Response to Reviewer 2:

This manuscript describes measurements of Nitrous Acid (HONO) and a suite of other trace gases at a mountaintop site (Mt. Tam Observatory) on the North China Plain. Their goal was to assess whether currently understood HONO sources could explain measured HONO mixing ratios at the (sometimes), free tropospheric site. The authors use their observations coupled with model output to calculate midday HONO photostationary state values (PSS) and compare their observations with Master Chemical Mechanism (MCM) model output. Closing the HONO budget has been a challenging long-standing issue within the community and this paper is a further attempt to do so. The publication is generally well written and the content falls within the scope of Atmospheric Chemistry and Physics. I recommend publication once the following comments are addressed.

Response: We appreciate the reviewer for the positive comments and helpful suggestions. We have carefully considered all of the comments, and revised the original manuscript accordingly. Below we provide the original referee's comments in *black italics*, followed by our responses and changes in the manuscript in blue and red, respectively.

Major Comments:

While the Long Path Absorption Photometer Technique (LOPAP) has been extensively tested for a variety of interferences (Heland et al., 2001; Kleffmann and Wiesen et al., 2008), it has been shown to have an interference from peroxynitric acid (HO_2NO_2, PNA), (Legrand et al., 2014). While in many studies ambient temperatures would have rendered this potential interference negligible, I cannot help but feel this is the type of scenario where it could potentially be a problem. The temperatures under which these measurements were performed (and NOx levels) should support a long enough PNA lifetime for it to be observed. In addition, the authors indicate that the missing HONO source should scale with solar radiation and NO_2. PNA should also scale with both of these parameters. While it would be nice to have a full interference test of the instrument for PNA, synthesizing or developing photolytic generation sources can be a challenge. The authors should address this by adding a section discussing the possibility of the interference. Using their MCM model runs they could provide an estimate of what best/worst case scenarios would look like. I doubt that PNA alone is the missing "HONO" source, however constraining the possibility of interference could give a more accurate picture to how much HONO is in fact missing.

Response: We appreciate the reviewer for the constructive comment that we did not consider carefully before. According to the suggestions, we reviewed more literatures and performed more MCM simulations to carefully explore the potential interferences from HO_2NO_2 to our HONO measurements. Below are some detailed results and our thoughts about this issue.

(1) We simulated the time series of HO_2NO_2 at Mt. Tai in winter and spring by the MCM chemical box model constrained with all our measured species including HONO. As shown in Figure R2-1, moderate concentration levels of HO_2NO_2 were predicted by the model at Mt. Tai, with average values (±SD) of 0.07±0.06 ppbv and 0.03±0.04 ppbv in winter and spring, respectively. If we took the HO_2NO_2 interference of 15% (Normal Case) reported by Legrand et al. (2014), the potential interference to the excess HONO (measured HONO minus the PSS HONO) were 16%±15% and 11%±10% in winter and spring, respectively. If we assumed a 100% interference (Worst Case), the potential interference from HO_2NO_2 to the excess HONO were 72%±30% and 66%±54% in winter and spring.

