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 thoroughly and substantially, to address these comments. Specifically, our major changes include (1) added analysis of hourly resolved HONO budget at night, (2) a dedicated section of detailed discussion of uncertainties for the nighttime budget, (3) removed the section on oxidation capacity, (4) a re-written introduction section, and (5) new title, new abstract, and new conclusion section to reflect these major changes and a sharpened focus on HONO budget and its uncertainties.

In the following, please find our detailed responses to the comments of the reviewers. Referee comments are given in *black italics*, and our responses and changes in the manuscript in blue and red, respectively.

Response to Reviewer 1:

I think the authors have adequately addressed my concerns and suggestions.
However, I do not think that they have fully addressed the concerns of the other reviewer (Referee #2). Although some of his/her comments are, in my opinion, overly critical, some are valid points.

In particular, Referee #2 states that some of the calculations (direct emissions and soil emissions) are incorrect and/or based on wrong assumptions. Now, one thing is to say that the conclusions drawn from the calculations are incorrect, but quite another thing is to say that the calculations themselves are

incorrect. The first may be acceptable as part of normal scientific discussions, the second is definitely not acceptable and should cause rejection of the paper.

Therefore, I think the authors have to demonstrate convincingly that the latter is not the case, that their calculations are correct, and that their disagreement with Referee #2 is a normal matter of differing opinion and interpretation of the outcomes of their analysis.

Author's Response: We would like to thank the reviewer for the helpful comments and suggestions. As shown in the following, we have carefully considered all the comments and revised the manuscript accordingly.

Response to Reviewer 2:

Overview

The Authors have made several changes to this manuscript to address some of the comments raised by the Reviewers yet did not fully address those made by both Reviewers in the first round of revisions. Additions of measurement intercomparison and QA/QC for the HONO measurements, as well as the inclusion of alkene and O3 chemistry are excellent and the Authors are thanked for these additions. The initial changes are a good start to reach an acceptable manuscript for acceptance into ACP, yet major revisions are still required. The Authors have requested specific and detailed constructive criticisms. Until the initial major issues raised are resolved, this Reviewer must point out that is not possible to assess the remainder of the work with constructive criticism as the existing flaws draw reasonable concern about the basis of this work and the potential over-interpretation of the dataset. In an effort to create a constructive dialogue towards a final accepted manuscript, one suggestion is that progress with the current work may be most easily accomplished if the Authors consider separating the HONO

chemistry and budget from its impact on oxidants into a second manuscript. Once the major issues are resolved around the HONO budget, then the oxidant impacts work can be submitted separately for peer review.

Author's Response: We thank the reviewer for the constructive comments and suggestions. Following the reviewer's suggestion, major revisions have been made to (1) add a more comprehensive discussion of the nighttime HONO budget including added analysis on an hourly basis and detailed discussion of uncertainties, and (2) remove the discussion related to the effect of HONO on atmospheric oxidative capacity. (3) remove the section on oxidation capacity, (4) a re-written introduction section, and (5) new title, new abstract, and updated conclusion section to reflect these major changes and a sharpened focus on HONO budget and its uncertainties.

The title thus has been revised to be "Budget of nitrous acid (HONO) at an urban site in the fall season of Guangzhou, China".

In the following, we address the reviewer's comments in the following point by point, and indicate revisions that we have made in light of these comments. We list the reviewer's comments below *in black italic*, our responses and changes in the manuscript in blue and red, respectively.

Major Comments

1. Both Reviewers raised concerns around the HONO budget, focusing on nighttime observations alone, and requested better description of the accounting of sources and sinks. These were to be compared against the averaged nocturnal observations to demonstrate that the chemistry and transformations of HONO suggested by the Authors were reasonably approximating the observations. This was not completed and a figure depicting the rates of HONO generated by the sources and sinks, along with the

resulting predicted HONO presented against the observations, was not made. The validity of the HONO budget remains questionable until this is presented and discussed with comparison to other reports, such as those extensively cited by the Authors in their response and more broadly for polluted urban environments. The Authors contend that comparing a single average value is sufficient for understanding HONO chemistry in the PRD as opposed to temporally-resolved diurnal data in order to minimize the impacts of fluctuations of other factors such as transport and dilution. The Reviewer finds such an argument to be of high concern for a dataset that spans several weeks of observations in a manuscript being considered in an atmospheric chemistry journal. The measurements are available to the Authors to do such a temporally-resolved representation of HONO nighttime chemistry and there is ample precedent in the literature demonstrating how to construct one (e.g. see the extensive work published by either Stutz or Kleffmann). Such an analysis has been a standard approach for assessing the impacts of HONO accumulated at night on oxidation chemistry the following day, which the Authors cite in their response and should revisit to improve this manuscript.

