG and 488m Canton Tower site as initial input in the residual layer in Fig.S11 (e) ~ (f) of the revised manuscript as follows. The results agreed well with each other. We have mentioned this point in line 75 ~ 78 in the revised Text S1 in SI as follows.

“In addition, the simulated nitrate and nitrate production rate from N_2O_5 uptake with the observation at the GIG site and 488 m Canton Tower as initial input were also compared in Fig.S11 (e ~ f), showing good agreement. Thus, we adopted this simulation method to perform the simulations at the Heshan site.”

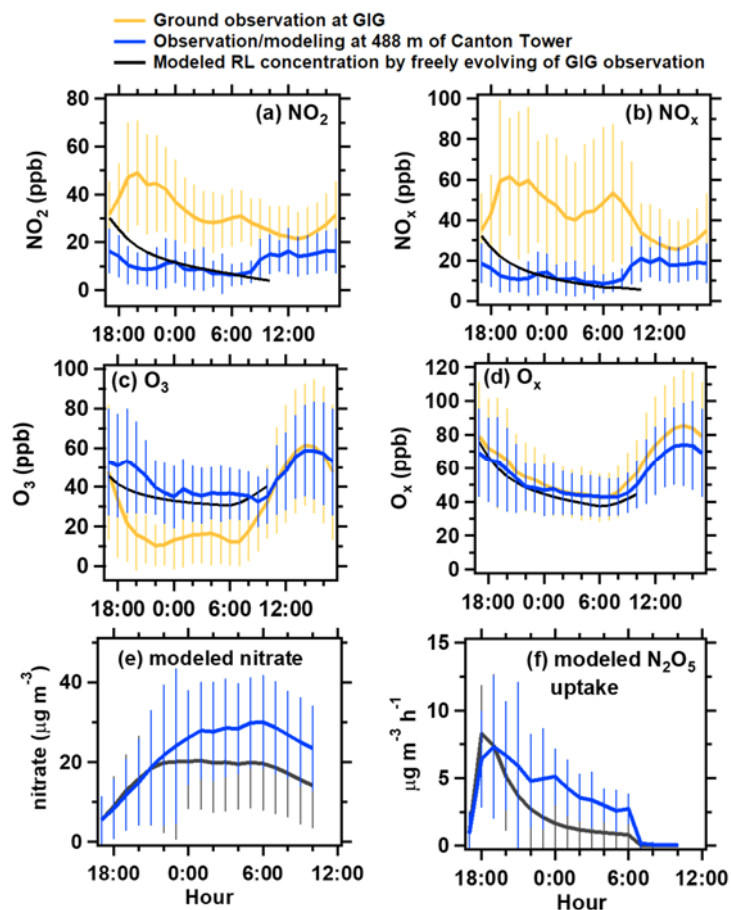


Figure S11. Time series of the simulated trace gases ((a) NO_2 , (b) NO_x , (c) O_3 and (d) O_x) in the RL, when the observations at 17:00 at GIG were setting as the initial inputs of the RL simulation and all chemical species were freely evolved in the box model. (e) the simulated nitrate and (f) nitrate production rate from N_2O_5 uptake with the observation data at the GIG (black line) and 488m Canton Tower (blue line) as the initial inputs in the RL. The observations at GIG and 488m site of Canton Tower are also shown for comparison. The error bars represent the standard deviation of the observations.

2. I am concerned with the roles of SO_4^{2-} and NH_3 in influencing NO_3^- chemistry. For example, even though the molar ratios of measured $[\text{NH}_4^+]$ to the sum of $2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-]$ are close to 1.0. at the two sites, that does not mean the regions have sufficient NH_3 to further neutralize nitrate as those experiments shown in Figs 8-9. One potential test is to check whether doubling NH_3 emissions yields doubling predicted

NO₃⁻.

Reply: We thank the reviewer for the insightful comment. Generally, H₂SO₄ is firstly neutralized by NH₃ to form sulfate due to its lower saturated vapor pressure. Then, the rest of NH₃ will react with HNO₃ to produce ammonium nitrate. The influence of sulfate and NH₃ on the nitrate production both lies on the available of NH₃ to neutralize nitrate. Thus, the test mentioned by you are needed to clarify the NH₃ effect on the nitrate formation.

Here, we use the thermodynamic ISORROPIA II model to evaluate the effect of NH₃ and sulfate in the nitrate formation. The same evaluation has been reported in the studies of Guo et al. (2018) and Nenes et al. (2020), which both suggest the particle fraction of nitrate in the sum of HNO₃ and nitrate ($\epsilon(\text{NO}_3^-)$) was affected by the pH values. In this work the ISORROPIA II model is based on the available input of total gas and particulate matter (HNO₃ + nitrate, NH₃ + ammonium, sulfate, and chloride), T and RH, and is run in the “forward” and “metastable” mode. The ISORROPIA II modeled results of nitrate, ammonium, HNO₃, and NH₃ at the GIG and Heshan site were displayed in **Fig.S8 ~ Fig.S9** in the revised manuscript as follows. The modeled components from ISORROPIA II showed good correlations with the observed concentrations at both sites.

The results of experiment by increasing total ammonium (NH_x, ammonium + NH₃) by 50% and 100%, keeping other parameters constant, are listed in Table R1. When doubling the total ammonium, the predicted nitrate increased 25% compared with the nitrate in the base case, suggesting doubling NH₃ would benefit the production of nitrate but not in a linear increase. This reveals both NH₃ and HNO₃ are important precursors for nitrate. It did not affect the experiments shown in original Figs 8-9. As NH₃ plays an important role in the nitrate partitioning, we further evaluated the effect of NH₃ and sulfate reduction by thermodynamic ISORROPIA II model in this study.

Table R1 ISORROPIA II predicted average nitrate and relative changes

ISORROPIA model case	predicted average nitrate ($\mu\text{g m}^{-3}$)	Relative changes
Base case	9.1	—
+ 50% NH _x	10.7	+ 18%
+ 100% NH _x	11.4	+ 25%

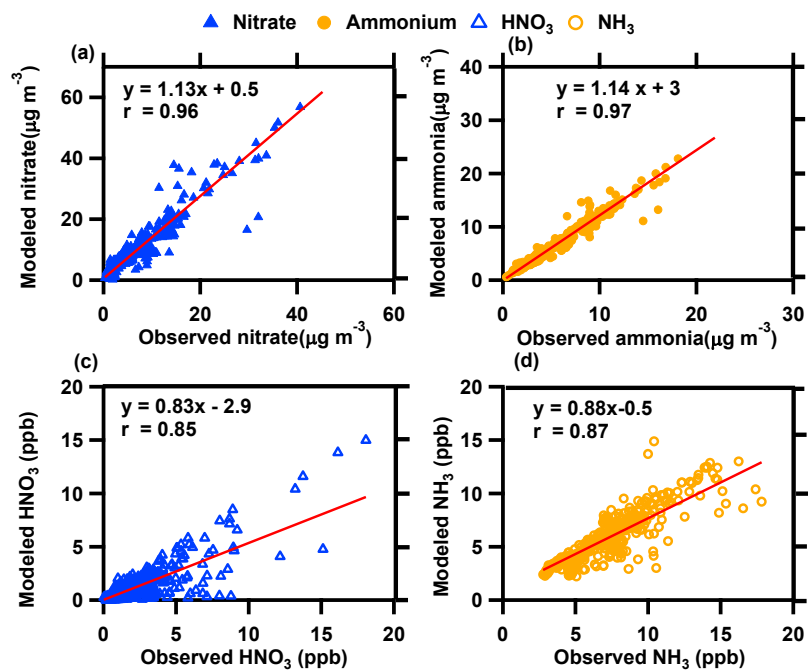


Figure S8. Scatter plot of observations vs ISORROPIA II modeled results of nitrate, ammonium, HNO₃ and NH₃ at the GIG site during the study period.

