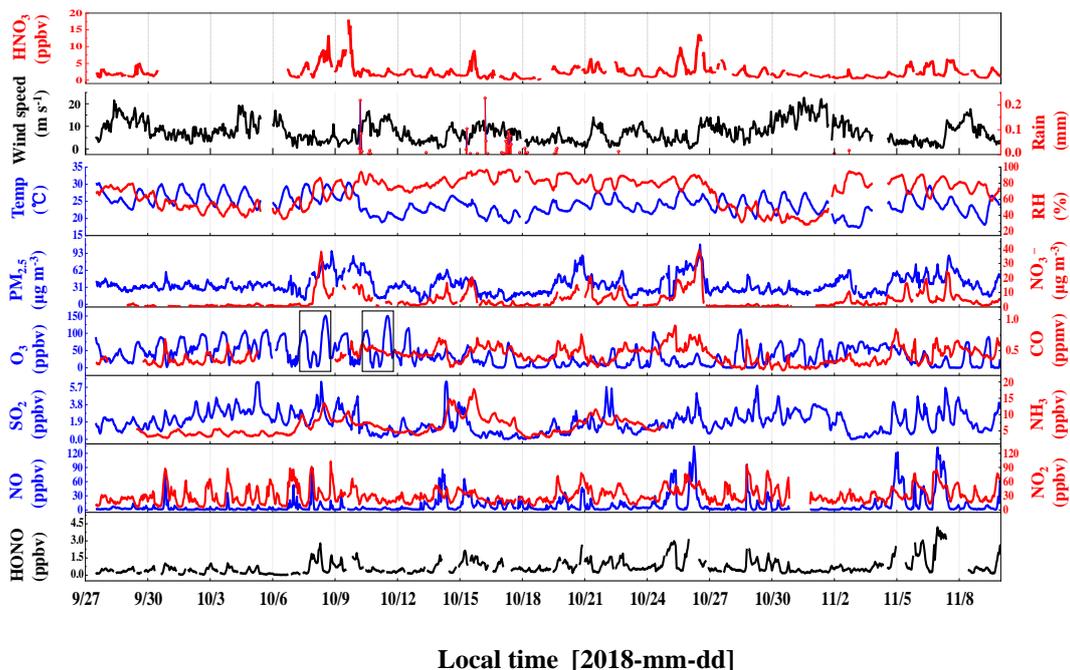
Point-by-point response to review comments on manuscript acp-2021-178 "Budget of nitrous acid (HONO) and its impacts on atmospheric oxidation capacity at an urban site in the fall season of Guangzhou, China"

We would like to thank the reviewers for valuable and insightful comments to improve the manuscript. We have carefully considered the comments and revised the manuscript accordingly. Below you find comments to the editor and our detailed answers to the comments of the reviewers. Referee comments are given in *black italics*, our responses and changes in the manuscript in blue and red, respectively.

Comments to editor:

We corrected a few minor errors which we discovered during the revision of the manuscript and we added clarifications in the response. The corrections and changes do not affect the results and conclusions of the paper.

1. In Figure 1 of the original manuscript, we found that the time series of ozone was the same for two days (in the black frames below). We have corrected it in the latest submitted manuscript.

Local time [2018-mm-dd]

2. The ratio of HONO/NO$_2$ (1.4 % to 3.0 %) in the original manuscript (Page 9 Line 212) is the result after processing into the daily average, not the ratio during the entire observation period. It has been corrected (0.2%−9.1% with an average of 2.3 ± 1.3%) in the latest submitted manuscript.

3. In Fig. S1 (the latest submitted manuscript), we marked the two arterial roads (The south Expressway and Guangyuan Expressway) near the observation site.

Response to Reviewer 1:

This paper presents a detailed analysis of the HONO budget in the Pearl River Delta region of China. The paper is well written, the data and the analysis are well presented. The subject is fit for publication in ACP and I would recommend the paper is accepted after the authors have addressed the following concerns.

Author's Response: We would like to thank the reviewer for the helpful comments and suggestions. We have carefully considered all the comments and revised the manuscript accordingly. For clarity, we list the original reviewer's comments below *in black italic*, and provide our responses and changes in the manuscript in blue and red, respectively.

Major comments:

1. Please add more information about the box-model. The MCM is not a model, it is just the chemical mechanism used in a model. Which software/modelling tool was used? Which VOCs were included? How was photolysis calculated for the non-measured photolysis rates? Were other processes (heterogeneous, deposition, etc..) included?

Author's Response: We thank the reviewer for the constructive comments. Accordingly, more detailed information about the box-model is introduced as follows:

To evaluate the influence of HONO chemistry on the atmospheric oxidation capacity, a zero-dimensional photochemical box model (Framework for 0-Dimensional Atmospheric Modeling–F0AM) based on the Master Chemical Mechanism (MCMv3.3.1) (Wolfe et al., 2016; Jenkin et al., 2003; Jenkin et al., 2015) was applied to calculate the concentrations of O_3 and OH radicals. The model was

implemented in MATLAB 2012. The hourly averaged measurement data were used to constrain the simulation, including HONO, NO, NO$_2$, CO, SO$_2$, VOC species (listed in Table S2), temperature, water vapor, wind speed, wind direction, pressure and photolysis frequencies J(NO$_2$), J(HONO), J(O^{1}D) and J(H$_2$O$_2$). Other non-measured photolysis frequencies were calculated according to Eq. (1) (Jenkin et al., 1997), and then scaled by the measured J(NO$_2$):

$$J_i = L_i \cos(\chi)^{M_i} exp(-N_i sec(\chi)) \tag{1}$$

where χ represents the solar zenith angle (SZA); L_i, M_i and N_i are the photolysis parameters under clear sky conditions which were taken from Jenkin et al. (1997). The heterogeneous processes as well as deposition of chemical species were not considered in this model.

Table S2. The VOCs species constrained in the F0AM model.

Classification	Measured hydrocarbons
Alkane	CYCLOHEXANE, ETHANE, N-BUTANE, N-DECANE, N-NONANE, N-OCTANE, PROPANE, 2-METHYLHEXANE, 2-METHYLPENTANE, 3-METHYLHEXANE, 3-METHYLPENTANE, 2-METHYLPROPANE, 2-METHYLBUTANE, PENTANE, HEXANE, HEPTANE, HENDECANE
Alkene	PROPENE, TRANS-2-BUTENE, TRANS-2-PENTENE, 1-BUTENE, 1-PENTENE, 1-HEXENE, CIS-2-BUTENE, CIS-2-PENTENE, STYRENE
ISO	ISOPRENE
Alkyne	ETHYNE
Aromatic	BENZENE, N-PROPYLBENZENE, 1-2-3-TRIMETHYLBENZENE, 1-2-4-TRIMETHYLBENZENE, 1-3-5-TRIMETHYLBENZENE, METHYLBENZENE, ETHYLBENZENE, 1,4-DIMETHYLBENZENE, 1,2-DIMETHYLBENZENE, I-PROPYLBENZENE, 1-ETHYL-3-METHYLBENZENE, 1-ETHYL-4-METHYLBENZENE, 1-ETHYL-2-METHYLBENZENE

2. The molybdenum converter used to measure NOx is subject to known interferences by other NOy species. Since a large part of the analysis in this paper relies heavily on NO and NO$_2$ data, this issue

cannot be neglected. I would expect the interference to be significant under the urban conditions considered here. The authors should address this issue and examine how the results of the studies are affected by it.

