Reviewer #3:

General comments

The manuscript reported the WRF-Chem model evaluation of several HONO sources and their impacts on multiple aspects of photochemistry, such as HONO production, O_3 production, OH production, nitrate production etc. The discussion is not limited to ground surface, by is spreading over regional and vertical distribution of pollutant budget. A rather comprehensive understanding on the HONO sources' impacts is thus shared with colleagues in our society. However, the model validation is not fully convincing. Also, discussion on the many results and figures appears to be oversimplified.

We sincerely appreciate 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 was 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 that these improvements could make our results more convincing and more profound.*

Specific comments

1.   Model-measurement comparison on regional and vertical distribution of pollutant budget would be helpful to convince that the HONO source is potentially missing process in current WRF-Chem scheme. Would it be appropriate to direct compare the stationary measurements with the model? If column density useful to verify model calculation on the regional and vertical distribution, considering vertical gradient measurements are rare?

*For model-measurement comparison, it is appropriate to direct compare simulations and observations at remote sites or representative regional sites for regional chemical model studies, because the grid-averaged concentrations of pollutants (i.e., simulations) at those sites are nearly equal to the measurements at those corresponding sites; otherwise, the simulations are usually lower than the corresponding observations at the other sites, 95 monitoring sites in the North China Plain were used for model validation, which is representative for this region (please see **Fig.3&4** in the revised manuscript).*

*The vertical evaluation of the model is indeed necessary, especially when conducting vertical analysis. The vertical comparison of simulated and observed HONO was actually conducted in our work, the description is given in **section 3.3.1** of the revised manuscript, and the model evaluation of the vertical HONO is shown in **Fig.S6**.*

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.

2. How the nitrate production and partitioning are setup in the model and compared with your measurements? Please refer to the reference of Kasibhatla et al., 2018.

We adopted the MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) module developed by Zaveri et al. (2008) in this study for nitrate production and partition, the nitrate in the MOSAIC was produced via the gas-phase reaction showed below:

$$HNO_3(g) + NH_3(g) \leftrightarrow NH_4NO_3(s)$$

This is a gas-particle equilibrium reaction, NH_4NO_3 is a volatile solid salt, and the equilibrium constant K(T) is calculated as below:

$$K(T) = K(T_0)^{e\left[\alpha\left(\frac{T_0}{T}-1\right)+\beta\left(1+\ln\left(\frac{T_0}{T}\right)-\frac{T_0}{T}\right)\right]}$$

Where T_0 = 298.15 K, $K(T_0)$ = 4.72×10^{-17}, α = -74.38 and β = 6.12.

In the study of Kasibhatla et al. (2018), the nitrate was formed via the gas-phase HNO_3 uptake on coarse-mode sea-salt aerosol, and calculated as below:

$$\frac{d[Nitrate]}{dt} = 4\pi D_g R_{cSSA} N_{cSSA} f(Kn)([HNO_3] - [HNO_3]^{eq})$$

Where [X] represents the mixing ratio, D_g is the gas-phase diffusivity of HNO_3, R_{cSSA} is the radius of coarse-mode SSA, N_{cSSA} is the number concentration of coarse-mode SSA, Kn is the Knudsen number, $[HNO_3]^{eq}$ is the equilibrium concentration of gas-phase HNO_3 associated with coarse-mode SSA.

*The model evaluation of nitrate is given in Fig.2b, the statistical metrics of mean bias (MB), root mean square error (RMSE) and the index of agreement (IOA) were 6.44/0.71 μg m^{-3}, 15.16/12.13 μg m^{-3} and 0.89/0.91 for the 6S/base case, respectively (**section 3.1.2** in the revised version).*

3.   Production of HONO from NO+OH route is offsetted by HONO photolysis, so is OH production from HONO photolysis. Was the net production of HONO or OH plotted in these figures?

HONO can be formed via the NO+OH reaction, which consumes OH and mainly occurs in daytime with high OH concentrations, nevertheless, the formed HONO can in turn be photolyzed to produce NO and OH during daytime, the net OH production from HONO is its photolysis to OH minus its homogeneous formation of HONO.

