

Response to Editors and Reviewers

Manuscript ID: egosphere-2023-1401.

We appreciate the reviewers for their careful reading and constructive comments on our manuscript. As detailed below, the reviewer's comments are shown in black, our response to the comments is in blue. New or modified text is in red.

All the line numbers refer to the revised Manuscript.

Response to Referee #1:

Comments:

Wang et al., present a field measurement report about dinitrogen pentoxide (N_2O_5) and relevant parameters in an island site in the South China Sea, where the nighttime chemistry is less studied compared with those in urban regions in China. They showed that this site is strongly affected by the outflow of urban polluted plumes from the Pearl River Delta, China, although the local anthropogenic emission is weak and has ~50 km from the coastline. High nitrate radicals (NO_3) production rate, moderate N_2O_5 concentrations, and short N_2O_5 lifetime are well characterized in the outflow plumes. The budget analysis is also convincing especially in the aspect of volatile organic compounds oxidation during the nighttime.

The data presented in this report has high quality although only valid for about half a month, this data set is valuable with respect to the nighttime chemistry in the marine regions that are frequently affected by anthropogenic activities, which can be helpful to the understanding of the interactions of anthropogenic and marine air masses. The results inspire that human emission in the coastal cities may have a significant impact on the air quality in the marine regions over a large spatial scale. Overall, the paper is well written and certainly within the scope of the measurement report type in ACP. I would like to recommend minor revisions before the publication.

Thanks for the review's positive comments.

General comments:

1. As shown in Figure 2, the N_2O_5 data is also available in one night (11-14), but it is not presented in Figure 3 as well as Table 2, I can understand the limited data did not have representativeness of average condition for CAM, but it should be clarified in the legend of Figure, Table, and the main text.

We highly acknowledged this suggestion. We have the statement in the Line 341 as “Daytime N₂O₅ and NO₃ in the IAM period were shown as NaN due to the absence of observation.” Also, we added the explanation in the note of Table 2 and in the caption of Figure 3 as follows.

Line 311: ° Without N₂O₅ measurement in the daytime and limited N₂O₅ data during the CAM period, N₂O₅, NO₃, and their lifetimes were not valid here.

Line 350: Figure 3. Mean diurnal profiles of N₂O₅, NO₃, P(NO₃), and relevant parameters in the two types of air masses. NO₃ was calculated from N₂O₅. Neither N₂O₅ nor NO₃ was shown during CAM period because of limited N₂O₅ measurement.

2. I strongly encourage the author to conduct more analysis about the nocturnal oxidation capacity of the different types of VOC by considering the nighttime ozone oxidation as well as the nitrate radicals.

Thanks, we added more discussion about the oxidation of VOC by NO₃ and O₃ at nocturnal time at section 3.4. The result showed that NO₃ accounted for 63.1% of the nocturnal VOC oxidation related to O₃.

Line 523. To better understand the nocturnal oxidation of VOCs, we compared the nighttime oxidation of VOCs by NO₃ with O₃. Since OH was not measured and OH is often regarded as a vital daytime oxidant (Finlayson-Pitts, 2000; Lu et al., 2010), we did not consider OH oxidation in the nighttime. Figure S4 showed the diurnal pattern of VOC loss rate by NO₃ and O₃, NO₃ predominantly achieves its peak oxidation rates (0.07 ppbv h⁻¹) during the initial half of the night, accounting for 63.1% of the total VOC oxidation on nocturnal average. Meanwhile, O₃ also makes a contribution to VOC oxidation, mainly owing to its relatively high nighttime concentration levels (42.9 ± 18.4 ppbv).

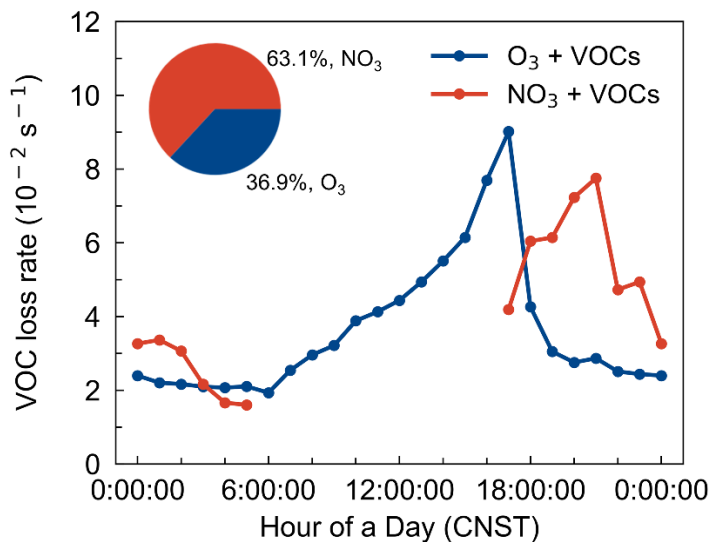


Figure S4. Diurnal profiles (mean \pm standard deviation) of VOC oxidation rate by atmospheric oxidants, NO₃ and O₃. The pie chart represents the nocturnal fractions of these two oxidants to VOC oxidation.

