Response to Reviewer #1

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:

General comments:

This study investigates the key controlling factors nitrate formation in YRD region during wintertime based on field observation and box model. They found large ALWC significantly promoted the uptake of $N_2O_5$ and gas-to-partition of gaseous $HNO_3$, the partitioning coefficient of which varied with pH values of particles. The model calculation showed that $N_2O_5$ uptake contribute to the major fraction of particulate nitrate formation in this region during the pollution periods. Further analysis on the correlation of nitrate with its precursors indicated the controlling effect on nitrate formation resulted from atmospheric oxidation, which could be the availability of ozone and OH radical. A comparison over various parameters associated with nitrate formation made between the data before and during the epidemics also provided confidence for the results derived above.

Overall, this work provides valuable data on analyzing nitrate formation. It shows the dominant contribution from $N_2O_5$ uptake to nitrate formation in YRD region which might be different from other regions in China, and reinforces the importance of atmospheric oxidation on mitigating secondary pollution. I would recommend publication of this paper in Atmospheric Chemistry and Physics after the following comments are well addressed.

Specific comments:

Line 240~243: A constant dilution rate for model is inappropriate. For example, the dilution should be significantly enhanced during the breakup of nocturnal boundary layer in the morning at sunrise. It therefore could influence the calculated abundance of long lifetime species, like particulate nitrate, and change the relative contribution from different pathways. Suggest the parameterization of dilution rate constant varying with PBL for a more accurate quantification.

Response: We agree that the evolution of planetary boundary layer (PBL) has a significant influence on the dilution process. When the PBL increases, the loss of species by dilution can be estimated by:

$$\frac{d[X]}{dt} = -\frac{\partial PBL(t)}{PBL(t) \times \partial t}(X - X_{FT}) \qquad (1)$$

Where $X_{FT}$ is the concentration of X in the residual layer or free troposphere. However, we did not have the measured data of $X_{FT}$, so it is difficult to parameterize this value in the model. If we set $X_{FT}$ to 0 or other values for simplicity, there might be significant uncertainties in the model results. Therefore, to evaluate the influence of the parameterization of dilution rate constant ($k_{dil}$) on the $HNO_3$ production rate from different pathways, we performed a sensitivity analysis for $k_{dil}$ by varying its value from 0.028 $h^{-1}$ to 0.2 $h^{-1}$ (corresponding to a dilution lifetime of 5 hours to 36 hours), which covers the typical range of $k_{dil}$ used in observation-constrained model simulations in the literature (Romer et al., 2018; McDuffie et al., 2019; Liu et al., 2020).

The results of sensitivity analyses during typical pollution episodes are shown in Figure R1. As the dilution lifetime varied from 5 hours to 36 hours, the average concentrations of $N_2O_5$ and OH radicals changed within -23%/+1% and -21.6%/+10.8%, respectively (Figure R1a, d), compared to the base case (dilution lifetime: 24 hours) during the episode. Accordingly, the $HNO_3$ production rates from the heterogeneous hydrolysis of $N_2O_5$ and gas-phase OH + $NO_2$ reactions changed within -17%/+1.2% and -33%/+12% (Figure R1b, e) and the relative contributions of the two pathways changed within -2.5%/+5.5% and -5%/+2.3% (Figure R1c, f), respectively. The relatively small changes in the rates and relative contributions of the two $HNO_3$ production pathways upon variations in $k_{dil}$ from 0.028 $h^{-1}$ to 0.2 $h^{-1}$ suggest that the simplified parameterization of the dilution process using a constant $k_{dil}$ would not result in significant uncertainty in the model results.

In the revised manuscript, we have added the following sentence to Section 2.3 of the main text.

"Considering the uncertainties in the parameterization of dilution process using a constant rate constant, we also conducted a sensitivity test for $k_{dil}$ with its value ranging from 0.028 $h^{-1}$ to 0.2 $h^{-1}$, which covers the typical values used in box model simulations to evaluate its influence on the model results."

In addition, we have added above sensitivity analysis results and Figure R1 to the supplement and rephrased discussions on the results of sensitivity tests in Section 3.4 of the main text (changes underlined).