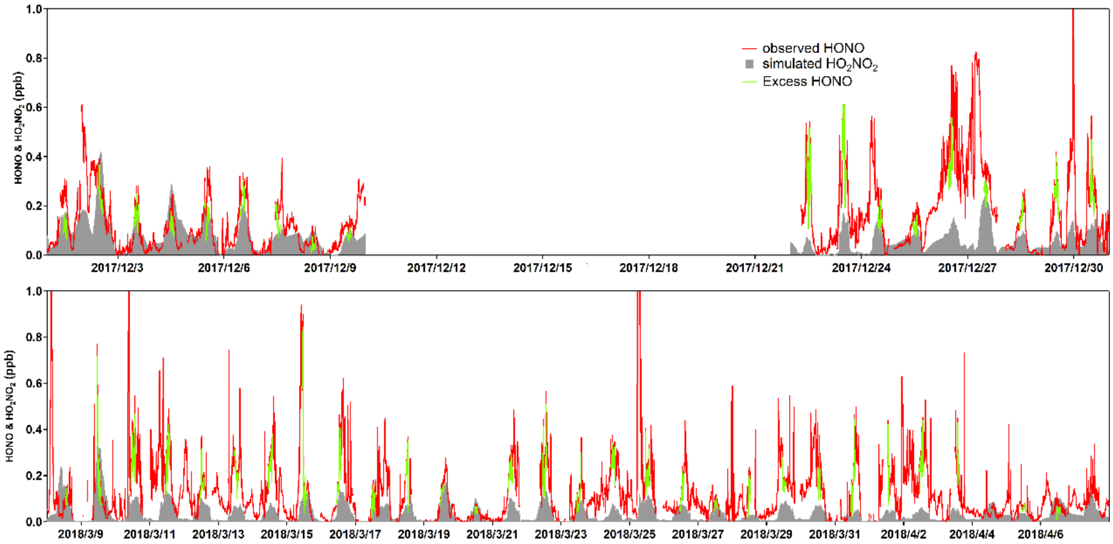


Figure R2-1. Model simulated HO_2NO_2 concentrations (grey) and comparison with the measured HONO (red) and excess HONO (green) at Mt. Tai in winter and spring.

(2) We examined the relationship between excess HONO (the measured HONO minus the PSS HONO) and $[NO_2]*J(NO_2)$, and the results are shown in Fig. R2-2. As we can see, the correlation was overall rather weak between excess HONO and $[NO_2]*J(NO_2)$, especially in winter. In comparison, the correlations were improved after the aerosol surface area was taken into consideration, with r of 0.54 and 0.48 between excess HONO and $[NO_2]*J(NO_2)*(S/V)a$ in winter and spring (see Fig. 6 in original manuscript). This indicates that the interference from HO_2NO_2 may not be a major factor in the determined excess HONO, and aerosol surface should play an important role.

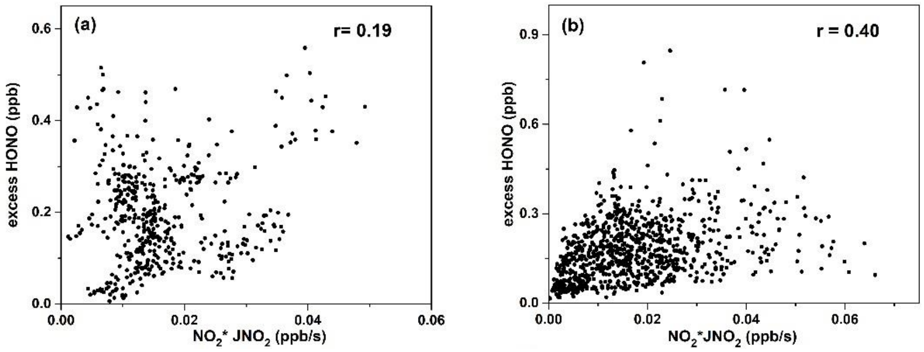


Figure R2-2. Scatter plots of excess HONO versus $[NO_2]*J(NO_2)$ at Mt. Tai in (a) winter and (b) spring.

(3) Based on the literature review, HO_2NO_2 is indeed a considerable interference to the LOPAP HONO measurements in the low temperature environments, such as polar regions and high mountain areas. Nonetheless, current studies haven't reached a consensus on the magnitude of HO_2NO_2 interference to the LOPAP measurements. For example, Legrand et al. (2014) reported that the HO_2NO_2 interference measured by LOPAP was about 15% in their lab experiments. Rappenglück et al. (2014) suggested that the interference could be higher than 15% from their wintertime measurements in an oil and gas field under severe O_3 pollution. Kerbrat et al. (2012) reported that an unpublished work by Ammann showed the HO_2NO_2 interference to the LOPAP was less than 3%. Obviously, more experiments are still needed to quantify the potential interference from HO_2NO_2 to the LOPAP HONO measurements.

In the revised manuscript, we have added a section (see below) to discuss the possible interference from HO_2NO_2 to the measured HONO in the present study.

