Reply to comments on "Measurement report: High contribution of N_2O_5 uptake to particulate nitrate formation in NO_2-limited urban areas" by Lin et al.

We would like to thank the editor and reviewers for their efforts in handling, reading, and critically reviewing our manuscript, which have helped us to further improve our manuscript. The comments on our paper are carefully addressed.

General Comments:

This study investigates the features of pNO_3^- production at a typical site in southeastern China. The nighttime N_2O_5 uptake was found to be efficient enough and play an increasing role in pNO_3^- formation. Multiple methods are applied to demonstrating the dominant effect of PNO_3 or precursor concentrations, in N_2O_5 uptake process. The manuscript is well organized. I recommend acceptance after carefully addressing the following concerns when revising this manuscript.

Response: We are grateful for your thoughtful comments on the manuscript and we have made careful revisions accordingly. Our point-to-point responses to each comment are as follows (reviewer's comments are in black font, our responses are in blue font and our revisions in the manuscript are italic font).

1. Method 2.1: I suggest more description of instrument deployment at least for I-Tof-CIMS in main text. It would be better to briefly introduce the sampling setup, calibration frequency and the variation of calibration factor, such that the reasonableness of measurements could be readily assessed.

Response: Thank you for this suggestion. We have added the detailed operation and calibration procedure for the I-TOF-CIMS in the revised manuscript (**line 112-127**), as follows:

"A nearly 2-meter long perfluoroalkoxy (PFA) tube with a 1/4-inch inner diameter was used for sampling. The total sampling flow rate was set as 10 standard liters per minute (SLPM), of which only 2SLPM was diverted to the CIMS. A nitrogen (N_2) flow (99.999%, 2.7 SLPM), carrying methyl iodide (CH_3I) vapor released from a heated permeation tube, passed through a soft X-ray source (Tofwerk AG, P-type) to generate reagent ions I^-. The I^- was combined with the target gas in an ion molecule reaction (IMR) chamber and then detected by the ToF-CIMS. Ambient N_2O_5 and $ClNO_2$ were detected as the $I(N_2O_5)^-$ and $I(ClNO_2)^-$ clusters at 235 and 208 m/z. The detailed calibration procedures of N_2O_5 and $ClNO_2$ are described in ***Text S2****, following established methods (Wang et al., 2022b; Wang et al., 2022a; Thaler et al., 2011). Briefly, N_2O_5 was generated from the reaction between O_3 and excessive NO_2, while $ClNO_2$ was synthesized via the reaction of Cl_2 (6 ppm in N_2) with a moist mixture of $NaNO_2$ and NaCl. The calibration curves for N_2O_5 and $ClNO_2$ at different RH are shown in* ***Figure S2,*** *with mean sensitivities of 0.110 ± 0.063 and 0.055 ± 0.018 ncps/ppb, respectively. The instrument background was determined by introducing dry N_2 into the inlet for 20 min. Based on three times the standard deviation (3σ) of the background signal, the typical 1-minute detection limits for N_2O_5 and $ClNO_2$ were estimated to be 1.3 and 0.61 ppt, respectively."*

2. Method 2.2: The algorithm proposed by Wagner 2013 should be termed as iterative box model instead of interactive box model.

Response: Thank you for the note. We have corrected it in the revised manuscript (**line 130,132 and 139**).

3. Line 212: Suggest clearly stating what simulate parameters exhibited good agreement here.

Response: As you suggested, we have rewritten the sentence in the revised manuscript (**line 225-228**) as follows:

*"As shown in **Figure S7,** the simulated kN_2O_5 and $\varphi ClNO_2$ exhibited good agreement with the classical steady-state method (R^2 = 0.76 and 0.73, respectively), demonstrating the model's capability to characterize heterogeneous uptake processes and thereby effectively evaluate pNO_3^- formation processes."*

4. Line 218-230: A direct comparison of pNO_3^- formation rate is also helpful to indicate the characteristics of pNO_3^- formation at this site.

Response: Thank you for the suggestion. We have added a direct comparison of pNO_3^- formation rate in the revised manuscript (**line 234-238**) as follows:

*"To exclude year-specific effects, we further analyzed pNO_3^- formation during the winters from 2019 to 2023. The results revealed that the pNO_3^- formation rates via N_2O_5 uptake (0.75 – 1.40 $\mu g\ m^{-3}\ h^{-1}$) were comparable to those from the OH + NO_2 reaction (0.88 – 1.66 $\mu g\ m^{-3}\ h^{-1}$; **Figure 3a**), with the N_2O_5 uptake pathway consistently*

*accounting for approximately half of the total pNO_3^- formation in the study area (**Figure 3b**).”*

5. Line 241: Please revise the text font of citation.

Response: Thank you for the note. We have corrected it in the revised manuscript (**line 253**).

6. Line 307-314: The SHAP of TVOC exhibit minor impact on N_2O_5 uptake and correlate not so well with its concentration. Replacing TVOCs with specific VOC species, such as monoterpene and styrene, could provide better correlation of this feature.