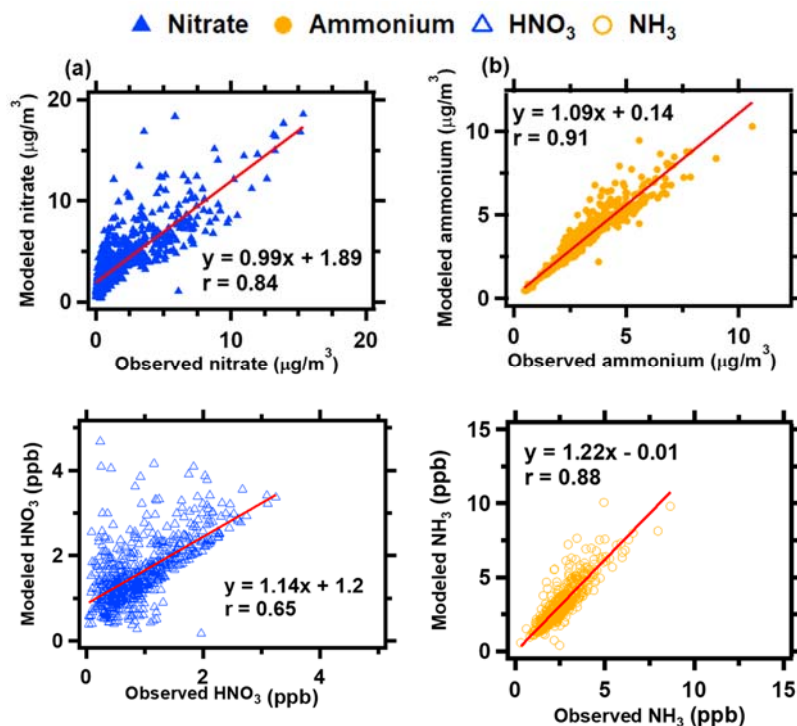


Figure S9. Scatter plot of observations vs ISORROPIAII modeled results of nitrate, ammonium, HNO₃ and NH₃ at the Heshan site during the study period.

The effect of ammonium on nitrate partitioning is related with the pH value. Thus, the aerosol pH at the GIG and Heshan site is also calculated. The aerosol pH, based on

the aerosol acidity and water content, is calculated by the following equation:

$$pH = -\log_{10} \frac{1000 H_{air}^+}{ALWC}$$

where H_{air}^+ ($\mu\text{g m}^{-3}$) is the hydronium concentration of the equilibrium particle and ALWC ($\mu\text{g m}^{-3}$) is the aerosol water content from ISORROPIA II modeled results.

In the ISORROPIA base model, the fraction of nitrate ($\varepsilon(\text{NO}_3^-)$) in the sum of HNO_3 + nitrate against pH at the GIG and Heshan site are depicted in **Fig.6** in the revised manuscript as follows. The pH data are colored by relative humidity and fit to an “s-curve”, as shown in Guo et al. (2018). The clustering of $\varepsilon(\text{NO}_3^-)$ data, mainly located between the pH values of 1~3, was sensitive to the changes in pH, and therefore may be sensitive to the changes of NH_3 and sulfate.

In the reduction cases, the input total ammonium (NH_x , ammonium + NH_3) and sulfate were reduced from 10% to 90% relative to the ISORROPIA II base model, respectively, while keeping other parameters constant. The response of ISORROPIA II simulated nitrate concentration and aerosol pH to changes in NH_x and SO_4^{2-} are shown in **Fig.7** in the revised manuscript as follows. The nitrate concentration decreased with the reduction of NH_x , and had little variation with the reduction of SO_4^{2-} (Fig.7 (a ~ b)) at both sites. Along with the reduction of NH_x , the pH values decreased significantly (Fig.7 (c ~ d)), which caused the further decrease of $\varepsilon(\text{NO}_3^-)$. The pH values showed a bit increase with the reduction of SO_4^{2-} , which may be caused by that there would be more available ammonium neutralized the hydronium. It is consistent with the study of Guo et al. (2018) and Nenes et al. (2020), which suggests the partitioning of nitrate was affected by the NH_3 in the pH values between 1~3. The partitioning of nitrate increased with the reduction of sulfate suggests the limited role of sulfate reduction on the mitigation of nitrate.

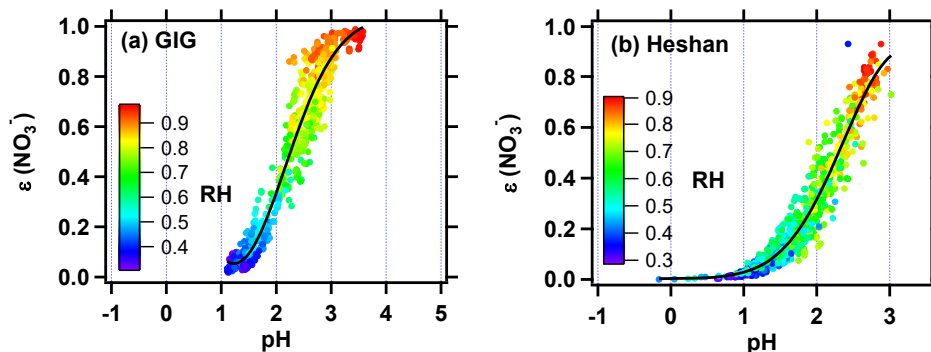


Figure 6. The fraction of total nitrate that is partitioned to the particle phase $\epsilon(\text{NO}_3^-)$ against aerosol pH. The pH data are colored by relative humidity and fit to an “s-curve” in black line, as shown in Guo et al. (2018).