Author's Response: We thank the reviewer for the comments. We parameterized the sources and sinks of nighttime HONO to represent their temporal variation. The summary of the parameterisations used for nighttime HONO budget calculation can be found in Table S5. We note here in particular that considering nighttime OH concentration 1.0×10^6 cm^{-3} has invited many concerns, we discussed with Dr. Zhaofeng Tan (Tan et al., 2019) and agreed on changing it to 0.5×10^6 cm^{-3}. This change does not change our conclusion.

Among all the terms in the nighttime HONO budget, the primary emission, the reaction of OH and NO have been discussed in the original manuscript. NO$_2$ heterogenous reaction on ground surface (P$_{ground}$) and aerosol surface (P$_{aerosol}$) can be estimated based on the empirical data derived from either experiments or observations.

$$P_{ground} = \frac{1}{8} \gamma_{NO_2 \rightarrow ground} \times [NO_2] \times C_{NO_2} \times \frac{S_g}{V} \tag{7}$$

$$P_{aerosol} = \frac{1}{4} \gamma_{NO_2 \rightarrow aerosol} \times [NO_2] \times C_{NO_2} \times \frac{S_a}{V} \tag{8}$$

$$\frac{S_g}{V} = \frac{2.2}{H} \qquad (9)$$

Where C_{NO_2} is the mean molecular velocity of NO_2 (m s^{-1}), $\gamma_{NO_2 \rightarrow ground}$ and $\gamma_{NO_2 \rightarrow aerosol}$ represent the uptake coefficient of NO_2 on ground surface and aerosol surface respectively, S_g/V and S_a/V are the surface area to volume ratio (m^{-1}) for both ground and aerosol, respectively. Considering the land use type of the study site, we treated the ground as an uneven surface, and a factor of 2.2 per unit ground surface measured by Voogt and Oke (1997) was adopted to calculate the total active surface. Hence, S_g/V can be calculated by Eq. (9), where H is the mixing layer height. The surface area-to-volume ratio S_a/V of PM$_{10}$ was not available in this study and was estimated according to PM$_{2.5}$ and S_a/V value in Guangzhou Xinken by Su et al. (2008). The uptake coefficients of NO_2 on ground surface and aerosol surface were assumed to be 4×10^{-6} following previous studies (Li et al., 2018; Liu et al., 2019; Zhang et al., 2021) (the summary of the parameterisations used for nighttime HONO budget calculation can be found in Table S5). With these assumptions, an average value of P$_{ground}$ of 0.27 ± 0.13 ppbv h^{-1} can be derived, which is far larger than P$_{aerosol}$ (0.03 ± 0.02 ppbv h^{-1}) (Fig. 5 (c) and (d)).

In response to reviewer's suggestion, we added a temporally-resolved budget analysis of nocturnal HONO, although we still note that such a detailed analysis is more appropriate for the daytime when HONO lifetime is much shorter and uncertainties in transport are negligible, whereas at night, transport is not negligible but is difficult to estimate with observational data like ours, which is why much more subtle and careful data filtering is necessary (Wong et al., 2011). The observed production rate of HONO P$_{obs}$ can be defined as the sum of the total loss rates and change rates of HONO (Gu et al., 2021). As shown in Fig. S6, our estimated P$_{obs}$ and the sum of sources and sinks agree reasonably well during most of the nighttime hours while P$_{obs}$ is markedly higher during 19:00, and 2:00–5:00, which reflects the expected larger uncertainties in such time resolved analysis than in an average estimate throughout the night.

We have added a section 3.2.5 with an extended discussion of the nighttime budget. The section reads as follows:

3.2.5 Nighttime HONO budget: relative importance of sources and their uncertainties

It is useful to evaluate the balance of HONO budget by evaluating calculated/parameterized sources and sinks against the observed HONO level and variability. The observed production rate of HONO P_{obs} can be defined as the sum of the total loss rates and change rates of HONO (Gu et al., 2021). When using the median values of parameters (Table S5) and taking an average throughout the night (18:00–6:00), all five sources are greater than or close to the average accumulating rate of HONO at night derived from observed HONO variation (0.02 ± 0.06 ppbv h^{-1}), indicating a balanced HONO budget considering all uncertainties. Ranking the source strengths with their median estimates suggested that heterogeneous conversion of NO_2 on ground surface (0.27 ± 0.13 ppbv h^{-1}), primary emission from vehicle exhaust (between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1} with a middle value of 0.16 ± 0.07 ppbv h^{-1}) and the homogeneous reaction of NO + OH (0.14 ± 0.30 ppbv h^{-1}) were major sources of HONO at night. Nighttime soil emission rate (0.019 ± 0.009 ppbv h^{-1}) and heterogeneous NO_2 conversion on the aerosol surfaces (0.03 ± 0.02 ppbv h^{-1}) were two other minor sources. Dry deposition (0.41 ± 0.31 ppbv h^{-1}) was the principal loss process of nighttime HONO, followed by dilution (0.18 ± 0.16 ppbv h^{-1}), while the homogeneous reaction of HONO + OH (0.008 ± 0.012 ppbv h^{-1}) and HONO uptake on the aerosol surfaces (0.008 ± 0.006 ppbv h^{-1}) were insignificant.

We also made an attempt to obtain a time resolved HONO budget on an hourly basis, although the results are not satisfactory for all the hours at night, with obvious differences between observed and calculated rates of HONO variation, e.g., at 22:00 and from 2:00 to 5:00 (Fig. S6). This is well expected considering much more amplified uncertainties associated with hourly variabilities of various quantities, which can be considerably reduced by averaging all hours. This is why subtle and careful data filtering is necessary when nightime HONO chemistry is examined in detail (Wong et al., 2011). Such a granular analysis is more appropriate for the daytime when HONO lifetime is much shorter and uncertainties affecting the interpretation of HONO chemistry (e.g., emission and transport) are much muted. As a matter of fact, because the rate of HONO change shown in Fig. S6 is a first order derivative of the HONO concentration itself, one can expect that HONO concentrations from each source would show greater variations, making it more difficult to compare on an hourly basis. Another challenge is that since those parameters used for

calculating HONO source strengths have a range in their estimates (Table S5), the HONO source strengths also have a wide range individually, and therefore there are numerous possible combinitions of these sources with different strengths and rankings to close the budget.

The comparison and ranking of sources considering variability and uncertainty becomes less straightforward than ranking nighttime average source strengths (Fig. 5). Among the three largest sources, both primary (non-soil) emission and NO_2 heterogenous source on ground showed an evening peak and decreased toward after midnight. The NO + OH source showed a different trend with its lowest level in the evening, making it the smallest source among the three at that time. Although the NO_2 heterogenous source on ground appeared the largest with its median parameter value, it also had the largest range of estimate, suggesting that its importance is more uncertain compared to the other sources. On the other hand, the other two minor sources, i.e., the NO_2 heterogenous source on aerosols and soil emission are unlikely more important than these three sources given their ranges of low estimates. The variability and uncertainty of dry deposition are largely dependant on other terms of sources and sinks since it is derived as a final term to balance the budget.
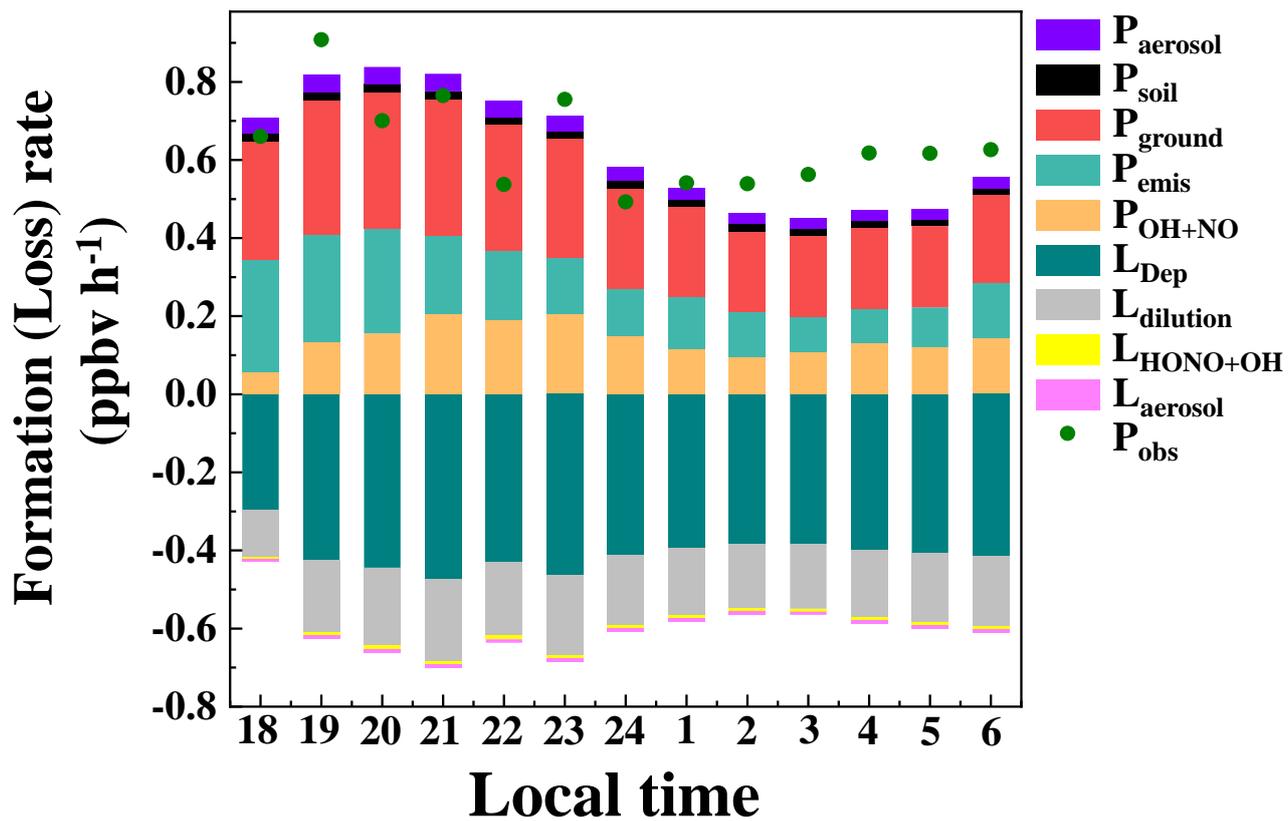
Figure. S6. Nighttime HONO budget in Guangzhou during the observation period.

