Dear editor:

We sincerely thank you and the three anonymous reviewers in reviewing the manuscript, the comments and suggestions are very precious and helpful to us. Point by point response to the reviewers' 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 that these improvements could make our results more reasonable.*

We are awfully sorry to have forgotten uploading the supplementary materials during our first submission. The revised supplementary material has been uploaded now.

With respect,

Best wishes,

Weigang Wang

Junling An

Reviewer#1

General comments:

The article entitled "Amplified role of potential HONO sources in O3 formation in North China Plain during autumn haze aggravating processes" by Zhang et al., is in line with several studies performed by the research group on this topic. North China Plain climate and atmospheric composition received higher attention in the last decade. The authors analyzed the impact of different HONO sources on the ozone concentrations by using the WRF-Chem model and performed investigations over various scenarios to study the effect of nitrate photolysis as the main HONO source.

The article is very well written and concise.

One main aspect regarding the complete evaluation of the present work has been related to missing supplementary material and the difficulties to understand the results and discussions despite the missing figures and text.

The comments of this review have been adapted and the eventual similar comments with the other reviewers have been removed to avoid double suggestions. However, some additional comments and suggestions remain to be solved.

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 that these improvements could make our results more reasonable.*

We are awfully sorry to have forgotten uploading the supplementary materials during our first submission. The revised supplementary material has been uploaded.

Specific comments:

1. An important finding of the present work is the effect of the photolytic and "volumic" HONO sources on the ozone high concentrations. These findings are related to haze episodes in NCP. The NCP area is highly correlated with biomass burning events where a high amount of aromatics are released into the atmosphere. The aromatics can strongly influence tropospheric chemistry on a regional scale. Could aromatics and especially nitroaromatics, both present in gas-phase and particle-phase, through their direct photolysis explain partly the amount of HONO? Could nitroaromatics play partially the role of nitrate in this study? Including photolysis of nitroaromatics for the conditions discussed in the model would influence the HONO formation

from the photolysis of nitrate. A chosen larger J(nitrate) would unbalance HONO sources from surface vs HONO sources from a higher altitude ("volumic"). Including similar sources with photolysis of nitrate could limit the J(nitrate)/J(HNO3) values.

We sincerely thank you for your support to our study. As you kindly pointed out, including similar sources with photolysis of nitrate may constrain the $J_{nitrate}/J_{HNO3}$ value to a more reasonable range. The photolysis of nitroaromatics was supposed as a potential HONO source in the atmosphere, and their representative chemical species are nitrophenols.

The concept of HONO formation via nitrophenol photolysis was proposed by Bejan et al. (2006) firstly, and they reported a $J_{(nitrophenol - HONO)}$ value of $(1.1–4.4) \times 10^{-5}$ s^{-1} for four typical nitrophenols with J_{NO2} reaching 10^{-2} s^{-1} (Table 1 in Bejan et al. (2006)). They collected a ortho-nitrophenol concentration of ~60 ppt in an urban area from Harrison et al. (2005), and calculated a HONO formation rate of ~6 ppt h^{-1} at noontime with J_{NO2} reaching 10^{-2} s^{-1} (the photolysis of 1 ppb of ortho-nitrophenol corresponding to ~0.1 ppb h^{-1} HONO production around noontime) (Bejan et al., 2006). While in rural areas the concentrations of nitrophenols were very low and usually <10 ppt, the maximum HONO production rate via the photolysis of nitrophenols was < 1 ppt h^{-1}. Thus, the HONO production rates are quite small via the photolysis of nitrophenols, compared with other stronger potential HONO sources in urban areas (Other HONO sources usually reached several ppb h^{-1} in urban areas during daytime).

