Response to Reviewer #2

We are grateful to the reviewer for the thoughtful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer's comments are in black font and our responses are in blue font).

Comments:

Zang et al., present a comprehensive study to identify the major nitrate formation pathways and their key controlling factors during the winter haze pollution period in the eastern YRD, China using two-year (2018-2019) field observations and detailed observation-constrained model simulations. They find that high atmospheric oxidation capacity is the reason for the winter nitrate aerosol pollution in YRD region in China. And N_2O_5 uptake contributes 60-70% in urban and suburban sites in polluted days. The analysis of the observation data is sound, I only have some comments to the model simulations.

Major Issues:

Line 24-27, The quantification of nitrate formation importance is derived from pollution episodes only. The campaign average result should be much more different. Please clarify it.

Response: Thanks for the reviewer's comment. In this study, we focused on the contribution of different processes to nitrate formation during the haze pollution episodes. To be more precise, we have revised this description as "We find that…, with contribution percentages of 69% and 29% in urban areas and 63% and 35% in suburban areas during the haze pollution episodes, respectively." (changes underlined).

The model includes the dry deposition of HNO_3, it seems that the authors want to simulate the variation the particle nitrate. I am very interesting whether the modelled nitrate comparable with the observation. Is it possible to provide more details about the intercomparison? In addition, when calculating the contribution of nitrate formation, are you just accumulate the nitrate production rate during a certain period from different channel? Are the only represent the formation potential without considering the dry deposition, what is the role of the dry deposition in the model simulation since it cannot influence any result in the paper?

Response: In this study, we simulated the formation rate (i.e., formation potential) of HNO_3 from different pathways but not the concentration of particulate nitrate. Accordingly, the contribution of nitrate formation was the accumulation of the HNO_3 production rate from different channel over a certain period (e.g., daytime or nighttime). In the manuscript, we have compared the increasing rates of particulate nitrate with the formation rates of HNO_3 for several typical episodes and found that the two rates were comparable. The dry deposition did not influence the formation potential of HNO_3, so we have removed its calculation in Section 2.3 of the main text.

The heterogeneous chemistry is well considered in the model simulation, such as the N_2O_5 and NO_2 uptake mechanism, but limited by the observation, the importance of these reactions cannot be confirmed, If the field measurement of N_2O_5 or $ClNO_2$ are available, the result would be more insightful with smaller uncertainties. Here, I suggest the author provide more information about the parameterized N_2O_5 uptake and $ClNO_2$ yield in the main text or SI, which could help people to connect the further observation studies that quantifying N_2O_5 uptake coefficient and/or $ClNO_2$ yield.

Response: We certainly agree that simultaneous measurements of N_2O_5 and $ClNO_2$ would provide strong constraints on the nitrate formation chemistry, but unfortunately such measurements are not available in this study. Instead, we carefully parameterized the heterogeneous nitrate formation pathways based on recent advances on the reaction kinetics and well-measured aerosol data. As mentioned in our replies to the previous comment, the modelled HNO_3 production rates were comparable to the measured increasing rates of particulate nitrate during several pollution episodes, indicating our model results are reliable.

According to the reviewer' suggestion, we have added more information about the parameterized N_2O_5 uptake and $ClNO_2$ yield in Section 2.3 of the revised manuscript (changes underlined).

"For the heterogeneous hydrolysis of N_2O_5, the N_2O_5 molecules accommodated on aqueous aerosols can undergo reversible hydrolysis to form NO_3^- and $H_2ONO_2^+$ (R1), followed by the reaction of $H_2ONO_2^+$ with H_2O or Cl^- to form HNO_3 and $ClNO_2$ (R2 and R3) (Finlayson-Pitts et al., 1989; Schweitzer et al., 1998; Thornton and Abbatt, 2005):

$$N_2O_5\,(aq) + H_2O\,(l) \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} H_2ONO_2^+\,(aq) + NO_3^-\,(aq) \quad (R1)$$

$$H_2ONO_2^+\,(aq) + H_2O\,(l) \xrightarrow{k_2} H_3O^+\,(aq) + HNO_3\,(aq) \quad (R2)$$

$$H_2ONO_2^+\,(aq) + Cl^-\,(aq) \xrightarrow{k_3} ClNO_2\,(g) + H_2O\,(l) \quad (R3)$$