Finlayson-Pitts, B. J., James N.: Chemistry of the upper and lower atmosphere: theory, experiments and applications, Academic Press, Calif2000.

Lu, K. D., Zhang, Y. H., Su, H., Brauers, T., Chou, C. C., Hofzumahaus, A., Liu, S. C., Kita, K., Kondo, Y., Shao, M., Wahner, A., Wang, J. L., Wang, X. S., and Zhu, T.: Oxidant (O₃ + NO₂) production processes and formation regimes in Beijing, Journal of Geophysical Research-Atmospheres, 115, Artn D07303, 10.1029/2009jd012714, 2010.

3. Line 402, the concentration of phenol and cresol is below 10 ppt on average, considering the high contribution to the NO₃ reactivities, I suggest the author add some discussion about the instrumental detection limit of the species.

Thanks. We added some discussion about the measurement uncertainties may be caused by the instrumental detection limit as following.

Line 446. Considering that the measured phenol and cresol concentration is low and near the instrumental detection limit, we note this may bring some uncertainties in quantifying the contribution to the total NO₃ reactivity and NO₃ loss rate.

4. Line 515, the two cases presented in Figure 9 are 0.04 ppb and 0.12 ppb, which is not consistent with the statement of 40-400 ppt, the author should clarify it. By the

way, I don't know why the two concentrations of NO are chosen in the two cases, respectively, since the budget is still not closed in the second half of the night.

Thanks. Here we choose the fixed NO concentration that can explain about 80% of the budget on average. Figure 9 illustrates two representative examples from many days. These results show that the required NO concentration varies for each day, yet consistently remains below the detection limit of the instrument. We change the caption of Figure 9 as follows and updated the figure.

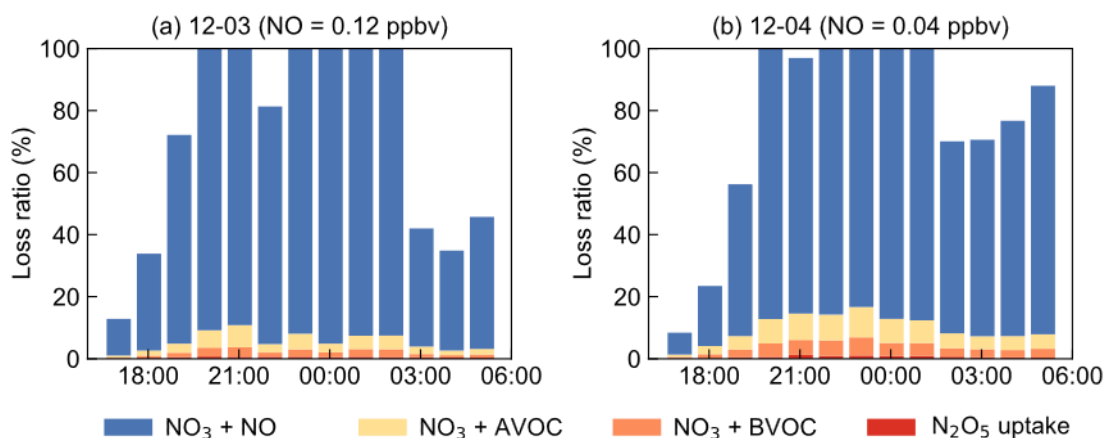


Figure 9. Examples for the assessment of NO₃ loss process by assuming NO as constant values to approximately explain about 80% of the budget.

5. The reaction rate constants of NO₃ with VOCs can be added as a table in the support information.

Thanks for your comment. We have added the reaction rate constants of NO₃ with VOCs in the supporting material as Table S2.

Table S2. Reaction rate coefficients of VOC with NO₃ used in this study.

	VOC	k (298K) (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	A Factor (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	Ea/R (K)	Ref
Anthropogenic compound					
1	Phenol	3800	/	/	1
2	Cresol	14000	/	/	1
3	Formaldehyde	0.00056	/	/	1
4	Hexanal	0.0027	/	/	1
5	i-Butane	0.106	/	/	1
6	n-Butane	0.046	/	/	1
7	Indene	4.1	/	/	1
8	Styrene	1500	/	/	1
9	Toluene	0.07	/	/	1
10	cis-2-Pentene	581	/	/	1
11	trans-2-Pentene	647	/	/	1
12	1-Pentene	15	0.39	0	2
13	cis-2-Butene	352	0.35	0	2
14	trans-2-Butene	390	/	/	1
15	n-Pentane	0.087	3.05	3060	2
16	Acetylene	0.21	/	/	3
17	Benzene	0.03	/	/	4
Biogenic compound					
18	Isoprene	700	3.15	450	1
19	α-Pinene	1190	1.19	-490	1
20	β-Pinene	6160	/	/	1
21	DMS	1100	/	/	5
22	Propane	0.03	/	/	1
23	Propene	9.49	/	/	1
24	1-Butene	14	3.3	2880	2

Ref1: (Atkinson et al., 2003)

Ref2: (Brown et al., 2011)

Ref3: IUPAC

Ref4: Estimated

Ref5: (Brown et al., 2012)

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem Rev*, 103, 4605-4638, 10.1021/cr0206420, 2003.

