Response to referee 3:

The authors would like to thank the anonymous referee 3 for taking the time to review the manuscript. We thank for validating our work and for providing us with valuable insights that allowed us to improve the manuscript. Comments by the reviewer are given in black normal font, and our response to the comments is shown in blue. Newly added and modified text in the revised manuscript and supporting information (SI) is given in italics.

Ye et al. examined HONO chemistry and its impact on ozone formation using a field campaign measurement and box modeling. They found a high HONO/NOx ratio of 0.17 around noon coinciding with high J(O1D), which suggests the importance of photo-induced sources for HONO formation. This is furthered verified by statistical analysis and box modeling with updated parameterization. They also demonstrated HONO chemistry can greatly enhance net ozone production by 45%.

Overall, this is a well-executed study and the key conclusions are reasonably defended. In particularly, the observational constraint for HONO chemistry from EXPLORE-YRD campaign adds important evidence to the understanding of HONO formation. However, I suggest the authors to discuss more broadly the HONO formation chemistry under different chemical conditions. I would recommend its publication after revision.

Thank you for your positive comments on this study.

We have expanded some discussion on HONO formation chemistry under different chemical conditions:

Line 446-454:

"Despite a good match between observed and measured HONO during most days, HONO was still underestimated after fertilization events, indicating the strong influence of soil HONO emission on HONO budget in areas surrounded by agricultural fields. Therefore, soil HONO emission should be well constrained, especially for rural areas during fertilization periods. In addition, while nitrate photolysis played a negligible role in HONO formation in our study, it may play a more important role in winter polluted periods with high nitrate loadings. Our study highlighted important role of NO_2 conversion on ground surface. Previous studies found some coexisted gas species like NH_3, CO_2 may promote HONO production by NO_2 heterogeneous reaction (Li et al., 2018; Xu et al., 2019; Liu et al., 2023; Xia et al., 2021). Thereby, laboratory experiments investigating heterogeneous NO_2 conversion on ground surface with these species present are needed for better representation of HONO formation in models."

The authors highlighted HONO production from NO2 heterogeneous conversion at ground. But how is daytime PM2.5 concentration during EXPLORE-YRD? I am wondering if the importance of aerosol update will increase over a severe PM2.5 pollution episode. Some discussion on the application of key conclusion from this study is required.

The times series of $PM_{2.5}$ was shown in Figure 1 in the revised manuscript. We can

clearly see that the maximum $PM_{2.5}$ concentration during the daytime was below 100 μg m^{-3}. HONO production by NO_2 uptake on aerosol surface can be expressed as follows:

$$P_{aerosol+h\nu}=\frac{1}{4}\gamma_{aerosol+h\nu}\times\frac{j(NO_2)}{0.005\ s^{-1}}\times[NO_2]\times\upsilon_{NO_2}\times S_a$$

If we take an $\gamma_{aerosol+h\nu}$ of 2×10^{-5} and double daytime $PM_{2.5}$ concentrations (assuming Sa was linearly correlated with $PM_{2.5}$ concentrations), then the HONO production by NO_2 uptake on aerosol surface was shown below (Figure R1):

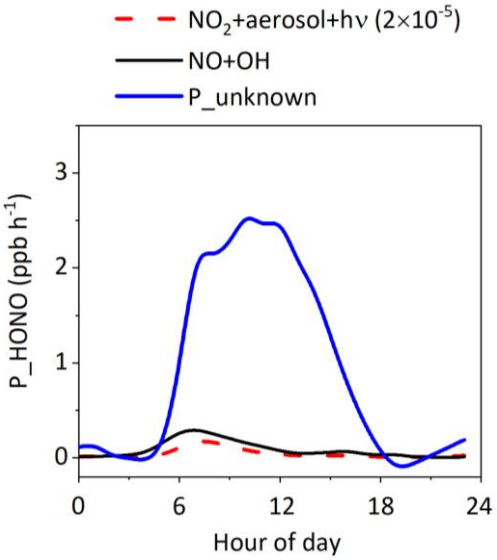

Figure R1. HONO production rates by photo-induced NO_2 conversion on the aerosol surface.

