## Response to Reviewer 1:

*The paper reports measurements of nitrous acid HONO at Mt Tai, a mountain site above the North China Plane in the Winter and Summer. The measurements were compared to the output of an MCM chemical box model to look for clues as to the processes that produce HONO values above those predicted by the NO-OH photostationary state (PSS). The measurements are interesting and their comparison to HONO measurements made at nearby surface sites are useful. I would like to see the authors expand their thinking about possible interferences in the chemical measurement, and use the MCM model to examine those. It is unfair to expect the authors to resolve these issues in this context, so I think the paper should be acceptable after some of that material is added and after the resolution of the following general and specific comments.*

**Response:** We thank the reviewer for the helpful comments to improve our original manuscript. We have carefully considered all the review comments and revised the manuscript accordingly. Especially, we adopted the constructive suggestion to examine the possible interference from $HO_2NO_2$ by the MCM modeling analysis. 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.

***General comments***

*Wintertime HONO measurements must consider the possibility of peroxynitric acid, $HO_2NO_2$, interferences. $HO_2NO_2$ is soluble in aqueous solution and forms $HONO/NO_2^-$ readily on surfaces and in aqueous solution. In addition, $HO_2NO_2$ is going to be favored at low temperatures when there is substantial $HO_x/NO_x$ photochemistry (Veres et al., 2015), which is the situation at Mt Tai in the Wintertime and Springtime. There is one study that has shown the $HO_2NO_2$ interference in the LOPAP method to be about 15% (Legrand et al., 2014). However, there is at least one other data set that implies the interference could be higher than that, see the Supplemental Material of Rappenglück, et al, (2014) which describes Wintertime LOPAP measurements in the middle of an oil and gas field when intense $O_3$ photochemical production was happening. One important piece of information in this regard is that modeling of this Wintertime photochemistry found that $O_3$ was overpredicted by substantial amounts when the LOPAP measured HONO was used in the model compared to PSS HONO (Carter and Seinfeld, 2012).*

*I am not expecting the authors to resolve this issue in this work. However, since this paper has extensive MCM modeling, I would like the authors to explore several questions: What are the $HO_2NO_2$ levels predicted by their model and how do they compare to the "excess HONO? What is the $O_3$ predicted when using both the PSS HONO and the LOPAP measured HONO and how*

*do those levels compare to measured $O_3$?*

*Modeled ozone levels that are much higher than measured would be clue that the HONO measurement has an interference. I would also note that the $HO_2NO_2$ source is $HO_2$ + $NO_2$, so one would expect the extra HONO (above PPS HONO) to scale with $NO_2$ and $J(NO_2)$. How does the quantity $[NO_2]*J(NO_2)$ correlate with $P_{HONO}$?*

**Response:** We thank 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 $HO_2NO_2$ on 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 from Figure R1-1, 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% 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% of interference (representing the worst case), the potential interference from $HO_2NO_2$ to the excess HONO were 72%±30% and 66%±54% in winter and spring.