Response: Thank you for the comment. We agree that specific VOCs species influence N_2O_5 formation due to the higher reactivity of NO_3 toward them. In this work, the loss of N_2O_5 was calculated using **eqs. R1-R2** (**eqs. S3-S4** in the supplementary material), where kN_2O_5 represents the rate of N_2O_5 uptake, and $kNO_3/Keq[NO_2]$ corresponds to the indirect chemical loss of N_2O_5 through NO_3 chemistry. As shown in **Table S6**, the reaction rate of $kNO_3/Keq[NO_2]$ was calculated to be 0.000136 s^{-1}, which is much smaller than that of kN_2O_5 (0.00764 s^{-1}). This indicates that the loss of N_2O_5 through the consumption of its precursors NO_3 by VOCs is relatively limited compared to its direct uptake. Considering this finding and the risk of model overfitting when including too many variables, we used TVOCs as a simplified indicator to represent the effect of VOCs on pNO_3^- formation via N_2O_5 uptake. As a result, the low SHAP value of TVOCs

is consistent with their limited influence on N_2O_5 removal, as determined by our calculations. We have included a detailed discussion in the supplementary material (**line 98-104**) and provided corresponding explanations in the revised manuscript (**line 319-324**).

$$\tau_{N_2O_5} = \frac{[N_2O_5]}{K_1(T)[NO_2][O_3]} \quad \text{(R1)}$$

$$(\tau_{N_2O_5})^{-1} = kN_2O_5 + \frac{k_{NO_3}}{K_{eq}[NO_2]} \quad \text{(R2)}$$

The corresponding explanations in the main text are as follows:

*"The total concentrations of the observed VOCs (TVOCs) showed a weak negative correlation with N_2O_5 uptake (**Figure 4e**). Similar to existing research (Hu et al., 2023), specific VOC species, such as styrene, 2-butene, and isoprene, can readily consume NO_3 radicals (**Figure S10**), thereby inhibiting N_2O_5 formation. However, the loss of N_2O_5 through the reaction between VOCs and NO_3 was relatively limited compared to its direct uptake, as determined by our calculations (Text S4), which supported the SHAP analysis."*

7. Section 3.4: The response of pNO_3^- and O_3 production rate to precursors is well investigated, while I figure out two confusing points in discussion part. First, the production of O_3 was clearly proved to be VOC-limited, resulting in effective mitigation on O_3 by reducing VOC. Meanwhile, the pNO_3^- production also shows larger sensitivity to VOC variation. However, the authors claim that the effect of VOC reduction is limited in mitigating both pNO_3^- and O_3, which is confusing. Second, the title of this manuscript, a NO_2-limited region, seems contradictory to the finding of O_3

production limited by VOC emission.

Response: We replied to this comment in the following two points.

(1) It is correct that O_3 production was VOC-limited and pNO_3^- production was sensitive to VOC variations. We apologize for the misstatement in the original manuscript. We had intended to state that VOC reduction is effective in mitigating both pNO_3^- and O_3, but its effectiveness in reducing pNO_3^- is relatively limited when compared to NO*x* reduction. We have rewritten the relevant sentence in the revised manuscript (**line 373-375**) as follows:

"As mentioned above, while VOCs reduction proved effective in mitigating both pNO_3^- and O_3, its effectiveness in reducing pNO_3^- remained limited compared to NOx reduction. However, the effectiveness of NOx reduction exhibited significant regional and temporal variations."

(2) We apologize for the misunderstanding. This study primarily focuses on nitrate formation and control. While evaluating the effectiveness of NO*x* reduction on pNO_3^-, we comprehensively assessed its impact on O_3 to help develop more optimized control strategies. Therefore, the NO_2 limitation discussed here specifically applies to N_2O_5 formation that further contributing pNO_3^- formation, not to O_3 formation. Our intention was to highlight that in the NO_2-limited regime, N_2O_5 uptake can act as the dominant pathway for pNO_3^- production. The results show that daytime NO*x* control has a limited effect on reducing pNO_3^- formation and may lead to an increase in O_3 concentrations. In contrast, nighttime NO*x* control can effectively suppress pNO_3^- production while avoiding O_3 enhancement. To avoid misunderstanding, we have revised the abstract

(**line 19-21**) to clarify that the NO_2 limitation refers specifically to pNO_3^- formation. The modifications in the abstract are as follows:

"However, the relative contributions of pNO_3^- formation pathways in urban areas remain poorly quantified, particularly under the NO_2-limited regime that governs its formation (as defined by the NO_2/O_3 ratio), which hinders effective particulate pollution control."

References:

Hu, H., Wang, H., Lu, K., Wang, J., Zheng, Z., Xu, X., Zhai, T., Chen, X., Lu, X., Fu, W., Li, X., Zeng, L., Hu, M., Zhang, Y., and Fan, S.: Variation and trend of nitrate radical reactivity towards volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 23, 8211-8223, https://doi.org/10.5194/acp-23-8211-2023, 2023.

Thaler, R. D., Mielke, L. H., and Osthoff, H. D.: Quantification of Nitryl Chloride at Part Per Trillion Mixing Ratios by Thermal Dissociation Cavity Ring-Down Spectroscopy, Analytical Chemistry. 83, 2761-2766, https://doi.org/10.1021/ac200055z, 2011.

Wang, H. C., Peng, C., Wang, X., Lou, S. R., Lu, K. D., Gan, G. C., Jia, X. H., Chen, X. R., Chen, J., Wang, H. L., Fan, S. J., Wang, X. M., and Tang, M. J.: N_2O_5 uptake onto saline mineral dust: a potential missing source of tropospheric $ClNO_2$ in inland China, Atmospheric Chemistry and Physics. 22, 1845-1859, https://doi.org/10.5194/acp-22-1845-2022, 2022a.

Wang, H. C., Yuan, B., Zheng, E., Zhang, X. X., Wang, J., Lu, K. D., Ye, C. S., Yang, L., Huang, S., Hu, W. W., Yang, S. X., Peng, Y. W., Qi, J. P., Wang, S. H., He, X. J., Chen, Y. B., Li, T. G., Wang, W. J., Huangfu, Y. B., Li, X. B., Cai, M. F., Wang, X. M., and Shao, M.: Formation and impacts of nitryl chloride in Pearl River Delta, Atmospheric Chemistry and Physics. 22, 14837-14858, https://doi.org/10.5194/acp-22-14837-2022, 2022b.