Reviewer #2:

General comments

Zhang et al. investigated the role of several HONO precursors in enhancing O_3 during haze aggravating processes using the WRF-Chem model. This manuscript analyzed the contribution of several different HONO sources (e.g., gaseous reaction between NO and OH, heterogeneous reactions on ground surface, and aerosol-related reactions) to O_3 enhancement. A key finding is that the importance of different HONO sources in affecting HONO formation, or in O_3 enhancement changed with height. The authors also reported the contribution of particulate nitrate photolysis to O_3 enhancement, nitrate concentrations, and HONO formation, after adjusting the $J_{nitrate}/J_{HNO3}$ ratios from 1–120. I have several comments/suggestions that could be considered in the revised version of the manuscript.

We sincerely thank you for the time and effort you spent in reviewing the manuscript, your kindly comments and suggestions are very precious and helpful to us. Point by point response to your comments has been made and attached beneath. The comments by the reviewer are in the plain format with black color*, and the responses are in the italic format with blue color, we hope these improvements could make our results more reasonable.*

1.The authors have indicated that ground-related heterogeneous reactions serve as the main HONO source at near-surface levels. The photolysis of HNO_3 adsorbed ($HNO_3(ads)$) on ground surfaces might also produce HONO, and this pathway is not discussed in the manuscript. If this source appears as negligible for HONO production, please explain why. Here is an example that reported $HNO_3(ads)$ as a daytime HONO precursor: Zhou, Xian liang, et al. "Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications." Geophysical Research Letters 30 (2003).

The photolysis of HNO_3 adsorbed ($HNO_3(ads)$) on ground surfaces might be a potential HONO source. We had made an attempt to insert this source into the model previously, however, this source showed a minor impact on HONO in our study region and was deleted in this research.

*Using the simulated HNO_3 deposition velocity (V_d), HNO_3 (g) concentrations and nitrate photolysis frequency (adopting a large $J_{nitrate}/J_{HNO3}$ ratio of 120), we calculated the HONO formation rate at the BUCT site during the study period (**Fig. reply1**). After several days when the dry deposition amount and the photolyzed amount were close to balance, the maximum HONO formation rate was <1 ng N m^{-2} s^{-1} around noontime. The formation of HONO via this reaction was contained in the first model layer above the ground, and the total HONO formation rate was relatively small, especially in high*

NO$_x$ emission areas like NCP compared with several other stronger HONO sources. However, this source might have a significant impact on HONO in the low-NO$_x$ environment, just as Zhou et al. (2003) pointed out.
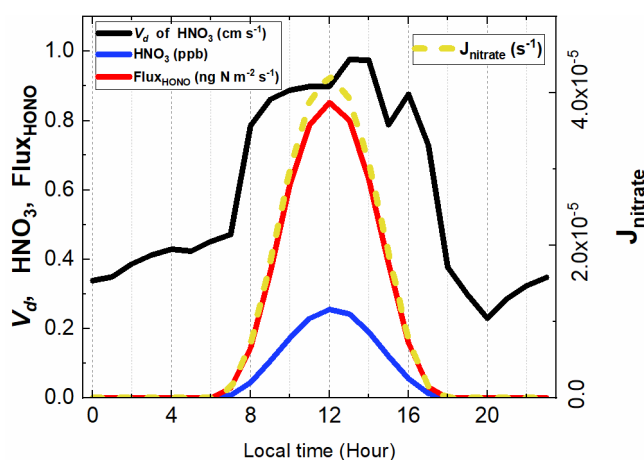

Fig.reply1 *the diurnal HONO formed (Flux$_{ion}$) via deposited HNO$_3$ photolysis on the ground, and the corresponding HNO$_3$ concentration, HNO$_3$ dry deposition velocity (V$_d$) and nitrate photolysis frequency (J$_{nitrate}$, assuming a J$_{nitrate}$/J$_{HNO3}$ ratio of 120) at the BUCT site during the study period.*

2.The information provided in the introduction section does not fully support the default J$_{nitrate}$/J$_{HNO3}$ setting of 30. Several previous studies have provided insights showing that J$_{nitrate}$/J$_{HNO3}$ seemed to change with several chemical properties of the aerosol samples (e.g., Ye et al., 2016, Bao et al. 2018), and the authors did not attempt to estimate J$_{nitrate}$/J$_{HNO3}$ based on the aerosol chemistry at their sampling sites. Also, it is not clear whether the J$_{nitrate}$/J$_{HNO3}$ reported in marine environment could be extrapolated to the atmospheric environment of the North China Plain. I would expect that the acidity of aerosols in the polluted environment might lead to enhanced J$_{nitrate}$/J$_{HNO3}$.