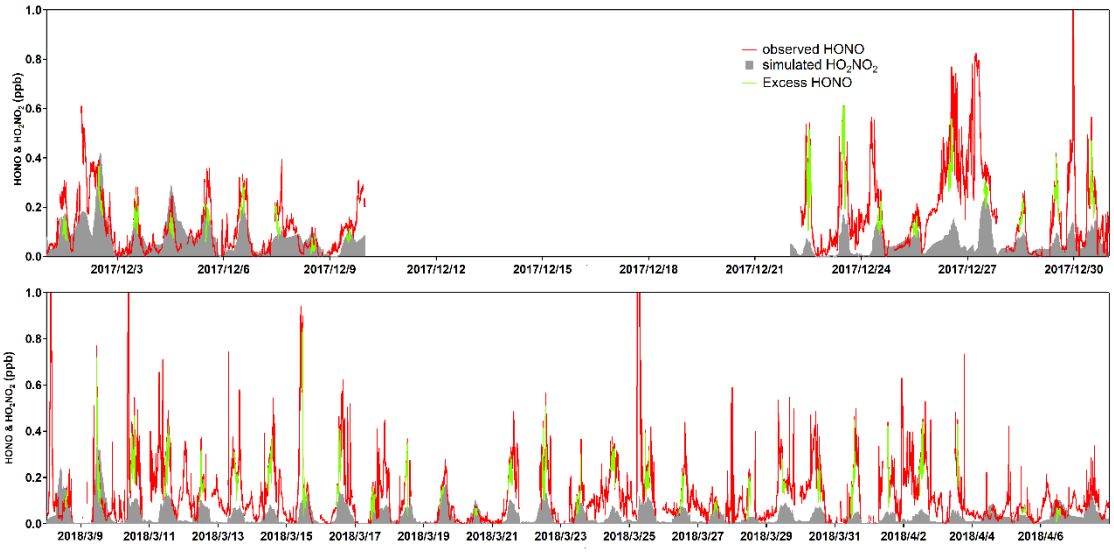


**Figure R1-1.** Model simulated $HO_2NO_2$ concentrations (grey) and comparison with the measured HONO (red) and excess HONO (green) at Mt. Tai in winter and spring.

(2) The observed $O_3$ concentrations at such a mountain site is mainly dominated by transport due to the mountain-valley breeze and strong winds at the mountaintop. It is really difficult for

a chemical box model with little consideration of physical processes to reproduce the observed variation pattern of $O_3$ at Mt. Tai. Although the model cannot reproduce the nighttime $O_3$ level observed at Mt. Tai, the modelled afternoon $O_3$ maxima (with measured HONO as constraints) were comparable to the observed $O_3$ peak levels (see Fig. R1-2 for examples with relatively weak winds). It should be noted that the modelling analyses presented in this study have used measured $O_3$ data (and other radical precursors) as constraints to estimate their impacts on the radical production and atmospheric oxidation capacity.

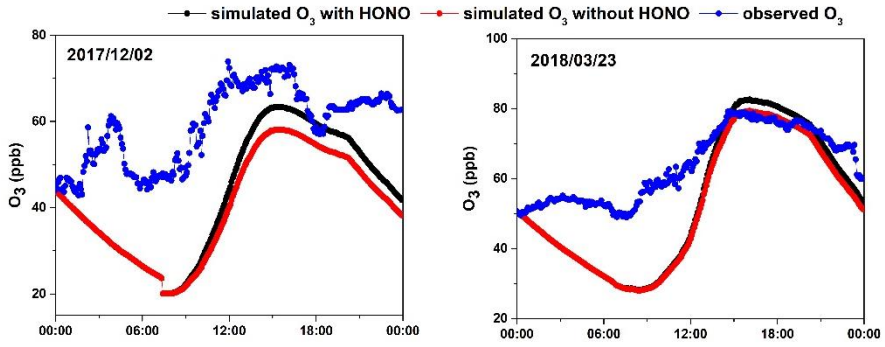


**Figure R1-2.** Model-simulated $O_3$ with HONO constraint (black) and without HONO constraint (HONO PSS; red) and comparison with the measured data (blue) on two cases with relatively weak daytime winds.

(3) 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. R1-3. 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 the 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.

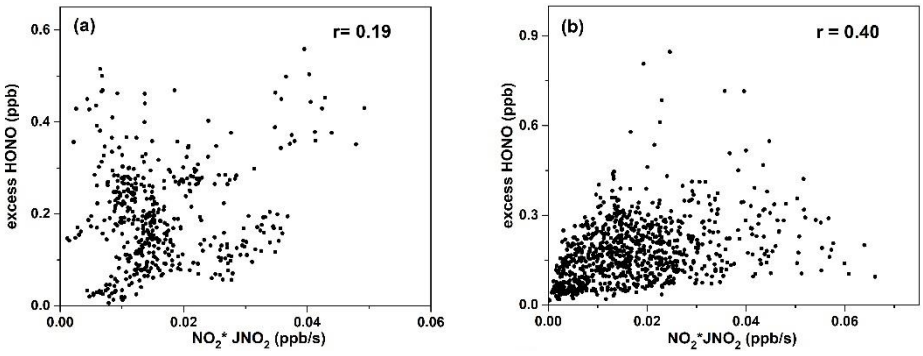


**Figure R1-3.** Scatter plots of excess HONO versus $[NO_2]*J(NO_2)$ at Mt. Tai in (a) winter and (b) spring.

(4) 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, as the reviewer mentioned, current studies have not 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 when intense $O_3$ production happened. 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 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***