…

$$\gamma N_2O_5 = \frac{4}{c}\frac{V_a}{S_a} K_H \times k_{1f} \times \left(1 - \frac{1}{\left(\frac{k_2}{k_{1b}} \times \frac{[H_2O]}{[NO_3^-]}\right) + 1 + \left(\frac{k_3}{k_{1b}} \times \frac{[Cl^-]}{[NO_3^-]}\right)}\right) \quad (3)$$

where V_a is the measured aerosol volume concentration; K_H is the Henry's law coefficient of N_2O_5, with a value of 51 M atm^{-1} (Bertram and Thornton, 2009); k_{1f} is the second-order reaction rate constant of N_2O_5 with water, which was calculated using a linear function with $[H_2O]$, as $3.0 \times 10^4 \times [H_2O]$ (Yu et al., 2020a); $\frac{k_2}{k_{1b}}$ and $\frac{k_3}{k_{1b}}$ are the relative rates of reactions of $H_2ONO_2^+$ (aq) with H_2O or Cl^- (R2 and R3) versus that with NO_3^- (the reverse reaction of R1), with values determined to be 0.033 and 3.4, respectively (Yu et al., 2020a); and $[H_2O]$, $[NO_3^-]$, and $[Cl^-]$ are the molarity of water, nitrate, and chloride in aerosol, respectively.

…

$$\Phi_{HNO3} = 1 - 1/\left(1 + \frac{[H_2O]}{\frac{k_3}{k_2} \times [Cl^-]}\right) \quad (4)$$

where $\frac{k_3}{k_2}$ is the ratio of reaction rates of R3 versus R2, which has been determined to be 105 (Bertram and Thornton, 2009; Yu et al., 2020)."

Monoterpene is very reactive to NO_3 radical, and we notice that monoterpene was not included in the model simulation, although the monoterpenes concentration may be low during the winter due to low temperature, but it maybe still have large contribution to the NO_3 loss and affect the budget, I encourage the authors do some sensitivity tests to assess the impacts to N_2O_5 uptake and following nitrate formation.

Response: We appreciate the reviewer's point. We have conducted a sensitivity test for monoterpenes to evaluate their influence on the HNO_3 formation. It should be noted that we only have the observation data of monoterpenes obtained using a proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS, Vocus, Tofwerk) at an urban site in Shanghai in early November, 2019. We selected the data on 9 November as the ambient temperature (average: 13.3 °C) that strongly affects monoterpene emissions (Guenther et al., 2012), was relatively low on this day, close to the temperature in the winter. The wind speed (average: 0.76 m s^{-1}) was also low on this day, which limits the transport and dilution of monoterpene emissions. The monoterpene concentration on this day ranges from 0.009 ppb to 0.070 ppb, with an average of 0.038 ppb. The sensitivity analysis shows that when the monoterpene chemistry was considered, the N_2O_5 concentration and HNO_3 production rate from N_2O_5 hydrolysis ($pHNO_{3(N2O5)}$) both had a decrease, especially during the nighttime with high N_2O_5 concentration (Figure S9a, b). However, such decrease was relatively small; the average N_2O_5 concentration and $pHNO_{3(N2O5)}$ decreased by 23% and 12% during the nighttime, respectively. In addition, the contribution of heterogeneous N_2O_5 hydrolysis to HNO_3 formation only decreased by 2.7% (Figure S9c). Notably, the average temperature in the selected winter haze episode was 8.1 °C, which was significantly lower than the temperature on 9 November, so the concentration of monoterpenes should be smaller, as is their impact on the HNO_3 formation. To sum up, the low monoterpene emissions had no significant impact on the budget of NO_3 radicals and N_2O_5 as well as the formation of HNO_3 during the winter haze pollution episodes in eastern YRD.

In the revised manuscript, we have added the above sensitivity analyses and Figure R1 to the supplement as a new section (Section S6. Potential influences of monoterpenes on HNO_3 production). In addition, we have added the following discussion to Section 3.4 of the main text.

"In addition, monoterpenes that are very reactive to NO_3 radicals (Atkinson and Arey, 2003) were not included in the model, because their measurements are not available in this study. However, a case study

considering the monoterpene chemistry in the model shows that the low monoterpene emissions during the winter did not significantly affect the budget of NO_3 radical and N_2O_5 and thereby the nighttime HNO_3 production (see Section S6 and Figure S9 for more details)."

