Response to Editors and Reviewers

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 Manuscript ID: acp-2022-408.

## Referee 2

This work conducted continuous field measurements of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> and performed comprehensive evaluation on the ClNO<sub>2</sub> chemistry as well as its contributions to radical and ozone formation under different transport pathways. The results highlight the N<sub>2</sub>O<sub>5</sub>-uptake-limited ClNO<sub>2</sub> formation and overall low contributions to RO<sub>2</sub> radical and O<sub>3</sub> formation in autumn in South China. The manuscript is generally well written with clear logic, deep analysis, and full discussion. It can be considered to accept after addressing the following minor comments.

Thanks for your positive and constructive comments.

Specific comments:

- Line 76-77, 78-79, etc., blanks are missed in the middle of different citations. The same suggestion is given to other parts of the main text.
   Corrected throughout the manuscript.
- 2. Line 87-88, the sentence requires modification. e.g., "the challenge to accurately predict ClNO<sub>2</sub> and particulate nitration production".

Here we modified as:

Line 87-89. These gaps in the parameterization of  $N_2O_5$  uptake coefficients and  $CINO_2$  yield result in the challenge of accurately predicting  $CINO_2$  and particulate nitrate production.

- Line 148, "seldom disturbs the sampling" can be written as "to have little influence on the sampling". Revised accordingly.
- Line 151, it's better to add "sometimes" after the word "are". Revised accordingly.
- Line 157, add "approximately" after the word "was". Changed accordingly.
- 6. Line 203, with and without the constrains of the observed ClNO<sub>2</sub>, or with and without taking ClNO<sub>2</sub> as the source of Cl radicals?

Yes, we revised it as:

Line 207. The impact of  $O_3$  by ClNO<sub>2</sub> chemistry was assessed by differing the scenario with and without taking ClNO<sub>2</sub> as the source of Cl radicals in the model simulation.

- Line 204-205, this operation will lead to overestimation on the contributions from CINO<sub>2</sub> chemistry. The potential uncertainty should be described here or somewhere else.
   Since the reaction rate constant is the upper limit, it does overestimate the contribution of CINO<sub>2</sub> chemistry. Here we added a brief discussion in the manuscript.
   Line 212. It should be noted that the setting will lead to an overestimation of the contributions from CINO<sub>2</sub> chemistry.
- Line 209, the average lifetime or a constant lifetime? Here we have rewritten it as a constant lifetime. Line 215. The constant lifetime corresponds to...
- 9. Line 210, the "was" should be "were". Corrected accordingly.
- Line 209-212, this sentence is not very clear. Is there any reference to support such lifetime setting? Yes, this set of trace gas lifetime is consistent with our previous studies for simulating the chemistry of HOx radicals. Here we added a reference as follows. Line 799.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Haseler, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO<sub>2</sub> concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, Atmospheric Chemistry and Physics, 12, 1541-1569, 10.5194/acp-12-1541-2012, 2012.

11. Line 249-250, what are the reasons for the lower abundances in 2019 than 2017? Smaller source strengths or larger sinks?

The higher  $CINO_2$  in 2017 is due to the much higher aerosol loading with a maximum of over 400 µg m<sup>-3</sup>, which largely promoted the conversion of  $N_2O_5$  to  $CINO_2$  (namely smaller source strengths as you mentioned). While the higher  $N_2O_5$  in 2017 is much more complicated since the concentration is closely related to the formation and loss of  $NO_3$ .

Line 259. The difference of  $CINO_2$  level between the two campaigns conducted in 2017 and 2019 may be caused by the aerosol loading.

12. Line 258, 500 m AMSL or AGL? Are the trajectories at 100 m similar to those at 500 m?Here we used the AMSL and stated the manuscript. We also tested the trajectories at 100 m and 500 m and found only a small difference between them.

Line 268. at the measurement site at 500 m AMSL height...

13. Figure 5, a RMA correlation coefficient may be better for comparing the consistent.

We appreciate the reviewer for this suggestion. We note that other studies used the regular correlation coefficient when comparing the derived and parameterized  $\gamma N_2O_5$  (e.g., Morgen et al., ACP, 2015; McDuffie et al., JGR, 2018). To keep in line with these studies, we did not used the RMA correlation coefficient, although RMA may be better here. Thus no change made with respect to this suggestion.

Ref:

McDuffie, E. E., Fibiger, D. L., Dube, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., Shah, V., Jaegle, L., Guo, H. Y., Weber, R. J., Reeves, J. M., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Dibb, J. E., Veres, P., Ebben, C., Sparks, T. L., Wooldridge, P. J., Cohen, R. C., Hornbrook, R. S., Apel, E. C., Campos, T., Hall, S. R., Ullmann, K., and Brown, S. S.: Heterogeneous N2O5 Uptake During Winter: Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of Current Parameterizations, Journal of Geophysical Research-Atmospheres, 123, 4345-4372, 10.1002/2018jd028336, 2018.

Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N2O5 uptake: airborne regional measurements in northwestern Europe, Atmospheric Chemistry and Physics, 15, 973-990, DOI 10.5194/acp-15-973-2015, 2015.

- Line 401, add "in this study" before "than".
   Added accordingly.
- 15. Figure 6 and Figure 7, suggest indicating the p values of the linear correlations. Added accordingly.
- Line 468, 470, 473, "power plants emissions" should be coal-fired power plant emissions. Revised accordingly.
- 17. Line 618, what does the "AH" mean? Double-check the unit mmol/mmol.
  Here the AH means absolute humidity. We added the explanation in the figure legend as "AH (absolute humidity)".

Line 657. The unit is a typo. We corrected it as "mmol mol<sup>-1</sup>".