Author's Response: Thanks for the suggestion. We are aware that the chemiluminescence technique combined with molybdenum converter, albeit widely used to detect NO and NO_2, suffers from the interference of some reactive nitrogen species (NOy) like HNO_3, HONO, Peroxyacetyl nitrate (PAN), other Organic nitrate, N_2O_5, etc., which can be reduced to NO by the molybdenum converter, leading to an overestimate of NO_2 concentration. The degree of overestimation depends on both air mass age and the composition of the oxidation products/intermediates of NOx. At urban sites that are greatly affected by fresh emissions, such interference has been estimated to be 3%−10% (Xu et al., 2013; Dunlea et al., 2007; Villena et al., 2012), while it could be substantially higher at the suburban sites that receive aged pollution (~30−50%) (Xu et al., 2013), even up to 100% or more at some sites with the mostly aged pollution air (Dunlea et al., 2007; Steinbacher et al., 2007).

Our site is a typical urban site with heavy traffic emissions, as indicated by high concentrations of NO and NOx. Meanwhile, the average concentration of HONO, gaseous HNO_3 and particulate nitrate during the campaign were 0.74 ± 0.70 ppbv, 2.1 ± 2.0 ppbv and 4.2 ± 5.8 µg m^{-3}, respectively. PAN was not measured and is estimated around 0.84 ppbv based on earlier data at Guangzhou (Wang et al., 2015a) and the other NOy species can be ignored. Based on these, we roughly estimate the relative interferences of NOz (NOy-NOx) to NO_2 to be around 10%. We believe such a discrepancy would not affect the validity of our findings, and the following statements have been added in our revised manuscript to acknowledge the limitation of the measurement technique.

It should be noted that the molybdenum oxide (MoO) converters may also convert some NOz (= NOy - NOx) (e.g., HONO, peroxyacetyl nitrate (PAN), HNO_3, and so on.) species to NO and hence could overestimate the ambient NO_2 concentrations. The degree of overestimation depends on both air mass age and the composition of NOy. At our site that was greatly affected by fresh emissions, the relative interferences of NOz to NO_2 have been estimated to be around 10%, which is closed to the results of Xu

et al. (2013) and negligible for our discussion of HONO budget.

3. I think the discussion in section 3.2 needs to be improved. First the observed HONO production rate should be presented and shown (how was it calculated, which are the mean values, etc..). This will make the following calculations easier to understand. Besides that, I have two main comments regarding this section.

One, the authors infer that a large missing sink of HONO is required to explain the observations (lines 274-275). However, their calculation of HONO primary emissions relies on emission inventories that are likely not very accurate. The possibility that HONO primary emissions are overestimated in the emission inventories cannot be neglected and needs to be discussed.

Two, the authors are deriving a primary emission rate of 0.04 ppb/h or more (line 272), a soil emission rare of 0.02 ppb/h (line 297) and a net production via OH+NO of 0.26 ppb/h (line 314), while the average observed HONO production rate is 0.02 ppb/h (line 271). From this an unknown sink of 0.25 ppb/h is inferred. First of all, in order to close the budget, the unknown sink should be 0.30 ppb/h (unless you mean that 0.05 ppb/h is lost via deposition, it is not clear from section 3.2.4). More importantly, the discussion in section 3.2.3 implies an additional, non quantified source due to NO2 reaction on surfaces, so the unknown sink is actually a lower limit (but see also the previous comment, regarding possible overestimation of primary emissions). These calculations should be make clearer, maybe with an extra "summary" subsection at the end of section 3.2.

Author's Response: Thanks for the suggestions. A number of changes have been made accordingly as follows.

First, as suggested by the reviewer, we have introduced the observed HONO production/accumulation rate in our revised manuscript:

The observed HONO production/accumulation rate P_{HONO} is calculated by Eq. (4):

$$P_{HONO} = \frac{[HONO]_{t_2} - [HONO]_{t_1}}{t_2 - t_1} \tag{4}$$

where $[HONO]_{t1}$ and $[HONO]_{t2}$ represent the HONO concentration at 18:00 and 6:00 Local Time, respectively. Then an average P_{HONO} of 0.02 ppbv h^{-1} can be derived.

In response to the other two comments:

(1) The uncertainty of the two sets of inventories is in the range of -25%–28% (Huang et al., 2021), leading to an uncertainty of HONO primary emissions. The HONO emission rates obtained at nighttime are 0.3 ± 0.15 ppbv h^{-1} and 0.04 ± 0.02 ppbv h^{-1}, as the upper and lower limits of the nighttime HONO emission rate, respectively, which are both larger than the observed HONO accumulation rate (0.02 ppbv h^{-1}). On the other hand, P_{emis} only contributed a minor fraction (8%) to the daytime HONO sources. Therefore, even though the HONO primary emissions are overestimated in the emission inventories, the results of HONO budget would not change much. As the reviewer suggested, the uncertainty of the inventories and its possible impact have been discussed in the revised manuscript as follows:

Considering the uncertainty of the inventories (-25%–28%), P_{emis} may be overestimated or underestimated to the same extent. Nevertheless, direct emission of HONO is still a large HONO source at night along with other sources of HONO that remain to be considered.

(2) We thank the reviewer for point out this error. Indeed, as the reviewer stated, a sink of 0.30 ppbv h^{-1} is required to close the budget, and it's just a lower limit. We re-checked the calculation process and found another error in deposition velocity, and the new value of V_d is 1.8 cm s^{-1}. We have revised the manuscript, and added an extra summary for section 3.2:

(2) except for HONO + OH, the strength of HONO sink should be at least 0.30 ppbv h^{-1}, 6 times larger than that obtained by Li et al. (2012) and comparable to that by Hao et al. (2020).

In sum, primary emission from vehicle exhaust (between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1}) and the homogeneous reaction of OH + NO (0.26 ± 0.08 ppbv h^{-1}) were major sources of HONO at night. Nighttime soil emission rate was calculated to be 0.019 ± 0.001 ppbv h^{-1}, which is comparable to the observed nocturnal increase rate of HONO (0.02 ppbv h^{-1}), further indicating the importance of direct emissions. Additionally, contribution from NO_2 heterogeneous reactions on surfaces should not be ruled out. To balance the nighttime HONO budget by assuming dry deposition to be the principal loss process, a dry deposition rate of at least 1.8 cm s^{-1} is required.