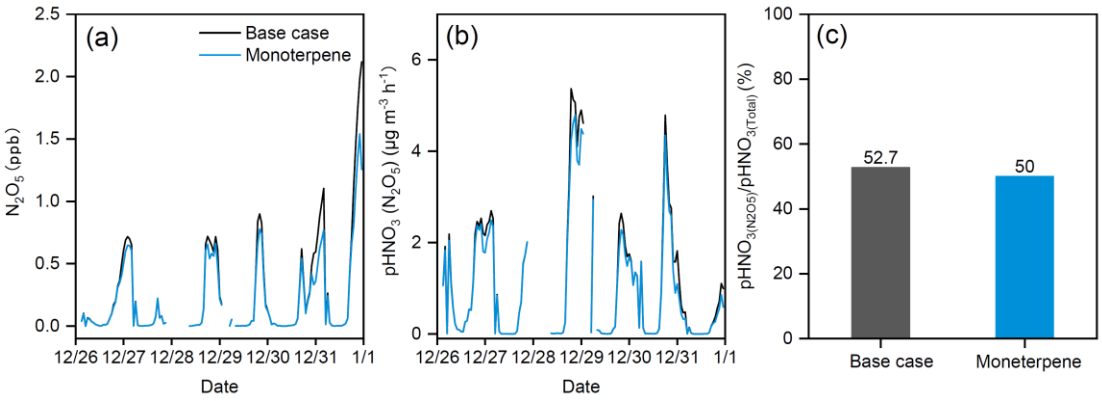

Figure R1 Sensitivity of N_2O_5 concentration, production rates of HNO_3 from N_2O_5 hydrolysis ($pHNO_{3(N2O5)}$), as well as its contribution to the HNO_3 formation ($pHNO_{3(N2O5)}$/ $pHNO_{3(total)}$), to the inclusion of monoterpenes in the model simulation. The chosen episode was from 26 to 31 December, 2019. The base case did not consider the effect of monoterpenes.

Line 249-250, why only constrain the sum NO and NO_2, if the NO and NO_2 not constrained separately but only the sum, I guess the modeled nocturnal NO always be zero when O_3 over ppb. While in fact NO spikes by local emission always observed in urban regions during the nighttime, which would lead to a bias of nitrate formation from N_2O_5 uptake (possibly an overestimation).

Response: Thanks for the reviewer's comment. We have tried to constrain NO and NO_2 separately in the model, but when we did this, the simulated nighttime concentrations of NO_3 radical and N_2O_5 were extraordinarily low during the whole observation period, owing to the titration of NO_3 by NO. In addition, high N_2O_5 peaks were simulated during the daytime likely due to the high O_3 concentrations in the model, which is unreasonable.

Therefore, we constrained the sum NO and NO_2 but let their specific ratios be simulated by the model. As shown in Figure 8 in the main text and Figure S5 in the supplement, the simulated NO_2 concentration was generally in good agreement with the observation, which would also be the case for NO given that the sum of NO and NO_2 was constrained by observation. The NO spikes did exist during the nighttime in some episodes, which could lead to an overestimation of NO_2. However, as discussed in the manuscript, as the O_3 concentration in the model was constrained by the observation, which was very low (below 5 ppb) during the NO spikes periods, the overestimation of NO_2 did not significantly affect the prediction of N_2O_5.

Figure 8 case 1, the observed NO_2 during daytime and nighttime had a lower and higher biases, are they mean the modelled nitrate during the daytime is lower and nighttime is higher. This phenomenon also happened in case 3.

Response: The overestimation of NO_2 during the nighttime was due to the NO spikes. As we explained in the previous comment, the O_3 concentration in the model was constrained by the measured value, which was very low, the overestimation of NO_2 did not significantly affect the modelled N_2O_5 and its contribution to HNO_3 formation. The bias of modelled NO_2 during the daytime is quite small compared to that during the nighttime, it therefore might also have no significant impact on the model results.

Line 81 or change to "and"

Response: We have revised this.

Line 361 weaker change to "weak".

Response: We have revised this.

Line 346 the value 15000 misses the unit, may be $pppbv^3$.

Response: We have added the unit ppb^3 for the value.

References:

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

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, doi, 2009.

Finlayson-Pitts, B. J., Ezell, M. J., and Pitts, J. N.: Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N2O5 and ClONO2, Nature, 337, 241-244, doi: 10.1038/337241a0, 1989.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geoscientific Model Development, 5, 1471-1492, doi, 2012.

Schweitzer, F., Mirabel, P., and George, C.: Multiphase chemistry of N2O5, ClNO2, and BrNO2, J. Phys. Chem. A, 102, 3942-3952, doi: DOI 10.1021/jp980748s, 1998.

Thornton, J. A., and Abbatt, J. P. D.: N2O5 reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, J. Phys. Chem. A, 109, 10004-10012, doi: 10.1021/jp054183t, 2005.

Yu, C., Wang, Z., Xia, M., Fu, X., Wang, W., Tham, Y. J., Chen, T., Zheng, P., Li, H., Shan, Y., Wang, X., Xue, L., Zhou, Y., Yue, D., Ou, Y., Gao, J., Lu, K., Brown, S. S., Zhang, Y., and Wang, T.: Heterogeneous N_2O_5 reactions on atmospheric aerosols at four Chinese sites: improving model representation of uptake parameters, Atmospheric Chemistry and Physics, 20, 4367-4378, doi: 10.5194/acp-20-4367-2020, 2020.