Reply to the comments of Anonymous Referee #2

Referee comment on "The formation and mitigation of nitrate pollution: Comparison between urban an suburban environments" by Suxia Yang et al., Atmos. Chem.Phys.Discuss., https://doi.org/10.5194/acp-2021-730-RC2, 2021

General comments

Yang *et al.* analyze data from several sites in the Pearl River Delta to assess mechanisms for the production of nitrate aerosol, an increasingly important component of PM2.5 pollution in China. The analysis shows that the contribution of photochemical and dark mechanisms varies by site and depends on both the chemistry and the dynamics of the planetary boundary layer. It further shows that NOx reductions are unlikely to improve nitrate pollution despite being the major precursor due to the dependence of NOx oxidation rates on NOx itself. Reductions in VOCs, by contrast, are effective at all sites in both NOx and O₃ reductions. The paper is well written, easy to follow and well organized. It is of substantial interest to the readership of ACP. I recommend publication following attention to the specific comments below.

Reply: We would like to thank the reviewer for the insightful comments, which help us tremendously in improving the quality of our work. Please find the responses to individual comments below.

Specific comments

1. Line 53: Nitrate reductions can be site specific, but the same is true for ozone and for the same reasons as detailed later in the manuscript. Can identify this effect here.

Reply: We thank the reviewer for the suggestion. The ozone production and synergistic control of nitrate and ozone pollution are also site-specific. "The results highlight that the relative importance of nitrate formation pathways can be site-specific, and the quantitative understanding of various pathways of nitrate formation will provide insights for developing nitrate mitigation strategies." has been revised in **line 53 ~ 55** in the revised manuscript as follow.

"The results highlight that the relative importance of nitrate and ozone formation can be site-specific, and the quantitative understanding of various pathways of

nitrate formation will provide insights for developing nitrate and ozone mitigation strategies."

2. Line 71-74: Nitrate photolysis to produce HONO remains uncertain. References that also place limits on this process should be included.

Romer, P.S., *Constraints on Aerosol Nitrate Photolysis as a Potential Source of HONO and NOx.* Environmental Science & Technology, 2018. **52**(23): p. 13738-13746.

Reply: We thank the reviewer for the valuable suggestion. Indeed, the photolysis of particulate nitrate to produce HONO had some limitations and uncertainties, as the enhancement of particulate nitrate photolysis may not be so fast. Thus, we rephrased the sentence in **line 71 ~76** in the revised manuscript as follows.

"In addition, the photolysis of particulate nitrate can increase the production of sulfate and nitrous acid (HONO), implying the importance of nitrate in the synergetic enhancement of the atmospheric oxidizing capability in haze events (Gen et al., 2019;Zhang et al., 2020;Ye et al., 2016;Ye et al., 2017), although the photolysis of particulate nitrate to produce HONO still remains highly uncertain (Romer et al., 2018)."

3. Lines 81-84: Aerosol pH is also an important process that should be identified and referenced for HNO$_3$ partitioning. See for example:

Guo, H., *Effectiveness of ammonia reduction on control of fine particle nitrate.* Atmos. Chem. Phys., 2018. **18**(16): p. 12241-12256.

Lawal, A.S., *Linked Response of Aerosol Acidity and Ammonia to SO2 and NOx Emissions Reductions in the United States.* Environmental Science & Technology, 2018. **52**(17): p.9861-9873.

Nenes, A., *Aerosol pH and liquid water content determine when particulate matter is sensitive to ammonia and nitrate availability.* Atmos. Chem. Phys., 2020. **20**(5): p. 3249-3258.

Franchin, A., *Airborne and ground-based observations of ammonium-nitrate-dominated aerosols in a shallow boundary layer during intense winter pollution*

episodes in northern Utah. Atmos. Chem. Phys., 2018. **18**(23): p. 17259-17276.

Reply: We agree with your comment that pH plays an important role in the nitrate formation by affecting the thermal equilibrium and gas-particle partitioning. We have reorganized the sentence in **line 83 ~ 88** in the revised manuscript as follows.

"The partitioning process of HNO$_3$ between the gas and particle phase is regulated by ambient temperature (T), relative humidity (RH) (Mozurkewich, 1993), aerosol pH and the abundance of NH$_3$ (R2) (Xue et al., 2014;Yun et al., 2018;Franchin et al., 2018). The pH value within a certain range plays an important role in the gas-particle partitioning of nitrate, which significantly impacts the nitrate formation (Guo et al., 2018;Lawal et al., 2018;Nenes et al., 2020)."

4. Line 87: Can also reference McDuffie 2018b for the variation of ClNO$_2$ yields.
McDuffie, E.E., *ClNO2 Yields From Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of the Current Parameterization.* Journal of Geophysical Research: Atmospheres, 2018. **123**(22): p. 12,994-13,015.