4. In section 3.4, I would suggest that if VOC data are available, than ozonolysis of alkenes should be added here. Several studies have suggested that these process may be important in urban conditions. In fact, why not use the model results from section 3.5 to calculate the OH production pathways? It would be more comprehensive than what is shown in figure 9.

Author's Response: Thanks for the suggestion. We have added the results of the reaction of ozonolysis of alkenes in Figure 9. Compared with HONO and O_3, this pathway seems insignificant at our site. Table S5 summarized the reaction rate constant of O_3 with alkenes at 298 K and the yields of OH. Results from model would be more comprehensive but suffer from uncertainties of other processes. Calculating the OH radicals' production rate based on observational data is a direct and standard method that was applied in many studies (Zheng et al., 2020; Shi et al., 2020; Su et al., 2008b; Liu et al., 2019; Yang et al., 2014; Ren et al., 2020; Alicke et al., 2002; Ge et al., 2021; Heard et al., 2004). Therefore, we also adopted this method and made a comparation with similar researches.

$$P_{(O_3+alkenes)-OH} = \sum k_{alkenes(i)+O_3} [alkenes(i)][O_3] Y_{OH_i} \tag{13}$$

In Eq. (13), $k_{alkenes(i)+O_3}$ represents the reaction rate constant for the reaction of O_3 with alkene (i), Y_{OH_i} represents the yield of OH from the gas-phase reaction of O_3 and alkene (i). Table S5 summarized the reaction rate constant of O_3 with alkenes at 298 K and the yields of OH. In daytime, the sum of OH production rates by ozonolysis of alkenes was 3×10^5 cm^{-3} s^{-1}, which is much smaller than that of HONO and O_3. This value (3×10^5 cm^{-3} s^{-1}) was comparable to the results in previous studies (Kim et al., 2014; Ge et al., 2021; Martinez et al., 2003; Ren et al., 2003; Lee et al., 2016; Alicke et al., 2002; Kleffmann et al., 2005; Ren et al., 2013), but smaller than some other studies (Shi et al., 2020; Zheng et al., 2020; Heard et al., 2004).

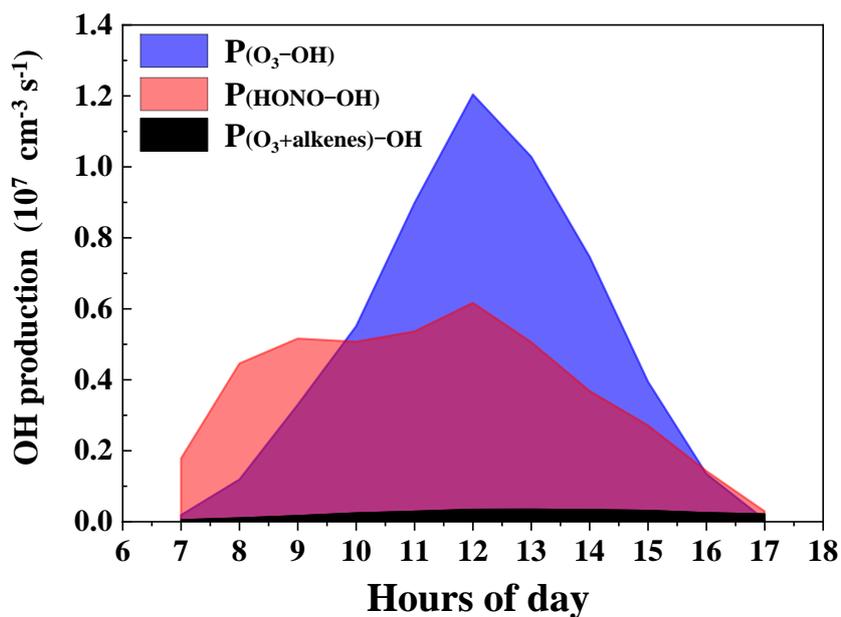



Figure 9. The yield and comparison of OH radicals by HONO, O₃ and ozonolysis of alkenes.

Table S5. Ozonolysis reaction rate constants and OH formation yields of the volatile organic compounds (VOC) used in the calculation.

VOC	k (298 K)/($\times 10^{-18}$ cm^3 molec. $^{-1}$ s^{-1})[a]	OH yield
PROPENE	10.1	0.34[b]
TRANS-2-BUTENE	190	0.59[b]
TRANS-2-PENTENE	160	0.47[c]
1-BUTENE	9.64	0.41[b]
1-HEXENE	11.3	0.32[b]
1-PENTENE	10.6	0.37[b]
CIS-2-BUTENE	125	0.37[b]
CIS-2-PENTENE	130	0.3[c]
STYRENE	17	0.07[c]
ISOPRENE	12.8[c]	0.13 ± 0.03[c]

[a] Atkinson and Arey (2003); [b] Rickard et al. (1999); [c] Alicke et al. (2002)

Minor comments:

1. lines 169-171: what does it mean that "the boundary layer diurnal cycle has been modified"? And what are the "solar altitude" and the "photolysis rate correction coefficient"?

Author's Response: The boundary layer diurnal cycle is a common application of the F0AM (Wolfe et al., 2016). It reflects the meteorology at the site where the model is applied for, and was modified to represent local geographical and meteorological conditions at our site.

"Solar altitude" in the original manuscript is inaccurate, and has been replaced by "solar zenith angle (SZA)". Photolysis rate correction coefficient is the ratio between measured $J(NO_2)$ and calculated $J(NO_2)$.

2. figure 3: a blue line with pink shading is confusing. It would be better to use a shade of blue. Also why not add the results obtained with the other two methods? It may be interesting to compare them.

Author's Response: Thanks for the suggestions. We have changed the color of the shade of the blue line in Figure 3 to light blue (see below). Basically, the results obtained by method (1) is not the HONO primary emission rate, but assumed HONO concentrations caused by emissions, which are often compared with observed HONO concentration to get the relative contribution of emissions. Additionally, we think that the calculation of method (2) is problematical, because a negative primary emission rate would be derived in NOx decline period, which is unrealistic. The result obtained by method (3) is the rate of change in HONO concentration, which is in line with the definition of emission rate. Specially, the unit of the quantity obtained from method (1) is ppbv, while that from method (3) is ppbv h^{-1}. They are not comparable.

