

Review “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.

Major comments:

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 HeShen 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.

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 NO_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?

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, update rate. See more details in specific comments.

Specific comments:

1. Page 3 lines 64-65: The increase of NH_3 is also a reason.
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.
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).
4. Page 4 line 93: Please define “the residual layer” here.

5. Page 4 line 111: How do you account for the role of SO₄ in adjusting this thermodynamic equilibrium reaction?
6. Pages 5-7 lines 144-192: A table that summarizes important information for the three measurement sizes would be helpful.
7. Page 5 line 156: When was the tower-based measurement conducted?
8. Page 6 lines 177-182: Why use different instruments? Have you calibrated the two instruments at the same time and location?
9. Page 6 lines 180-182: Same question.
10. Page 6 line 189: “campaign” should be “campaigns”? Otherwise please indicate which campaign.
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?
12. Page 8 lines 227-228: How do you get these y.
13. Page 8 lines 233-236: How large could the uncertainty in the simulated particulate nitrate be with this approach?
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(RH) calculation?
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?
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”.
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?
18. Page 11 lines 315-317: I do not understand this sentence.
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, ...”.
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.
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?
22. Page 13 lines 388-389: Is there any data to support this conclusion?
23. Page 13 line 411-412: What is the N₂O₅ 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.
24. Page 14 line 417: Is it the column or surface to the “total nitrate production”?
25. Page 14 line 444: Please define “the transition regime” here.
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?
27. Page 17 line 523: It might be more appropriate to use the word “difference” instead of “opposite” here.

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

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

Technique corrections:

1. Page 4 line 109: Please define ϕ in the paragraph right after this equation.
2. Page 7 line 221: Please define S_a in the paragraph right after this equation, similar to w_l and r .
3. Page 8 line 222: Please define J_{ClNO_2} .
4. Page 8 line 223: Please give the unit to w_l .
5. Page 8 line 224: Please delete the definition of ϕ here.
6. Page 8 line 236: Please move the definition of S_a to line 224.
7. Page 8 line 249: Please give the unit to R_a .
8. Page 8 line 250: Please give the unit to w .
9. Page 17 line 514: Please define “PRD”.
10. Page 14 Figure S3c: Please change label “Hehan N_2O_5 ” to “HeShan N_2O_5 ”.

Bian, H., Chin, M., Hauglustaine, D. A., Schulz, M., Myhre, G., Bauer, S. E., Lund, M. T., Karydis, V. A., Kucsera, T. L., Pan, X., Pozzer, A., Skeie, R. B., Steenrod, S. D., Sudo, K., Tsigaridis, K., Tsimpidi, A. P., and Tsyro, S. G.: Investigation of global nitrate from the AeroCom Phase III experiment, *Atmos. Chem. Phys.*, 17, 12911-12940, <https://doi.org/10.5194/acp-17-12911-2017>, 2017.