Reply: We thank the reviewer for the suggestion. We have added this reference in **line 110** in the revised manuscript.

5. Line 95: Also suggest earlier references from California, e.g.
Brown, S.G., *Wintertime Vertical Variations in Particulate Matter (PM) and Precursor Concentrations in the San Joaquin Valley during the California Regional Coarse PM/Fine PM Air Quality Study.* Journal of the Air & Waste Management Association, 2006. **56**(9): p.1267-1277.
Chow, J.C., *PM2.5 chemical composition and spatiotemporal variability during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS).* Journal of Geophysical Research: Atmospheres, 2006. **111**(D10): p. n/a-n/a.

Reply: We thank the reviewer for the valuable suggestion. We have added these references in **line 121** in the revised manuscript.

5. Line 190-191: There is a reference to integrity and temporal coverage of the measurements as a limitation on the data, without much explanation. More detail on which instruments were functioning at which times could be given in the introduction to this section or the SI.

Reply: Considering the different measurement time between the instruments, we choose the overlapping time as the study period. To clarify this issue, we have added the temporal coverage of different instruments at GIG site, Ganton Tower site and Heshan site in **Table S1~ Table S3** in the revised manuscript as follows.

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_2O_5	TOF-CIMS	1 min	< 10 ppt	± 25%	2018.10.07~2018.11.19
$ClNO_2$	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 $\mu g\ m^{-3}$	± 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_2O_5	TOF-CIMS	1 min	< 10 ppt	± 25%	2019.10.01~2019.11.16
$ClNO_2$	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/NO₂/NOx	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 $\mu g\ m^{-3}$	± 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

6. Line 216: How was the dilution rate determined? This is an important parameter that is normally fit to achieve agreement with observations in box modeling approaches. The 24 hour inverse rate constant appears to be rather an arbitrary guess.

Reply: We thank the reviewer for the constructive comments. The box model

cannot replicate the effects of meteorology, and the dilution is not accurately quantitated. 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, or determined combining 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 (MVK+MACR), O_3, HNO_3 and nitrate at the GIG and Heshan site, as shown in **Fig.S2 and Fig.S3** in the revised manuscript as follows. A dilution rate of 24 h^{-1} for all species was determined at the GIG site, due to the reasonable consistency between the simulation and observation for the chosen species. Comparing with the diurnal average observation, 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. The simulated diurnal data had relative minor deviation with the observation by dilution constant of 8 h^{-1}. Thus, the lifetime of 24 h and 8 h were used at the GIG and Heshan site, respectively. We have clarified these issues in the revised manuscript and SI as follows.
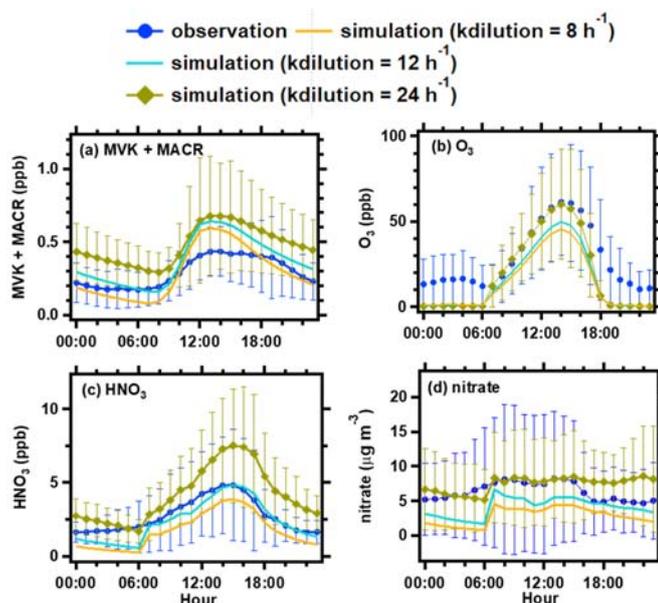
Figure.S2 Sensitivity tests with different dilution constant (kdilution) at the GIG site by box model.
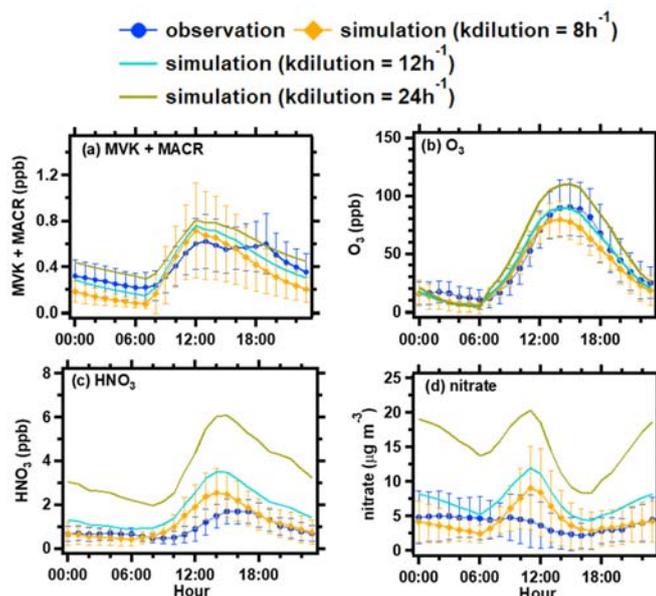
Figure.S3 Sensitivity tests with different dilution constant (kdilution) at the Heshan site by box model.