"Significant uncertainties remain in the key parameters of the heterogeneous HONO formation pathways and the dilution process in the model, which could affect the prediction of OH radicals and $N_2O_5$ and thereby the production of $HNO_3$. However, sensitive analyses for various parameters show that the current parameterization of the heterogeneous HONO formation and dilution process in the model allows for robust quantitative constraints ... (see Section S5 and Figures S7, S8 for more details)."

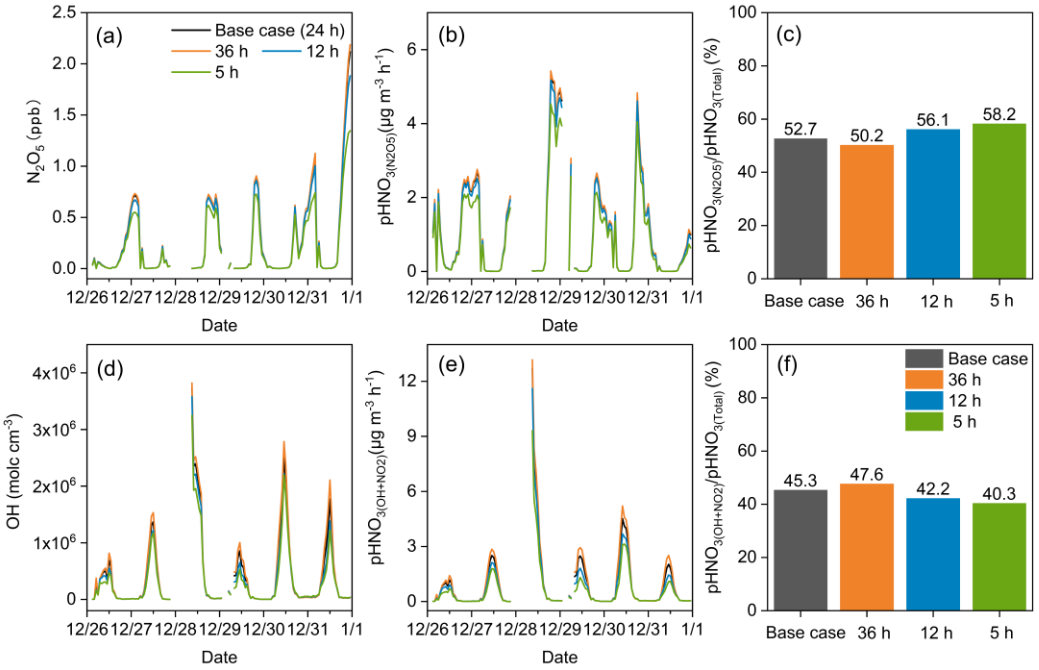


Figure R1 Sensitivity of $N_2O_5$ and OH radical concentrations, production rates of $HNO_3$ from different pathways, as well as their contributions to the $HNO_3$ production to the variations in the value of dilution lifetime from 5 hours to 36 hours in the model. The chosen pollution episode was from 26 to 31 December, 2019. In the base case, a typical dilution lifetime of 24 hour was assumed.

Line 338: The sentence of "The nitrate formation mechanism is different during the different time of a day" is a wrong statement, as the chemical mechanism should be basically the same throughout the day while the dominant formation pathway could change. It should be rephrased or deleted since it is closed to following sentence.

Response: Thanks for the reviewer's comment. We have rephrased this sentence as "The dominant nitrate formation pathway is different during the different time of a day."

Line 340~350: There are two major problems on the evaluation of nighttime nitrate formation pathway. First, the concentration of particulate nitrate observed during nighttime is composed of both daytime remainder and nighttime formation, as it is a long lifetime species. Thus the positive correlation of particulate nitrate concentration with $[NO_2]^2 \times O_3$ might fail to represent the contribution from $N_2O_5$ uptake pathway. Second, what is the time resolution of data points showed in Figure 6? If it is one hour, the level of $[NO_2]^2 \times O_3$ at the point just after sunset, when nighttime formation of nitrate starts, should be the highest over the night under a stable condition without transports. The positive correlation tends to unreasonable accordingly. Suggest replacing the point-to-point correlation with nighttime averages correlation. Similar problems also apply to the daytime cases.