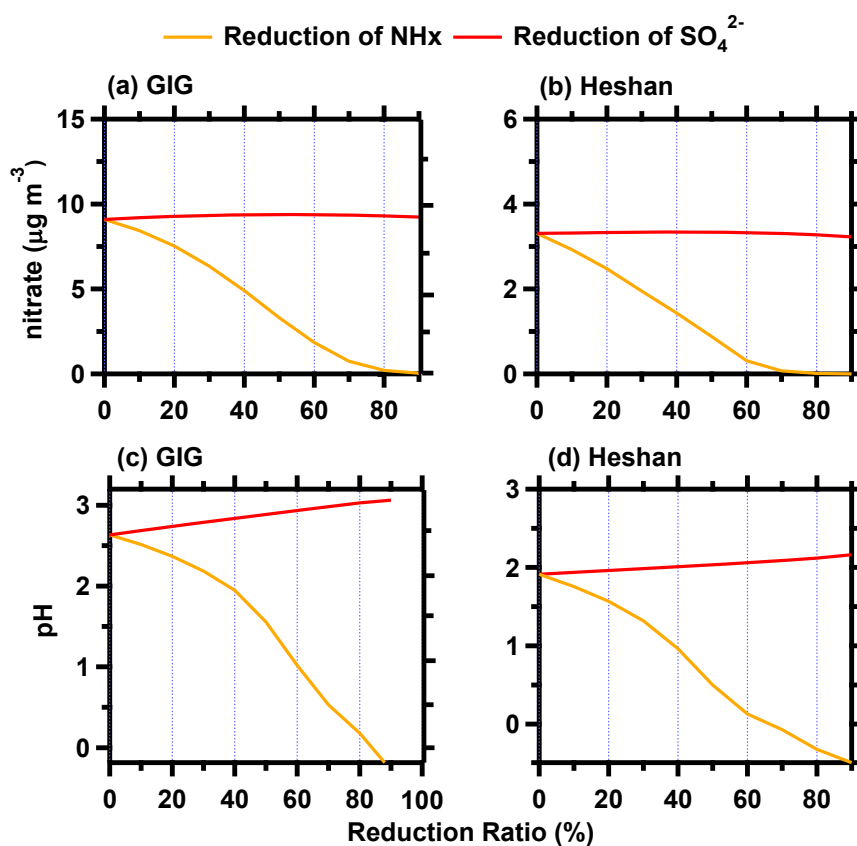


Figure 7. ISORROPIA-predicted average nitrate (a, b) and pH (c, d) as a function of changes in NH_x (ammonium + NH_3 , orange line) and SO_4^{2-} (red line) at the GIG and Heshan site during the study period.

The ISORROPIA II model setting was described in Test S2 in the revised SI manuscript as follows. The influence of NH_3 reduction on the nitrate partitioning based on ISORROPIA II model results was added in line 378 ~ 407 in the revised manuscript.

“Text S2 Thermodynamic ISORROPIA II model description

The presence of HNO₃ and NH₃ are conducive to form ammonium nitrate, which influenced by the aerosol pH and partitioning process of nitrate (Guo et al., 2018; Nenes et al., 2020). Thus, the thermodynamic ISORROPIA II model was used to evaluate the NH₃ and sulfate impacts on the gas-particle partitioning process of nitrate (Fountoukis and Nenes, 2007). The model is run in the “forward” and “metastable” mode, which is used to calculate the gas-particle equilibrium concentrations. The model is based on the available input of total gas and particulate measured matter (HNO₃ + nitrate, NH₃ + ammonium, sulfate, and chloride), T and RH. The low concentration of nonvolatile cations (such as sodium, calcium, potassium, magnesium) in the PRD region is assumed to have minor impact on the thermodynamic equilibrium in PM_{1.0} (Franchin et al., 2018; Guo et al., 2018).”

We described the results of ISORROPIA II model in **Line 378 ~ 407** in the revised manuscript:

“The ISORROPIA II model setting is described in Test S2 in detail. The ISORROPIA II modeled results of nitrate, ammonium, HNO₃, and NH₃ at the GIG and Heshan site were displayed in Fig.S8 ~ Fig.S9. The particle-phase nitrate and ammonium showed a bit overestimation at the GIG site, while the gas-phase HNO₃ and NH₃ showed overestimation at the Heshan site. Overall, the simulated components showed good correlations with the observed concentrations at both sites. We use the ISORROPIA II model results to evaluate the fraction of total nitrate that is partitioned to the aerosol phase $\epsilon(\text{NO}_3^-)$ against aerosol pH. Aerosol pH, which depends on the aerosol acidity and water content, was calculated by the following equation:

$$\text{pH} = -\log_{10} \frac{1000 H_{\text{air}}^+}{\text{ALWC}} \quad (\text{Eq.5})$$

where H_{air}^+ ($\mu\text{g m}^{-3}$) is the hydronium concentration of the equilibrium particle and ALWC ($\mu\text{g m}^{-3}$) is the aerosol water content from ISORROPIA II simulation.

The $\epsilon(\text{NO}_3^-)$ against pH at the GIG and Heshan site are shown in Fig.6. The

pH data are colored by relative humidity and fit to an “s-curve” as in Guo et al. (2018). The clustering of pH data, mainly located between 1~ 3, and the $\epsilon(\text{NO}_3^-)$ are sensitive to the change of pH. To further evaluate the sensitivity of NH_3 and sulfate on this effect, the input of total ammonium (NH_x , ammonium + NH_3) and sulfate were reduced from 10% to 90% relative to the ISORROPIA II base model, respectively, while keeping other parameters constant. The response of ISORROPIA II simulated nitrate concentration and aerosol pH to changes in NH_x and SO_4^{2-} are shown in Fig.7. The nitrate concentration decreased with the reduction of NH_x , and had little variation with the reduction of SO_4^{2-} (Fig.7 (a ~ b)) at both sites. Along with the reduction of NH_x , the pH values decreased significantly (Fig.7 (c ~ d)), which caused the further decrease of $\epsilon(\text{NO}_3^-)$. The pH values showed a bit increase with the reduction of SO_4^{2-} , which may be caused by that there would be more available ammonium neutralized the hydronium. It is consistent with the study of Guo et al. (2018) and Nenes et al. (2020), suggesting the partitioning of nitrate was also affected by the NH_3 in the pH values between 1~3. Thus, the control of NH_3 is effective for the reduction of nitrate by affecting the partitioning process of nitrate at both GIG and Heshan site in this study. The partitioning of nitrate increased with the reduction of sulfate suggests the limited role of sulfate reduction on the mitigation of nitrate.”

3. It would be good to explain the diffusive time scale used. Is the lifetime of 24 h applied to every species or only for the secondary species? How sensitive is it to the simulation results? Is there any evidence or reference for the chosen lifetime?

Reply: We thank the reviewer for the constructive comments. A “physical loss” lifetime of 6 h ~ 48 h is used to prevent long-lived species to build-up (Wolfe et al., 2016). The empirical lifetime of 24 h was often used in box model and determined through the combination with the performance of OVOCs and target species (Lu et al., 2017;Decker et al., 2019;Zhao et al., 2020;Novak and Bertram, 2020;Souri et al., 2020;Liu et al., 2021). A lifetime of 8 h was used in the study of nitrate formation at the Heshan site in 2017 by Yun et al. (2018). We did the sensitivity tests combined with the unconstrained OVOCs species (the sum of MVK + MACR), O_3 , HNO_3 and nitrate at

the GIG and Heshan site, as shown in **Fig.S3** and **Fig.S4** in the revised manuscript. A dilution rate of 24 h^{-1} for all species was determined at the GIG site, due to the good consistency between the simulation and observation for the chosen species. Comparing with the diurnal average observation, the simulation diurnal data had relative minor deviation with the observation by dilution constant of 8 h^{-1} . The average variations were -19% for MVK + MACR, -10% for O_3 , 25% for HNO_3 , and 12% for nitrate with the dilution constant of 8 h^{-1} at the Heshan site. Thus, the lifetime of 24 h and 8 h were used at the GIG and Heshan site, respectively. We have addressed this issue in the revised manuscript and SI as follows.