Line 241~244 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;Yun et al., 2018). To achieve agreement with the observation, a life time of 24 h and 8 h were used at the GIG and Heshan site, respectively. The sensitivity tests were shown in Fig.S2 and Fig.S3."

Line 79~89 in the 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), O_3, HNO_3 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 O$_3$, 25% for HNO$_3$, and 12% for nitrate with the dilution constant of 8 h^{-1} at the Heshan site. Thus, the dilution constant of 24 h^{-1} and 8 h^{-1} were used at the GIG and Heshan site, respectively."

7. Line 264-265: Explain why this approach is meaningless.

Reply: The N$_2$O$_5$ production was affected by the O$_3$ and NO$_2$, which would change with the VOCs and NOx emission. If we constrain N$_2$O$_5$ as the observation, the concentration of N$_2$O$_5$ would keep constant as NOx or VOCs concentrations change in different simulation scenarios, which could not provide the feedback of nocturnal nitrate formation due to the precursors change. In addition, the modeled results without N$_2$O$_5$ constrained were comparable to the observations. Thus, we did not constrain N$_2$O$_5$ in the simulation. We have rephrased it in the revised manuscript in **line 298 ~ 300** in the revised manuscript as follows.

"Since the N$_2$O$_5$ is affected by the chemistry between ozone and VOCs, constraining N$_2$O$_5$ concentrations with the change in NOx ratio arbitrarily during the isopleth simulations is improper."

8. Lines 271-273: Large N$_2$O$_5$ mixing ratios were present elsewhere in the time series in S3 but do not appear to be associated with poor representation of nitrate in S2. Is this explanation consistent with the data?

Reply: Indeed, large N$_2$O$_5$ mixing ratios were present elsewhere at the GIG site, such as the early nighttime in October 22 and late nighttime in October 26 in **Fig.S6** as follows in the revised manuscript (original Fig.S3); and the simulated nitrate with N$_2$O$_5$ constrained were also higher than the base case at that time in **Fig.S5** as follows in the revised manuscript (original Fig.S2). Besides, the observed nitrate increased with the high concentration of N$_2$O$_5$. It is consistent with the results. The simulated nitrate with N$_2$O$_5$ constrained on October 9 and October 10 were significantly higher, so we specially pointed out the simulation on these days. The GIG site is located near traffic avenues, impacted by traffic emissions during the nighttime. The abnormally high observed concentrations of N$_2$O$_5$ lasted for short periods (10-30 minutes) at the