Table S5. Parameterisations of HONO production and loss mechanisms.

Mechanism	HONO formation/loss reactions	Parameterisation			Reference
		Median	Lower	Upper	
Primary emission		$P_{emis} = 0.16$ ppbv h^{-1}	Emission source inventory 1	Emission source inventory 2	1
NO + OH	NO + OH $\rightarrow$ HONO	OH $= 0.5 \times 10^6$ cm^{-3}	1.0×10^5 cm^{-3}	1.0×10^6 cm^{-3}	2
NO$_2$ on aerosol	NO$_2$ + aerosol $\rightarrow$ HONO	$\gamma_{NO_2 \rightarrow aerosol} = 4 \times 10^{-6}$	2×10^{-7}	1×10^{-5}	3, 4, 5
NO$_2$ on ground	NO$_2$ + ground $\rightarrow$ HONO	$\gamma_{NO_2 \rightarrow ground} = 4 \times 10^{-6}$	2×10^{-7}	1×10^{-5}	3, 4, 5
Soil emission		water content: 35%–45%	45%–55%	25%–35%	6, 7, 8
Deposition		$V_d = 2.5$ cm s^{-1}	0.077 cm s^{-1}	3 cm s^{-1}	9, 10, 11,12
Vertical transport		$k_{(dilution)} = 0.23$ h^{-1}	0.1 h^{-1}	0.44 h^{-1}	13, 14, 15
HONO on aerosol		$\gamma_{HONO \rightarrow aerosol} = 4 \times 10^{-5}$	3×10^{-7}	5×10^{-4}	16, 17, 18
HONO + OH	HONO + OH $\rightarrow$ NO$_2$ + H$_2$O	OH $= 0.5 \times 10^6$ cm^{-3}	1.0×10^5 cm^{-3}	1.0×10^6 cm^{-3}	2