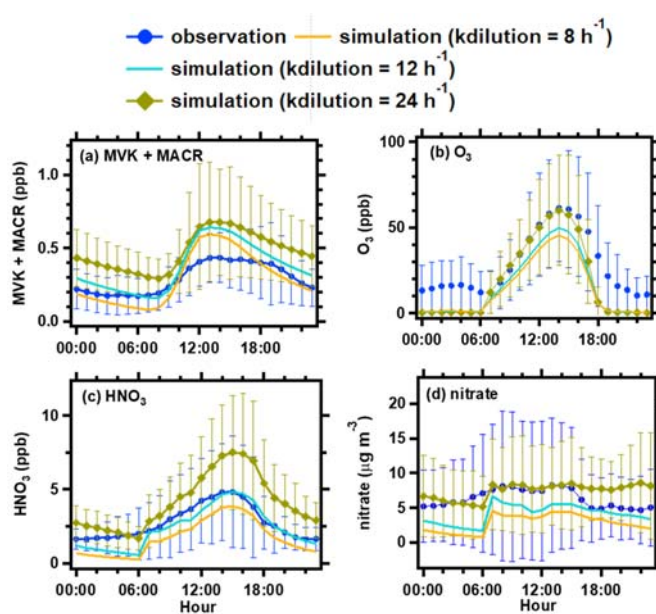


Figure.S2 Sensitivity tests with different dilution constant (kdilution) at the GIG site by box model.

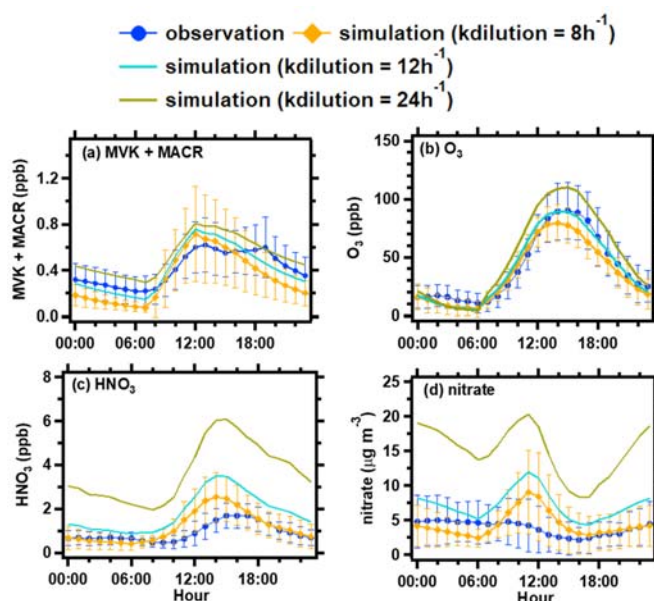


Figure.S3 Sensitivity tests with different dilution constant (kdilution) at the Heshan site by box model.

Line 242~246 in the Method of revised manuscript:

“To prevent the build-up of long-lived species to unreasonable levels, an additional physical dilution process was applied in the model (Lu et al., 2017;Decker et al., 2019;Novak and Bertram, 2020;Liu et al., 2021). To achieve agreement with the observation, a life time of 24h and 8 h were used at the GIG and Heshan site, respectively. The sensitivity tests with different dilution constant at the GIG and Heshan site were shown in Fig.S2 and Fig.S3, respectively.”

Line 79~89 in the revised SI:

“The physical loss that parameterized as a first order dilution process was the same as the daytime simulation in both the NBL and RL. We did the sensitivity tests combined with the unconstrained OVOCs species (MVK+MACR), O₃, HNO₃ and nitrate at the GIG and Heshan site, as shown in Fig.S2 and Fig.S3. A dilution rate of 24 h⁻¹ for all species was determined at the GIG site, due to the good consistency between the simulation and observation for the chosen species. Comparing with the diurnal average observation, the simulated diurnal data had relative minor deviation with the observation by dilution constant of 8 h⁻¹. The

average variations were -19% for MVK + MACR, -10% for O₃, 25% for HNO₃, and 12% for nitrate with the dilution constant of 8 h⁻¹ at the Heshan site. Thus, the dilution constant of 24 h and 8 h was used at the GIG and Heshan site, respectively.”

4. I also feel it is hard to follow the description of the measurement at the three sites and of the experiment set up. The authors might consider summarizing the relevant important information in tables. Clarification is also needed of several definitions used in the text, such as residual layer, transition regime, uptake rate. See more details in specific comments.

Reply: We thank the reviewer for the useful suggestion. We have revised the measurement information at the three sites in **Table S1 ~ Table S3** separately in the revised manuscript, and summarized the important modeling information in **Table S5** in the revised manuscript as follows. Some definitions about residual layer, transition regime and uptake rate were revised in the manuscript, according to the reviewer’s specific comments.

Table S1. Measured chemical species and the analytical methods, time resolution, limit of detection, the accuracy of the instruments used for different measured species, and sampling period at the GIG site.

chemical species	methods	time resolution	limit of detection	accuracy	sampling period
NMHC	GC-FID-MS	1 h	10 ~ 84 ppt	0.65% ~ 9.14%	2018.09.14~2018.11.19
Formaldehyde	PTR-TOF-MS	1 min	20 ppt	11.80%	2018.09.12~2018.11.19
Acetaldehyde	PTR-TOF-MS	1 min	33 ppt	12.50%	2018.09.12~2018.11.19
MVK+MACR	PTR-TOF-MS	1min	8 ppt	5.8%	2018.09.12~2018.11.19
HNO ₃	TOF-CIMS	1 min	< 10 ppt	± 20%	2018.10.07~2018.11.19
N ₂ O ₅	TOF-CIMS	1 min	< 10 ppt	± 25%	2018.10.07~2018.11.19
CINO ₂	TOF-CIMS	1 min	< 10 ppt	± 25%	2018.10.07~2018.11.19
NH ₃	CRDS	1 min	1.0 ppb	± 35%	2018.09.30~2018.10.29
HONO	LOPAP	1 min	6.0 ppt	± 20%	2018.09.28~2018.11.19
O ₃	UV absorption	1 min	0.5 ppb	± 10%	2018.09.11~2018.11.20
NO/NO ₂ /NO _x	Chemiluminescence	1 min	0.4 ppb	± 10%	2018.09.11~2018.11.20
CO	Infrared absorption	1 min	0.04 ppm	± 10%	2018.09.11~2018.11.20
NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺	TOF-AMS	300 s	0.005~0.024 μg m ⁻³	± 20%	2018.09.29~2018.11.20
Sa	APS (500 nm to 20 μm), SMPS (10 to 650 nm)	300s	—	± 10%	2018.09.29~2018.11.20
Photolysis frequencies	Spectrometer	10 s	—	± 10%	2018.09.18~2018.11.19

Table S2. Measured chemical species and the analytical methods, time resolution, limit of detection, the accuracy of the instruments used for different measured species, and sampling period at the Canton Tower site.