"Possibility of measurement interference from peroxynitric acid (PNA; HO_2NO_2): While the LOPAP instrument has been extensively tested for a variety of interferences (Heland et al., 2001; Kleffmann and Wiesen, 2008), some recent studies reported that it may be subject to positive interference from HO_2NO_2 (e.g., Legrand et al., 2014). Due to the thermo decomposition nature of HO_2NO_2, its interference is generally negligible at ambient temperatures at the ground level, but may become important in the circumstances with low temperature and active photochemistry. Legrand et al. (2014) reported that the interference from HO_2NO_2 to their HONO measurements was about 15% according to laboratory experiments. In the present study, we did not conduct in-situ measurements of HO_2NO_2. To estimate the potential interference for our HONO measurements, we simulated the HO_2NO_2 concentrations at Mt. Tai in both campaigns by the MCM chemical box model constrained with all measured species including HONO. Figure S6 shows the time series of modelled HO_2NO_2 and its comparison with the measured HONO and missing HONO (measured HONO minus

[HONO]$_{pss}$) concentrations. Overall, moderate concentration levels of HO_2NO_2 were predicted by the model at Mt. Tai, with average values (±SD) of 0.07±0.06 ppbv and 0.03±0.04 ppbv in winter and spring, respectively. If we took the HO_2NO_2 interference of 15% (Legrand et al., 2014), the potential interference to the missing HONO were 16%±15% and 11%±10% in winter and spring, respectively. Figure S7 shows the scatter plots of missing HONO versus $[NO_2]*J(NO_2)$, an indicator of the HO_2NO_2 production. As we can see, the correlation was rather weak between missing HONO and $[NO_2]*J(NO_2)$, especially in winter (r=0.19). This indicates that the interference from HO_2NO_2 may not be a major factor in the determined missing HONO, and more experiments are needed to confirm and quantify the possible interferences to the ambient HONO observations."

Kleffmann, J., and Wiesen, P.: Technical Note: Quantification of interferences of wet chemical HONO LOPAP measurements under simulated polar conditions, Atmos. Chem. Phys., 8, 6813-6822, 2008.

Legrand, M., Preunkert, S., Frey, M., Bartels-Rausch, T., Kukui, A., King, M. D., Savarino, J., Kerbrat, M., and Jourdain, B.: Large mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic Plateau) in summer: a strong source from surface snow?, Atmos. Chem. Phys., 14, 9963-9976, 2014.

Rappenglück, B., Ackermann, L., Alvarez, S., Golovko, J., Buhr, M., Field, R. A., Soltis, J., Montague, D. C., Hauze, B., Adamson, S., Risch, D., Wilkerson, G., Bush, D., Stoeckenius, T., and Keslar, C.: Strong wintertime ozone events in the Upper Green River basin, Wyoming, Atmos. Chem. Phys., 14, 4909-4934, 2014.

Kerbrat, M., Legrand, M., Preunkert, S., Gallee, H., and Kleffmann, J.: Nitrous acid at Concordia (inland site) and Dumont d'Urville (coastal site), East Antarctica, J. Geophys. Res. Atmos., 117, 2012.

Specific Comments

1. Please indicate where the data and model output are available to readers. Title: Should be "The North China Plain"?

Response: The measurement data and model output used in the present study have been deposited in the Mendeley Dataset, which can be accessed from the following weblink (https://data.mendeley.com/datasets/wcn84cybx9/draft#folder-defadc56-944c-4f33-af54-14019d73ac61). The title has been changed as suggested.

"Data availability. The measurement data and model output used in the present study can be accessed from https://data.mendeley.com/datasets/wcn84cybx9/draft#folder-defadc56-944c-4f33-af54-14019d73ac61. The code for the MCM model can be downloaded from the MCM website (http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt)".

Title: "Sources of nitrous acid (HONO) in the upper boundary layer and lower free troposphere of the North China Plain: insights from the Mount Tai Observatory"

2. P1 L20: Are the mixing ratios means or medians? What are they? I believe it is mentioned further in the text, but it should be noted here as well.