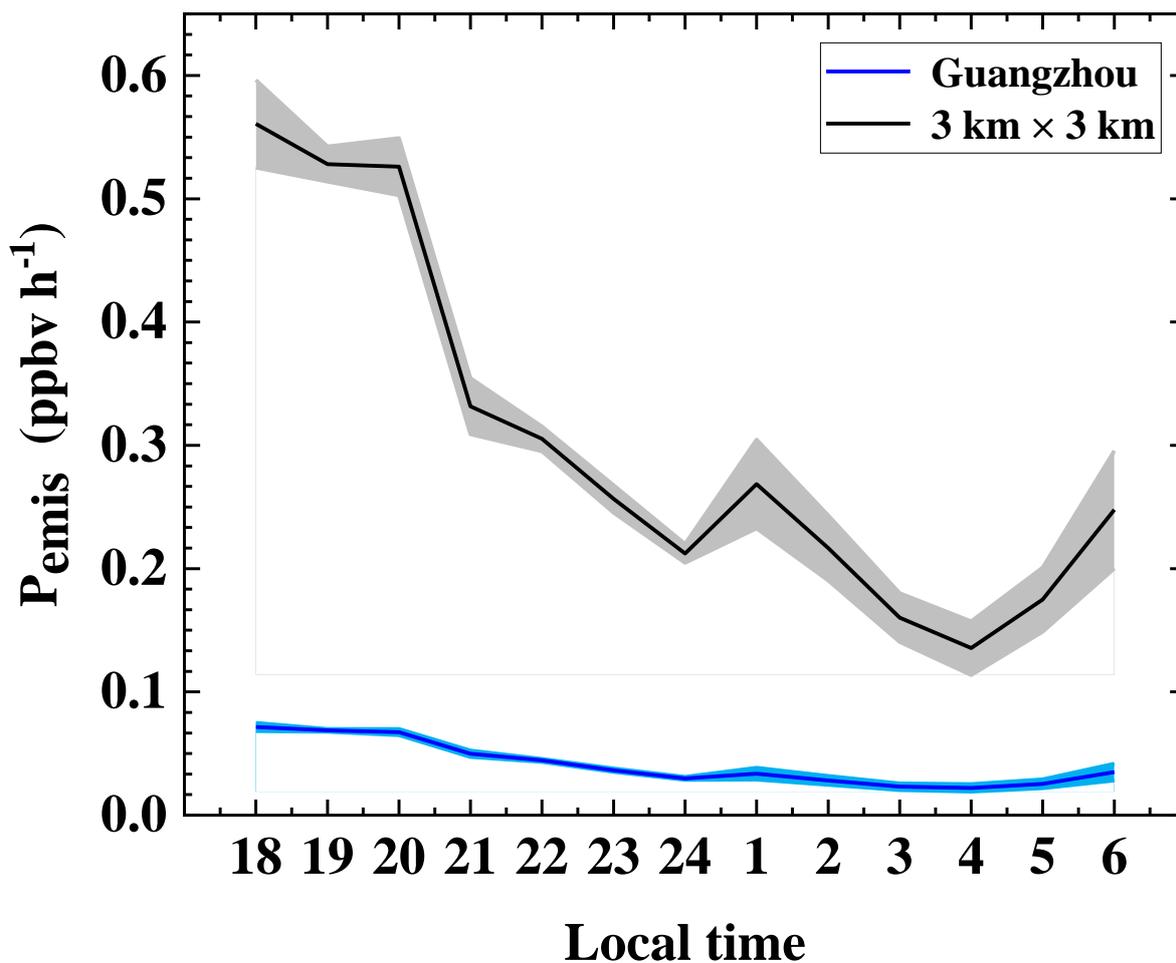



Figure 3. The nocturnal variation of HONO primary emission rates. The black and blue lines represent the HONO primary emission rates calculated by the 2017 NOx emission source inventory of the 3 km × 3 km grid cell centred on the Guangzhou Institute of Geochemistry and the 2017 NOx emission source inventory of Guangzhou city respectively. The coloured areas represent 1 – σ standard deviations.

3. figure 5: I would not consider the correlation netween HONO and NO, "a good correlation". In fact

it is not even linear, meaning it doesn't really provide evidence that OH+NO is a major pathway.

Author's Response: We agree that the relationship between HONO and NO is non-significant linear. We found that under conditions with low NO concentration, high concentration of HONO also appeared, suggesting processes other than primary emissions or homogeneous reaction of OH + NO were involved in HONO formation. Nevertheless, the correlation ($R^2 = 0.5927$) is relatively high compared to many nighttime observations (Zhang et al., 2019; Fu et al., 2019; Yang et al., 2014; Yang et al., 2021; Tong et al., 2016; Ge et al., 2021; Li et al., 2021). Although correlation cannot indicate the causal relationship between HONO and NO, it does suggest that these two may be related. The original text has been revised to convey this point more accurately.

The relatively high correlation ($R^2 = 0.5927$) between HONO and NO is in line with this finding (Fig. 5 (a)).

4. figure 6: can you explain why you are averaging only the top five HONO/NO2 values?

Author's Response: In the study of Stutz et al. (2004), the pseudo steady state (PSS) of $HONO/NO_2$, which is characterized by a maximum $HONO/NO_2$ ratio, was interpreted as the balance between the heterogeneous conversion of NO_2 to HONO and the loss of HONO on surfaces. For each RH, $HONO/NO_2$ ratios can be influenced by the time of the night, the surface to volume ratio, and other parameters, such as advection. Concentrating solely on these maxima (reaching pseudo steady state) will therefore eliminate much of the uncertainty connected with the influence of other parameters (like the time of the night, the surface density, advection, etc.).

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Response to Reviewer 2:

In this work, data collected from the Pearl River Delta in China have been used to explore potential nitrous acid (HONO) sources and their impacts on the production of hydroxyl radical (OH) and photochemical ozone (O3). The Authors perform a large number of calculations that are replicated from a variety of other publications to assess sources and sinks of HONO for their observational dataset. Despite the results of these calculations being grossly erroneous (e.g. direct emissions calculated exceeding the observations by over an order of magnitude), limited to single value comparisons (e.g. average accumulation rates calculated and observed), and using clearly erroneous assumptions (e.g. 10^6 molec cm-3 of OH at night) the Authors press on to calculate a radical budget and impact on O3 chemistry in the PRD. Overall, this work does not demonstrate any progress in our understanding of the impacts of HONO on oxidation chemistry due to fundamentally flawed data interpretation. The extreme mismatches between the calculated HONO sources and those observed are never depicted and raise serious questions regarding quality control of this work. Given that the topic of HONO sources and sinks is only the first part of this manuscript, it is not possible to consider the remainder of this work that draws on this analysis to try and improve understanding of oxidation chemistry and radical budgets. As this manuscript currently stands, it is unsuitable for publication in ACP and requires extensive re-work.

Below is an incomplete list of outstanding issues that require addressing, which may not yield an acceptable manuscript once completed, as the issues impacting this work are pervasive and beyond the scope of the requirements of peer review. The Authors are encouraged to significantly revisit the contents of the manuscript and independently ascertain that the work presents valid findings and communicates a complete understanding of the chemistry explored. As it currently stands, the manuscript replicates the prior work of others without careful reflection on whether the findings are consistent with the established knowledge of the related atmospheric chemistry.

Author's Response:

We thank the reviewer for taking the time to review our paper. It is always constructive in a peer-review process to directly point out any concerns and issues from the reviewer's perspective and urge us as authors to provide reasons and clarifications whenever necessary.