The J$_{nitrate}$/J$_{HNO3}$ setting of 30 was referred to the recommendations of Romer et al. (2018) (ratio of 1–30) and Kasibhatla et al. (2018) (ratio of 25–50), a recent HONO study also adopted the J$_{nitrate}$/J$_{HNO3}$ ratio of 30 for nitrate photolysis by using the CMAQ model (Zhang et al., 2021). The purpose of using these constant J$_{nitrate}$/J$_{HNO3}$ values (1, 7, 30 and 120) is to be easier to compare with other relevant studies (Fu et al., 2019; Kasibhatla et al., 2018; Romer et al., 2018; Shi et al., 2021; Shi et al., 2020; Xue et al., 2020; Zhang et al., 2021; Zheng et al., 2020), because these studies adopted one or more constant J$_{nitrate}$/J$_{HNO3}$ values in their nitrate photolysis studies. The propose of conducting a group of J$_{nitrate}$/J$_{HNO3}$ sensitivity tests in our study is to evaluate the impacts and uncertainties of these J$_{nitrate}$/J$_{HNO3}$ ratios.

We sincerely thank you for your good suggestion to explore the role of the acidity of aerosols on $J_{nitrate}/J_{HNO3}$. The concept has been proposed by Ye et al. (2016a) and explored by Bao et al. (2018) through laboratory experiments. In the results of Bao et al. (2018), they found introducing HCl flow enhanced HONO formation under irradiation condition, but no HONO enhancements were found after introducing HCl flow under dark condition, these results indicated the essential role of the acidic proton in the HONO production during nitrate photolysis.

*Based on previous studies, directly measure particle pH is very difficult (Rindelaub et al., 2016), proxy methods such as thermodynamic equilibrium models and phase partitioning are commonly used to predict particle pH in the United States, in the Europe and in China (Bougiatioti et al., 2016; Liu et al., 2017; Weber et al., 2016). To calculate the aerosol acidity, we used the ISORROPIA II model (Fountoukis and Nenes, 2007) combined with the simulated concentrations of gas and aerosol (e.g., NH_3, NH_4^+, H_2SO_4, SO_4^{2-}, HNO_3, NO_3^-, Na^+, and H_2O) from our results. The ISORROPIA II model is widely adopted to calculate the pH value of the aerosol and has been coupled into a number of models including GEOS-Chem and Cam. The calculated pH values of the aerosols for the base and 6S cases are shown in **Fig.reply2**, with a mean pH of ~3.8 for both cases and a minor difference between the two cases. Our calculated pH values in NCP were comparable with the results of Liu et al. (2017), who also used the ISORROPIA II model combined with field observations of gases and aerosols in Beijing during wintertime and reported a pH range of 3.0–4.9 with a mean value of 4.2.*
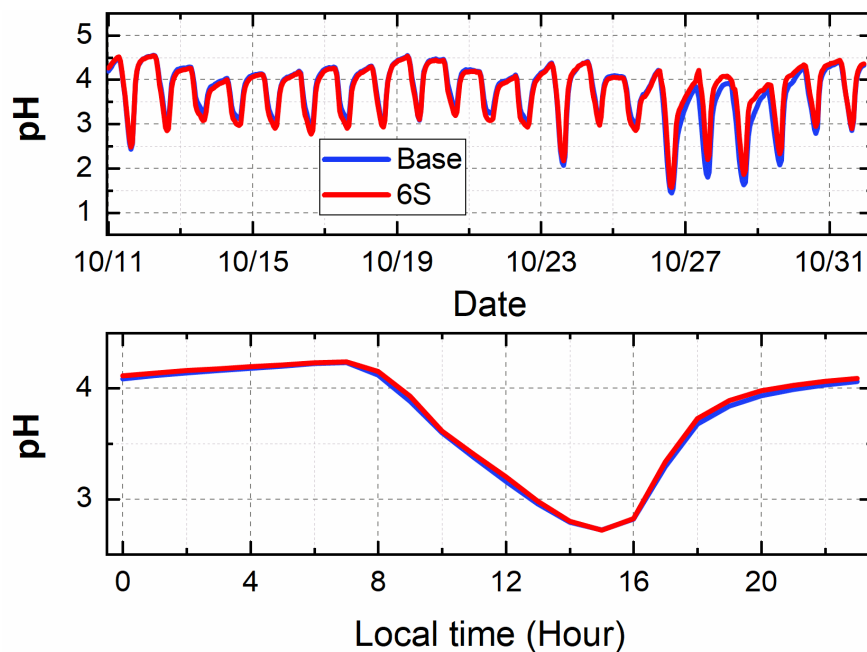