Limited to the current understanding on the mechanisms of nitro-aromatic compounds and the lack of nitro-aromatic compounds in the anthropogenic inventory, the nitro-aromatic compounds are temporarily not available in the WRF-Chem model. To evaluate their potential impact on the HONO formation, we estimated by using the reported observations from the literature. Here are some recent observations of nitro-aromatic compounds in NCP. Li et al. (2020b) reported a total concentration of ~80 ng m^{-3} for eight nitro-aromatic compounds in urban Beijing from autumn to winter of 2017–2018, being the highest concentration among the four seasons, and corresponding to ~12–15 ppt. Li et al. (2020a) reported a total concentration of 19–585 ng m^{-3} (mean is 173 ng m^{-3}) of twelve nitro-aromatic compounds in January of 2016 in urban Beijing, the maximum concentration was corresponding to ~100 ppt. Wang et al. (2018) observed the fine particulate nitrated phenols at four sites in northern China (including urban, rural and mountain areas) during 2013–2014, the maximum value was found in urban Jinan during winter, with a mean value of <50 ng m^{-3}, i.e., <10 ppt. Yang et al. (2020) reported the concentration of nitro-aromatic compounds was ~80 ng m^{-3} in urban Beijing and 8 ng m^{-3} in rural Xinglong. Recently Song et al. (2021) reported a maximum concentrations of ~ 1.2 ppb in hazy days for the gas-phase nitrated phenols in urban Beijing during winter of 2018, and the averaged concentration in clean days was ~170 ppt.

From the above, the nitro-aromatic compounds were usually 1–100 ppt in NCP, and rarely exceeded 1ppb even in the heavy haze events in winter. The calculated maximum HONO production rate around noontime was 0.1–10 ppt h^{-1} in most cases, quite small compared with the calculated unknown HONO sources (several ppb h^{-1}). Some modeling studies have evaluated the impact of this source and found that this source is minor. Lee et al. (2016) adopted an upper limit constant concentration of 1 ppb and the photolysis rate of $\sim 3 \times 10^{-5}$ s^{-1} in their MCM (Master Chemical Mechanism) box model but found that the contribution of this source can be neglected. Recently Chen et al. (2021) reported an average peak HONO production rate of 16.9 ppt h^{-1} from the photolysis of nitro-phenolic compounds in south China with the MCM model, so the HONO production rate was also small.

*Although $J_{(nitrophenol - HONO)}$ and $J_{nitrate}$ values may be similar, e.g. 10^{-5} s^{-1}, the concentration of nitro-aromatic compounds (in the unit of "ng m^{-3}") in the atmosphere is quite low compared with that of nitrate (in the unit of "μg m^{-3}"), dwarfing their atmospheric contribution to HONO. Nevertheless, the introduction of this potential HONO source has been added into the revised manuscript, please see **Line 75–76 in Page 3–4** in the **introduction section**.*

2. HONO is formed from NO and OH but HONO photolysis would produce back those products. HONO formation by this source is a net production?

*HONO can be formed via the NO+OH reaction, which consumes OH and mainly occurs in daytime when OH concentrations are high, and 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**), accordingly, the daytime-averaged net HONO formation rate was 0.02 ppb h^{-1} at the 95 NCP sites.*

Based on the above results, the OH+NO reaction slightly increased HONO concentrations but consumed more OH as a cost, so reduced the concentrations of atmospheric oxidants essentially.

*For more details, please see **Line 517–544 in Page 28–29** in the **Section 3.3.2**.*

3. Table 3 has not been easy to understand since missing the definition of the metrics...

*The definitions were given in **text S1** in the supplementary materials previously, and the supplementary materials have been uploaded.*

Briefly, the definition of MB, NMB, RMSE and IOA are calculated as:

$$MB = \frac{\sum_{i=1}^{N}(P_i - O_i)}{N}$$

$$NMB = \frac{\sum_{i=1}^{N}(P_i - O_i)}{\sum_{i=1}^{N}O_i} \times 100\%$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(P_i - O_i)^2}{(N-1)}}$$

$$IOA = 1 - \frac{\sum_{i=1}^{N}(O_i - P_i)^2}{\sum_{i=1}^{N}(|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$$

Where P_i represents the simulated data and O_i represents the observed data. N means the number of data pairs. $\bar{O}$ is the mean of observations. These statistical measures are commonly used for model validation.

4. In figure 2 at the end of the haze period, it seems to accumulate significant precursors of HONO, other than those included in the 6S scenario. How could be explained the missing correlations of HONO between the observed and 6S on 15.10.2018 and 22-23.10.2018?