It is true that there have been a large body of literatures on the HONO sources and sinks, and many theories and findings have emerged from these studies, many of which are conflicting between each other. As a ripple effect, more confusions and new challenges emerged for studies that followed. As a participant in numerous HONO studies (e.g., Su et al., 2008, Su et al., 2011, Cheng et al., 2013, Yang et al., 2017, Tian et al., 2018), the corresponding author of this paper sincerely shares the reviewer's understanding that it takes patient efforts to make any progress in this small yet important field of atmospheric chemistry, due to the lack of information on many processes being considered in the HONO budget. As such, it is crucial to acknowledge all kinds of uncertainties and be transparent on assumptions and caveats in the process of conducting measurements and calculations, in order to provide useful and accurate information and findings for future studies to rely on to make any further meaningful progress. Bearing these considerations in mind, we tried to consider all possible varying and uncertain factors as far as we deem appropriate and tried to be conservative in our estimates of the terms.

For instance, direct emission is one of the main points of our paper that this source of HONO and its uncertainties need to be further investigated in future studies. We considered multiple methods and estimated a range of possible direct emission rates; we used two emission inventories to account for the uncertainty in this kind of input data in estimating emissions. Yet it is inevitable for such an effort to lead to a lengthy and in some cases tedious documentation of all the methods adopted and all the outcomes derived, which might become a cause of confusions. We hope to do whatever we can to make our paper clear, accurate, and scientifically sound. To answer the reviewer's question why the direct emissions calculated exceeding the observations by over an order of magnitude, it is because the two

terms are related but not consistent, since the latter is a result of many processes, e.g., emission, reaction, transport, etc. For example, NOx level often decreases at daytime, during which the emission rates of NOx are obviously greater than the observed growth rates. To answer another question why the comparison between Pemis and observed HONO was limited to averaged values, it is because averaging can smooth out the influence of fluctuation and uncertainties in various influencing factors (transport, dilution, OH, etc.). Because of the long lifetime of HONO at night, and effect of transport and large uncertainties in the dilution/diffusion conditions, a temporally-resolved budget appears desirable but would not be meaningful given all uncertainties. Otherwise, the assumption of the nocturnal OH concentration to be 1.0×10^6 cm^{-3} appears problematic but is possible in the PRD region. Sensitivity tests also showed limited impact from this assumption on our conclusion about HONO.

In light of the reviewer's comments, we have re-examined and revised our paper for better clarity, accuracy, and completeness toward a good reception of our paper by a broad range of a readers of ACP. Indeed, addressing those critical comments from the reviewer turned out very useful for us to improve our paper. We welcome the reviewer to review our responses and revisions, and provide any further comments and discussions, if any, with the goal of reaching a comprehensive and objective assessment of the scientific contributions made by our paper.

We list the original reviewer's comments below *in black italic*, and provide our responses and changes in the manuscript in blue and red, respectively.

Major issues:

1. The introduction of the manuscript is unorganized and simply lists topics in nearly random order (e.g. the sources and sinks of HONO). There are basic concepts of atmospheric chemistry that do not seem to be correctly understood (e.g. microbial production of HONO is not a heterogenous reaction). There is extensive discussion of mechanisms that have been thoroughly refuted (e.g. two photon excitation of

NO2 followed by reaction of the excited state with water or termolecular reactions with NH3) which are presented as topics of open debate. The Authors should significantly rework the introduction for clarity, but also with a focus on having it reflect the contents of the work being done in the manuscript. Very little text presents the outstanding issue of poor air quality and oxidation chemistry in the PRD, despite significant work having been done in this area over the past 10 years. As it currently stands, the introduction is only weakly motivating this work and can be significantly improved.

Author's Response: Thanks for the comments. In fact, as we introduced in Line 54, HONO sources generally include (1) direct emissions, (2) homogeneous reactions and (3) heterogeneous reactions. And then, part (1) was introduced in Line 54–63; part (2) was introduced in Line 63–75; part (3) we introduced in Line 76-91. Particularly, microbial production of HONO is obviously treated as emission source in Line 59.

Li et al. (2008) suggested that the reaction of photolytically excited NO_2 with H_2O can be a substantial OH/HONO source. But this reaction has been proven to be unimportant in the real atmosphere (Carr et al., 2009; Wong et al., 2011; Amedro et al., 2011; Dillon and Crowley, 2018). The original expression is not very accurate and has been deleted as the reviewer suggested.

Theoretical simulations suggested that NH_3 can promote the hydrolysis of NO_2, significantly decrease the free-energy barrier to HONO formation as well as stabilize the product state (Wang et al., 2016b; Zhang and Tao, 2010; Li et al., 2018b). Some field observations also found ambient NH_3 was involved in HONO formation (possibly through the heterogeneous reactions) (Ge et al., 2019; Xu et al., 2019; Wang et al., 2016a). Based on these, we think the reaction of NH_3, NO_2 and H_2O has not been testified, but it should not be ruled out.

In addition, the discussion of air quality and oxidation chemistry in the PRD region have been revised to reflect its connection with this work.

The Pearl River Delta (PRD) region is one of the biggest city clusters in the world with dense population and large anthropogenic emissions. Rapid economic development and urbanization have led to severe deterioration of air quality in this region, which was characterized by atmospheric "compound

pollution" with concurrent high fine particulate matter (PM$_{2.5}$) and ozone (O$_3$) (Tang, 2004; Chan and Yao, 2008; Yue et al., 2010; Wang et al., 2017; Xue et al., 2014; Zheng et al., 2010). While O$_3$ has been increasing along with reduced PM$_{2.5}$ over recent years in the region (Li et al., 2019; Li et al., 2014; Liao et al., 2020; Wang et al., 2009; Zhong et al., 2013; Lu et al., 2018), and has become the dominant factor of the air quality index exceeding the national standard (Feng et al., 2019), indicating the enhancement of atmospheric oxidation capacity in this region. By far two comprehensive atmospheric observations were conducted in the PRD region to detect OH radicals. High concentrations of OH radicals were observed both times, especially in the first time it was the highest ever-reported, which cannot be explained by the current knowledge of atmospheric chemistry (Hofzumahaus et al., 2009). Substantial level of HONO was suggested to be the major source of the OH–HO$_2$–RO$_2$ radical system in above two campaigns (Lu et al., 2012; Tan et al., 2019). Moreover, high concentrations of HONO have also been confirmed in other observations in this area during last two decades (Li et al., 2012; Su et al., 2008b; Shao et al., 2004; Hu et al., 2002; Qin et al., 2009; Su et al., 2008a). Fast OH production through HONO photolysis may be a key factor for the increasing atmospheric oxidation capacity and ozone concentration in this area.

2. This manuscript uses the performed HONO measurements extensively. The Authors' data is collected using a custom-built instrument that uses similar principles to the LOPAP. No prior work demonstrating the accuracy, precision, reliability through intercomparison, etc are made. Instead the Authors cite the manuscripts that established the commercial LOPAP instrumentation as though they apply to their apparatus. It is not clear if the presented QA/QC values were determined from data collected during this study or from statements others have made in the literature.

