Response to 2nd round review

1. Editor's comments to the author:

Please address as quantitatively and in as much detail as possible the comments of the re-review from Reviewer #2.

These predominantly concern the quantitative implications of the selection of MLH and also the implications of the results for other locations.

Response: Thanks for the comments. We added our understanding and corresponding texts about MLH for HONO in the manuscript. Besides, a new section (Section 3.3.4) was supplemented to explain the translation of new methods we developed and conclusions we obtained in this study to further studies worldwide.

Please see the point-to-point response below (Comments in Black; Response in Blue; Changes in Red).

2. Report #1 from Reviewer #2

The manuscript has been improved after revision, and can be accepted to publish.

Response: Thank you.

3. Report #2 from Reviewer #1

ACP-2021-531 second review. The numbered comments correspond to the authors' replies to reviewer #1 in document "acp-2021-531-AC1-supplement" and line numbers to the authors' revised manuscript.

[Comment 1] This is a high quality observational dataset of HONO and related parameters that merits publication. My main concerns from the first review focused on the data interpretation side of the work, and particularly because the outcomes from the authors' 0-D modeling analysis rely heavily on the "correct" choice of the mixing layer height. MLH is set at 50 m, and two sensitivity tests are performed with the MLH set at 35 and 100 m.

The authors' response provides further qualitative discussion of the MLH based on their study and other literature studies. This is helpful. But it hasn't fully answered the question. I was hoping that the authors could be *quantitative* in their response and thus they would add numerical values of the MLH found in other studies into the main text, against which the reader can judge the authors' choice of the MLH. This would give confidence that 50 m is indeed a reasonable, *objective* choice. MLH = 50 m brings the authors' simple 0-D model into closest agreement with their HONO observations. But a different, more sophisticated model might produce a significantly different optimum MLH. Thus "50 m is best" is a consequence of the model, and not necessarily what is happening in the atmosphere itself. This part of the manuscript still needs further work:

* I accept the authors' response that it isn't possible to prove the MLH by comparing these ground-based observations with HONO measured at the mountain summit in their comparison paper.

* Were any numerical values of the MLH for HONO derived/quoted in the papers by Brown et al (2013) or Vandenboer et al (2013) or any other studies in the literature? If so, please add the MLH numbers into the main text.

* Numerical data of vertically resolved HONO measurements from Xing et al (2021) were given in

the main text (and repeated in the authors' response). Did Xing et al derive a number for the MLH? Can their data be fitted to provide a value(s) of the MLH?

* Do the sensitivity tests performed at 35 m and 100 m cover the likely range of how the MLH varies with wind speed, time of day, day vs night etc? i.e. do 35 and 100 m encompass the lower and upper limits of what is happening at their measurement site?

I'm entirely comfortable with the authors' conclusion that ground-based HONO sources dominate at the Tai'an city measurement site, and consequently the MLH for HONO is small (of the order of 50 m). I also recognise that the exact value of the MLH is changeable with conditions at their measurement site, and the MLH will likely be different at other locations. But at the moment the manuscript asks its readers to accept 50 m as the correct choice based on the authors' assertion. And this has consequences for the understanding of the atmospheric chemistry that follows.

Response to the above comments concerning MLH:

Thanks for the further comments. A proper choice of MLH is challenging but very important for 0D box model outcomes when constrained with near ground surface measurements, which is the reason why the reviewer and we are very serious with this issue.

In the supporting information, we added a new section to explain in detail.

2. A detailed explanation for the used MLH

Currently, some studies with ground measurements directly used the boundary layer height (BLH, 1-2 km at noon) instead of MLH. This would largely underestimate the contribution of ground-derived sources, leading to the misunderstanding of HONO formation. In the present study, we could not conclude that the MLH of 50 m (and sensitivity tests for 35-100 m) is the best, but it significantly reduces the uncertainties compared to the use of BLH. Additionally, a reasonable MLH for model study on ground HONO measurements should be in the range we tested. See the explanation below.

Here we assume that the ground surface is the main source of HONO in the atmosphere. This is for example confirmed by recent MAX-DOAS studies (Garcia-Nieto et al., 2018; Ryan et al., 2018; Wang et al., 2019; Xing et al., 2021), in which strong gradients were observed in the lower daytime atmosphere. The gradients can be explained by fast photolysis of HONO during the vertical updraft from the ground surfaces (source region of HONO) during the daytime. The mixing layer higher (MLH), i.e., the height to which ground surface produced HONO will be transported, will depend on both the photolytic lifetime of HONO (inverse of J(HONO)) and the vertical mixing of the atmosphere described e.g., by the eddy-diffusion coefficient. In response to the solar zenith angle (SZA), the lifetime of HONO will decrease from morning to noon, which will solely lead to a decreasing MLH. In contrast, caused by the increasing turbulence from morning to noon (Jacob, 1999), the vertical transport of HONO increase (increasing MLH). If the vertical transport is increasing in the same way as the photolytic lifetime of HONO is decreasing, both effects will exactly compensate leading to a constant MLH as used for simplicity in the present study.