Response: We appreciate the reviewer's suggestion. The time resolution of data points shown in Figures 6 and 7 was one hour. We have replaced the point-to-point correlation with nighttime or daytime average correlation in these two figures (see Figures R2 and R3 below) in the revised manuscript. In addition, to reduce the influences of daytime or nighttime remainder on the analysis of nighttime or daytime nitrate formation, only the data with an obvious peak or increasing trend during the nighttime or daytime were included in the plots.

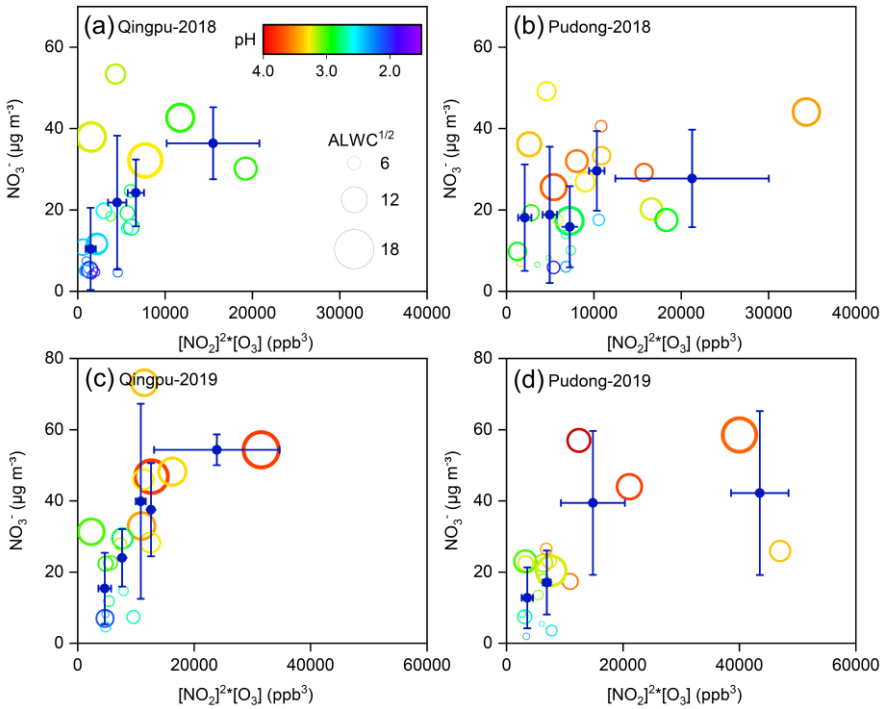


Figure R2 Nighttime average particulate nitrate concentration (empty circles) as a function of $[NO_2]^2 \times [O_3]$ at (a, c) Qingpu and (b, d) Pudong sites in 2018 and 2019. The circles are colored according to aerosol pH and their size is linearly scaled with square root of ALWC. The blue filled circles represent the average of nitrate concentration within a certain $[NO_2]^2 \times [O_3]$ interval.