nighttime, which may be caused by the transported air masses from upwind regions or vertical transport without well-mixed with fresh urban NO emissions. The high N_2O_5 in short period may be related to the short lifetime of N_2O_5 (Brown et al., 2006b) , which will be investigated in the future.
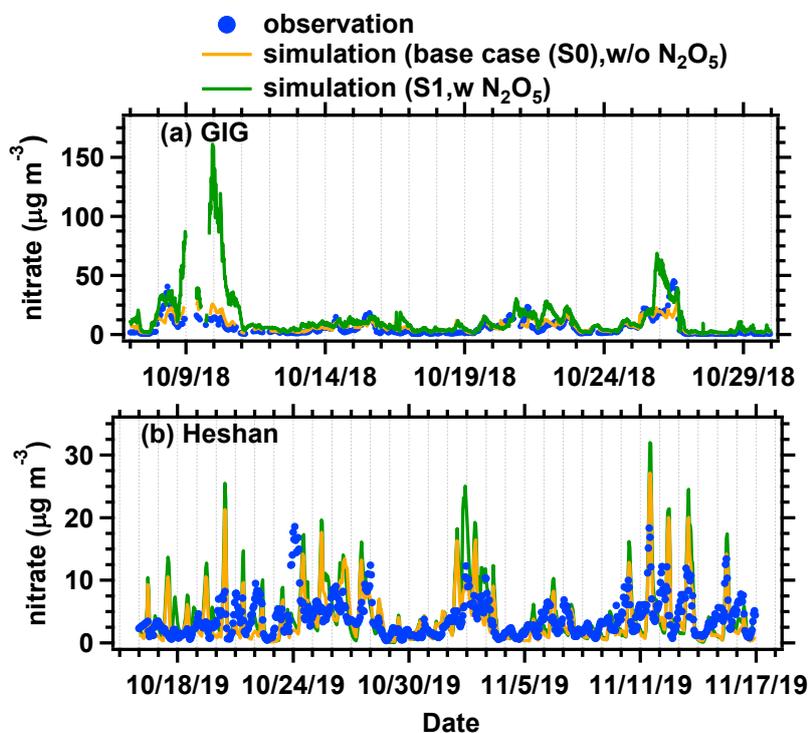
Figure S5. Comparison of the box model simulated and observed nitrate concentrations at (a) GIG site and (b) Heshan site. The orange lines represent simulated results of the base case (S0) without N_2O_5 constrained, and green lines represent the simulated results with N_2O_5 constrained (S1).
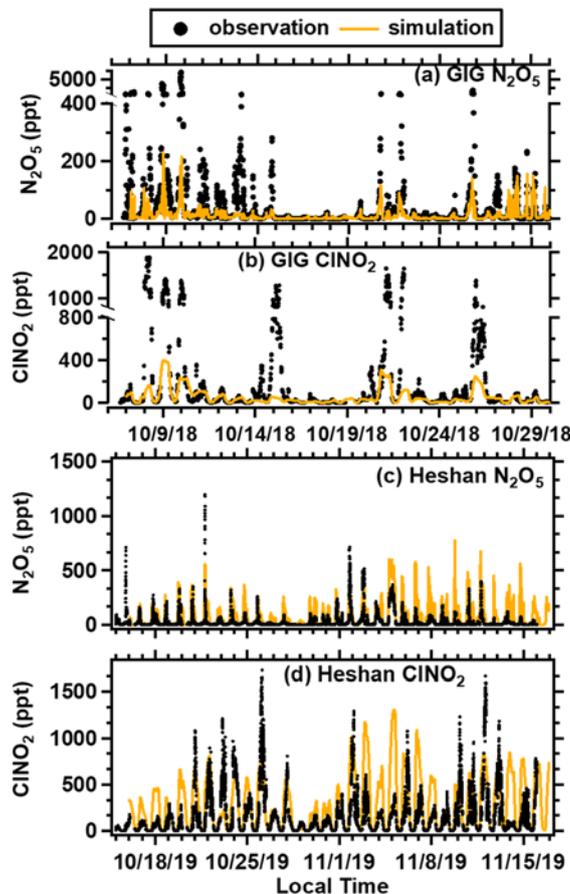
Figure S6. Comparison of the box model simulated and observed N_2O_5 and $ClNO_2$ concentrations at (a, b) GIG site and (c, d) Heshan site.

9. Line 289-294: Suggest comparing this result to that of the Franchin paper above, which shows the same effect but more dramatically for aircraft data in northern Utah, USA.

Reply: As you suggested, we have compared the results with those from Franchin's paper, and have added the corresponding sentences in **Page 11 line 329 ~ 330** in the revised manuscript.

"The significant increasing ratio of nitrate fraction from clean condition to polluted condition (~ 43%) was also revealed in the airborne observations in Utah Valley, US (Franchin et al., 2018)."

10. Line 309-311: Meaning of this sentence is not clear. Is the morning increase in nitrate being attributed to photochemical NO_2 oxidation in the residual layer, or does

the word "might" here indicate uncertainty? If the former, the later discussion of nighttime accumulation of nitrate would appear to conflict with this statement.

Reply: We thank the reviewer for the comment. We inferred the increase of nitrate was induced by the aloft transportation, so the word "might" indicate uncertainty. At the GIG site, with the rapid increase of nitrate during morning time, the precursors of HNO_3 and NH_3 did not increase sharply. HNO_3 mainly formed by the photochemical reaction of $OH + NO_2$. So, this process might be caused by the vertical transport from aloft. In order to clarify this issue, we have rephrased the sentence (original line 309 ~ 311) "The concentration of NO_2 exhibited a decreasing trend during the nitrate growth period. As gaseous HNO_3 is mainly produced by the reaction of OH and NO_2, the accumulation of nitrate after sunrise might largely be attributable to the downward transport from the residual layer to the ground." in **Page 11 line 344 ~ 348** in the revised manuscript as follows.

"At the GIG site, nitrate rapidly increased from 4:00 to 9:00, but the concentrations of NH_3 and HNO_3 increased slowly, which suggests the minor contribution of direct production of HNO_3 from the reaction of OH and NO2. The increase of nitrate during this period might be associated with the downward transport from the residual layer to the ground."