Emission source inventory 1 denotes the 2017 NOx emission source inventory of Guangzhou city; Emission source inventory 2 denotes the 2017 NOx emission source inventory of the 3 km × 3 km grid cell centred on the Guangzhou Institute of Geochemistry. Reference: 1: Huang et al. (2021); 2: Tan et al. (2019); 3: Li et al. (2018); 4: Liu et al. (2019); 5: Zhang et al. (2021); 6: Oswald et al. (2013); 7: Liu et al. (2020a); 8: Liu et al. (2020b); 9: Stutz et al. (2002); 10: Harrison and Kitto (1994); 11: Harrison et al. (1996); 12: Spindler et al. (1999); 13: Dillon et al. (2002); 14: Lin et al. (1996); 15: Kalthoff et al. (2000); 16: El Zein et al. (2013); 17: El Zein and Bedjanian (2012); 18: Romanias et al. (2012).
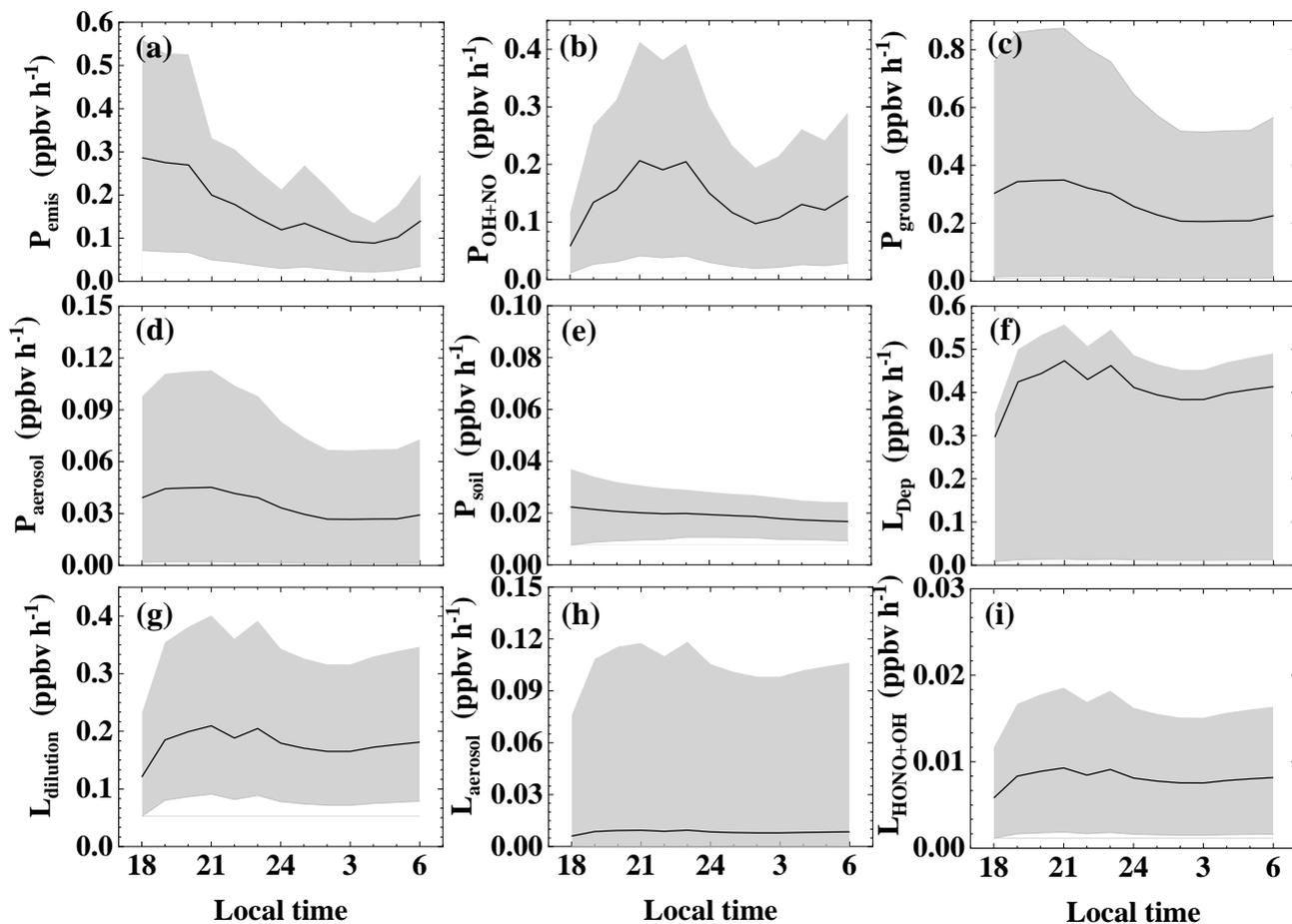
Figure 5. The nocturnal variation of the terms of HONO budget (a) primary emission from vehicle exhaust, (b) homogeneous reaction of NO + OH, (c) heterogeneous conversion of NO₂ on ground surfaces, (d) heterogeneous conversion of NO₂ on aerosol surfaces, (e) soil emission and HONO loss from (f) dry deposition, (g) dilution, (h) uptake on aerosols, (i) HONO + OH during Sep. 27–Nov. 9 2018 in Guangzhou. The black line is the HONO production rates with the median values of parameters, and the grey shadow represents their lower and upper limits.