Generally, the MLH could be defined as the height where the HONO concentration – or more precisely the excess HONO concentration exceeding (height-dependent) $HONO_{PSS}$ – has decreased to 1/e from its ground surface concentration. Caused by the gradients, a formal source determined from the excess over PSS will be height dependent and stronger when measured close to the ground as done in the present study. The reason for this problem is that the sources are not correctly implemented as flux from the ground surface (molecules m^{-2} s^{-1}) in a 1D vertical model, but are mathematically treated as a gas phase source in a homogeneously mixing box model, which we used here for simplicity. Thus, the box height has to be even lower than the above-defined MLH and will

be better described by the height where the HONO mixing ratio is decreasing to lower values than the measured near the ground surface. A better definition of the height used would be the homogeneous mixing height of the 0D box, for which we used the term MLH for simplicity.

Then we did several steps to scale the MLH used in this study.

A minimum MLH of 35 m was derived based on the assumption that all the $P_{unknown}$ could be wholly explained by photosensitized heterogeneous NO_2 reaction on the ground surface in our recent study (Xue et al., 2021).

To scale the maximum of the MLH of HONO, theoretically, the vertical turbulence process within the lifetime of HONO should be considered. For instance, Zhang et al. (2009) estimated the maximum vertical transport distance by turbulent diffusion (Jacob, 1999). A maximum of 350 m at noontime that HONO could reach was obtained. Therefore, MLH for HONO should be much lower than 350 m, which is in agreement with vertical measurements.

Brown et al. (2013) and Vandenboer et al. (2013) are under the same project of Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT-11) and the latter one was focused on HONO formation. Vandenboer et al. (2013) conducted similar model simulations with a model height of 150 m. They found significant underestimation in HONO levels, which was attributed to the higher model height compared to the measurement height of 20 m. Hence, to model measurements near the ground surface, a lower MLH than 150 m is needed.

Vertical measurements could furtherly scale the MLH. A declining HONO trend with altitude was frequently observed in previous vertical measurements (Kleffmann et al., 2003; Meng et al., 2020; Vandenboer et al., 2013; Vogel et al., 2003; Xing et al., 2021; Ye et al., 2018; Zhang et al., 2009). We would like to take the measurements in Germany (Vogel et al., 2003), the USA (Vandenboer et al., 2013) and China (Xing et al., 2021) as examples to scale the MLH. From the ground level (4-10 m) to 100 m above the ground surface, Vogel et al. (2003), Vandenboer et al. (2013), and Xing et al. (2021) observed declining HONO levels from ~0.6 to 0.3 (a representative case from Figure 4), from 0.6 to 0.3 (case from Figure 8), and from 4.8 to 1.6 ppbv (case from Figure 5), respectively. All of those cases suggest that near-ground surface measurements were more weighted by ground-derived sources. Moreover, this phenomenon was observed during their whole campaigns including daytime and nighttime, suggesting a similar level of MLH. Hence, the maximum of MLH could be furtherly scaled to 100 m for near-ground surface measurements.

In summary, 0-D modeling with the utilization of ~50 m level could represent a general MLH for studying HONO measurements near the ground surface. Nevertheless, we still should highlight that accompanied efforts, e.g., performing sensitivity tests, should always be made to underline the uncertainties.

Regrading deriving MLH from vertical measurements like Xing et al. (2021), we need to conduct 1D modeling simulations with reasonable transport and a real surface flux of HONO. The model results should be compared with near-ground surface measurements or gradient measurements. However, currently, we don't have the tool of a 1D model and gradient measurements. Instead, in this study, we tried to scale the MLH using the above methods, which significantly improved the model performance.

In Section 3.2.2.4 of the main text, we added a brief discussion on how we scale MLH:

A similar phenomenon could also be found in tower-based vertical measurements in Germany and USA. For instance, from the ground level (4-10 m) to 100 m above the ground surface, Vogel et al.