*The data used in this paper, and ideally the code used for the model, must be made available to the community. Please deposit your data in an acceptable repository (see the ACP Instructions to Authors), or an accessible repository of your choosing. If the model code is already generally accessible, please specify where it may be obtained.*

**Response:** The measurement data used in the present study has been deposited in Mendeley Dataset (https://data.mendeley.com/datasets/wcn84cybx9/draft#folder-defadc56-944c-4f33-af54-14019d73ac61). The code used for the chemical box model was downloaded from the MCM website (http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt), and was modified for the current location and period. The following statements have been added in the revised manuscript.

"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)".

***Technical Comments/Corrections***

*1. Page 1, Line 16: should be "conducted at the surface"*

**Response:** Changed.

*2. Page 1, Line 20: Are these averages and standard deviations?*

**Response:** Yes. This statement has been revised as follows.

**"**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. Page 1, Line 21: Should be "with broad noontime maxima"*

**Response:** Changed.

*4. Page 1, Line 29: the statement about $HO_x$ radical levels is misleading. You don't have actual measurements of $HO_x$ radicals, only two different model cases, one based on PSS HONO and the other base on what the model says $HO_x$ would be given LOPAP measured HONO. You need to be clear about how you talk about it. When you say "underestimated" you are implying that the higher modeled $HO_x$ is in some sense "true" or "correct", when really, it's only a different estimate. This language is found other places in the paper and needs to be changed.*

**Response:** We agree with the reviewer, and the original statements have been revised as follows in the revised version.

Page 1, Line 29: "The model only considering homogenous HONO source predicted much lower levels of the $HO_x$ radicals and atmospheric oxidation capacity, compared to the model constrained with measured HONO data."

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."

*5. Page 2, Line 9: Should be "affects human health"*

**Response:** Changed.

*6. Page 2, Line 19: The PROPHET site is 238 m in elevation, so is not a high-altitude site.*

**Response:** Thanks for the suggestion. This reference has been deleted, and a new reference for a high-elevation site was added in the revised manuscript.

**"**Existing modelling studies may underestimate the AOC of high-altitude atmospheres owing to the lack of observational data constraints (Kukui et al., 2014).**"**

Kukui, A., Legrand, M., Preunkert, S., Frey, M. M., Loisil, R., Roca, J. G., Jourdain, B., King, M. D., France, J. L., and Ancellet, G.: Measurements of OH and $RO_2$ radicals at Dome C, East Antarctica, Atmos. Chem. Phys., 14, 12373-12392, 2014.

*7. Page 5, Line 12: What does "SHARP" stand for?*

**Response:** We have spell out "SHARP" in the revised manuscript as follows.

"The fine particle ($PM_{2.5}$) mass concentration was measured using a Synchronized Hybrid Ambient Real-time Particulate monitor (SHARP; *Thermo Scientific Model 5030*)."

*8. Page 6, Line 1: What are the uncertainties in the J($NO_2$) measurements and estimates?*

**Response:** The J($NO_2$) monitor was mounted at the rooftop of the station and higher than all the other instruments' inlets (also without any shelter), and should be free from additional errors other than the monitor's inherent uncertainty. However, the in-situ J($NO_2$) observations were only available during the spring campaign. So, we had to estimate the J($NO_2$) for the winter campaign as well as J(HONO) and J($O^1D$) for both seasons, based on the concurrent J($NO_2$) observations and the TUV model calculations (scaling the TUV-calculated clear-sky J values with the ratio of measured J($NO_2$) to TUV J($NO_2$)). Such estimation should be subject to some uncertainties, although this is the best what we can do with the available measurement data. The following statements have been added in the revised manuscript to elaborate the potential uncertainty of the estimation of J values.

"It should be noted that such estimation of J values is subject to some uncertainties, especially for those in winter when direct J($NO_2$) measurements were unavailable. Nonetheless, scaling the TUV-calculated clear-sky J values with the same ratio should not alter the major conclusion of this study regarding the impacts of HONO photolysis on the HOx sources and atmospheric

oxidation capacity."