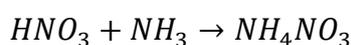
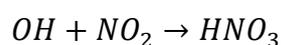
*Near the ground, when only the NO+OH reaction was considered (Base case), the consumed OH for HONO formation was 0.11 ppb h^{-1} at the 95 NCP sites during daytime, while the corresponding production rate of OH via HONO photolysis was 0.09 ppb h^{-1} during daytime, HONO had a negative contribution (-0.02 ppb h^{-1}) and became a small sink of OH when the NO+OH reaction was considered as the only HONO source (**section 3.3.2** in the revised version). However, when the six potential HONO sources were added into the model, the production rate of OH via HONO photolysis was 1.81 ppb h^{-1} at the 95 NCP sites during daytime, while the corresponding HONO production rate via NO+OH was 0.48 ppb h^{-1}. The net contribution of HONO photolysis to OH reached 1.33 ppb h^{-1}. After considering the six potential HONO sources, HONO indeed had a net contribution to OH. One important thing we should notice is that the enhanced OH by HONO is amplified in the radicals' cycling involving OH, HO_2 and RO_2 and thus the atmospheric oxidation processes are enhanced, that is why the enhancement of the total OH production/loss is higher than the enhancement caused by the direct HONO photolysis (please see **Fig.9** and **section 3.3.2** in the revised version).*

*The net production enhancement of OH was calculated between the cases considering potential HONO sources (e.g., case 6S) and the base case (e.g., **Fig.10** and **Fig.12** and **section 3.3.2** in the revised version).*

4.   In figure 2, why nitrate loading is still higher in 6S model as it is consumed in the photolysis reaction, compared to base model?

The nitrate photolysis reaction indeed consumed nitrate to a certain extent, however, the products of Phot$_{nitrate}$ especially HONO favored nitrate formation and in turn mitigated nitrate consumption. The photolysis of HONO elevated OH concentrations, favoring the formation of gaseous nitric acid (HNO_3) and nitrate, the main reactions are:

$$OH + NO_2 \rightarrow HNO_3$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

*The detailed nitrate enhancement at the BUCT site is given in **Fig S3** and **section 3.1.2** in the revised version, among the six potential HONO sources, Phot$_{nitrate}$ slightly consumed nitrate and lowered its concentrations, but Het$_{aerosol}$ and Het$_{ground}$ significantly promoted nitrate formation and increased nitrate concentrations, the 6S case contained the six potential HONO sources and this is why the nitrate concentration in the 6S case is higher than that in the base case.*

*A number of studies have also proven the enhanced role of nitrate by HONO, for example, the nitrate was significantly increased in **Fig.8** of Fu et al. (2019) after considering six potential HONO sources (**Fig.reply1**), with a J$_{nitrate}$/J$_{HNO3}$ ratio of ~120 for Phot$_{nitrate}$.*

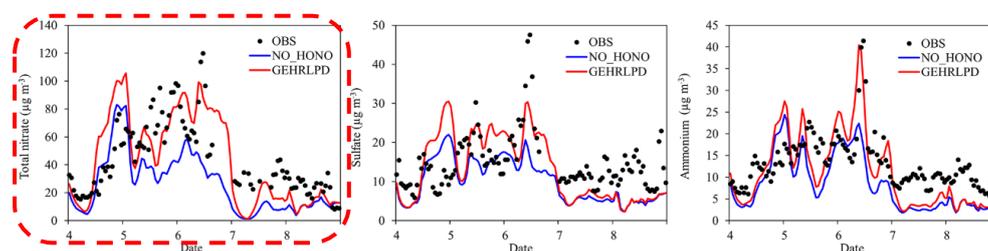



Figure 8. Temporal variation of observed and simulated total nitrate, sulfate, and ammonium concentrations in the NO_HONO and GEHRLPD cases at the Heshan site during 4–8 January 2017.