Author's Response: Thanks for the suggestion. The parameters of the instrument and the QA/QC values were determined independently. Moreover, we made an intercomparison with a commercial LOPAP (QUMA, Germany) during the campaign, showing good agreement. Detailed information about the instrument has been introduced in the supplementary, and the manuscript has been revised accordingly:

Manuscript: HONO was measured by a custom-built LOPAP (LOng Path Absorption Photometer) according to the design in literatures (Heland et al., 2001; Kleffmann et al., 2006). More information about our custom-built LOPAP (including principle, quality assurance/quality control, instrument parameters and intercomparison) are introduced in supplement information.

Supplement information: The LOPAP instrument was first developed by Heland et al. (2001), which is based on wet chemical sampling and photometric detection. Ambient air is sampled into an external sampling unit consisting of two similar stripping coils in series. Almost all the HONO and a small fraction of interfering substances (PAN, HNO_3, NO_2, etc.) are absorbed in solution in the first stripping coil, while in the second stripping coil only the interfering species are absorbed. To minimize the potential interferences, we assume the interferences absorbed in the first and the second coil are the same, so the real HONO concentration in the atmosphere is determined by subtracting the measured signal of the second coil from the measured signal of the first coil. The absorption solution R1 is a mixture reagent of 1 L hydrochloric acid (HCl) (37% volume fraction) and 100 g sulfanilamide dissolved in 9 L pure water. The dye solution R2, 2 g n-(1-naphtyl)-ethylendiamine-dihydrchloride (NEDA) dissolved in 10 L pure water, is then reacted with the absorption solution from two stripping coils pumped by a peristaltic pump to form colored azo dye. The light-absorbing colored azo dye is then pumped through a debubbler by the peristaltic pump and flows into the detection unit, which consists of two liquid waveguide capillary cells (World Precision Instrument, LWCC), one LED light source (Ocean Optics), two miniature spectrometers (Ocean Optics, Maya2000Pro) and several optical fibers. To correct for the small zero-drifts in the instrument's baseline, the zero measurements were conducted every 12 h by introducing zero air (highly pure nitrogen). During the instrument's operation, the instrument calibration was performed every week using the standard sodium nitrite ($NaNO_2$) solution.

Detection limit is defined as 3σ of HONO concentration measured in zero air measurement. The detection limit of 5 pptv for this campaign was determined by zero air measurement. This 5 pptv also serves as the precision of the instrument. Time resolution is defined as the time interval between HONO signal decreases from 90% of the signal when start zero air running to 10% higher than the zero signal. It also relates to the liquid flow. The determined time resolution during the campaign is about 15 min considering the air flow of 1 L min^{-1} and liquid flow of 0.4 mL min^{-1}. Measurement error is the sum of

statistic error and systematic error. Statistic error is defined as 1σ of HONO signal in zero air measurement. Systematic error is coming from the uncertainties of air flow rate, liquid flow rate and calibration factor, and is about 8% of measured HONO by applying "Gaussian Error Propagation" method (Trebs et al., 2004). The instrument parameters are listed in Table S1.

Table S1. The parameters of our custom-built LOPAP.

Parameters	Values
Air flow	$1\ \mathrm{L\ min^{-1}}$
Liquid flow	$0.4\ \mathrm{mL\ min^{-1}}$
Length of LWCC	100 cm
Detection limit	5 pptv
Detection range	5 pptv–10 ppbv
Time resolution	15 min
Uncertainty	8%

A commercial LOPAP (QUMA, Germany) operated by the Guangzhou Institute of Geochemistry Chinese Academy of Sciences (GIGCAS) also measured HONO during the observation. Unfortunately, only less than 10 days data were obtained by the commercial LOPAP due to malfunction. Our custom-built LOPAP was validated against the commercial LOPAP instrument with good agreement ($R^2 = 0.910$) (see Fig. S2), which further demonstrated the reliability of our instrument.
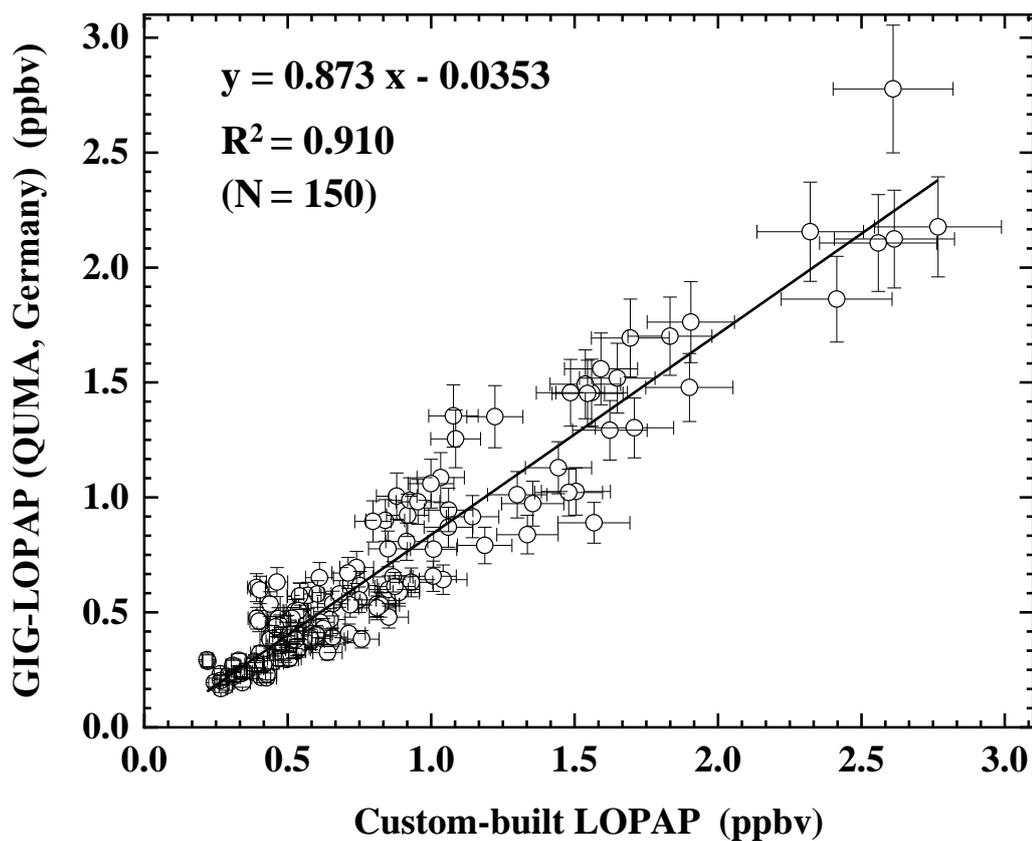
Figure S2. Intercomparison between the custom-built LOPAP with the commercial LOPAP (QUMA, Germany). The linear fitting line has an intercept of A = -0.035 ± 0.022, a slope of B = 0.873 ± 0.023 and R^2 = 0.910 (N = 150). The error bars represent the uncertainties of our custom-built LOPAP (8%) and commercial LOPAP data (QUMA, Germany) (10%). The data from October 15-18 and November 1-6, 2018 was used for comparison.