2. A good example of remaining questions around the HONO budget comes from the major error in the deposition of HONO that was corrected by the Authors using reactive uptake coefficients in the literature.

This major error was identified by both Reviewers and it is now contended by the Authors that this correction makes the production and loss terms explored in this work robust enough to represent the observations. This is not depicted, nor summarized, to provide a convincing argument that the chemical controls on HONO are understood well enough to extend the analysis to oxidant impacts. The work performed by the Authors for representing the HONO deposition is well done and needs to be extended to the inclusion of NO2 heterogenous hydrolysis and a full HONO budget analysis that is compared to the observations.

Author's Response: Thanks for the suggestions. In the original manuscript, we calculated the deposition rate considering only primary emission and NO + OH and set it as a low limit. In a more comprehensive nocturnal budget (see the response above) as suggested by the reviewer, we calculated the deposition of HONO L_{Dep}, HONO uptake on aerosols $L_{aerosol}$, and transport processes, e.g. entrainment of background air $L_{dilution}$ using the typical/recommended parameter values (see Table S5) (heterogeneous conversion of NO_2 on ground and aerosol surface were also considered) and found that the sources and sinks of HONO at night were in balance and able to explain the observed production rate of HONO P_{obs}.
The manuscript has been revised accordingly:

As discussed above, strong sinks are required to balance the nighttime HONO production. Since the reactions of HONO + OH and HONO + HONO are negligible (Kaiser and Wu, 1977; Mebel et al., 1998), it is conceivable that nighttime HONO is mainly removed through deposition L_{Dep} (El Zein and Bedjanian, 2012; Li et al., 2012; Hao et al., 2020; Meng et al., 2020), transport processes, e.g. entrainment of background air $L_{dilution}$ (Gall et al., 2016; Meng et al., 2020), and uptake on aerosols $L_{aerosol}$,. These terms can be expressed as follows:

$$L_{Dep} = \frac{V_d \times [HONO]}{H} \tag{10}$$

$$L_{aerosol} = \frac{1}{4} \, \gamma_{HONO \rightarrow aerosol} \times [HONO] \times C_{HONO} \times \frac{S_a}{V} \tag{11}$$

$$L_{dilution} = k_{(dilution)} \times ([HONO] - [HONO]_{background}) \tag{12}$$

where V_d is the average deposition velocity, $\gamma_{HONO \to aerosol}$ is the uptake coefficient of HONO on aerosol surface, $k_{(dilution)}$ is the dilution rate (including both vertical and horizontal transport) (Dillon et al., 2002). C_{HONO} is the mean molecular velocity of HONO (m s^{-1}), and [HONO] and [HONO]$_{background}$ represent the HONO concentration at the observation site and the background site, respectively. In this work, the lowest nighttime HONO concentration was taken as the [HONO]$_{background}$.

The average loss rate of HONO by dilution was calculated to be 0.18 ± 0.16 ppbv h^{-1}, which is in the range of prior results (Gall et al., 2016; Liu et al., 2020a; Liu et al., 2020b). The average value of $L_{aerosol}$ and $L_{OH+HONO}$ was 0.008 ± 0.006 ppbv h^{-1} and 0.008 ± 0.012 ppbv h^{-1}, respectively. In order to balance the nighttime HONO budget and assuming dry deposition to be responsible for the remaining amount of HONO loss, a dry deposition rate of ~ 2.5 cm s^{-1} was adopted accounting for an average loss rate of 0.41 ± 0.31 ppbv h^{-1} by deposition between 18:00–6:00, when using the median parameter values in Table S5 to calculate the HONO sources and sinks. This result is consistent with previous studies suggesting dry deposition as the dominant loss way for HONO during night (Li et al., 2012; Hao et al., 2020; Meng et al., 2020). The upper limit of $L_{aerosol}$ is only 0.10 ± 0.08 ppbv h^{-1}, suggesting that HONO loss on aerosols was not a major sink, as also suggested by prior studies (El Zein and Bedjanian, 2012; El Zein et al., 2013; Romanias et al., 2012).