*ived from the six additional HONO sources***Fig.reply1** *(From Fig.8 in Fu et al. (2019)), the red line contained additional HONO sources including nitrate photolysis with a J$_{nitrate}$/J$_{HNO3}$ ratio of ~120, the blue line was the base case.*

Recently Zhang et al. (2021) compared nitrate concentrations between the base case and the case after adding six potential HONO sources including nitrate photolysis (J$_{nitrate}$/J$_{HNO3}$=30), the enhanced nitrate also can be found after adding the six potential HONO sources.

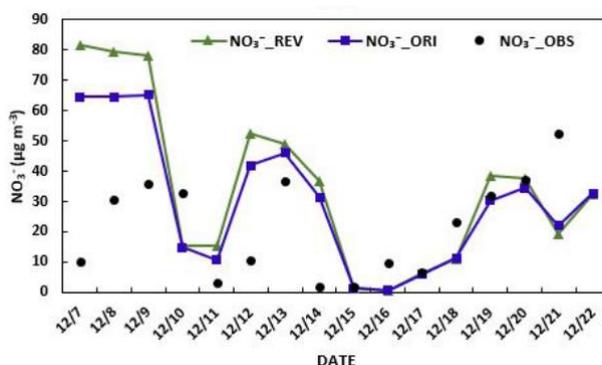



Fig.reply2 *Nitrate comparison before and after adding six potential HONO sources (From Fig.4 in Zhang et al. (2021)), the green line contained six additional HONO sources including nitrate photolysis, the blue line was the base case.*

5.   The impacts of those tested HONO sources varies from clean day to pollution day and from the surface to higher levels. What are the key parameters mediating it?

The discussion on the detailed impact of potential HONO sources from clean days to pollution days and from the surface to higher levels was rare in previous studies, we made an attempt to find the key potential HONO sources for the atmospheric environment. The added six potential HONO sources in this study can be classified into two categories, i.e., ground related sources (three direct emission sources ($E_{traffic}$, E_{soil} and E_{indoor}) and the NO_2 heterogeneous reaction on ground surface (Het_{ground})), and aerosol related sources (the NO_2 heterogeneous reaction on aerosol surface ($Het_{aerosol}$) and nitrate photolysis ($Phot_{nitrate}$))(Abstract and section 2.2 in the revised version). The $E_{traffic}$, E_{soil}, E_{indoor} and Het_{ground} were added in the first layer of the model, the strong photolysis frequency of HONO (~1×10^{-3} s^{-1} around noontime) reduced the concentrations of these ground related HONO sources at higher altitude; while $Het_{aerosol}$ and $Phot_{nitrate}$ were added at each of the vertical modelling layers, their variation with altitude was slow, and their relative contribution to HONO concentrations increased with altitude. The emission rates of $E_{traffic}$, E_{soil} and E_{indoor} were relatively stable under different pollution levels, while the HONO formation via Het_{ground}, $Het_{aerosol}$ and $Phot_{nitrate}$ were enhanced in haze aggravating processes because of higher concentrations of NO_2, $PM_{2.5}$ and nitrate favored these reactions Please see Section 3.3.1 in the revised version.

6.   Figure 10&13 infers an underestimated P(OH)/O3 as a function of PM2.5? Was this verified anywhere? What is the reason of it?

The propose is to evaluate the impact of potential HONO sources on the atmospheric oxidation capacity under different pollution levels ($PM_{2.5}$ concentrations).

Some recent studies have found the positive correlation between observed $PM_{2.5}$ and observed O_3 (Tie et al., 2019), especially during haze events with co-occurrences of high $PM_{2.5}$ and O_3 concentrations (Feng et al., 2021; Fu et al., 2019) (please see the Abstract and Section 1 in the revised version). Researchers speculated the significant role of HONO in O_3 formation in these haze events, however, by using the models only with the default HONO formation mechanism (NO+OH), the HONO concentration was seriously underestimated, resulted in a severe underestimation of atmospheric oxidation capacity and O_3 concentrations, which can be found in our manuscript (Figs 2–4 and sections 3.1.2 and 3.1.3 in the revised version) and many previous studies. For example, the simulated O_3 without additional HONO sources (blue line) in the results of Fu et al. (2019) (represented in the top right corner of Fig.reply3). Under higher $PM_{2.5}$ concentrations, the HONO sources were stronger, especially for Het_{ground}, $Het_{aerosol}$ and $Phot_{nitrate}$, higher concentrations of NO_2, $PM_{2.5}$ and nitrate, and larger surface to volume ratio for the aerosols both favored these reactions (please see Section 2.2 of the revised version). The differences between the 6S case and the base case were