11. Line 316: A sustained level of nearly 2 ppbv of NO in excess O_3 at 488 m implies very rapid mixing with surface NO emissions. Is this likely to be the case, and if so, would it be consistent with an analysis of an isolated residual layer? More likely might be that the NO instrument zero is not well characterized, and that NO was in fact zero at this altitude. If so, the reaction of $NO_3 + NO$ would present no limit for nighttime chemistry at 488 m.

Reply: We thank the reviewer for the valuable comments. The observed NO concentration was between 1 ~ 3 ppb at the 488 m site on the Canton tower when O_3 concentration was almost 50 ppb during the nighttime, as shown in the following Fig.R1 (a). However, the NO concentration was nearly zero in the nighttime when O_3 was high at both GIG and Heshan site (Fig.R1 (b ~ c)). We compared the nighttime NO concentration against O_3 at the GIG site, Heshan site and 488 m site of Canton Tower.

When the O_3 concentration was between 50 ppb to 60 ppb during the nighttime, the average concentration of NO was 0.8 ppb, 0.05 ppb and 2.1 ppb at the GIG site, Heshan site and 488 m site of Canton Tower, respectively. In addition, the modeled concentration of NO was also shown in Fig.R2, which was simulated by freely evolved NO at the residual layer. The average simulated concentration of NO was 0.02 ppb when the O_3 was between 50 ppb to 60 ppb.

As pointed by the reviewer, we agree that the NO measurements at the 488 m on the Caton tower may be somewhat biased. Actually, it is a common issue for NO measurements at continuously monitoring stations in China, as the result of infrequently instrumental background measurements. Thus, NO concentrations should be close to zero at the 488 m site of Canton Tower, rather than 1-3 ppb based on the measurement.

It should be noted that the potential NO measurement errors do not affect the modelling results in this study. In the modelling of the residual layer for the urban region, only NO_2 and O_3 were constrained using measurements at the 488 m site of Canton Tower and NO was freely evolved (see details in Text S1 in SI).
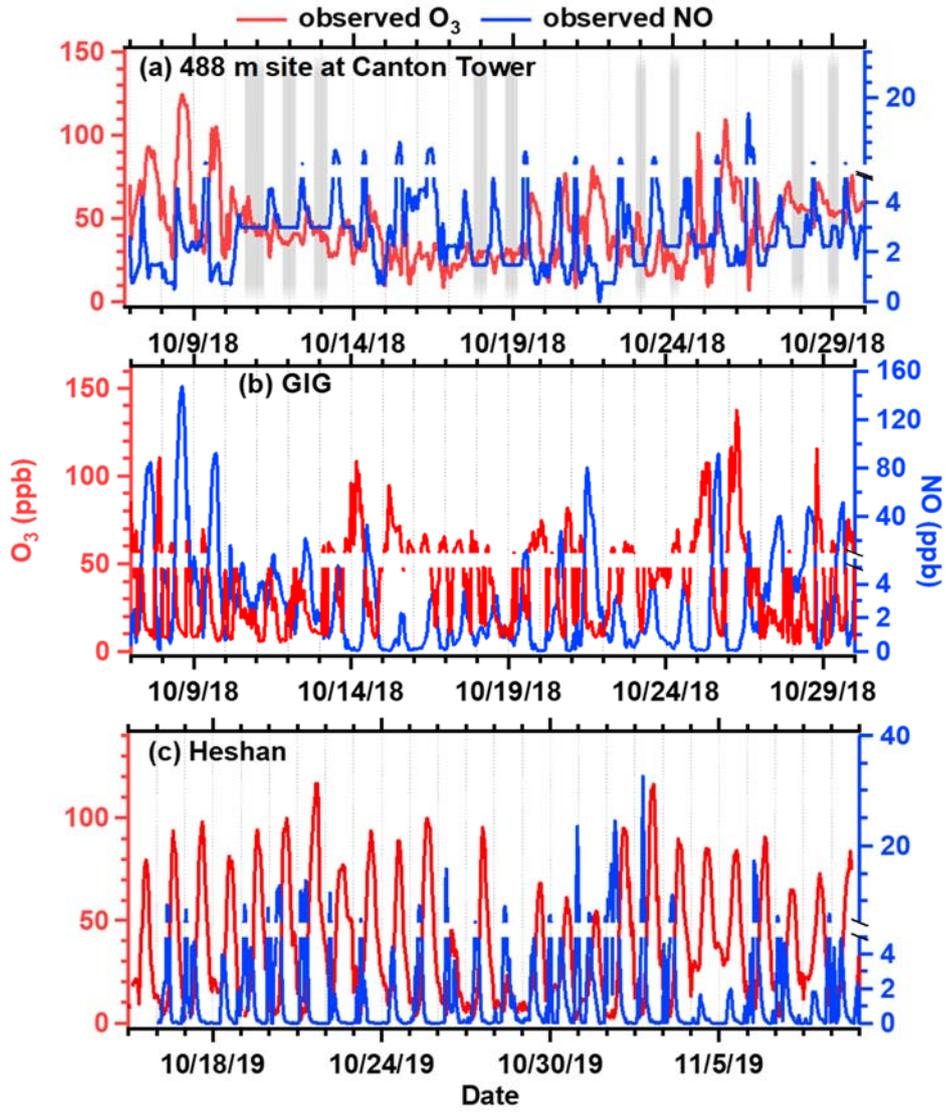
Figure R1 Time series of observed O_3 (left) and NO (right) concentration at the (a) 488 m site of Canton Tower, (b) GIG site and (c) Heshan site. The shadows at the 488 m site of Canton Tower represent the stage that the concentration of O_3 was high, while NO still kept a higher concentration.
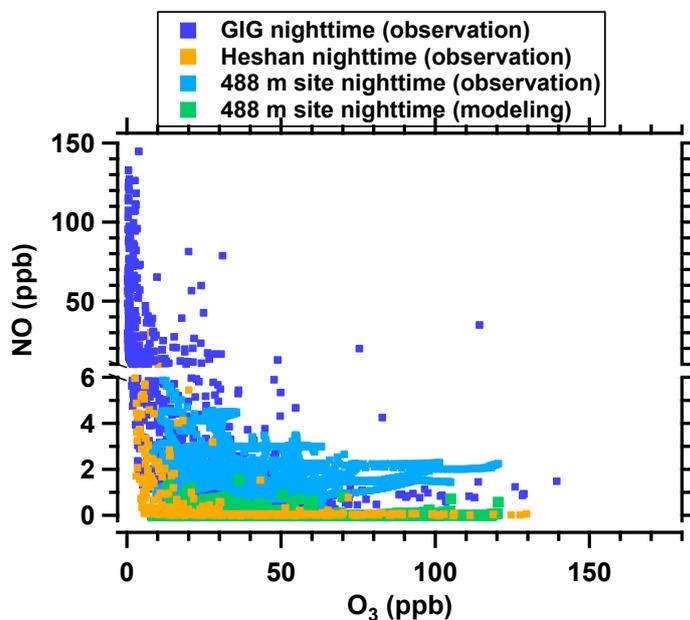
Figure R2 scatter plot between nighttime NO and O_3 at GIG site (blue blocks), Heshan site (orange blocks), at 488 m site of Canton Tower (light blue and green blocks). The green blocks represent the modeling concentration of NO at 488 m site of Canton Tower