Brown, S. S. and Stutz, J.: Nighttime radical observations and chemistry, *Chem Soc Rev*, 41, 6405-6447, Doi 10.1039/C2cs35181a, 2012.

Brown, S. S., Dube, W. P., Peischl, J., Ryerson, T. B., Atlas, E., Warneke, C., de Gouw, J.

A., Hekkert, S. T., Brock, C. A., Flocke, F., Trainer, M., Parrish, D. D., Feshenfeld, F. C., and Ravishankara, A. R.: Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study, *Journal of Geophysical Research-Atmospheres*, 116, Artn D24305 10.1029/2011jd016544, 2011.

Technical comments:

1. Figure 6a, the standard deviation should be added to the bar plot.

Thanks, we have revised the boxplot of $k(\text{NO}_3)$ for both IAM and CAM period in Figure 6a to better demonstrate the statistical distribution as follows.

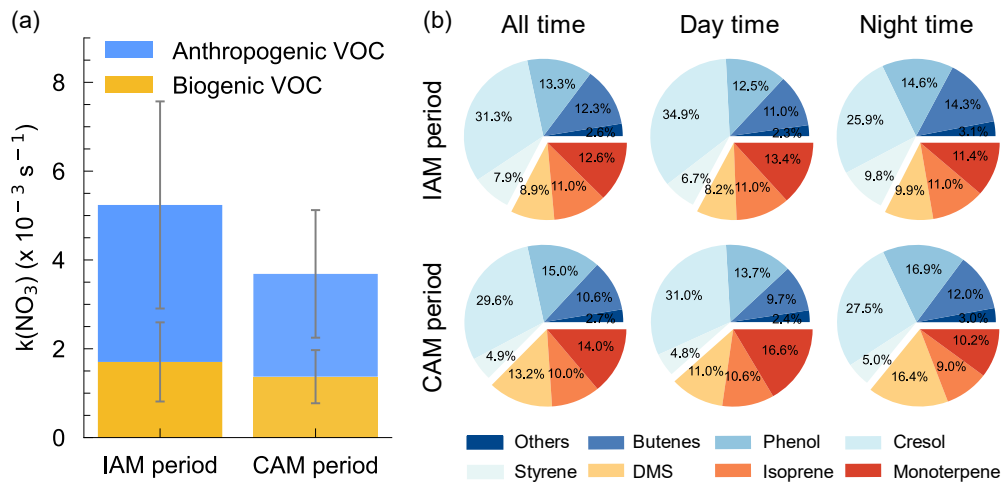
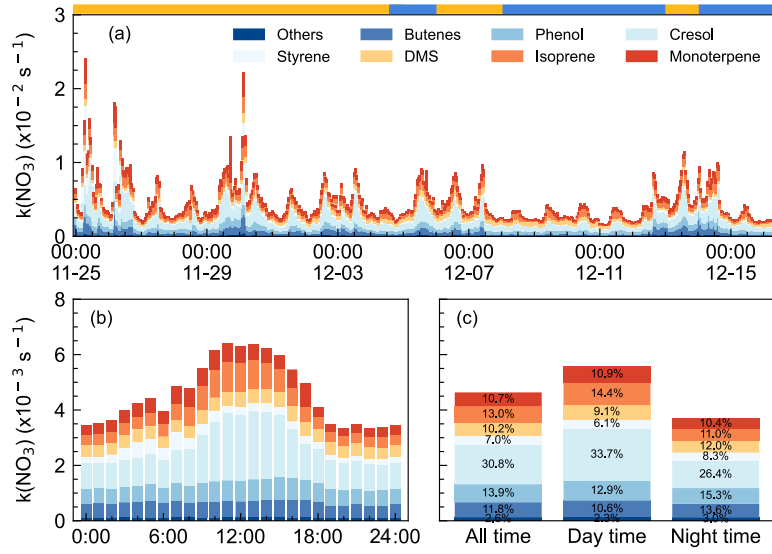


Figure 6. (a) Distributions of $k(\text{NO}_3)$ from AVOC and BVOC for both IAM and CAM period. The error bar indicates the standard deviation. (b) The relative contribution of VOC categories to the $k(\text{NO}_3)$.

2. Figure 5c, the font size of the percentages is too small, it can be further improved.

Thanks for your suggestion and we updated Figure 5 as follows. Due to the limited space, I have tried to make the font size of percentage larger to facilitate the readability.



3. Line 138, 3000 change to 3, 000.

Thanks, and we revised it accordingly.