larger in hazy days than in clean days, this is the reason why the enhanced P(OH), OH and O$_3$ showed positive correlation with PM$_{2.5}$.

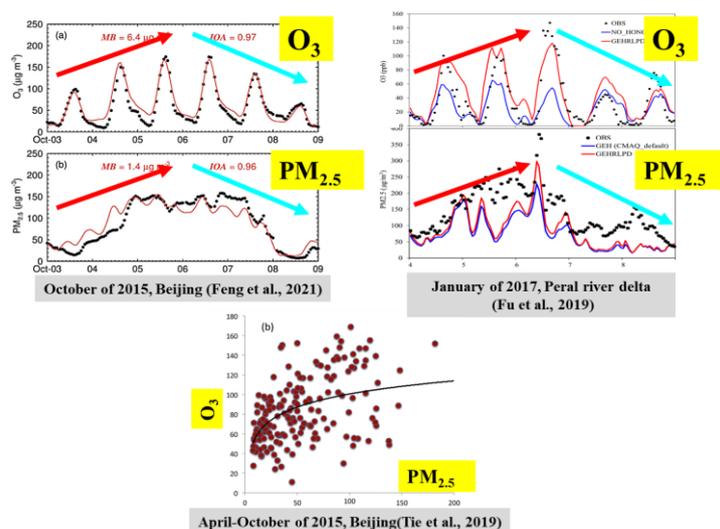



Fig.reply3 *The variation patterns of PM$_{2.5}$ and O$_3$, and the positive correlation between PM$_{2.5}$ and daytime O$_3$ collected from some recent relevant studies.*

7. Figure 18 suggests less perturbation of nitrate budget by Phot$_{nitrate}$? Is there a measurement confirmation of this? What is the reason of it?

*The discussions on the nitrate budget by Phot$_{nitrate}$ in previous studies were very few to the best of our knowledge. Romer et al. (2018) found a J$_{nitrate}$/J$_{HNO3}$ ratio of 10 or 30 would have a much larger effect on HONO than on HNO$_3$, and Phot$_{nitrate}$ accounted for an average of 40% of total HONO production, and only 10% of HNO$_3$ loss with a J$_{nitrate}$/J$_{HNO3}$ ratio of 10 (**Fig.5** in Romer et al. (2018)), consistent with our study (**section 4.2.2** in the revised version).*

*In brief, the produced HONO and NO$_x$ from Phot$_{nitrate}$ are both favorable for nitrate formation. From the gaseous HNO$_3$ production rate (P$_{HNO3}$) in **Fig.S10**, we can find that an increase in the J$_{nitrate}$/J$_{HNO3}$ ratio simultaneously enhances the HNO$_3$ production rate, i.e., nitrate consumption is mitigated by the faster nitrate formation, this is the main reason for less perturbation of the nitrate budget influenced by Phot$_{nitrate}$ (please see **section 4.2.2** in the revised version).*

8. Long sentences for example in the abstract are not easy to follow.

Long sentences in the abstract and the main text were revised as short sentences according to your suggestions (please see the revised version).

References:

Feng, T., Zhao, S., Bei, N., Liu, S., Li, G., 2021. Increasing atmospheric oxidizing capacity weakens emission mitigation effort in Beijing during autumn haze events. Chemosphere 281, 130855.

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.

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Zaveri, R.A., Easter, R.C., Fast, J.D., Peters, L.K., 2008. Model for Simulating Aerosol Interactions and Chemistry (MOSAIC). J Geophys Res-Atmos 113. doi:10.1029/2007JD008782.

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