Fig.reply2 *the hourly and diurnal mean aerosol pH at the 95 NCP sites for the base and 6S cases during the study period.*

Due to the lack of equation between $J_{nitrate}/J_{HNO3}$ and pH in previous studies (Ye et al., 2016a; Bao et al., 2018), directly evaluating the impact of aerosol acidity on

$J_{nitrate}/J_{HNO_3}$ and related parameters is very difficult for model studies. Nevertheless, an increasing trend for acidity was indeed found based on calculated daytime pH variation. By comparing the results of the four constant $J_{nitrate}/J_{HNO_3}$ values (1, 7, 30 and 120) in the revised manuscript, we could reasonably speculate that if the $J_{nitrate}/J_{HNO_3}$ ratio was enhanced by the acidity of aerosols during daytime, the atmospheric oxidation capacity and the formation of secondary pollutants will probably be enhanced, e.g., ozone and secondary aerosols will probably be elevated as a result.

Ye et al. (2016b) found Phot$_{nitrate}$ in the marine environment could increase the formation of tropospheric oxidants and secondary atmospheric aerosols on a global scale. Assuming that the $J_{nitrate}/J_{HNO_3}$ reported in marine environment was the same as that in the atmospheric environment of NCP, the Phot$_{nitrate}$ in the marine environment had a small impact on the ozone pollution in the coastal areas of NCP, with a maximum DMA8 O$_3$ enhancement of 1–2 ppb shown in **Fig. reply3**.
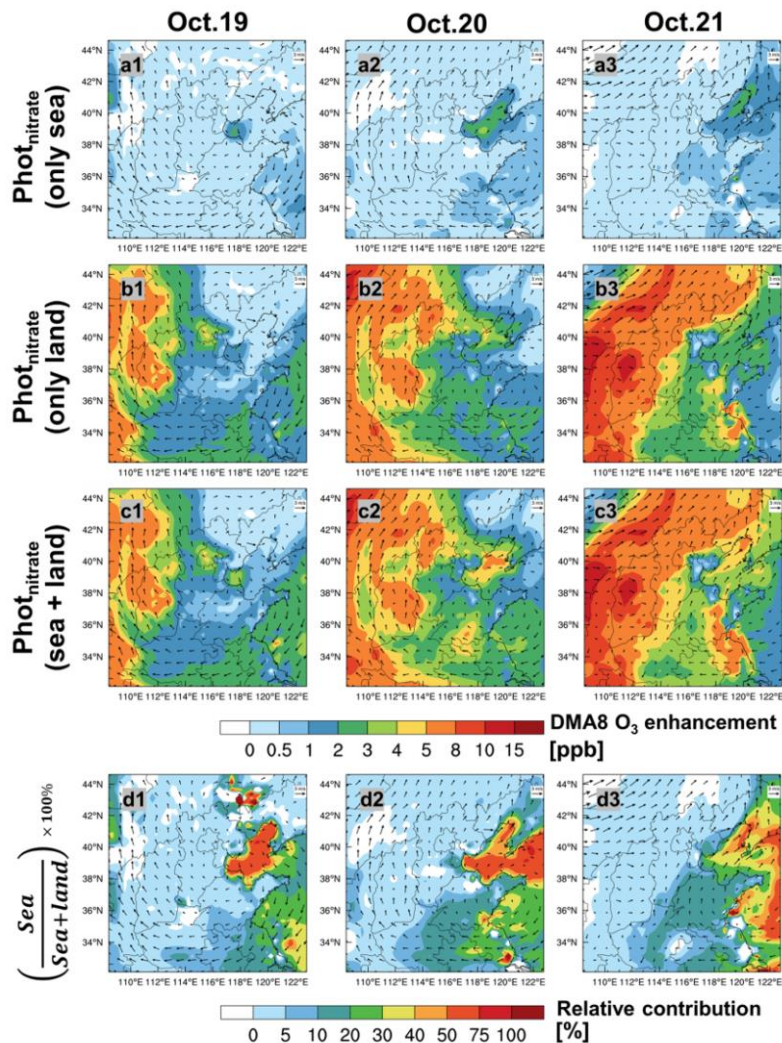
Fig.reply3 *Comparison of surface DMA8 O$_3$ enhancements caused by nitrate photolysis only above the sea (a1–a3, case Desae minus base), only above the continent (b1–b3, case DeLand minus base), above both sea and continent (c1–c3, case D minus base), and the proportion of enhanced O$_3$ by*

