Reply to the comments of Anonymous Referee #1

General Remarks:

The authors describe a recent field campaign at an urban, suburban, and tower measurement site near Guangzhou, China. They use these observations to construct a box model for the production of nitrate aerosol, and demonstrate that the urban area is in a VOC-limited regime, while the suburban site is at a transition point. The tower measurements yield critical information about the contribution of different production mechanisms in the nocturnal boundary and residual layers.

Overall, this is a very good paper that provides new constraints on an important pollution issue, and I recommend publication. I have only a few minor comments.

Reply: We thank the reviewer for the comments. These comments are valuable and very helpful for improving this paper. We reviewed these comments carefully and made corresponding revisions according to the reviewer's comments. Our replies to the comments are itemized below in blue color.

General comments:

1. Would the authors include more details about what (if any) biogenic VOCs are included in the model.

Reply: We thank the reviewer for the comment. Isoprene was included as other researchers done in the box models (Tan et al., 2018). To clarify this issue, we have added the corresponding descriptions in **line 294~297** in the revised manuscript as follows.

"Isoprene was included in the simulation as biogenic VOC (BVOC). Reducing BVOCs such as isoprene is impractical, so it is not scaled with AVOCs concentrations in the sensitivity simulations on control of precursors."

2. Line 82 – Previous work has emphasized the importance of particle pH in nitrate aerosol formation, so this should be discussed at some point.

See Guo, H., Otjes, R., Schlag, P., Kiendler-Scharr, A., Nenes, A., and Weber, R. J.:

Effectiveness of ammonia reduction on control of fine particle nitrate, Atmos. Chem. Phys., 18, 12241-12256, 2018 as an example.

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 added the sentences in **line 86~88** in the revised manuscript and cited this paper as you have suggested.

"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)"

3. Line 134 – What is meant by "different environments"? The authors should be a little more clear about what makes this paper different than other recent papers discussing NOx and VOC sensitivity in urban areas in China.

Reply: The "different environments" means different emission ratios of NOx and VOCs in ambient atmosphere, such as urban and suburban sites. The nitrate formation impacted by the NOx-VOCs-O_3 chemistry was evaluated in this study, which combined ground- and tower-based measurements to simulate the nitrate formation aloft at urban and suburban sites. This issue has not been systematically evaluated in reported field studies. To address this issue clearly, we have modified the "different environments" to **"urban and suburban areas"** in **line 154** in the revised manuscript as follows.

"In addition, few studies have comprehensively evaluated the relative influence of NOx and VOCs reductions on nitrate production in the urban and suburban areas."

4. Line 155 – Change "upward" to "upwind"

Reply: We modified the "upward" to **"upwind" in line 175** in the revised manuscript.

5. Line 157 – It's not clear here whether the tower measurements were taken during the same timeframe as the GIG ground site.

Reply: The tower measurements were taken during the same period as the GIG

ground site, we have added the field measurement period in **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 concurrent with the measurements at the GIG site, which are approximately 5.7 km apart each other."

6. Line 164 – Were the aethelometer and particle size distributions taken at the GIG site? If so, change line 157 to read "The chemical components of PM1, trace gases, NMHC, and particle BC content and size were measured…."

Reply: Yes, the BC and particle size distribution were measured at the GIG site. We have revised this sentence in **line 180** in the revised manuscript as you have suggested.

"The chemical components of PM_1, trace gases, and non-methane hydrocarbons (NMHC), and particle BC content and particle size distribution were both measured at the GIG and Heshan sites, whereas only trace gases (NOx and O_3) and meteorological parameters were measured at the Canton Tower site".

7. Line 196 – A reference detailing the MCM should be cited here.

Reply: We thank the reviewer for the suggestion. Some references which described the MCM in detail were cited in the revised manuscript as follows.

Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, Atmos. Chem. Phys., 5, 641-664, 10.5194/acp-5-641-2005, 2005.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181-193, 10.5194/acp-3-181-2003, 2003.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the

development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-180, 10.5194/acp-3-161-2003, 2003.

The revisions have been made in **line 218~222** are as follows:

"The F0AM box model uses a subset of the Master Chemical Mechanism (MCM) v3.3.1 (Saunders et al., 2003;Jenkin et al., 2003;Bloss et al., 2005), which explicitly describe chemical reactions of VOCs, ROx radicals (including OH, HO_2 and RO_2), ozone and nitrate, and was widely used in laboratory and theoretical researches (Edwards et al., 2017;Anderson et al., 2017;D'Ambro et al., 2017;Womack et al., 2019). "

8. Line 229 – State what the observed parameters were.

Reply: The observed mean data of γ at the Heshan site, combined with flow-tube system, was 0.020 ± 0.019. We have revised the sentence in **line 251~ 253** in the revised manuscript as follows.