Location	chemical species	methods	time resolution	limit of detection	accuracy	sampling period
Ground site and 488 m site	O ₃	UV absorption	1 min	0.5 ppb	± 10%	2018.09.20~2018.11.20
	NO/NO ₂ /NO _x	Chemiluminescence	1 min	0.4 ppb	± 10%	2018.09.20~2018.11.20
	CO	Infrared absorption	1 min	0.04 ppm	± 10%	2018.09.20~2018.11.20

Table S3. Measured chemical species and the analytical methods, time resolution, limit of detection, the accuracy of the instruments used for different measured species, and sampling period at the Heshan site.

chemical species	methods	time resolution	limit of detection	accuracy	sampling period
NMHC	GC-FID-MS	1 h	0.01 ~ 0.41 ppb	—	2019.09.25~2019.11.16
Formaldehyde	PTR-TOF-MS	1 min	29 ppt	15.6%	2019.10.16~2019.11.16
Acetaldehyde	PTR-TOF-MS	1 min	18 ppt	4.2%	2019.10.16~2019.11.16
MVK+MACR	PTR-TOF-MS	1min	7.3 ppt	5%	2019.10.16~2019.11.16
HNO ₃	TOF-CIMS	1 min	< 10 ppt	± 20%	2019.10.01~2019.11.16
N ₂ O ₅	TOF-CIMS	1 min	< 10 ppt	± 25%	2019.10.01~2019.11.16
CINO ₂	TOF-CIMS	1 min	< 10 ppt	± 25%	2019.10.01~2019.11.16
NH ₃	GAC	30 mins	0.08 ppb	—	2019.09.25~2019.11.16
HONO	GAC	30 mins	0.1 ppb	—	2019.09.25~2019.11.16
O ₃	UV absorption	1 min	0.5 ppb	± 10%	2019.09.25~2019.11.16
NO/NO ₂ /NO _x	Chemiluminescence	1 min	0.4 ppb	± 10%	2019.09.25~2019.11.16
CO	Infrared absorption	1 min	0.04 ppm	± 10%	2019.09.25~2019.11.16
NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺	TOF-AMS	300 s	0.005~0.024 μg m ⁻³	± 20%	2019.10.02~2019.11.16
Sa	APS (500 nm to 20 μm), SMPS (10 to 650 nm)	300s	—	± 10%	2019.10.02~2019.11.16
Photolysis frequencies	Spectrometer	10 s	—	± 10%	2019.09.28~2019.11.16

Table S5 Box model scenarios performed at the GIG and Heshan site

Site	Scenarios	description about simulation	Other information
GIG	base case (S0)	set lifetime as 24 h, without N ₂ O ₅ constrained	NBL: with observation at the GIG site; RL: with Observation at the 488m site of Canton Tower
	S1	set lifetime as 24 h, with N ₂ O ₅ constrained	
Heshan	base case (S0)	set lifetime as 8 h, without N ₂ O ₅ constrained	NBL: with observation at the Heshan site; RL: with observation at the Heshan site freely evolved
	S1	set lifetime as 8 h, with N ₂ O ₅ constrained	

Specific comments:

1. Page 3 lines 64-65: The increase of NH₃ is also a reason.

Reply: We thank the reviewer for the useful comment. In the limited regulation of NH₃ emission, larger emission reduction of SO₂ than NO_x was implemented in recent years, more free ammonia could react with gas HNO₃ (Guo et al., 2018;Liu et al., 2019;Zhai et al., 2021). Indeed, this is also one reason that the percentage of nitrate in PM_{2.5} increased in recent years. We revised the original sentence (original line 64 ~ 65) “Due to the larger emission reduction of SO₂ than NO_x was implemented since the clean air actions in China” in **Page 3 line 65** in the revised manuscript as follows.

“Due to the larger emission reduction of SO₂ than NO_x and little change of NH₃ since the implementation of the clean air actions in China (Guo et al., 2018;Liu et al., 2019;Zhai et al., 2021), a considerable increase in the nitrate fractions in aerosols has been observed in haze periods in the northern China Plain (Wen et al., 2018;Li et al., 2018;Lu et al., 2013;Fu et al., 2020), southern China (Pathak et al., 2009;Pathak et al., 2011) and eastern China (Griffith et al., 2015;Tao et al., 2018;Yun et al., 2018;Li et al., 2018), which indicates the growing significance of nitrate in the formation of haze events.”

2. Page 3 line 77: The chemistry processes described here are for inorganic nitrate only.

Thus, the term “Particulate nitrate” should be “Particulate inorganic nitrate” to be more accurate.

Reply: We have revised the term “Particulate nitrate” to **“Particulate inorganic nitrate”** in **Page 3 line 79** as follows.

“Particulate inorganic nitrate is primarily produced through two processes: the photochemical reaction of hydroxyl radical (OH) and NO₂ during daytime (R1) and the heterogeneous uptake of N₂O₅ (R2–R5) during nighttime.”

3. Page 3 lines 84-85: Please check Table 1 and the corresponding discussion for the gamma values used in the nine global chemistry models in Bian et al., (2017).

Reply: We have checked the reference about **Bian et al., (2017)**, and updated the references in **Page 4 line 109**.

4. Page 4 line 93: Please define “the residual layer” here.

Reply: We thank the reviewer for the comment. The nocturnal layer and residual layer are defined at the beginning of that paragraph in **Page 4 line 112 ~ 114** in the revised manuscript as follows.

“With the radiative cooling in the afternoon, the mixed layer decoupled into a steady, near surface nocturnal boundary layer (NBL) and a residual layer (RL), which is a neutral layer and formed aloft during the turbulence attenuation process (Prabhakar et al., 2017).”

5. Page 4 line 111: How do you account for the role of SO₄²⁻ in adjusting this thermodynamic equilibrium reaction?

Reply: H₂SO₄ is preferred to be neutralized by ammonia to form sulfate, due to its lower saturated vapor pressure. The ammonia that does not react with sulfate will react with HNO₃ to form nitrate. We have evaluated the role of sulfate in the thermodynamic reaction by ISORROPIA II model in detail in the Major #2 comment.

6. Pages 5-7 lines 144-192: A table that summarizes important information for the three measurement sizes would be helpful.

Reply: We summarized the important information in **Table S1 ~ Table S3** in the revised manuscript as shown in Major # 4 comments.

7. Page 5 line 156: When was the tower-based measurement conducted?

Reply: The tower-based measurement was conducted from late September to mid-November in 2018 concurrently with the measurement at the GIG site, we have added this information in **Page 6 line 176~179** in the revised manuscript.

“The tower-based measurements were conducted simultaneously at the ground and 448 m on the Canton Tower from late September to mid-November in 2018 concurrently with the measurements at the GIG site, which are approximately 5.7 km apart each other.”

8. Page 6 lines 177-182: Why use different instruments? Have you calibrated the two instruments at the same time and location?

Reply: We thank the reviewer for the comment. Because there was no available LOPAP instrument at the Heshan site, we measured HONO by GAC instrument at the Heshan site. The HONO concentrations measured by LOPAP and GAC have been compared in the southern and northern China by (Dong et al., 2012; Yang et al., 2014). The wet chemistry/ions chromatography method (as same as GAC method) had a better performance during the low HONO concentration (Xu et al., 2019; Xue et al., 2019; Cheng et al., 2013). The HONO concentration range was from 0.01 ppb ~ 2.2 ppb (mean value of 0.56 ppb) at the Heshan site. Thus, we used the HONO data measured by GAC instrument at the Heshan site.