*The simulated HONO on Oct.15 and Oct.22 was indeed underestimated compared with the observations. The underestimation was mainly caused by the earlier scavenging of pollutants at the urban Beijing site (BUCT) in the model. From the comparison of PM$_{2.5}$ in **Fig.2a**, we could clearly find that the observed PM$_{2.5}$ reached its peak on Oct.15 and Oct.22 in the first two haze episodes, especially on Oct.22; but the simulated PM$_{2.5}$ reached its peak on Oct.14 and Oct.21 in the first two haze episodes and decreased fast on Oct.15 and Oct.22. For a specific site like the BUCT, limited to the spatial/temporal resolution of meteorological and chemical inputs, biases may occur in the beginning or ending of a haze event, nevertheless, the model usually performs better on a regional scale because of less local effects. For example, the increasing and scavenging patterns of PM$_{2.5}$ were both well captured at the 95-NCP-sites in **Fig.4d**. Discussions on the underestimation of simulated HONO has been added in **Section 3.1.2** in the revised manuscript, please see **Line 299–305** in **Page 15**.*

5. In this figure, the nitrate by 6S is overestimated constantly? Why? It is correlated with the NO$_2$ overestimation?

The detailed nitrate enhancement in case 6S 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 NO_2 heterogeneous reactions especially Het_{ground}, which was overestimated due to the overestimation of NO_2, significantly promoted nitrate formation and increased nitrate concentrations. 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 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 due to potential HONO sources, for example, the nitrate was significantly increased in Fig.8 of Fu et al. (2019) after considering six potential HONO sources in southern China (Fig.reply1), with a $J_{nitrate}/J_{HNO3}$ ratio of ~120 for $Phot_{nitrate}$. An overestimation of ~20–40 μg m^{-3} for nitrate could be found on January 4 and January 6 of 2017.
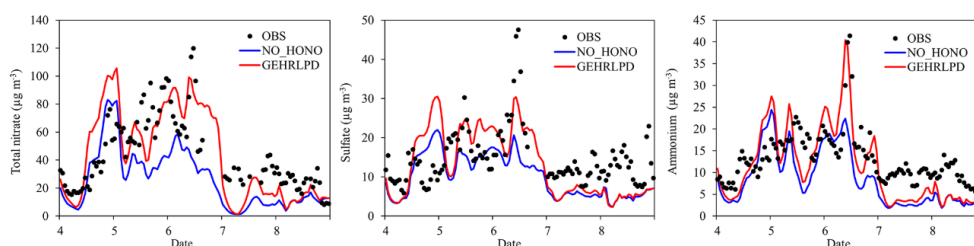

Figure 8. Temporal variation of observed and simulated total nitrate, sulfate, and ammonium concentrations in the NO_HONO and GEHRLPD cases at the Heshan site during 4–8 January 2017.

***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 ($J_{nitrate}/J_{HNO3}=30$) in urban Beijing, the enhanced nitrate can also be found after adding the six potential HONO sources. The overestimation of nitrate (reached 10–70 μg m^{-3}) could also be found in more than half of their study period. When using the hourly concentration rather than the daily mean concentration for nitrate, the overestimation would be probably even larger.
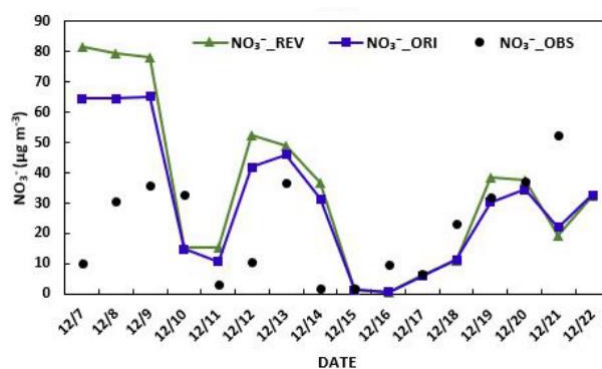
Fig.reply2 Nitrate comparison before and after adding six potential HONO sources (From Fig.4 in Zhang et al. (2021)), the green line contained six additional HONO sources including nitrate photolysis, the blue line was the base case.

For our nitrate results in Fig.2, the observed nitrate pattern was well reproduced. The model performed well in clean days, but overestimated by 10–50 $\mu g\ m^{-3}$ in some period of the first two haze aggravating processes. From the above, using the CMAQ model by Fu et al. (2019) and Zhang et al. (2021) or using the WRF-Chem model by us, the nitrate concentrations were usually overestimated. The overestimation could be partially caused by the uncertainties in the anthropogenic emission inventory, e.g., the overestimation of NO_x emissions, as you kindly pointed out. The inadequate understanding of the nitrate formation mechanism could also be related to nitrate simulation bias.