We have updated the description about NO concentration at the 488 m site of Canton Tower **in line 351 ~ 354** in the revised manuscript as follows.

"However, the average concentration of O_3 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 NO_3 and N_2O_5 (Wang et al., 2018b;McDuffie et al., 2019)."

12. Line 336: The instrument descriptions indicate that NH_3 was measured. Was there excess gas phase NH_3 as implied by the ion balance in Figure S5?

Reply: We thank the reviewer for the insightful comment. We also calculated the excess NH_3 by molar concentration of Total ammonia（$[NH_3]$ +$[NH_4^+]$）- Total nitrate($[HNO_3]$ + $[NO_3^-]$) -2*sulfate($2*[SO_4^{2-}]$) (Seinfeld &Pandis et al., 2008), as shown in the following Fig. R3. The average excess ammonia at the GIG and Heshan

site were 0.18 μmol m^{-3} and 0.05 μmol m^{-3}, respectively, indicating excess gas NH$_3$ at the two sites.
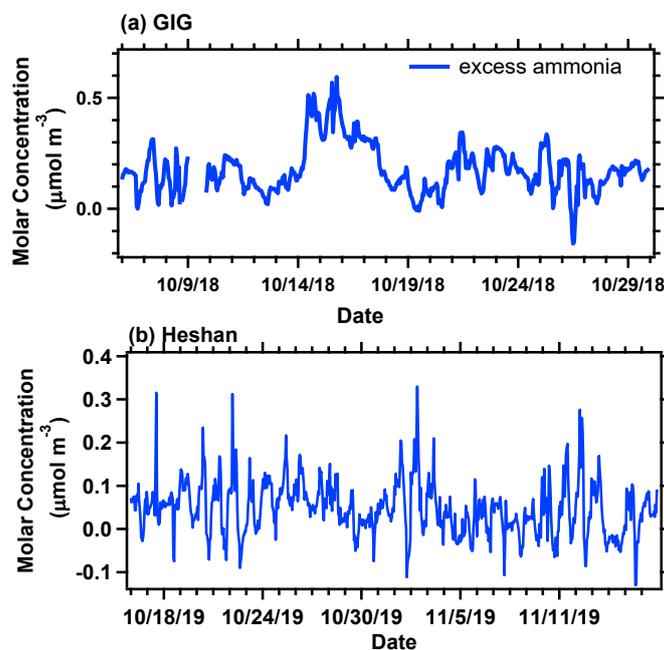
Figure R3. The excess ammonia calculated by molar concentration of Total ammonia （[NH$_3$] +[NH$_4^+$] - Total nitrate([HNO$_3$] + [NO$_3^-$]) -2*sulfate(2*[SO$_4^{2-}$]) at the GIG and Heshan site.