3. This mechanism has been demonstrated for decades to be a major source of nocturnal HONO, such that this has become the textbook mechanism for secondary HONO chemical formation. In a concerning rebuttal regarding the conversion of NO2 on surfaces at night, the Authors contend that this does not need to be performed because their other mechanisms make enough HONO already. This is not a factual position to take, as Figure 5e looks nearly identical to that presented previously by Stutz et al. (2004) when exploring this mechanism (i.e. a conversion ratio that increases with RH above 70 %). The Authors need to draw from the work that includes reactive uptake coefficients for this conversion to be calculated

(e.g. see the extensive modeling work from Stutz) and numerically demonstrate that all sources and sinks are reasonably represented.

Author's Response: We thank the reviewer for the constructive comments. A main point of this paper is that at our site that is strongly influenced by vehicle emissions, the contributions of primary emission and consequential NO + OH emissions to HONO are higher than most previous observations. This does not rule out the heterogeneous reaction of NO_2 as a major source of HONO (see our response to Comment 1). In fact, correlation analysis and Fig. 5 (e) has qualitatively indicated the role of heterogeneous reaction of NO_2, which is further confirmed by calculations on sources and sinks.

As proposed in 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. The reaction probability ratios $\gamma_{NO2}/\gamma_{HONO}$ of 0.05 can be approximated from the nocturnal, emission-corrected HONO measurement plotted against their respective NO_2 mixing ratios (see Fig. R3). Assuming a typical γ_{NO2} varlue of 4×10^{-6}, $\gamma_{HONO} = 8 \times 10^{-5}$ can be deduced, which is within the range of previous studies (Donaldson et al., 2014; VandenBoer et al., 2013).
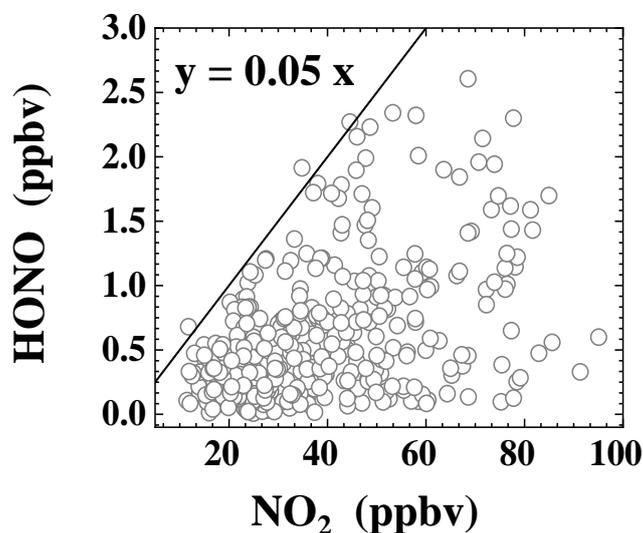
Figure R3. Scatter plot of emission-corrected HONO against NO₂ in the time interval of 18:00–00:00 LT. The straight line indicates the maximum values of HONO/NO₂ ratio, as predicted for the PSS in Stutz et al. (2004) with a heterogeneous reactivity ratio of 0.05.

4. Given the long-standing history of the importance of NO2 heterogeneous hydrolysis in the literature, it is confusing to see soil emissions given a highly weighted role in this work. It is similarly confusing to see the error in the soil HONO emission estimate being so tightly constrained (+/- 0.001 ppb hr-1), given that clear observations of this process have predmoninantly been seen in lab samples. Those field observations that do exist remain limited to agricultural soils. The literature cited in the Authors' response regarding the approach in constraining the soil emissions include a PhD thesis that has not been published in a peer-reviewed journal and a second article that indicates the approach is semiquantitative in the title. While it is commendable to bring the dimension of soil emissions into the analysis, it cannot be made at the expense of much more thoroughly described HONO production chemistry, and without the approach being very clearly presented in this manuscript (or its SI).

Author's Response: We thank the reviewer for pointing out "error in the soil HONO emission estimate being so tightly constrained". We clarify here that this is because in the original manuscript, when calculating soil HONO emission, we used fixed values of soil temperature and water content. The error of soil emission rates has been recalculated to be around 48% by taking the two factors into account.

It appears that our estimated soil emission rate being on par with the observed HONO growth rate has led to the impression that soil emissions played a role in nocturnal HONO formation. This should also be clarified here and in the revised manuscript. As a matter of fact, Figure 5 shows that the contributions of soil emission are far lower than heterogenous reactions of NO₂, primary emissions and the reaction of NO + OH. We also acknowledge that estimating the HONO emission from soil by extrapolating the laboratory results is prone to errors, due to the lack of comparison between laboratory results and field

observations. The manuscript has been revised to note the minor contribution of soil emissions in HONO budget and the potential errors in its estimate using laboratory data.