*For more details, please see **Line 287–298** in **Page 14–15** in **Section 3.1.2**.*

6. In figure 2 the NO_2 concentrations are constantly overestimated. Could you explain why the observations are constantly lower at maxima? It may be the reason for interferences in the NO_2 measurements?

The NO_2 observations were obtained by using commercial instrument (Thermo 42i), and we deemed these observations as the truth value in the atmosphere. Generally speaking, the interferences in the NO_2 measurement like HONO or NO_y tend to slightly elevate the NO_2 observations rather than lower their values, the current bias was probably caused by the model overestimation. For the simulations, our results followed the pattern of the observations at both BUTC and 95-NCP sites but were overestimated especially during nighttime. The overestimation of NO_2 could be partially attributed to the uncertainty in the anthropogenic emission inventory due to the dramatic changes in anthropogenic emissions in China over the past few years (Zheng et al., 2018).

*In the study of Zhang et al. (2021), they used the CMAQ with the ABaCAS national emissions inventory (http://www.abacas-dss.com, last access: 14 October 2021), a large bias of NO_2 simulations compared with the observations could also be found (**Fig.reply3**).*
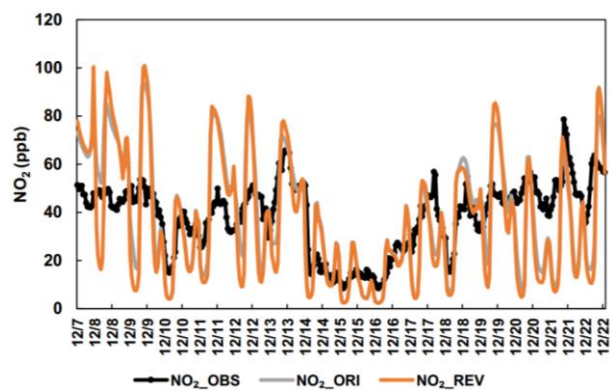
Fig.reply3 Comparison of simulated and observed NO2 at urban Beijing (Fig.S6 in Zhang et al. (2021))

A recent modelling study conducted by us (Lu et al., 2021) compared NO_2 simulations and observations from November of 2019 to March of 2020, covering the COVID-19-induced lockdown period in eastern China with 174 cities. The anthropogenic inventory and the model setup were consistent with the Base case in this study. The NO_2 concentration was well simulated before the COVID-19 lockdown (November to December). In January and February an apparent bias occurred between the simulations and observations, because of the human activity came to a standstill, while the model still performed the "regular" results and approximately reflected the observations without the COVID-19 impact. When the lockdown was gradually got over the gaps were narrowed and almost appeared in late March. The overall NO_2 performance in our model is acceptable, and we speculate that on a larger spatial and temporal scale or using an updated NO_x emission inventory, the model performance on NO_2 will possibly be better and more reasonable.
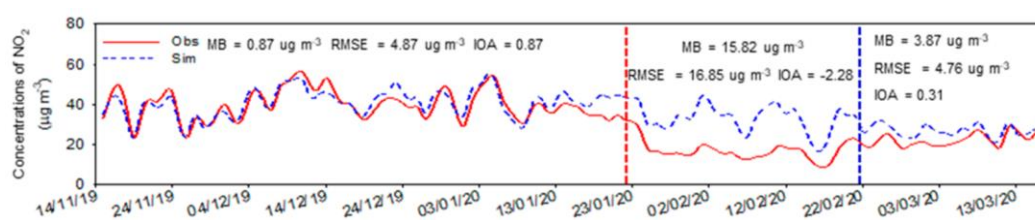
Fig.reply4 Comparison of simulated and observed NO_2 at 174 cities in eastern China from Nov.14, 2019 to March 15, 2020 (Lu et al., 2021) by using the same model and same inventory as this manuscript.

7. Could the authors add some information about the interferences which are related to each instrument measurements, especially for HONO, nitrate, and NO_2?

Thanks for your suggestions. HONO was measured with a homemade water-based long-path absorption photometer which was described in Chen et al. (2020). Briefly, the interferences were determined by the dual-channel absorption system because the real HONO concentration was the difference between the two channels. One of the known HONO interferences is NO_2, which had a relatively low solubility in water, and had almost the same concentration in both channels.