9. Page 6 lines 180-182: Same question.

Reply: There was no CRDS instrument to measure NH₃ at the Heshan site during the campaign. The wet chemistry method (the same method as GAC instrument) and spectroscopic techniques (CRDS technique) agreed closely with each other in the comparing study of von Bobrutzki et al. (2010). Thus, we used the NH₃ data measured by GAC instrument at the Heshan site.

10. Page 6 line 189: “campaign” should be “campaigns”? Otherwise please indicate which campaign.

Reply: We have changed the “campaign” to **“campaigns”** in **Page 7 line 212** in the revised manuscript as follows.

“The photolysis frequencies of O₃, NO₂, HCHO, and HONO (PFS-100,

Focused Photonics Inc., China) were also measured during the campaigns.”

11. Page 7 line 206-209: What if the simulation of the residual layer at the GIG site also freely evolved from sunset time using the ground observation data?

Reply: We thank the reviewer for the useful suggestion. The simulation suggested by the reviewer which treated the GIG site with a similar methodology at the Heshan site, allowing the ground measured chemical fields to evolve freely, has been already included in the original manuscript (original Fig.S6), as described in **Text S1** in the revised manuscript. The comparing results are shown in **Fig.S11** in the revised manuscript. The detailed reply was given in the Major #1 comment.

12. Page 8 lines 227-228: How do you get these γ (γ).

Reply: The uptake parameter of N_2O_5 (γ) is calculated by the observation-based empirical parameterization method proposed in Yu et al. (2020) (Eq. R1), combined with chemical compositions of aerosol (nitrate and chloride), and the aerosol liquid water content (ALWC, $[H_2O]$). The nitrate and chloride were measured by the AMS instrument, and ALWC was calculated by the thermodynamic ISORROPIA model, as described in Franchin et al. (2018). The equations to determine γ and ϕ are:

$$\gamma_{N_2O_5} = \frac{4}{\omega_{N_2O_5}} * \frac{Va}{Sa} * K_H * 3.0e^4 * [H_2O] * \left(1 - \frac{1}{1 + 0.033 * \frac{[H_2O]}{[NO_3^-]} + 3.4 * \frac{[Cl^-]}{[NO_3^-]}}\right) \quad \text{Eq. R1}$$

$$\phi_{ClNO_2} = \frac{1}{1 + \frac{0.033 * [H_2O]}{3.4 * [Cl^-]}} \quad \text{Eq. R2}$$

Where $\omega_{N_2O_5}$ is the mean molecular speed of N_2O_5 ($m s^{-1}$), Va/Sa is the measured aerosol volume to surface area ratio (m), K_H is the Henry's law coefficient, $[H_2O]$, $[NO_3^-]$, and $[Cl^-]$ are the aerosol water content, aerosol nitrate and chloride molarity (M), respectively.

13. Page 8 lines 233-236: How large could the uncertainty in the simulated particulate nitrate be with this approach?

Reply: As we shown in Eq. R1 and Eq. R2, the N_2O_5 uptake parameter(γ) and $ClNO_2$ production yield (ϕ) exhibited non-linear dependence on multiple factors, such as nitrate and organic matter concentration, aerosol liquid water content, chloride content and so on. Nitrate and organic matter can suppress the N_2O_5 uptake reaction in previous field studies, while higher RH and liquid water content likely promote N_2O_5

aqueous solvation and reaction (McDuffie et al., 2019). The ClNO_2 production yield is a function of the aerosol chloride to liquid water, with a negative dependence on aerosol liquid water and positive dependence on aerosol chloride (Bertram and Thornton, 2009; Yu et al., 2020). There was higher RH, and lower chloride at the 488 m site compared to the ground site of Canton Tower. The nitrate concentration was comparable at the 488 m site to the ground site in the study of Zhou et al. (2020). It is inferred that there are negative deviations for γ and positive deviations for ϕ in the residual layer, but the deviation may not be significant based on the results from McDuffie et al. (2018). The sensitivity tests about different γ and ϕ values have been included in **Fig.S14** in the revised manuscript as follows. When we reduced or increased the γ and ϕ by a factor of two, the relative deviations of modeled nitrate were less than 10%, compared to the base case at the GIG site. We revised the sentence in **Page 9 line 258 ~ 266** in the revised manuscript as follows.

“The γ and ϕ exhibited complicated nonlinear dependence on aerosol composition, aerosol liquid water and RH (Bertram and Thornton, 2009; McDuffie et al., 2019; Yu et al., 2020), such that γ and ϕ has positive and negative dependence with RH, respectively. There was higher RH, and lower chloride at the 488 m site, compared to the ground site of Canton Tower. The nitrate concentration was comparable at the 488 m site to the ground site in the study of Zhou et al. (2020). Combined with the higher RH and lower $\text{PM}_{2.5}$ concentrations in the residual layer in this study (as shown in Fig.S4), we inferred the negative deviations for γ and positive deviations for ϕ in the residual layer.”

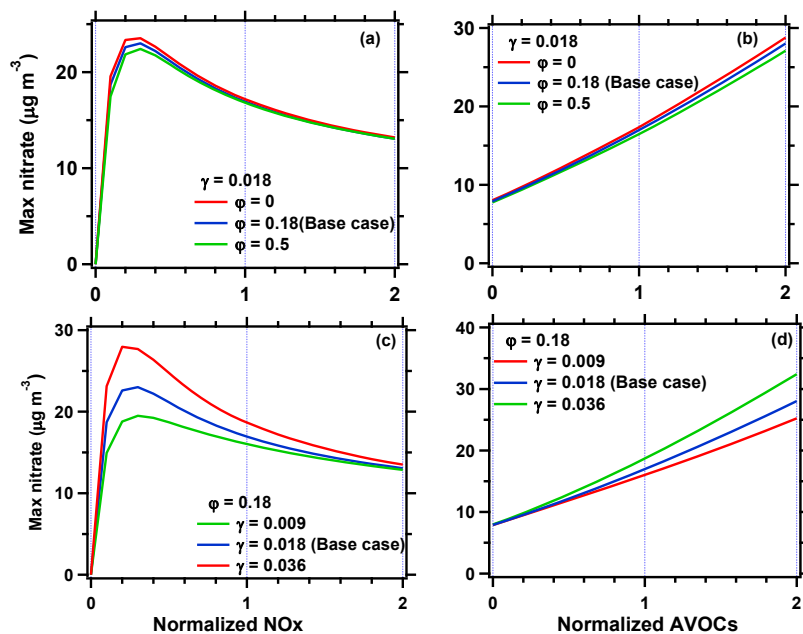


Figure S14. Sensitivity tests of the production yield of ClNO_2 (ϕ value) and the uptake parameter of N_2O_5 (γ value) on maximum nitrate concentrations as a function of the normalized NO_x and AVOCs relative to the base concentration at the GIG site.

14. Page 8 line 239: Is it the overall aerosol liquid water or the liquid water for different aerosol compositions? Could the authors elaborate a bit more on the $f(\text{RH})$ calculation?