Response: They are mean mixing ratios. For clarity, the statement has been revised as follows in the revised version.

"HONO showed moderate concentration levels (average ± standard deviation: 0.15±0.15 and 0.13±0.15 ppbv), with maximum values of 1.14 and 3.23 ppbv in winter and spring, respectively."

3. P1 L21: Could the noontime max be biased by measuring HO_2NO_2 (see major comments)?

Response: As discussed in the "Response to Major Comments", we estimated the potential interferences from HO_2NO_2 to our HONO measurements in both Normal and Worst cases, and the relatively weak correlation between missing HONO and $[NO_2]*J(NO_2)$ suggested that the bias by the HO_2NO_2 interference should be small.

4. P1 L27: Would a source consistent with NO_2 not also be consistent with HO_2NO_2 (see major comments)?

Response: As discussed in the "Response to Major Comments", the correlations between missing HONO and $[NO_2]*J(NO_2)$ were rather weak, especially in winter. In comparison, the correlations were improved after the aerosol surface area was taken into consideration, with r of 0.54 and 0.48 between excess HONO and $[NO_2]*J(NO_2)*(S/V)a$ in winter and spring. This suggests that the HO_2NO_2 interference should not be a major factor in the determined missing HONO, and aerosol surface may play an important role.

5. P4 L9: Change the wording of "Observatory has been widely deployed". You don't really deploy a building. Perhaps "Observatory has been widely used as a sampling location"?

Response: This statement has been revised as suggested in the revised version.

"The Mt. Tai Observatory has been widely used as a sampling location to investigate the regional air pollution in the North China Plain region in the past decade (e.g., Gao et al., 2005;

Sun et al., 2016; Wen et al., 2018)."

6. P6 L22: What do the authors mean by approximated by the CO (Temperature) data? Was it approximated by CO or temperature? Please clarify.

Response: We are sorry that the original descriptions may be too simplified and unclear. In the present study, the measurements of VOC and carbonyls were made offline by taking air samples followed by laboratory chemical analysis. The VOC and carbonyl samples were only collected during the daytime (7:00-19:00 local time) on some days, and there were no data available for the nighttime period. To facilitate the model simulations, these measured VOC and carbonyl data were approximated to a high resolution (i.e., 5 min) time series as follows. During the daytime when multiple VOC and carbonyl samples were available, the measurement data were directly interpolated to a time resolution of 5 min. For the period when measurement data were unavailable, the VOC concentrations (except for isoprene) were estimated with the real-time CO data by assuming a linear regression relationship between VOCs and CO (the regression was established with the concurrent measurement data of VOCs and CO). The same method was also applied for isoprene and carbonyls, but ambient temperature was used instead of CO for isoprene, and multi-linear regression with CO and O_3 was used for carbonyls to account for the primary and secondary sources of carbonyls. For clarify, the following descriptions have been provided in the revised manuscript.

"For VOCs and carbonyls for which the measurements were not in real-time, the high-resolution data were approximated as follows. During the daytime when multiple VOC and carbonyl samples were available, the measurement data were interpolated to a time resolution of 5 min. For the period when measurement data were unavailable, the VOC concentrations (except for isoprene) were estimated with the real-time CO data by assuming a linear regression relationship between VOCs and CO (note that the regression was established with the available measurement data of VOCs and CO). The same method was applied for isoprene and carbonyls, but ambient temperature was used instead of CO for isoprene, and multi-linear regression with CO and O_3 was used for carbonyls to account for the primary and secondary sources of carbonyls (Yang et al., 2018; Xue et al., 2016). Such approximation may be subject to some uncertainties but should not significantly interfere the estimation of the role of HONO photolysis in OH sources (Yang et al., 2018)."

7. P7 L27: I find the description of AOC to be confusing. Are the authors simply trying to describe OH-Reactivity or something else? Please clarify.