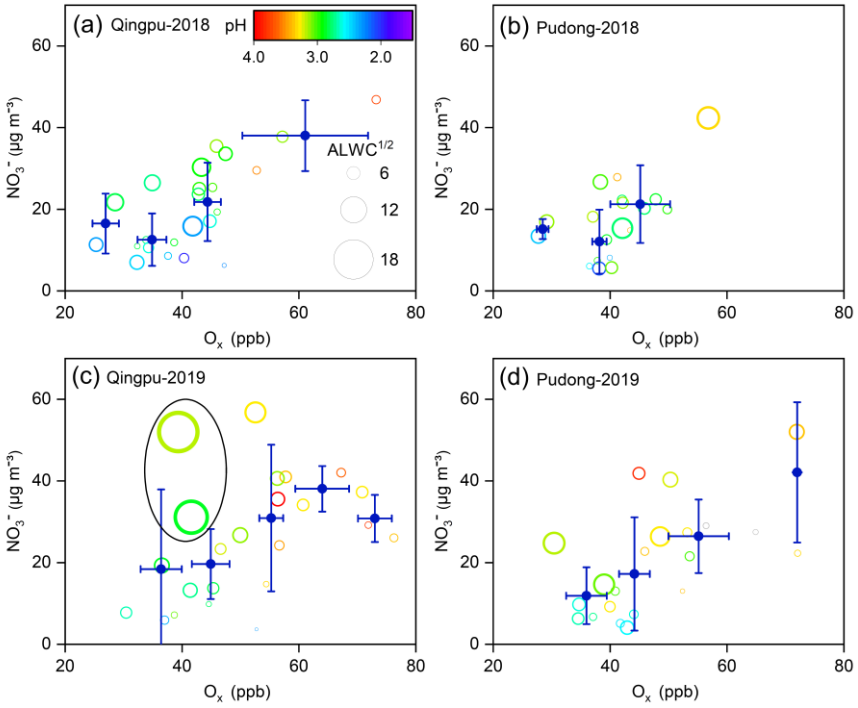


Figure R3 Daytime average particulate nitrate concentration as a function of $O_x$ at (a, c) Qingpu and (b, d) Pudong sites in 2018 and 2019. The circles are colored according to aerosol pH and their size is linearly scaled with square root of ALWC. The blue filled circles represent the average of nitrate concentration within a certain $O_x$ interval. The data points inside the black circle in (c) correspond to low $O_x$ levels but high ALWC and nitrate concentrations.

Line 473~474: References as to the statement that reduction of $NO_2$ could result in the increase of $O_3$ and OH radical are suggested to be provided here.

Response: We have added the relevant references to this statement in the revised manuscript.

Line 522~523: Please explain why regional transport with more aged air plume leads to higher NOR and SOR values before the epidemic periods than that during the epidemic periods? It seems confusing to readers.

Response: The Qingpu site was more easily influenced by the transport of air pollutants from Jiangsu, which is usually more polluted than Shanghai. Before the epidemic, the transport of aged air plume with relatively high nitrate and sulfate concentration from Jiangsu would result in a relatively high NOR and SOR values at the Qingpu site. However, during the epidemic, the emission reduction not only happened in Shanghai, but also in the surrounding areas. As a result, the nitrate and sulfate concentration in the aged air plume from Jiangsu would decrease significantly, leading to a lower NOR and SOR during the epidemic at the Qingpu site.

We have revised manuscript to explain the reason more explicitly.

"In addition, before the epidemic, the transport of aged air plume with relatively high nitrate and sulfate concentrations from upwind regions resulted in relatively high NOR and SOR values at the Qingpu site. However, during the epidemic, the significant decrease in nitrate and sulfate concentrations in the aged air plume due to regional emission reductions leaded to lower NOR and SOR at this site."

References:

Liu, Y. C., Zhang, Y. S., Lian, C. F., Yan, C., Feng, Z. M., Zheng, F. X., Fan, X. L., Chen, Y., Wang, W. G., Chu, B. W., Wang, Y. H., Cai, J., Du, W., Daellenbach, K. R., Kangasluoma, J., Bianchi, F., Kujansuu, J., Petaja, T., Wang, X. F., Hu, B., Wang, Y. S., Ge, M. F., He, H., and Kulmala, M.: The promotion effect of nitrous acid on aerosol formation in wintertime in Beijing: the possible contribution of traffic-related emissions, Atmos. Chem. Phys., 20, 13023-13040, doi: 10.5194/acp-20-13023-2020, 2020.

McDuffie, E. E., Womack, C. C., Fibiger, D. L., Dube, W. P., Franchin, A., Middlebrook, A. M., Goldberger, L., Lee, B., Thornton, J. A., Moravek, A., Murphy, J. G., Baasandorj, M., and Brown, S. S.: On the contribution of nocturnal heterogeneous reactive nitrogen chemistry to particulate matter formation during wintertime pollution events in Northern Utah, Atmos. Chem. Phys., 19, 9287-9308, doi: 10.5194/acp-19-9287-2019, 2019.

Romer, P. S., Wooldridge, P. J., Crounse, J. D., Kim, M. J., Wennberg, P. O., Dibb, J. E., Scheuer, E., Blake, D. R., Meinardi, S., Brosius, A. L., Thames, A. B., Miller, D. O., Brune, W. H., Hall, S. R., Ryerson, T. B., and Cohen, R. C.: Constraints on Aerosol Nitrate Photolysis as a Potential Source of HONO and NOx, Environ. Sci. Technol., 52, 13738-13746, doi: 10.1021/acs.est.8b03861, 2018.