The average nighttime P_{soil} varied from 0.011 to 0.035 ppbv h^{-1}, with a mean value of 0.019 ± 0.009 ppbv h^{-1}. The HONO emission rate from soil at our site is slightly larger than the result reported in Shijiangzhuang urban area (Liu et al., 2020a) and comparable to that in Beijing urban area (Liu et al., 2020b). A caveat is that the calculation relies on laboratory results and is therefore prone to errors due to any possible inconsistency between laboratory simulations and field observations. Overall, soil emission is a minor source compared to other sources.

The reviewer pointed out that we cited a PhD thesis that has not been published in a peer-reviewed journal and a second article that indicates the approach is semiquantitative in the title. We deleted the thesis considering the reviewer's comment. A reference on the OH observation of Pearl River Delta region has been added for our OH value (Tan et al., 2019). Besides, we double checked the manuscript and the previous response, and found that the article containing semi-quantitative in the title is "Semi-quantitative understanding of source contribution to nitrous acid (HONO) based on 1 year of continuous observation at the SORPES station in eastern China". The article does not discuss HONO emission from soils.

5. Finally, the order of magnitude uncertainty presented in the direct HONO emission rate and in the NO + OH production of HONO at night continue to raise major concern when the sources and sinks, along with propagated error, are not fully communicated. The Authors have made good progress towards being able to do this, and with the inclusion of NO2 hydrolysis, can likely complete the analysis successfully. The range of direct emissions and the NO+OH sensitivity study then need to be combined with that result. Having pieced the presented facts for the latter two mechanisms together, a resulting difference of P(HONO) at 0.02 ppbv hr-1 between the large sources and sinks (each up to an order of magnitude larger) to match the observations seems possibly insignificantly different from zero or an overall loss once the error is propagated. One way to negate this issue could be to continue with the conservative approach that the Authors state they are taking in exploring the dataset: i) put sources at the lower limit and sinks

at the upper limit, and ii) vice versa. Then present the resultant HONO production rates at both boundaries against that which was observed, including propagation of the error at both limits. This should then be followed in the discussion by a synthesis of the most likely combination of production and loss processes, the average temporal representation of these, and a demonstration that this compares well to the measurements. The extension of such results to the impact on oxidation capacity can then use the upper and lower limits of the HONO budget to set more reasonable boundaries on the potential impact that it has on chemical processes at this location.

Author's Response: We thank the reviewer for the comments. The upper and lower limits of parameters in Table S5 were adopted to evaluate the uncertainties of HONO sources and sinks. As shown in Fig. 5, there is a big range between the upper and lower limits of each source and sink, as one can expect. The lower limits of both primary emission and P_{OH+NO} are still higher than the average accumulating rate of HONO (0.02 ± 0.06 ppbv h^{-1}), indicating the significance of these sources regardless of uncertainty. The uptake efficiencies of NO_2 on surfaces vary in a range of 2 ~ 3 orders of magnitude. As a result, the resulting lower limits of NO_2 hydrolysis on ground is 0.014 ± 0.007 ppbv h^{-1}, while the higher limits of NO_2 hydrolysis on ground is 0.68 ± 0.33 ppbv h^{-1}, far larger than the other sources. The HONO formation rates by NO_2 hydrolysis on aerosols ranges between 0.002 ± 0.001 ppbv h^{-1} to 0.09 ± 0.04 ppbv h^{-1}, indicating its small contribution regardless of uncertainty. The limits of soil emissions mainly depend on the soil temperature and water content. It can be seen clearly from Fig. 5 that soil emissions can be regarded as negligible during the observation. More detailed discussion can be found in Section 3.2.5.

6. The Reviewer hopes that the Authors find these suggested revisions more constructive such that the manuscript can be improved to meet the expectations of publication in ACP. Further constructive criticism and suggestions to improve this manuscript are currently out of the scope of peer review, as the time required is too substantial given the current state of this work. Obtaining such a detailed review is the responsibility of the Authors by addressing the major concerns that currently exist. The Authors are strongly encouraged to again consider revising their introduction to improve the narrative being outlined,

as it remains a collections of statements/facts obtained from the literature instead of synthesizing the state of knowledge such that outstanding gaps are clearly presented for the current work to address. The quality of writing in this section significantly lowers the impact of this work.

Author's Response: We thank the reviewer for the constructive comments. We have revised the introduction according to the reviewer's suggestion.

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