Phot$_{nitrate}$ only above the sea to that above both sea and continent (d1–d3) in NCP during a typical haze aggravating process. Setting a J$_{nitrate}$/J$_{HNO3}$ of 30.

3.Could you explain why uncertainty analyses were only conducted for J$_{nitrate}$/J$_{HNO3}$? Are there uncertainties associated with the parameters in R3 and R4? Also, does uncertainties in HONO/NO$_2$ production ratio in R2 affect your results?

The uncertainty of Het$_{ground}$ on O$_3$ formation was also discussed and can be found in **Text S2** *in the supplementary material. The impact of Het$_{aerosol}$ was small, thus its uncertainty analysis was not provided.*

Phot$_{nitrate}$ could in turn change NO$_x$ concentrations to some extent. From the 95-site-averaged NO$_2$ concentrations shown in **Fig. 20***, we can find that Phot$_{nitrate}$ slightly increased NO$_2$ concentrations in hazy days. The elevated NO$_2$ concentration could enhance HONO formation via the NO$_2$ heterogeneous reactions, nevertheless, due to the high background NO$_2$ concentrations in NCP (up to ~ 40 ppb at nighttime), the increment of NO$_2$ and the enhanced HONO formation from NO$_2$ caused by Phot$_{nitrate}$ were small (<10%) but might have a larger impact on NO$_x$ budgets in clean regions. A positive feedback relationship between the NO$_2$ heterogeneous reactions and the Phot$_{nitrate}$ reaction could be found, these multi-processes worse the air quality during the haze aggravating processes (please see* **section 4.4** *in the revised version).*

4.Please make sure that the supplement information is provided. Now the supplement is not available from the preprint webpage.

We are very sorry to have found that the supplementary materials are not available on the ACPD website. In our initial submission, we uploaded the manuscript and the supplementary material, while the format of Table 4 in the manuscript was in landscape format rather than in the portrait format, the landscape format might be unable to operate, and the editor reminded us to provide a new manuscript file with proper format. In the following operation of updating the manuscript with the corrected format handled by the editor, we misunderstood that the supplementary material is NOT needed, so we deleted the supplementary material. The revised supplementary material has been uploaded.

Reference:

Bao, F., Li, M., Zhang, Y., Chen, C., Zhao, J., 2018. Photochemical Aging of Beijing Urban PM$_{2.5}$: HONO Production. Environmental science & technology 52, 6309-6316.

Bougiatioti, A., Nikolaou, P., Stavroulas, I., Kouvarakis, G., Weber, R., Nenes, A., Kanakidou, M., Mihalopoulos, N., 2016. Particle water and pH in the eastern Mediterranean: source variability and implications for nutrient availability. Atmos. Chem. Phys. 16, 4579-4591.

Fountoukis, C., Nenes, A., 2007. ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H2O aerosols. Atmospheric Chemistry and Physics 7, 4639-4659.