Despite doubling daytime $PM_{2.5}$ concentrations, HONO production was still much lower than unknown sources, and also lower than NO+OH, implying NO_2 uptake on aerosol surface was not important in our study. Compared to NO_2 conversion on ground surface, NO_2 conversion on aerosol surface was minor, which was ascribed to much smaller surface area to volume ratio (<0.01 m^{-1} vs 0.3 m^{-1})

Our study provides three important hints: 1) NO_2 heterogeneous on ground surface dominated HONO production; 2) soil HONO emission may become an important source in rural area with large areas of agricultural fields during fertilization period; 3) HONO greatly aggravated O_3 pollution in China. Our study has important implication on O_3 mitigation for policymakers. Controlling HONO production may provide an alternative pathway for O_3 mitigation. We have added the following discussion on the application from our study in the revised manuscript:

Line 492-504:

"In addition, now most studies are focusing on VOCs and NO_x reduction to achieve O_3 mitigation. However, O_3 formation showed non-linear relationship on VOCs and NO_x, making it difficult to decrease O_3 by solely reducing VOCs or NO_x. For instance, during COVID-19 lockdown period, O_3 showed an evident increase while NO_x and VOCs

showed a decrease trend, highlight the complexity of O_3 mitigation (Zhao et al., 2020; Wang et al., 2022). Our results suggested HONO contributed significantly to O_3 production in China, and thereby, reducing HONO production may be an alternative way for O_3 control. As NO_2 heterogeneous reactions on the ground surface were important sources for HONO production, reducing NO_x emissions would be beneficial for reducing HONO emissions. However, NO_x reduction may also lead to more O_3 production if O_3 formation is in a VOC-limited regime, and hence the overall effects of NO_x reduction on O_3 should be evaluated by chemical transport models. Moreover, soil HONO emissions may become an important source in rural area with large areas of agricultural fields. Decreasing soil HONO emissions is beneficial for O_3 pollution control, especially during fertilization period in June when the O_3 pollution was severe. Therefore, more environmental-friendly fertilization amount and fertilization mode should be investigated to decrease soil HONO emissions."

L43: please spell out "SOA"

As suggested, "SOA" has changed to "secondary organic aerosol (SOA)".

L166-167: any reference for "a lifetime of 8 hours"?

For reference, we have added a study by Ma et al. (2020). We assumed a lifetime of 8 hours with the aim of considering the loss by transportation and deposition. If this loss was incorporated, the modeled PAN agreed very well with observed PAN in this campaign (Figure S1), suggesting this incorporation was reasonable.

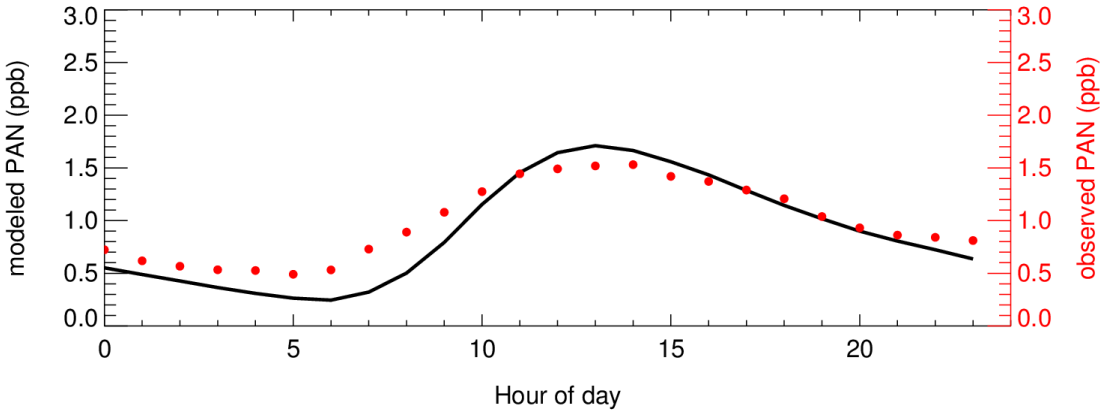

Figure S2. Averaged diurnal pattern of observed and modeled PAN if A first-order dilution loss term with a lifetime of 8 hours was incorporated.