3. Direct emissions of HONO calculations are grossly incorrect. The Authors present several methods from the literature that have been used previously, none of which give a reasonable result when they compare to their observations (e.g. they calculate- direct emission rates of 0.3 ppbv hr-1 versus 0.02 observed). Despite having CO measurements, they do not draw on these to arrive at more reasonable estimate and belabour a number of other ways to estimate the direct HONO emission values. While one can appreciate the work done to arrive at an unexpected finding, the results conflicting with the

observations in such an extreme way require some significant reflection on the state of understanding of direct HONO sources and why the established literature approaches fail to reach reasonable results with this observational dataset. Instead of taking the opportunity to make a meaningful contribution in this respect, the Authors simply press forward with further calculations on HONO sources and sinks. The absence of a temporally-resolved intercomparison between the measured and calculated direct HONO emission sources in a figure raises serious concerns. The Authors state that the site is more impacted by direct emissions than previously considered, but this result comes from a calculation that does not compare within the same order of magnitude of the observations.

Author's Response: Thanks for the comments. At first, 0.30 ppbv h^{-1} is the upper limit of the nighttime HONO emission rate. Secondly, according to the literature retrieval, the method (3) was applied at four sites for calculation of the HONO emission rates. Results close to our study were obtained at urban sites (Liu et al., 2020a; Liu et al., 2020b) and a suburban site (Michoud et al., 2014), while much smaller values were obtained at a rural site (Su et al., 2008b). What's more, it's perfectly reasonable that direct emission rates are larger than the observed growth rates. It is well known that, the concentration variation of a certain species in the atmosphere is determined by the joint effect of emission, reaction, transport, etc. It can be independent of a single process. For example, NOx level often decreases at daytime, during which the emission rate of NOx is obviously greater than the observed NOx growth rate. We are aware that CO is often treated as a tracer of primary emissions. However, by far as we know, CO has never been used to estimate the direct HONO emission values. Use NO instead of CO as a tracer, besides excluding the potential impact of the carbon-nitrogen ratio of different fuels on the emission rate, the more important advantage is that the criteria for NO/NOx (Line 225–231) can be used to filter out fresh air masses, that is crucial to identify emitted HONO.

Because of the long lifetime of HONO at night and effect of transport, and large uncertainties in the dilution/diffusion conditions, we cannot estimate emission/formation rate by using measured HONO concentrations (Su et al., 2008a). Thus, intercomparison (whether temporally-resolved or not) between the measured and calculated direct HONO emission sources can't be done. Whereas the intercomparison between P_{emis} with HONO increasing rate is realistic, by which we can assess the

relative contribution of the single source. As the reviewer commented, the intercomparison was limited to averaged single values but not temporally-resolved data. The reason for that is the average can better smooth out the influence of fluctuation in other factors (transport, dilution, etc.). Many previous studies also adopted this approach, such as Li et al. (2012), Hao et al. (2020), Tong et al. (2015), Tong et al. (2016), Zhang et al. (2019), Tian et al. (2018) and Wang et al. (2019).

As the reviewer suggested, we compared our results (from 2 methods) with prior studies using the same method. The text has been revised as follows:

The average of P_{emis} is 0.30 ± 0.15 ppbv h^{-1}, far larger than the average accumulating rate of HONO at night (0.02 ppbv h^{-1}) derived from observed HONO variation. By contrast, P_{emis} with the city level emission data (Guangzhou) is much lower (0.04 ± 0.02 ppbv h^{-1}) and varied smoothly throughout the night. Similar results have been obtained at urban sites (Liu et al., 2020a; Liu et al., 2020b) and a suburban site (Michoud et al., 2014), while the result at a rural site is much lower (Su et al., 2008b). The lower limit of the calculated P_{emis} is still larger than the observed HONO accumulation rate, indicating direct emission of HONO is a large HONO source at night along with other sources of HONO that remain to be considered.

Method (1) is also adopted here to calculate [HONO]$_{emis}$, and [HONO]$_{emis}$/[HONO] can simply represent the primary emission's contribution to HONO. We summarized [HONO]$_{emis}$ /[HONO] ratios obtained from urban sites in China (Table S3). The values varied at a wide range from 12% to 52%, and the difference of 2 times or more existed in different seasons at the same site. These indicate the complexity of the impact of source emissions on observation site. The ratio of [HONO]$_{emis}$/[HONO] at our site is at a high level of 47%, indicating that the site during the campaign is more strongly affected by primary emission from vehicle exhaust compared to most previous studies.

Table S3. The overview of percentage of nighttime primary emissions of HONO from urban sites in China.

Location	Date	Nighttime NOx (ppbv)	[HONO]$_{emis}$/[HONO] (%)	Emission ratio HONO/NOx	Reference

				(%)	
Guangzhou	Oct 2015	57.9	15.1	0.65	1
Guangzhou	Sep–Nov 2018	47.7	47	0.9	2
Shanghai	May 2016	–	12.5	0.65	3
Changzhou	Apr 2017	–	31.4	0.69	4
Zhengzhou	Jan 2019	41	17[a]	0.65	5
		68.7	16[b]		
		107.3	16[c]		
Ji'nan	Nov 2013–Jan 2014	–	42	0.58	6
Ji'nan	Sep–Nov 2015	38	18	0.53	7
	Dec 2015–Feb 2016	78.5	21		
	Mar–May 2016	47.3	12		
	Jun–Aug 2016	29.1	15		
Beijing	Jan–Feb 2007	–	20.59	0.65	8
	Aug 2007	–	11.68		
Beijing	Oct–Nov 2014	94.5	39.6	0.65	9
Beijing	Dec 2015	–	48.8	0.8	10
Beijing	Dec 2015	–	52[b]	1.3	11
		–	40[c]		
Beijing	Dec 2016	–	29.3	0.78	12
Beijing	May–Jul 2018	–	14.21	0.78	13
	Nov 2018–Jan 2019	–	30.79		

[a]: clean; [b]: polluted; [c]: severely polluted. Reference: 1. Tian et al. (2018); 2. This work; 3. Cui et al. (2018); 4. Shi et al. (2020); 5. Hao et al. (2020); 6. Wang et al. (2015b); 7. Li et al. (2018a); 8. Spataro et al. (2013); 9. Tong et al. (2015); 10. Tong et al. (2016); 11. Zhang et al. (2019); 12. Meng et al. (2020); 13. Liu et al. (2021).

4. Soil emissions of HONO are not justified and rely on a set of assumptions that are not justified (e.g. boundary layer height and surrounding landscape properties) and are quite clearly in error. The HONO production rates calculated again exceed those observed significantly, raising many questions around attention to the validity of data interpretation in this manuscript.