13. Line 351-353: The effect of periodic large N$_2$O$_5$ and ClNO$_2$ is more likely due to vertical than horizontal transport – so these concentrations may be associated with the overlying residual layer.

Reply: We thank the reviewer for the comment. Indeed, the periodic large N$_2$O$_5$ and ClNO$_2$ may be associated with vertical transport from residual layer. In general, when the residual layer decoupled from the nocturnal layer, the vertical mixing is weak since the residual layer is one neutral stable layer. Due to lacking of radar or related vertical observation, we did not emphasize the vertical transport effect of periodic large N$_2$O$_5$ and ClNO$_2$. We considered your suggestion and modified the sentence in **Page 14 line 424 ~ 427** in the revised manuscript.

"The abnormally high observed concentrations of N$_2$O$_5$ and ClNO$_2$ that lasted for short periods (10-30 minutes) at the GIG site may be caused by

transported air masses from upwind regions or vertical transport without well-mixed with fresh urban NO emissions.”

14. Line 430: The model of residual and boundary layer mechanisms for nitrate production is certainly more complete than most similar analyses. However, horizontal transport in the residual layer, especially as part of nocturnal jets, has been invoked in some analyses of winter nitrate production in the California central valley (see Brown and Chow references above). Some comment in this section about the differences in horizontal transport would be useful, even if it is not possible to quantitatively analyze this effect for the data in this study. The assumption here is that the residual layer and the nocturnal boundary layer originate at the same location, which is not necessarily the case. As noted later in the paper, this is one of the limitations of box modeling.

Reply: We thank the reviewer for the constructive comments. The horizontal transport occurred in the residual layer, which would facilitate the formation and transportation of nitrate ammonium in regional scale. As you have mentioned in the comment that it is not possible to conduct horizontal simulation via box model, thus, we have added the related implications and suggestions on the possibility of horizontal transport to the nitrate production in the residual layer. The revisions are shown in **Page 16 line 509 ~ 513** in the revised manuscript as follows.

“The horizontal transport in the residual layer from nocturnal jets may also contribute to the different nitrate production at urban and suburban sites, which has been discussed in the research of Chow et al. (2006) and Brown et al. (2006a). Due to the limitation of box model, this issue could be studied by the chemistry transport model in further research.”

15. Line 445-446: The NOx sensitivity at Heshan looks neutral or near peak – that is O_3 and nitrate would stay approximately constant for an initial NOx reduction. Also, could define what is meant by "initial' here – just an infinitesimal increment, or a fixed number such as 5 or 10%.

Reply: We thank the reviewer for the comment. It is true that the maximum ozone and nitrate concentration show little decrease for an initial NOx reduction. The maximum ozone decreased from 116 ppb to 115.3 ppb, and the maximum nitrate

concentration decreased from 20.8 μg m^{-3} to 20.5 μg m^{-3} with 10% reduction of NOx. With the increased reduction ratio of NOx, the decrease rate of ozone and nitrate enhanced. Thus, the nitrate and ozone at the Heshan site were in the transition regime. A less than 70% reduction of NOx emission would increase nitrate and ozone concentrations at the GIG site, an "initial" reduction meant the reduction ratio before the turning point of O$_3$ or nitrate appeared. To clarify this issue, we have rephrased the sentence **in Page 17 line 527 ~ 530** in the revised manuscript.

"As shown in Fig. 11, the reduction of NOx emissions from 0-70% would increase nitrate and ozone concentrations at the GIG site, but decrease those concentrations at the Heshan site. The decrease in VOCs concentrations would decrease nitrate and ozone concentrations at both sites."

Supplement

16. Lines 135-138: The sensitivity to the ClNO$_2$ yield is explored, but not the N$_2$O$_5$ uptake coefficient. Can the authors comment on the sensitivity to this parameter? Importantly, there may be almost no sensitivity here if the system is limited by the reaction of NO$_2$ + O$_3$. If so, the N$_2$O$_5$ uptake coefficient would need to be reduced substantially before the heterogeneous reaction becomes important or rate limiting. Canthe authors comment on these aspects of the model sensitivity?