L251: this argument should be further justified.

As suggested, we have revised the corresponding texts:
Line 249-251:
"In addition, considering that the observation period covered the fertilization period in June, the high HONO/NO_x in our study may be partially explained by direct soil HONO

emissions around the sampling sites."

In Fig.1, The website of TROPOMI NO2 data product should be provided.

We have provided the following website of TROPOMI NO_2 data product: https://s5phub.copernicus.eu/dhus

Reference:

Li, L., Duan, Z. Y., Li, H., Zhu, C. Q., Henkelman, G., Francisco, J. S., and Zeng, X. C.: Formation of HONO from the NH3-promoted hydrolysis of NO2 dimers in the atmosphere, P Natl Acad Sci USA, 115, 7236-7241, 10.1073/pnas.1807719115, 2018.

Liu, J., Li, B., Deng, H., Yang, Y., Song, W., Wang, X., Luo, Y., Francisco, J. S., Li, L., and Gligorovski, S.: Resolving the Formation Mechanism of HONO via Ammonia-Promoted Photosensitized Conversion of Monomeric NO2 on Urban Glass Surfaces, Journal of the American Chemical Society, 145, 11488-11493, 10.1021/jacs.3c02067, 2023.

Ma, X. F., Tan, Z. F., Lu, K. D., Yang, X. P., Chen, X. R., Wang, H. C., Chen, S. Y., Fang, X., Li, S. L., Li, X., Liu, J. W., Liu, Y., Lou, S. R., Qiu, W. Y., Wang, H. L., Zeng, L. M., and Zhang, Y. H.: OH and HO2 radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018, Atmos Chem Phys, 22, 7005-7028, 10.5194/acp-22-7005-2022, 2022.

Wang, H., Huang, C., Tao, W., Gao, Y., Wang, S., Jing, S., Wang, W., Yan, R., Wang, Q., An, J., Tian, J., Hu, Q., Lou, S., Pöschl, U., Cheng, Y., and Su, H.: Seasonality and reduced nitric oxide titration dominated ozone increase during COVID-19 lockdown in eastern China, npj Climate and Atmospheric Science, 5, 24, 10.1038/s41612-022-00249-3, 2022.

Xia, D. M., Zhang, X. R., Chen, J. W., Tong, S. R., Xie, H. B., Wang, Z. Y., Xu, T., Ge, M. F., and Allen, D. T.: Heterogeneous Formation of HONO Catalyzed by CO2, Environ Sci Technol, 55, 12215-12222, 10.1021/acs.est.1c02706, 2021.

Xu, W., Kuang, Y., Zhao, C., Tao, J., Zhao, G., Bian, Y., Yang, W., Yu, Y., Shen, C., Liang, L., Zhang, G., Lin, W., and Xu, X.: NH3-promoted hydrolysis of NO2 induces explosive growth in HONO, Atmos. Chem. Phys., 19, 10557-10570, 10.5194/acp-19-10557-2019, 2019.

Zhao, Y., Zhang, K., Xu, X., Shen, H., Zhu, X., Zhang, Y., Hu, Y., and Shen, G.: Substantial Changes in Nitrogen Dioxide and Ozone after Excluding Meteorological Impacts during the COVID-19 Outbreak in Mainland China, Environmental Science & Technology Letters, 7, 402-408, 10.1021/acs.estlett.0c00304, 2020.