Other parameters were measured with respective commercial instruments. The 42i (Thermo Scientific) used molybdenum NO_2-to-NO converter, there would be a NO_2 overestimation for the conversion of HONO, HNO_3, and other NO_y. Compared with NO_2, the concentrations of other components were relatively low, so their impacts could be small. ToF-ACSM (Aerodyne) was developed via Fröhlich et al. (2013) for Non-refractory $PM_{2.5}$ measurement. The detailed usage could be found in Liu et al. (2020), where ionization efficiency calibration of nitrate was performed using 300 nm dry NH_4NO_3 every month during the observation.

*These descriptions have been added into the revised manuscript, please see **Line 151–163** in **Page 7–8** in **section 2.1**.*

8. It could be simulated a missing HONO source presence for additional contribution to ozone formation on vertical average over the J(nitrate)/J(HNO3)=30 ratio?

For the missing HONO source study, Su et al. (2008) proposed the calculation of unknown HONO source in their study, usually described as $R_{Unknown}$. The below equation shows the processes influencing the concentration of HONO at a site:

$$\frac{d(HONO)}{dt} = (R_{OH+NO} + R_{Unknown} + R_{Emiss} + R_V + R_H) - (R_{OH+HONO} + R_{Phot} + R_{Depo})$$

Where $\frac{d(HONO)}{dt}$ is the observed variation of HONO concentrations, R_{OH+NO} is the homogeneous HONO formation rate via OH+NO , $R_{Unknown}$ is the combination of HONO production from unknown sources, R_{Emiss} is the emission rate, R_V describes the vertical transport process, R_H describes the horizontal transport process, $R_{OH+HONO}$ is the HONO loss rate from reaction OH+HONO, R_{Phot} is the photolysis loss rate and R_{Depo} is the deposition loss rate.

This method is commonly used in the $R_{Unknown}$ calculation. By combining with the HONO observations, assuming a pseudo steady state for HONO and neglecting small terms, $R_{Unknown}$ was calculated via the following equation by Su et al. (2008):

$$R_{Unknown} \approx J_{HONO}[HONO] + k_{OH+HONO}[OH][HONO] + \frac{d(HONO)}{dt}$$
$$- k_{OH+NO}[OH][NO]$$

The calculated $R_{Unknown}$ is an estimation of the whole missing HONO sources and usually used in box model for a typical observation site near the ground. The $R_{Unknown}$ excluded horizontal and vertical transport.

*$R_{Unknown}$ impacts on RO_x (=OH +HO$_2$+RO$_2$) cycles and O$_3$ formation can be found in our previous studies (Guo et al., 2020; Tang et al., 2015). In this study, each of the other five potential HONO sources except the traffic source can be grouped as $R_{Unknown}$ according to Su et al. (2008), and have been discussed, including your suggestion, shown in **sections 3.2, 3.3 and 4** in the revised version.*

9. Line 39 and line 802: "one order of magnitude"

*Thanks for your suggestions. The expression of "one order of magnitude" has been changed to "ten times" in the revised manuscript. Please see **Line 37, 207, 481, 578, 639 and 891**.*

10. Lines 66-68: Please add more sources of HONO from homogeneous reactions ... For direct emissions and heterogeneous HONO sources are plenty of references and would be great for the consistent state of the art to include homogeneous HONO sources too, even if they have a lower contribution in comparison with NO + OH.

*Thanks for your good suggestion. A number of references about homogeneous reactions formed HONO have been added to the revised manuscript, including via NO+OH reaction (Pagsberg et al., 1997; Stuhl and Niki, 1972), via nucleation of NO$_2$, H$_2$O, and NH$_3$ (Zhang and Tao, 2010), via the photolysis of ortho-nitrophenols (Bejan et al., 2006), via the electronically excited NO$_2$ and H$_2$O (Crowley and Carl, 1997; Dillon and Crowley, 2018; Li et al., 2008) and via HO$_2$·H$_2$O+NO$_2$ reaction (Li et al., 2015; Li et al., 2014; Ye et al., 2015). Except for the NO+OH reaction, the contribution of other homogeneous HONO sources was minor in the atmosphere. Please see **Line 71–78 in Page 3–4** in the revised manuscript.*

11. Again, I could not see the entire work and a general view of the paper since up to 9 figures in SM were missing. The work presented here adds interesting inputs for the effect of HONO sources on the concentrations of ozone, especially during haze events.