Reply: We thank the reviewer for the comment. The liquid water here means the inorganic-associated and organic-associated water in the aerosol. The inorganic-associated water was estimated from ISORROPIA II model, and the organic-associated water was estimated from the organic aerosol mass which was measured by AMS, and the organic hygroscopicity constant. To make it clear, we have revised the original sentence (original line 239) “ $f(\text{RH})$ was calculated using the aerosol compositions measured by AMS and estimated liquid water by thermodynamic model of ISORROPIA, according to the study conducted by McDuffie et al. (2018).” in **Page 9 line 268 ~ 273** in the revised manuscript as follows.

“The $f(\text{RH})$ was estimated from the aerosol composition measured by AMS and the aerosol liquid water content, which included the inorganic-associated and organic-associated water. The sum of inorganic-associated water estimated from

ISORROPIA thermodynamic model and organic-associated water estimated from the organic aerosol mass, was used to calculate the growth of wet matter contributions, as described in the study of McDuffie et al. (2018)."

15. Page 9 line 266: What do the authors mean by "N₂O₅ constrained"? Do you refer to inclusion of the heterogeneous uptake of N₂O₅? Or does it mean to assimilate observed N₂O₅ in the calculation?

Reply: The "N₂O₅ constrained" means that the observed N₂O₅ was entered into the model in each modeled step. The N₂O₅ concentration at the beginning of each step is consistent with the observation.

16. Page 9 lines 267-268: Please describe more for the base case setup. Could the authors give a table to summarize the designed simulations? The authors pointed out, in lines 265-266, that the base case is the one without N₂O₅ constrained. Thus, I am confused with the sentence here: "The base case simulation was comparable to the results without N₂O₅ constrained".

Reply: We thank the reviewer for the suggestion. The base case (S0) is simulated without N₂O₅ constrained, and to test the results of base case, we design another simulation with N₂O₅ constrained (S1). The model scenarios were described in **Table S5** in the revised manuscript as follows. We have revised the legend in **Fig.S5** in the revised manuscript and the sentence in **Page 10 line 298 ~304** in the revised manuscript.

Table S5 Box model scenarios performed at the GIG and Heshan site

Site	Scenarios	Description about simulation	Other information
GIG	base case (S0)	set lifetime as 24 h, without N ₂ O ₅ constrained	NBL: with observation at the GIG site;
	S1	set lifetime as 24 h, with N ₂ O ₅ constrained	RL: with Observation at the 488m site of Canton Tower
Heshan	base case (S0)	set lifetime as 8 h, without N ₂ O ₅ constrained	NBL: with observation at the Heshan site;
	S1	set lifetime as 8 h, with N ₂ O ₅ constrained	RL: with observation at the Heshan site evolved freely

Page 10 Line 309 ~316 in the revised manuscript:

“Since the N_2O_5 is affected by the chemistry between ozone and VOCs, constraining N_2O_5 concentrations with the change in NO_x ratio arbitrarily during the isopleth simulations is improper. Thus, we set the simulation of base case (S0) without N_2O_5 constrained. To evaluate the results of the base case, we design another simulation with N_2O_5 constrained (S1) and compare the two simulated nitrate with the observation in Fig. S5. The model scenarios were described in Table S5 in detail. The base case simulation (S0) was comparable to the observation.”

17. Page 9 lines 275-280: The authors discussed the various potential uncertainties in simulation, but how about the uncertainty of the diffusion adopted in the study?

Reply: The concept of deposition rate meant the diffusion rate in the referenced studies (Lou et al., 2010; Lu et al., 2012). Considering the different diffusion rate adopted in this study, we evaluated the sensitivity of dilution rate in the **Fig.S2 and Fig.S3** in the revised manuscript, as described in the Major comment #3. In order to avoid inappropriate expression, we have rephrased the sentences in **Page 10 line 311 ~315** in the revised manuscript as follows.

“Gaussian error propagation was used to evaluate the uncertainties about measurement parameters and reaction rates in the model, as described in Lu et al. (2012). The uncertainties of various measurement parameters (VOCs, trace gases, meteorological parameters, etc.) ranged from 0 to 20%, and uncertainties of reaction rates are in the order of ~20% (Lu et al., 2012).”

18. Page 11 lines 315-317: I do not understand this sentence.

Reply: We emphasized that the difference of ozone and NO_x concentration between the GIG site and the 488 m of Canton Tower site. The ozone concentration at the 488 m site was higher than the concentration at the GIG site, while NO concentration at the 488 m site was much lower than the concentration at the GIG site. The lower concentration of NO and higher concentration of ozone at the 488m site were favorable for the reaction of NO_3 and N_2O_5 in the residual layer. We have rephrased the

original line 315 ~ 317 “However, the average concentration of O₃ at 488 m was 2.4 times higher than that at the ground site during nighttime, and the low nocturnal concentrations of NO at the 488 m site would enhance the production of NO₃ and N₂O₅.”in **Page 12 line 351 ~ 354** in the revised manuscript as follows.

“However, the average concentration of O₃ at 488 m of Canton Tower site was 2.4 times higher than that at the GIG site during nighttime, and the lower nocturnal concentrations of NO (nearly zero) at the 488 m site would enhance the production of NO₃ and N₂O₅ (Wang et al., 2018;McDuffie et al., 2019).”

19: Page 11 lines 322-325: These lines seem to describe the performance of GIG and should be moved ahead before the discussion of HeShan, i.e., before the sentence in line 319 starting with “At the Heshan site, ...”.

Reply: The original lines 322~325 describe the pollutants at the Heshan site, we have clarified it in **Page 12 line 358** in the revised manuscript.

“Subsequently, there was a significant increase in nitrate from 7:00 to 9:00. The concentration of NH₃ showed variation pattern that was similar with that of nitrate and increased after 7:00, while the concentrations of HNO₃ and NO₂ showed a decreasing trend from 7:00 to 9:00 at the Heshan site.”

20. Page 12 line 348: I do not think “comparable” is the right word. The simulated N₂O₅ in HeShan is significantly higher than that of measurement.

Reply: We thank the reviewer for the suggestion. We agree with you that the simulated N₂O₅ and ClNO₂ at Heshan were higher than their observed concentrations, but the overall trend is consistent and comparable. We have modified the “comparable” as **“higher”** in **Page 14 line 425** in the revised manuscript as follows.

“The temporal variations in simulated N₂O₅ and ClNO₂ concentrations were higher than the observations at the Heshan site as shown in Fig. S6 (c, d), the simulated results at the GIG site from October 9 to 10 were significantly lower than the observations (Fig.S6 (a, b)).”

21. Page 12 lines 356-358: Here, the authors pointed out that it is not necessary to use observed N₂O₅ constraining for the nitrate simulation. However, the authors also pointed out that the nighttime uptake of N₂O₅ is important for the nitrate simulation.

How do you reconcile these points?