(2003) and Vandenboer et al. (2013) observed similarly declining HONO levels from ~0.6 to 0.3 (representative cases from Figure 4 in Vogel et al. (2003) and Figure 8 in Vandenboer et al. (2013)), respectively. All of those cases suggest that near-ground surface measurements were more weighted by ground-derived sources. Moreover, this phenomenon was observed during their whole campaigns including daytime and nighttime, suggesting a similar level of MLH. Hence, the maximum of MLH could be furtherly scaled to 100 m for near-ground surface measurements. A minimum MLH of 35 m was derived based on the assumption that all the $P_{unknown}$ could be wholly explained by photosensitized heterogeneous NO_2 reaction on the ground surface in our recent study (Xue et al., 2021). Therefore, in the present study, the MLH for HONO was set at a constant height of 50 m, with sensitivity tests performed with the MLH set at 35 and 100 m. In general, ~50 m level could represent a general MLH for 0D models to study HONO measurements near the ground surface. Similar values (25 – 100 m) were also used in previous box model studies (Harrison et al., 1996; Lee et al., 2016; Xue et al., 2020, 2021). Nevertheless, it should be highlighted that a box model as used in the present study is not an ideal tool for studying a ground source when comparing with near-ground surface measurements in the atmosphere. For the future, gradient measurements are recommended, which should be compared with 1-D model simulations.

[Comment 2]
Fig 4 & line 269. The addition of the J-HONO photolysis frequency to the diurnal profile in Fig 4 is informative and welcome. Likewise the more explicit reference in the text to the asymmetric shape of P_unknown. I think Line 269 should now read "Note that the profile of P_unknown *is* asymmetric around *12:00 solar noon*, indicating the unknown source is not simply photolytic…" The important point here is that the diurnal profile exhibited by P_unknown is offset with respect to the peak photolysis activity of J-HONO and/or J-NO2 at solar noon (rather than any asymmetry before/after the peak in P_unknown at 11:00).
Response: Changed as the reviewer suggested.

It is good the authors have added campaign-averaged diurnal profiles of HONO, O3, NO, NO2 etc as a new figure S3 in the supporting information (also requested by referee #3). Personally I would put this new figure into the main body of the paper because its information is very important for telling the scientific story.
Response: Thanks for the suggestion. The average diurnal profiles were moved to the main body.

Continuing discussion of the sentence that began on line 269: The second half of the sentence reads "…but also includes its precursors that also have an asymmetric distribution (e.g., NO2, Figure S3)". The text need to be much more explicit here. Panel (E) in new figure S3 certainly shows that NO2 concentrations were higher in the morning than in the afternoon – so are the authors saying the faster P_unknown HONO production rate observed before midday (and peaking at 11:00) is attributed to the greater NO2 concentrations present in the morning? This would fit with the authors' finding that P_unknown has its biggest contribution from heterogeneous NO2 to HONO conversion at the ground (Figure 8).
Response: Yes, this is a good point. We added
Note that the profile of $P_{unknown}$ is asymmetric around 12:00 solar noon, indicating the unknown source is not simply photolytic but also includes its precursors. For instance, higher NO_2 levels were

observed in the morning than that in the afternoon (Figure 3E), which preliminarily implies the importance of NO_2-to-HONO conversion.

[Comment 3]

I asked the authors to expand about how the conclusions of this paper translate to other locations in China and other countries? The revisions here are disappointing and I had hoped to see more discussion. The authors have added a sentence at line 523 "Model results may have uncertainties but shed light on the atmospheric chemistry in this polluted region", which is certainly true but fails to answer the reviewer's question.

Response: Regarding implications of conclusions in this study to further studies worldwide, we added a new section as follows:

3.4 Implications for Further Studies

For the first time, we considered HONO and NO_x lifetimes to quantify the contribution of direct emission to daytime HONO formation. The method developed here remarkably reduced the overestimation of contribution from direct emission. It is universal and should be used for all ground measurements to quantify the contribution of direct emission to daytime HONO formation.

In the present study, we also conclude that heterogeneous NO_2 reaction on the ground surfaces is the major HONO source. Constraints on aerosol-derived sources, including NO_2 uptake on the aerosol surfaces and particulate nitrate photolysis, are conducted by our measurements at the summit of Mt. Tai and recent laboratory studies. Therefore, it could be expected that similar conclusions can be found in other studies when considering ground measurements. Additionally, parametrizations of HONO sources used for box model simulations are applicable for other studies. The values of some parameters, such as NO_2 uptake coefficients, MLH and particulate nitrate photolysis frequency, are obtained or derived from laboratory or field studies. Further studies may improve the understanding of the variation of those parameters, for instance, NO_2 uptake coefficients may vary with locations that have different landscapes. In particular, based on three vertical measurements in Germany, the USA, and China, similar levels of MLH (<100 m) were derived, indicating the potential application of this method to ground measurements worldwide. This could significantly reduce the underestimation of HONO formation from ground-derived sources compared to models in which the BLH was used. Meanwhile, sensitivity tests should be conducted and uncertainties should be discussed accordingly.