We sincerely thank you again for your precious comments and suggestions to our study. We are awfully sorry again to have forgotten uploading the supplementary materials during our first submission. The revised supplementary material has been uploaded.

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. reply5**). 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.
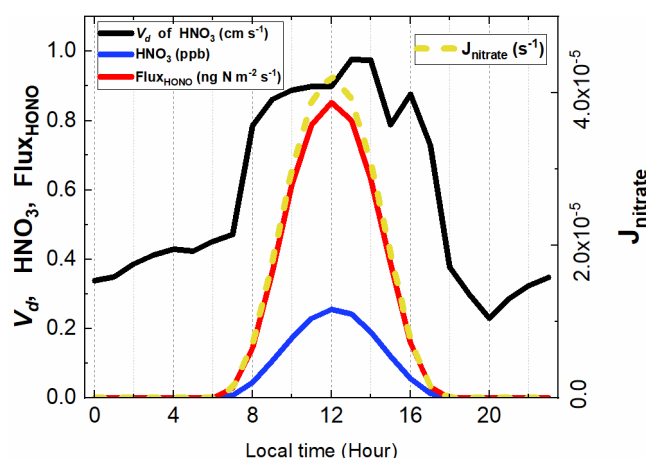

***Fig.reply5** the diurnal HONO formed (Flux$_{ion}$) via deposited HNO$_3$ photolysis on the ground, and the corresponding HNO$_3$ concentration, HNO$_3$ dry deposition velocity (V$_d$) and nitrate photolysis frequency (J$_{nitrate}$, assuming a J$_{nitrate}$/J$_{HNO3}$ ratio of 120) at the BUCT site 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. Please see **Line 100–101 and 111–112 in Page 5**.*

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.reply6**, 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.*
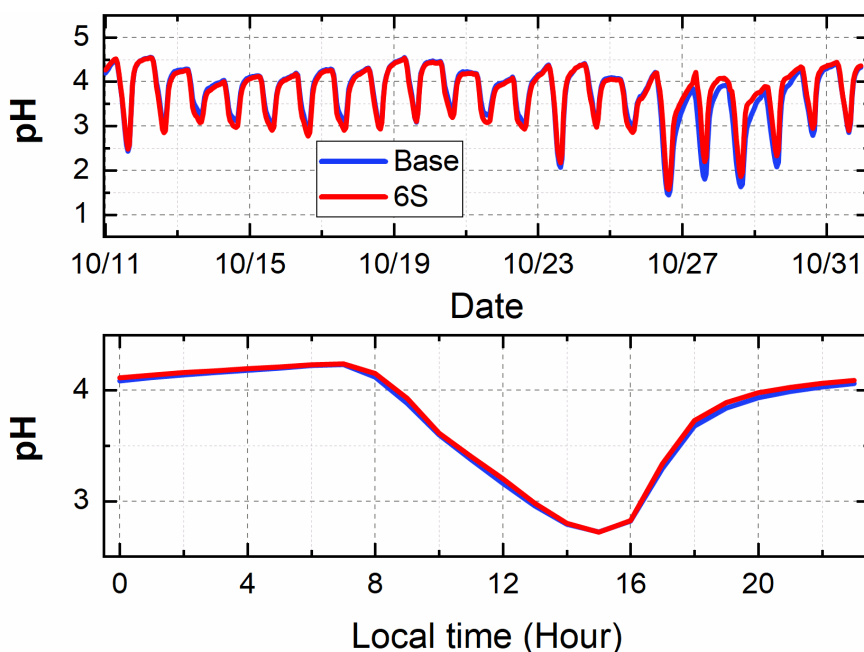

Fig.reply6 *the hourly and diurnal mean aerosol pH at the 95 NCP sites for the base and 6S cases during the study period.*