"The average values of γ were 0.018 ± 0.01 and 0.019 ± 0.01 at the GIG and Heshan sites, respectively, which were comparable with the observed mean data of γ (0.020 ± 0.019) at the Heshan site in 2017 (Yu et al., 2020)."

9. Line 373 – Where does the estimate of the nocturnal boundary layer and residual layer fractions as 0.4 / 0.6 come from? Is this an empirical observation during the study or an estimate based on theory?

Reply: The PBL height data were derived from the NOAA Air Resource Laboratory website (https://ready.arl.noaa.gov/READYamet.php). The average diurnal boundary layer height was 400 m and 1000 m in the nighttime and daytime during the study period, respectively, which are shown in **Fig. S1** in the revised manuscript as follows. Thus, the heights of the nocturnal boundary layer and residual layer were set as 400 m and 600 m, and the nocturnal boundary layer and residual layer fraction was estimated as 0.4 and 0.6, respectively.

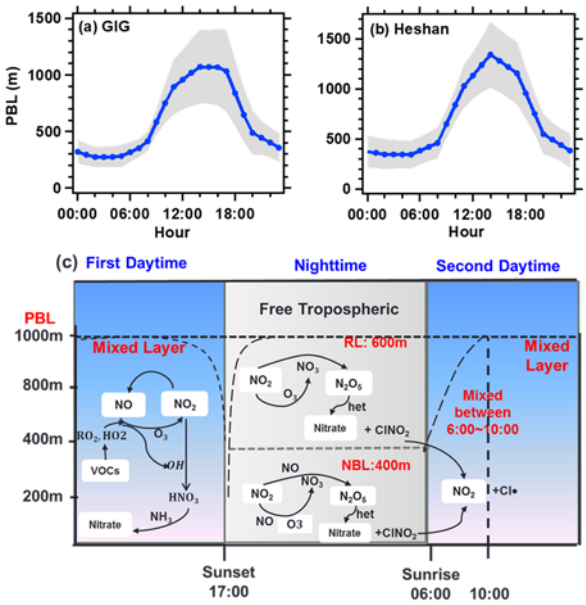

Figure S1. Diurnal variations of mean Planetary Boundary Layer (PBL) heights at (a) GIG site and (b) Heshan site, which were obtained from the NOAA Air Resource Laboratory website (https://ready.arl.noaa.gov/READYamet.php); (c) Schematic of PBL evolution and chemistry in the box model.

10. Figure 4: I would suggest putting the modeled diurnal observations on the observation to make the comparison more clear.

Reply: We thank the reviewer for the suggestion. We have added the modeled and observed diurnal nitrate concentrations in **Fig.S10** in the revised manuscript, and described the comparison in **line 414 ~ 419 of Page 14** in the revised manuscript as follows.

"The diurnal simulated nitrate was comparable with the observation at the GIG site, especially when considering the vertical transport from the residual layer in the morning. Unlike the GIG site, the diurnal simulated nitrate performed higher in the daytime, and little bit lower in the late nighttime, compared with the observation. It may be related to the lack of quantitative transport in the box model."

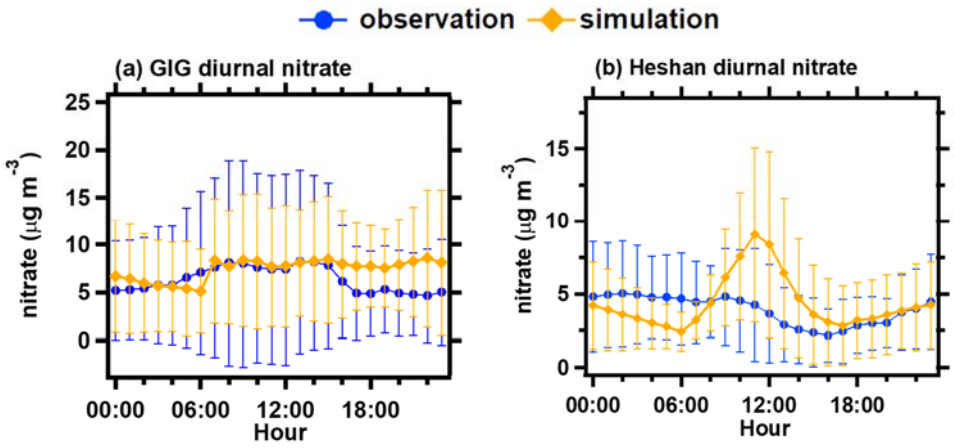

Figure S10. Comparison of daily-averaged box model simulated and observed nitrate at the GIG and Heshan site

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