It has been recognized that HONO photolysis could initiate daytime atmospheric chemistry in the early morning and also acts as a substantial OH source during the daytime in polluted regions. The significant contribution and impact of HONO on radical levels could motivate studies by chemistry-transport models, most of which have currently not included HONO chemistry.

Furthermore, O_3 pollution is becoming a key environmental issue in China. While high levels of O_3 are present, moderate levels of NO_x are frequently accompanied. In this case, NO_3 chemistry could make a considerable contribution to atmospheric oxidization capacity, especially during the nighttime. Its follow-up impacts on atmospheric composition, such as the formation of nitrate and SOA, need further field measurements and model quantifications.

General comments:

The authors have done a lot of work on their manuscript. Overall, the revised manuscript is a great improvement because the authors have acted on the comments from 3 detailed, extensive reviews.

The authors have also thoroughly proof-read their manuscript, which has removed most of the English language problems in the original manuscript. Whilst the authors thanked the reviewers in the authors' individual responses to the 3 referees, perhaps they might also consider acknowledging the referees' efforts in the acknowledgements section of the main manuscript?

Response: Yes, we should do that. In the acknowledge section, we added the below sentence:

We appreciate the three anonymous reviewers and the editor, John Orlando, for their careful reading of our manuscript and many insightful comments, suggestions, and discussion.

Minor errors (These are errors I spotted whilst reviewing, so not an exhaustive list):

Caption to Fig 4, line 260. "The relative contribution of NO + OH and … *are* shown…in the pie charts". I also suggest moving this sentence to the end of the caption, i.e. to after the sentence about the "blue shaded area" which seems to refer to the main plot (and not the blue shading in the pie charts). Or does the blue shading in the plot and the pie charts both represent the same observed-minus-model differences? I was unsure, please clarify and re-word as necessary.

Response: The caption was improved as:

Simulated HONO by the default mechanism (Sce-1, left axis) compared with the observations (Obs, left axis), unknown source strength ($P_{unknown}$, right axis), HONO photolysis frequency (J(HONO), right axis). The shaded area in blue in the plot and the pie charts represent the difference between the observation and modeled values. The relative contributions of NO + OH to the observations at night (19:00 – 4:50) and day (5:00 – 18:50) are shown in the left and the right pie charts, respectively.

Line 267. "… were calculated *from* the measurements [plural]…".

Response: Changed as commented.

Line 317. "…upper limit derived from the summit measurements [plural] *in our companion paper*, see Xue et al. (2021b)…"

Response: Changed as commented.

Line 389. "The only major exception was a period of heavy rain from 25th to 28th June…"

Response: Changed as commented.

Line 392. "While the modified model could generally predict…, [add comma & delete "but"] it largely failed…"

Response: Corrected as commented.

Fig 10, line 470. The authors have improved the colors and now the distinctions are a lot clearer between the various OH sources in panel (A) and NO3 sources in panel (B). However the new fig 10 now uses a light scale of pastel colors. I actually preferred the style of bold colors in panels (C) and (D) of the original – it was easier to distinguish the bold colors.

Response: The figure was modified by using style of bold colors.

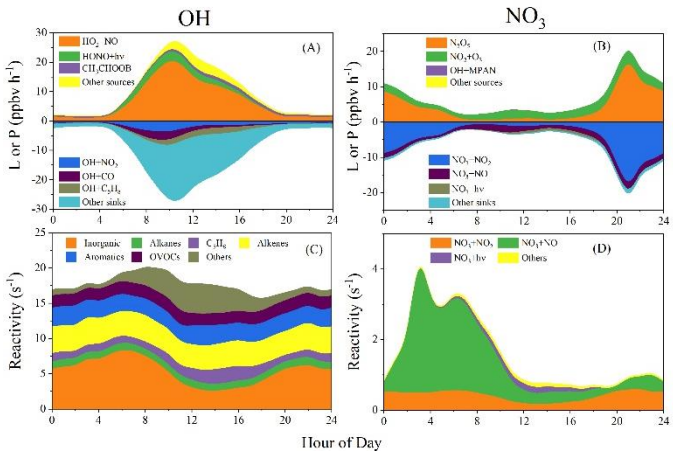

Figure 11: Production rates (P), loss rates (L) and reactivities of radicals. (A): L and P of OH; (B): L and P of NO_3; (C): Reactivities of OH and (D): Reactivities of NO_3. In (A) and (B), the top-3 sources or sinks are shown, and all the others are summarized in "Other sources" or "Other sinks". In (C), OH reactivities with different families of the measured species are shown and reactivities with all the unmeasured species are summarized in "Others". In (D), NO_3 reactivities from top-3 reactions are shown and all the others are summarized in "Others".

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