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

$J_{nitrate}/J_{HNO3}$ 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 $J_{nitrate}/J_{HNO3}$ values (1, 7, 30 and 120) in the revised manuscript, we could reasonably speculate that if the $J_{nitrate}/J_{HNO3}$ 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 $J_{nitrate}/J_{HNO3}$ 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. reply7.**
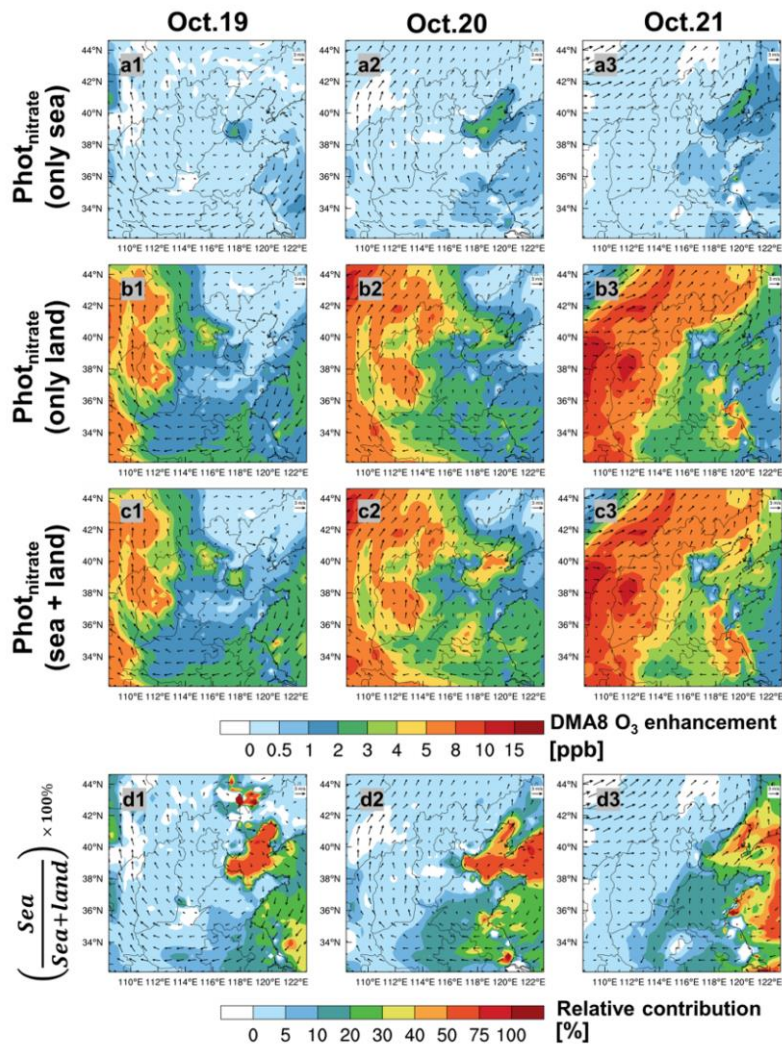
Fig.reply7 Comparison of surface DMA8 O_3 enhancements caused by nitrate photolysis only above the sea (a1–a3, case Desae minus base), only above the continent (b1–b3, case DeLand minus base), above both sea and continent (c1–c3, case D minus base), and the proportion of enhanced O_3 by

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.*

*The above discussion has been added into the revised manuscript, please see **Line 839–861** in **Page 47–49** in **Section 4.3**.*

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

We are awfully sorry to have forgotten uploading the supplementary materials during our first submission. The revised supplementary material has been uploaded.

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 **Line 381–388** in **Page 20** and **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 **Line 438–448** in **Page 23–24** in **section 3.3.1** of the revised manuscript, and the model evaluation of the vertical HONO is shown in **Fig.S6**.*

We are awfully sorry to have forgotten uploading the supplementary materials during our first submission. The revised supplementary material has been uploaded.

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, $K(T_0) = 4.72\times10^{-17}$, $\alpha = -74.38$ and $\beta = 6.12$.