Reply: We thank the reviewer for the comment. The simulated nitrate without N_2O_5 constrained (base case (S0)) was comparable with the observation, while the results with N_2O_5 constrained by S1 were significantly higher than observation on October 9 to 10 at the GIG site. The significantly higher nitrate by S1 may be caused by the upwind transported air masses without well-mixed with fresh urban NO emissions in short period (10 ~ 30 mins). Thus, the base case by S0 could represent the characterization of nitrate formation at the GIG site, suggesting the abnormal high concentration of N_2O_5 was negligible in short period. The well performance of modeled nitrate at the nocturnal and residual layer by S0 was based on the empirical calculation of the uptake coefficient of N_2O_5 and the production yields of ClNO_2 , which also affected by the nocturnal chemistry in the model. In addition, the nighttime N_2O_5 uptake reaction was significant higher in the residual layer at the GIG site, which we emphasized the nighttime N_2O_5 uptake is important.

22. Page 13 lines 388-389: Is there any data to support this conclusion?

Reply: We thank the reviewer for the comment. The mean NO concentration in the early nighttime at the GIG site was 12.1 ppb. The lower concentration of NO (nearly zero) at the 488m site was favorable to produce NO_3 radical and N_2O_5 . We have revised the sentence in **Page 15 line 466 ~ 468** in the revised manuscript.

“This may be caused by the fresh NO surface emissions, which titrate the NO_3 radical and ozone in the nocturnal boundary layer, as the mean NO concentration in the nighttime at the GIG site was 12.1 ppb.”

23. Page 13 line 411-412: What is the N_2O_5 uptake rate? Is it the reaction rate defined in Eq. 1? If yes, please keep the same name throughout the paper. If not, please define it and describe the method of its calculation.

Reply: We thank the reviewer for the comment. The term “ N_2O_5 uptake rate” is nitrate production rate from N_2O_5 uptake, which was defined in **Text S3** in the revised manuscript. The k_6 defined in Eq.1 is the reaction constant. To make it clear, we have changed the N_2O_5 uptake rate as **“nitrate production rate from N_2O_5 uptake”** in the revised manuscript.

24. Page 14 line 417: Is it the column or surface to the “total nitrate production”?

Reply: It means the contribution to the surface nitrate production; we have clarified it in **Page 16 line 494~497** in the revised manuscript.

“The nitrate production rate from OH and NO₂ reaction (19.9 μg m⁻³ day⁻¹) and nocturnal N₂O₅ uptake (15.6 μg m⁻³ day⁻¹) were the major nitrate formation pathways, which contributed 56% and 44% to the surface total nitrate production, respectively.”

25. Page 14 line 444: Please define “the transition regime” here.

Reply: We have revised the sentence in **Page 17 line 527** in the manuscript.

“The production of nitrate and ozone were in the VOCs-limited regime at the GIG site, and in the transition regime at the Heshan site, where nitrate and ozone are sensitive to both VOCs and NO_x reduction.”

26. Page 16 line 491-494: What was the “the titration effect of NO on NO₃ radical and ozone at the GIG site” and why did it not occur at the HeShan site?

Reply: The NO consumes the NO₃ radical and ozone quickly during the higher NO concentration condition, which is called the titration effect. The ground surface average concentration of NO was 12.1 ppb and 0.5 ppb in the nighttime of GIG and Heshan site, respectively. As the lower NO concentration at the Heshan site, we did not emphasize the titration effect of NO. Another reason caused the N₂O₅ changes with NO_x/VOCs emission was that ozone was in the NO_x-saturation regime at the GIG site and in the transition regime at the Heshan site. It caused the initial ozone that participated in the nocturnal chemistry increase/decrease with the less than 70% NO_x reduction at the GIG and Heshan site. We rephrased the sentences in **Page 18 line 576 ~ 580** in the revised manuscript.

“During nighttime, the initial ozone concentration participated the nocturnal chemistry increased/decreased with the reduction of NO_x at the GIG/Heshan site. In addition, the decrease in NO_x will reduce the titration effect of NO on NO₃ radical and ozone at the GIG site, which enhances production of N₂O₅ and promotes nitrate production in both the nocturnal boundary layer and the residual layer (Fig.13).”

27: Page 17 line 523: It might be more appropriate to use the word “difference” instead of “opposite” here.

Reply: We thank the reviewer for the suggestion. We have modified the word “opposite” to “**different**” in **Page 20 line 614~618** in the revised manuscript.

“The spatial differences of nocturnal reactions and the different contributions from downward transport of the residual layer to surface nitrate at urban and suburban sites were attributed to different fresh emissions and concentration levels of NO_x at the two sites during the night time, suggesting that nitrate production under different NO_x conditions should be explored to better understand the its formation pathways.”

28: Page 18 line 545: What are these limitations and how large could their possible impact be on the study?

Reply: We thank the reviewer for the comment. The direct vertical transport and horizontal transport cannot be quantified in the 0-D box model, resulting in a lack of assessment about the transport contribution. Thus, three-dimensional models should be used to further investigate the synergistic control of ozone and particles on the regional scale.

We have added these limitations in **Page 20 line 635 ~ 638** in the revised manuscript.

“As the result of limitation for the 0-D box model, vertical transport and horizontal transport cannot be considered explicitly in this study. Given the limitations of the box model, three-dimensional models should be used to further investigate the synergistic control of ozone and particles on the regional scale.”

29. S Page 4 line 78: Was there any precipitation occurred during the studied period?

Reply: There was mild rain on 10/15/2018~10/19/2018, and the precipitation intensity was 0.3 mm at the GIG site. At the Heshan site, there was no precipitation during the studied period. Thus, we did not consider the wet deposition in this study.

Technique corrections:

1. Page 4 line 109: Please define ϕ in the paragraph right after this equation.

Reply: We have defined ϕ in **Page 4 line 101** after the equation in the revised

manuscript.

2. Page 7 line 221: Please define S_a in the paragraph right after this equation, similar to w_1 and r .

Reply: We have defined S_a , ωl and γ in **Page 4 line 101 ~103** in the revised manuscript.

3. Page 8 line 222: Please define J_{ClNO_2} .

Reply: We have defined J_{ClNO_2} in **Page 4 line 106** of the revised manuscript as follows.

“Here the reaction rate k_6 was denoted as the photolysis rate of $ClNO_2$ (J_{ClNO_2}).”

4. Page 8 line 223: Please give the unit to w_1 .

Reply: The unit of ωl is $m s^{-1}$, we have added the unit in **line 101** in the revised manuscript.

5. Page 8 line 224: Please delete the definition of ϕ here.

Reply: We have removed the definition of ϕ in the revised manuscript.

6. Page 8 line 236: Please move the definition of S_a to line 224.

Reply: We have moved the definition of S_a to **line 102** in the revised manuscript.

7. Page 8 line 249: Please give the unit to R_a .

Reply: The unit of R_a is m , we have added the unit in the revised manuscript.

8. Page 8 line 250: Please give the unit to w .

Reply: The unit of ω is $m s^{-1}$, we have added the unit in the revised manuscript.

9. Page 17 line 514: Please define “PRD”.

Reply: We have defined the Pearl River Delta as PRD in the Abstract.

10. Page 14 Figure S3c: Please change label “Hehan N_2O_5 ” to “Heshan N_2O_5 ”.

Reply: We thank the reviewer for the reminder. We changed label “Hehan N_2O_5 ” to **“Heshan N_2O_5 ”**.

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