Reply: We thank the reviewer for the suggestion. Indeed, parameterized N$_2$O$_5$ uptake parameter (γ) is also an important parameter for nocturnal chemistry, and changes widely between laboratory and field studies. We used the median parameterized γ and φ as the base input, and changed the two parameters respectively to perform the sensitivity tests. The results showed that the nitrate sensitivity did not change with different values of γ and φ. It is consistent with the research by Womack et al. (2019) in the Salt Lake of US. When γ is in a certain range, the nocturnal nitrate production is limited by the formation of NO$_3$ and N$_2$O$_5$ (Chen et al., 2020;McDuffie et al., 2019). We have revised these sentences in **line 157 ~ 163** in the revised SI manuscript as shown below, and updated the **Fig.S14** (original Fig.S9) in the SI manuscript.

"Here we chose the median value of γ (0.018) and φ (0.18) as the base input

parameters; thus, different values of γ and φ were selected to perform sensitivity simulation (Fig. S14). Compared with the base case, the sensitivity of nitrate did not change with different values of γ and φ although the peak values of nitrate showed difference with the changing of γ and φ".
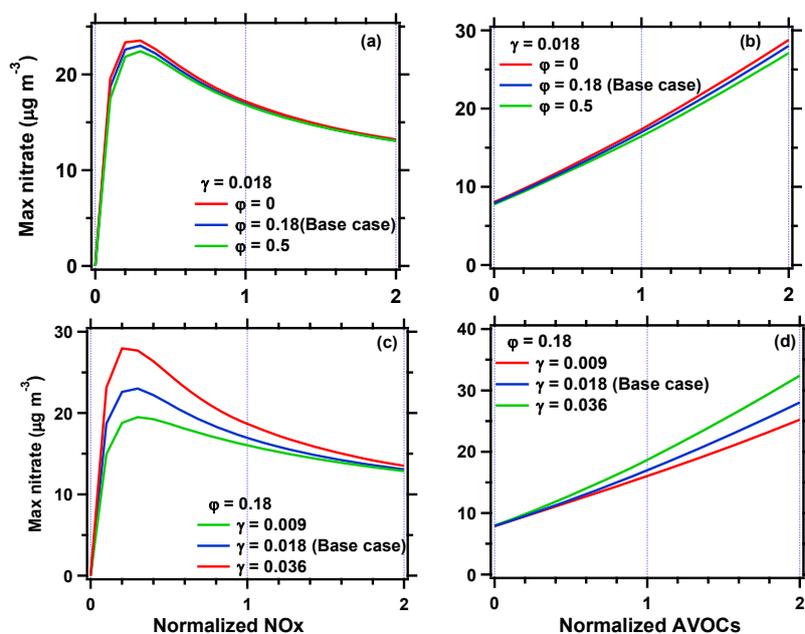
Figure S14. Sensitivity tests of the production yield of ClNO₂ (φ value) and the uptake parameter of N₂O₅ (γ value) on maximum nitrate concentrations as a function of the normalized NOx and AVOCs relative to the base concentration at the GIG site.

Technical corrections

1. Line 43: replace "are" with "is an"

Reply: We have replaced the "are" with **"is an" in line 43** in the revised manuscript.

2. Line 62: hygroscopic properties

Reply: We have changed the word "hygroscopic property" to **"hygroscopic properties" in line 63** in the revised manuscript.

3. Line 231: particle rather than particles

Reply: We have revised the word "particles" to **"particle" in line 255** in the revised manuscript.

4. Line 365-367: Check sentence grammar

19

Reply: We have rephrased the sentence (original line 365 ~ 367) "Since the nitrate produced in the residual layer is only gradually mixed to the surface as the boundary layer develops during the following morning, while the nitrate contributed to the boundary layer column concentration always included the N_2O_5 uptake in the residual layer during the whole nighttime (Wang et al., 2018a;Womack et al., 2019)." **in line 439 ~ 443** in the revised manuscript.

"The nitrate produced in the residual layer is only gradually mixed to the surface as the boundary layer develops during the following morning, while the nitrate contributed to the boundary layer column concentration always included the N_2O_5 uptake in the residual layer during the whole nighttime"

5. Line 399-400: Check meaning – what is "nitrate of nitrate"

Reply: We have changed the original sentence (original line 399 ~ 400) "The relative magnitudes of the contributions to the daily-averaged surface nitrate of nitrate differ somewhat from the contributions to the entire boundary layer." in **line 477** in the revised manuscript as follows.

"The relative magnitudes of the contributions to the daily-averaged surface nitrate differ somewhat from the contributions to the entire boundary layer"

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