Response: We are sorry that the original description is misleading. It is not the OH reactivity, but is defined as sum$\{k_{OH}[OH][Xi]\}$. For clarity, the original statements have been modified as follows in the revised manuscript.

"Also calculated by the model was the AOC by OH, which is defined here as the reaction rate of OH with NO, NO_2, SO_2, CO and VOCs (AOC = $\Sigma(k_{OH}[OH][Xi])$: [Xi] is the concentration of the individual reactant species, and K_{OH} is the rate coefficient of OH with Xi)."

8. P7 L8: This wording is a bit ackward "The atmospheric conditions at Mt. Tai were featured by a cold and dry weather". Perhaps "The atmospheric conditions at Mt. Tai were dominated by cold and dry weather."?

Response: Changed as suggested.

"The atmospheric conditions at Mt. Tai were dominated by cold and dry weather (especially in winter with average (±standard deviation; SD) temperature and RH of -5.2±3.8 °C and 48±20%) as well as relatively lower concentrations of air pollutants."

9. P9 L18: "It can be argued that the heterogeneous formation of HONO should be stronger at the mountaintop, which may be due to the more intense solar radiation at the high altitudes." Why can this be argued? The ratios are almost within one standard deviation of each other. This would potentially be true assuming the source scales with light intensity, but what would the difference in surface area for the heterogeneous reaction be? That's not clear.

Response: We agree with the reviewer that this statement is a little bit arbitrary. In the revised manuscript, this statement has been revised as follows.

"Third, although the HONO/NO_2 ratios were almost comparable at both surface and Mt. Tai during the night, the daytime ratios were significantly higher at the mountaintop (0.065±0.093 and 0.093±0.094) than at the surface (0.047±0.090 and 0.052±0.040). It implies the enhanced HONO formation from the NO_2-involved sources at the mountaintop, especially in spring (see Fig. 3)."

10. P9 L31: Is there no newer reference than 1973? Surely there have been some advances.

Response: A new and more recent reference has been cited in the revised version.

"Around noontime, the PBL has been developed and K_z is generally in the order of 10^6 cm^2 s^{-1} (Zhang et al., 2009)."

"Zhang, N., Zhou, X., Shepson, P. B., Gao, H., Alaghmand, M., and Stirm, B.: Aircraft measurement of HONO vertical profiles over a forested region, Geophys. Res. Lett., 36, ,172-173, 2009."

11. P10 L6: The surface HONO would most certainly be extensively diluted by the time it reached the elevated site. Could the authors not use a conserved tracer to estimate the dilution? Or for that matter the upslope time?

Response: As we did not conduct the measurements concurrently both at surface and on the mountaintop, it was indeed difficult for us to find a conserved tracer to accurately estimate the dilution during the upslope transport. Here we only estimated the maximum transport height driven by the turbulent diffusion and mountain-valley breeze, to prove the potential important role of upslope transport in the observed daytime HONO at Mt. Tai.

12. P13 L20: How do you know the model underestimated the HO_x radical levels? I am unaware of HO_x measurements as part of this campaign constraining this. They aren't noted anywhere. This (as well as in the conclusion) should be re-worded.

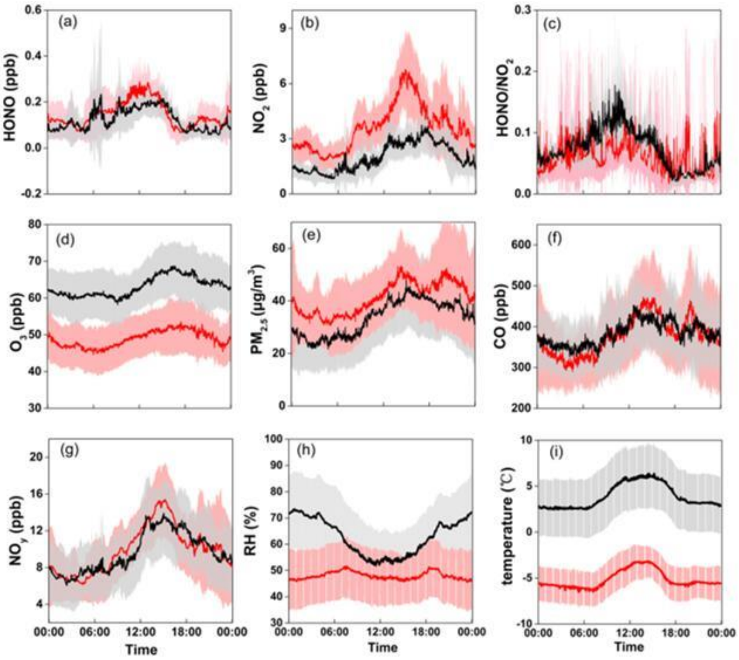
Response: The original statements are misleading. We didn't have in-situ HOx measurements in this study, and the inter-comparison was only made between two model scenarios with and without the measured HONO constraints. For clarity, these statements have been revised as follows in the revised version.