Fu, X., Wang, T., Zhang, L., Li, Q.Y., Wang, Z., Xia, M., Yun, H., Wang, W.H., Yu, C., Yue, D.L., Zhou, Y., Zheng, J.Y., Han, R., 2019. The significant contribution of HONO to secondary pollutants during a severe winter pollution event in southern China. Atmospheric Chemistry and Physics 19, 1-14.

Kasibhatla, P., Sherwen, T., Evans, M.J., Carpenter, L.J., Reed, C., Alexander, B., Chen, Q.J., Sulprizio, M.P., Lee, J.D., Read, K.A., Bloss, W., Crilley, L.R., Keene, W.C., Pszenny, A.A.P., Hodzic, A., 2018. Global impact of nitrate photolysis in sea-salt aerosol on NO_x, OH, and O_3 in the marine boundary layer. Atmospheric Chemistry and Physics 18, 11185-11203.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., Zhu, T., 2017. Fine particle pH during severe haze episodes in northern China. Geophysical Research Letters 44, 5213-5221.

Rindelaub, J.D., Craig, R.L., Nandy, L., Bondy, A.L., Dutcher, C.S., Shepson, P.B., Ault, A.P., 2016. Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and Variation in Acidity with Relative Humidity. The Journal of Physical Chemistry A 120, 911-917.

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., Cohen, R.C., 2018. Constraints on Aerosol Nitrate Photolysis as a Potential Source of HONO and NOx. Environmental science & technology 52, 13738-13746.

Shi, Q., Tao, Y., Krechmer, J.E., Heald, C.L., Murphy, J.G., Kroll, J.H., Ye, Q., 2021. Laboratory Investigation of Renoxification from the Photolysis of Inorganic Particulate Nitrate. Environmental science & technology 55, 854−861.

Shi, X., Ge, Y., Zheng, J., Ma, Y., Ren, X., Zhang, Y., 2020. Budget of nitrous acid and its impacts on atmospheric oxidative capacity at an urban site in the central Yangtze River Delta region of China. Atmospheric Environment 238, 117725.

Weber, R.J., Guo, H., Russell, A.G., Nenes, A., 2016. High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. Nature Geoscience 9, 282-285.

Xue, C., Zhang, C., Ye, C., Liu, P., Catoire, V., Krysztofiak, G., Chen, H., Ren, Y., Zhao, X., Wang, J., Zhang, F., Zhang, C., Zhang, J., An, J., Wang, T., Chen, J., Kleffmann, J., Mellouki, A., Mu, Y., 2020. HONO Budget and Its Role in Nitrate Formation in the Rural North China Plain. Environmental science & technology 54, 11048-11057.

Ye, C., Gao, H., Zhang, N., Zhou, X., 2016a. Photolysis of Nitric Acid and Nitrate on Natural and Artificial Surfaces. Environmental science & technology 50, 3530-3536.

Ye, C., Zhou, X., Pu, D., Stutz, J., Festa, J., Spolaor, M., Tsai, C., Cantrell, C., Mauldin, R.L., 3rd, Campos, T., Weinheimer, A., Hornbrook, R.S., Apel, E.C., Guenther, A., Kaser, L., Yuan, B., Karl, T., Haggerty, J., Hall, S., Ullmann, K., Smith, J.N., Ortega, J., Knote, C., 2016b. Rapid cycling of reactive nitrogen in the marine boundary layer. Nature 532, 489-491.

Zhang, S., Sarwar, G., Xing, J., Chu, B., Xue, C., Sarav, A., Ding, D., Zheng, H., Mu, Y., Duan, F., Ma, T., He, H., 2021. Improving the representation of HONO chemistry in CMAQ and examining its impact on haze over China. Atmospheric Chemistry and Physics 21, 15809-15826.

Zheng, H., Song, S., Sarwar, G., Gen, M., Wang, S., Ding, D., Chang, X., Zhang, S., Xing, J., Sun, Y., Ji, D., Chan, C.K., Gao, J., McElroy, M.B., 2020. Contribution of Particulate Nitrate Photolysis to Heterogeneous Sulfate Formation for Winter Haze in China. Environmental Science & Technology Letters 7, 632-638.

Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S.B., Civerolo, K., Schwab, J., 2003. Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications. Geophysical Research Letters 30. Doi:10.1029/2007JD008782.