Author's Response: Thanks for the comments. Contribution of soil emissions is indeed a challenge for the community and has not been discussed in most early studies. Here, we made a trial to bring this into the budget analysis, following the method of Liu et al. (2020a) and Liu et al. (2020b), that has been published recently. We also refer to Wu et al. (2015) to determine the landscape types in Guangzhou (this part has been added in our revised manuscript as follows). Otherwise, we believe it's reasonable to assume the night boundary layer to be 200 m, which comes from a prior study in Guangzhou in autumn by Fan et al. (2008). In addition, as discussed in response 3, we insist that the emission/production rate is greater than the observed growth rate is justified.

HONO emission flux from soil depends on the temperature, water content and nitrogen nutrient content of soil, which have been considered according to the parameters reported in the literature (Oswald et al., 2013). Since grassland, coniferous forest and tropical rain forest are the typical plants in Guangzhou city area (Wu et al., 2015) and their emission fluxes are comparable (Oswald et al., 2013), emission flux from grassland was adopted to represent the soil HONO emission in Guangzhou.

5. The use of a static OH value of 10^6 at night based on one measurement. Again, the result of the calculation differs from the observations (and again only comparing single values instead of temporally-resolved data) by over an order of magnitude

Author's Response: Thanks for the suggestion. In our study OH measurement is unavailable thus a static nocturnal OH value was assumed. The same estimation was applied in many literatures (Spataro et al., 2013; Huang et al., 2017; Hao et al., 2020; Cui et al., 2018; Tong et al., 2015; Tong et al., 2016; Liu et al., 2020a; Li et al., 2021). Because of the uncertainties in OH concentrations, as well as fluctuation of transport and dilution/diffusion, a temporally-resolved analysis can be problematic.

In the previous discussion with the editor, we have learned that nighttime OH concentration of 1.0×10^6 cm^{-3} would cause serious concerns. We still stick to our point because of the two reasons: (1) Only two observations measured OH concentration in the PRD region (Hofzumahaus et al., 2009; Lu et al., 2014; Liu, 2017), in which the average nighttime OH concentrations were both around 1.0×10^6 cm^{-3}. We believe that the data obtained from the observations at the location nearby and in the similar season are

the most valuable reference. (2) We have performed sensitivity tests of nighttime OH concentration within the range of 0.1×10^6 cm^{-3} to 2×10^6 cm^{-3}, as editor suggested (Table S2). Results indicate that the production rate from homogeneous reaction of NO + OH are always larger than the measured accumulation of HONO and taking a value within the range of the observed nighttime OH concentration will not affect the conclusion of this study.

6. Deposition losses of HONO rely on reasonable production terms. Since the production terms have major errors, and this calculation propagates those, the result cannot be correct. Further considerations for this section are the large body of work that has investigated the reactive uptake coefficients for HONO on surfaces, from which dry deposition velocities can be approximated, in order to make literature comparisons that are much more recent and detailed.

Author's Response: As discussed above, since the production terms listed by the reviewer are reasonable within their respective uncertainties, deposition can be derived consequently. It should be noted that some production terms such as heterogeneous conversion of NO$_2$-HONO has not been taken into account, we can only get the lower limit of dry deposition velocity. We re-checked the calculation process and found an error in deposition velocity, and the new value of V$_d$ is 1.8 cm s^{-1}.

Dry deposition velocities can be derived from uptake coefficients using V$_d$ = γω/4 (Dentener et al., 1996; Donaldson et al., 2014a), where ω is the average thermal speed of the HONO molecules in the gas phase. According to the reviewer's suggestions, we investigated a large amount of literatures about the uptake coefficients of HONO on various surfaces (Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, Arizona test dust, sodium chloride aerosols, Na$_2$CO$_3$, NaHCO$_3$, kaolinite, ammonium sulphate aerosols, plant surfaces, asphalt surface, ground surface, soil surface, and aqueous surfaces). Generally, the uptake efficiencies of HONO on solid surfaces varies at a range of 3×10^{-7} to 2.8×10^{-3} (El Zein and Bedjanian, 2012; El Zein et al., 2013; Romanias et al., 2012; Harrison and Collins, 1998; VandenBoer et al., 2015; Donaldson et al., 2014b; Schimang et al., 2006; Trick, 2004; VandenBoer et al., 2013; Donaldson et al., 2014a), and measurements of HONO uptake onto aqueous surfaces find much higher γ$_{HONO}$ values of

10^{-4} to 4×10^{-2} (Msibi et al., 1993; Kirchner et al., 1990; Mertes and Wahner, 1995; Hirokawa et al., 2008). Therefore, the composition of the ground and the content of adsorbed water can greatly affect the uptake coefficient. Especially, γ_{HONO} measured for soil surface and ground surface (the most representative surfaces) were around 1.1×10^{-5} to 2.5×10^{-4}, 2×10^{-5} to 2×10^{-4} (Donaldson et al., 2014a; VandenBoer et al., 2013), respectively, corresponding to V_d of 0.1 to 2.3 cm s^{-1}, and 0.18 to 1.8 cm s^{-1}. On the other hand, previous field measurements reported that V_d for HONO ranged between 0.077–3cm s^{-1} (Harrison and Kitto, 1994; Harrison et al., 1996; Li et al., 2012; Stutz et al., 2002; Spindler et al., 1999). Our result falls in the range of theirs. The original text has been revised accordingly as follows

The average deposition velocity V_d between 18:00–6:00 was calculated to be 1.8 cm s^{-1}, which is within the range of prior researches (0.077–3 cm s^{-1}) (Harrison and Kitto, 1994; Harrison et al., 1996; Li et al., 2012; Stutz et al., 2002; Spindler et al., 1999), is also consistent to the results derived from the HONO uptake coefficient on soil and ground (Donaldson et al., 2014a; VandenBoer et al., 2013). It should be noted that heterogeneous conversion of NO$_2$-HONO has not been taken into account, so 1.8 cm s^{-1} is the lower limit of dry deposition velocity. High RH at night probably increased the amount of adsorbed water on the ground surfaces and facilitates dry deposition of HONO.

7. The daytime HONO budget compounds all of these errors further and the manuscript henceforth cannot be seen as scientifically reliable for further evaluation.

Author's Response: HONO chemistry during daytime is completely different from that at night. The budget of the two are not comparable. For example, we choose a period from 9:00 to 15:00 with intense solar radiation and low wind speed to ignore some small terms such as vertical transport, horizontal transport, etc. Meanwhile, with very high levels of photolysis loss rate of HONO, the relative uncertainties of deposition and emissions can be also minimized. Such an approach was applied in a large body of literatures and the results have been compared and discussed (Hao et al., 2020; Huang et

al., 2017; Li et al., 2018a; Li et al., 2021; Spataro et al., 2013; Su et al., 2008b; Xu et al., 2019; Zhang et al., 2019; Zheng et al., 2020; Liu et al., 2019).

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