Page 14, Line 26: "Clearly, the model only considering the homogeneous source and without observational constraints predicted much lower levels of the HO_x radicals and AOC at Mt. Tai. Specifically, the discrepancy in the mid-day (9:00-15:00) average P_{OH}, OH, HO_2, and AOC can be up to 83.4% (63.7%), 47.2% (27.1%), 39.7% (20.3%), and 44.8% (24.9%) in winter (spring), compared to the base scenario with constraints of the measured HONO data."

Page 15, Line 19: "With only inclusion of the OH+NO reactions, significant reductions of the modelled OH (by ~47.2%; 27.1%), HO_2 (by ~39.7%; 20.3%), P_{OH} (by ~83.4%; 63.7%), and AOC (by ~44.8%; 24.9 %) were found, compared with being constrained by observed HONO data."

13. Figure 2: While the shaded areas currently represent standard error of the measurement, perhaps showing standard deviation of the measurement might be more useful so that the reader can get a better feel for the range of values observed.

Response: The suggestion has been adopted in the revised manuscript. For a better clarity of the figure, half standard deviation of the measurement data was used in the revised figure, see below.



Revised Figure 2. Average diurnal variations of (a) HONO, (b) NO_2, (c) $HONO/NO_2$, (d) O_3, (e) $PM_{2.5}$, (f) CO, (g) NO_y, (h) RH, and (i) temperature in winter (red) and spring (black) at Mt. Tai. Shaded area indicates half standard deviation of the measurement data.

14. Figure 5: A figure showing the relative contribution of each of known HONO formation pathways would also be nice so that readers can get a visual idea of the importance of each pathway at this location.

Response: Thanks for your helpful suggestion. The following figure showing the relative contributions of PSS HONO and unknown HONO formation pathways has been provided in the supporting information in the revised version.

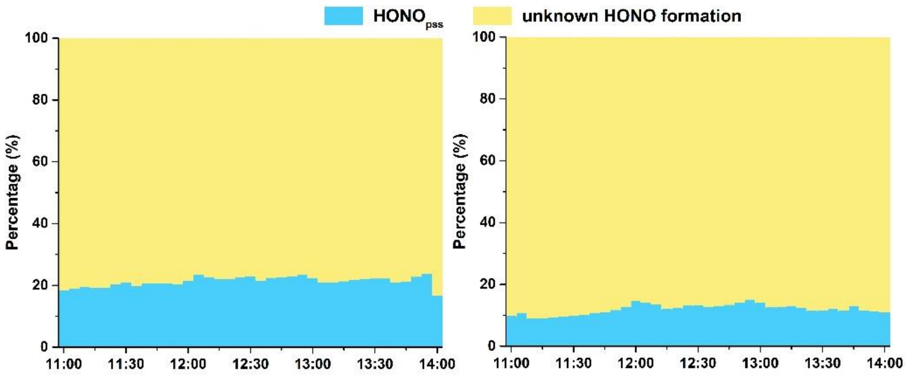


Figure S4. Relative contributions of $HONO_{PSS}$ and unknown HONO formation to the observed HONO around noon in winter (left) and spring (right).