*9. Page 6, Line 5: What does FNL stand for?*

**Response:** It is the final version of the NCEP reanalysis data and can be obtained from this website (https://rda.ucar.edu/datasets/ds083.3/index.html#sfol-fw?g=201608). The original statement has been revised as follows for clarity.

"The Weather Research and Forecasting (WRF) Model, driven by the NCEP FNL reanalysis data (https://rda.ucar.edu/datasets/ds083.3/index.html#sfol-fw?g=201608), was run to produce the high spatial resolution meteorological field."

*10. Page 6, Line 27: The definition of AOC is hard to follow based on this description. At first I thought the authors meant Sum{kOH[Xi]}, where [Xi] is the concentration of the individual species listed. That is properly termed "OH reactivity". I think the authors mean Sum{kOH[OH][Xi]}, but they need to make that explicitly clear.*

**Response:** We are sorry that the original description is misleading. Yes, it was 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)."

*11. Page 7, Line 22: I don't understand what the authors mean by "inspection of data reveals the higher than expected concentration levels of HONO". At this point in the paper, we have no context with which to judge this, i.e. we don't know what PSS HONO is or what [HONO] at remote sites might be expected.*

**Response:** We agree with the reviewer, and this statement has been revised as follows in the revised version.

**"**The above inspection of data reveals the overall moderate HONO concentration levels as well as the frequent occurrence of HONO-laden plumes in the upper PBL and lower FT of the NCP region.**"**

*12. Page 8. Line 21: It seems to me, the authors could use a tracer to more precisely determine the timing of upslope arrival at the site.*

**Response:** Thanks for the suggestion. As shown in Figure 2, most species including HONO, $NO_2$, NOy, $O_3$, CO and $PM_{2.5}$ showed daytime concentration peaks at Mt. Tai, confirming the upslope transport of boundary layer pollution to the mountaintop. To determine the timing of upslope arrival at the site, we chose CO as a tracer, which is relatively chemically inert and can represent the contribution of transport. During the two observation campaigns, the average CO concentrations increased from the morning and reached the maximum around noontime (e.g., 12:00-15:00 local time), which were almost coincided with the observed daytime HONO peak (~11:00-15:00 local time). The following statements have been added in the revised manuscript to elaborate this.

"The noontime HONO maximum (e.g., ~11:00-15:00 LT) at Mt. Tai suggested the potential upslope transport of HONO to the mountaintop and/or the presence of 'additional' daytime sources. The almost coincident noontime concentration peak of CO (e.g., ~12:00-15:00 LT) confirmed the upslope transport of boundary layer air to the mountaintop."

*13. Page 10, Line 1: I think there are better references for this than Donahue et al., (1973).*

**Response:** Thanks for the suggestion. 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."

*14. Page 10, Line 26. The phrase the "air masses ..... facilitate a pseudo-steady state" doesn't make sense. The short lifetimes facilitate steady state.*

**Response:** The original statement has been revised as follows in the revised version.

**"**Given such short lifetimes, the air masses arriving at Mt. Tai at noon should facilitate a steady state for HONO.**"**

*15. Page 12, Line 16: "dissected" seems like the wrong word here. I think "examined" or "explored" would be better.*

**Response:** It has been changed to "explored" in the revised version.

"The detailed chemical budget of $RO_x$ radicals was explored by the observation-based MCM box model."

*16. Page 13, Lines 20, 21: You are phrasing these results like you know what HOx and AOC is or should be, when really, you are comparing two different model results, one with and one without the additional HONO implied by the LOPAP measurements. The same kind of language is used in the Conclusions. These statements should be rephrased.*

**Response:** We agree with the reviewer. 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."

*17. Page 13, Baergen and Donaldson reference – this is a talk not a journal publication. I am fairly sure this group has a journal publication about this.*

**Response:** Thanks for the suggestion. We have found the journal publication of Baergen and Donaldson et al. in 2016, and cited it in the revised manuscript.

"Baergen, A. M. and Donaldson, D. J.: Formation of reactive nitrogen oxides from urban grime photochemistry, Atmos. Chem. Phys., 16, 6355–6363, 2016."