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 $\mu g\ m^{-3}$, 15.16/12.13 $\mu g\ m^{-3}$ and 0.89/0.91 for the 6S/base case, respectively (**section 3.1.2** in the revised version). For more details, please see **Line 287–298 in Page 14–15**.*

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 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). For more details, please see **Line 511–544** in **Page 28–29** of 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:

$$OH + NO_2 \rightarrow HNO_3$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$
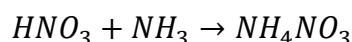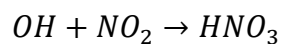
*The detailed nitrate enhancement at the BUCT site is given in **Fig S3** and **Line 287–298** in **Page 14–15** in the revised version. Among the six potential HONO sources, Phot$_{nitrate}$ slightly consumed nitrate and lowered its concentrations, but Het$_{aerosol}$ and Het$_{ground}$ significantly 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.reply8**), with a $J_{nitrate}/J_{HNO3}$ ratio of ~120 for $Phot_{nitrate}$.*
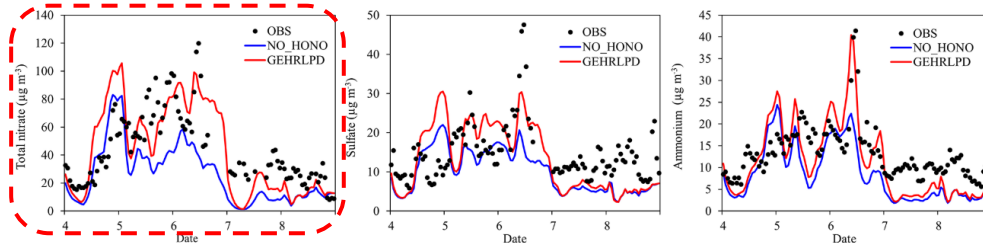
Figure 8. Temporal variation of observed and simulated total nitrate, sulfate, and ammonium concentrations in the NO_HONO and GEHRLPD cases at the Heshan site during 4–8 January 2017.

Fig.reply8 (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.
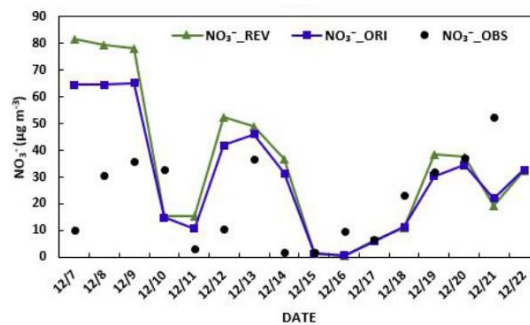
Fig.reply9 Nitrate comparison before and after adding six potential HONO sources (From Fig.4 in Zhang et al. (2021)), the green line contained six additional HONO sources including nitrate photolysis, the blue line was the base case.

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$_{nitrate}$)). The detailed parameterizations of these sources were added, please see **Line 177–208** in **Page 8–10**. 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 **Line 437–508** in **Page 23–28** 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 **Line 306–318** in **Page 15–16** and **Line 364–372** 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.reply10**). 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 **Line 177–208** in **Page 8–10** 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$_{2.5}$.*
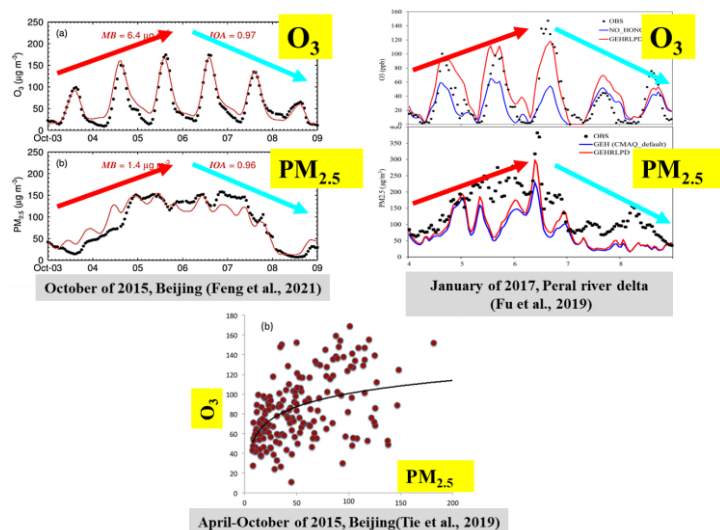
Fig.reply10 *The variation patterns of PM$_{2.5}$ and O$_3$, and the positive correlation between PM$_{2.5}$ and daytime O$_3$ collected from some recent relevant studies.*

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 **Line 754–762** in **Page 42** of the revised manuscript).*

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. In most of the case, the length of the sentences was less than three lines now (~30 words). Please see **Line 23–50** in **Page 2**.*

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