

Response to the Anonymous Referee #1 and #2's comments,

We thank the Anonymous Referees for our manuscript's thorough and constructive comments.

Referee#1's comment: Heterogeneous chemistry of HONO formation and sink in the atmosphere is one of the least quantified issues in tropospheric chemistry, which induce serious uncertainty in the global and regional CTM to predict O₃ formation, CH₄ lifetime, and so on. The present article implements the heterogeneous HONO chemistry into the chemistry-climate model CHASER to show the inclusion of HONO chemistry reduces the model bias against the measurements for PM_{2.5}, NO₃-/HNO₃, NO₂, OH, O₃ and CO in the lower troposphere.

Since the importance of heterogeneous production and loss of HONO has rarely been treated by a global CTM, it is interesting and worthwhile to evaluate the role of the chemistry of HONO in a global scale, and the present study is a challenging effort toward the direction. The most serious problem of the present article, however, is that the effects of HONO chemistry in the global atmosphere are discussed in 3.1 and 3.2 without enough validation of the processes and assumed uptake coefficients for heterogeneous formation and loss of HONO. At the present stage of understanding of heterogeneous HONO chemistry, selection of appropriate processes and uptake coefficients to reproduce the HONO concentration in the urban and remote field measurements should be the starting point for the model discussion. I am afraid that the present article does not fulfill such requirement.

Therefore, I rather reject the present version of the paper for publication, but do encourage the authors to revise the paper considering the following comments and resubmit the paper after conducting appropriate recalculation.

Author comment: We are thankful for your dedicated time and interest in our manuscript. We acknowledged the shortcoming of this manuscript version. From the perspective of a global modeller, we tried to add the HONO chemistry into our global model CHASER to better predict the chemistry of O₃, HO_x, and CH₄ lifetime, etc. This decade, HONO chemistry has received considerable interest, yet modelling studies for HONO on a global scale are still scarce. Implementation of HONO chemistry in a global model is a real challenge due to its significant uncertainties; the most relevant to this study is which one among various possible HONO formation mechanisms is dominant globally. The current manuscript version tried to give a fresh outcome on how the troposphere will respond to the basic mechanisms of HONO. Taking the chance to have the measured HONO levels within the free troposphere, we tried to reproduce the daytime HONO that was surprisingly high already for such an Asian coastal region.

We tried out your suggestion on a photochemical heterogeneous formation in an updated version this time. This new production resulted in better agreement with EMERGE's HONO measurement. Therefore, the main new results are added in Sect. 3.1.2 and related places in the revised manuscript version, highlighted in yellow. We hope this version finds you more satisfactory since we also discussed the uncertainties of each potential HONO formation mechanism and its global effects (Sect. 3.2.1 and 3.2.3).

Referee#1 comment:

Specific suggestions for improving the paper:

Many field observations and regional CTMs have revealed that the concentrations of daytime HONO in urban area is much higher than expected by models considering only dark heterogeneous formation process (e.g., Lee et al., 2016; Lu yet al., 2018; quoted in the present paper). Since photochemical heterogeneous formation is now widely accepted to be important as a source of HONO, it should be taken into account as one of the important processes in the global model as well. The present paper discusses such photochemical process only later in 3.1.5.

Further, it has been generally accepted that every surface including soil dust and PM₅, and the Earth's ground would be effective for the formation of HONO. These processes should be taken into account in the global model as well.

Author comment:

We agree that photochemical heterogeneous formation is an important source of HONO that should be coupled into modelling works of HONO. We also acknowledged that surface-related sources from Earth's ground, soils, and atmospheric particles might also be significant sources of HONO for dense and polluted regions. In this manuscript version, we added our new results of implementing such a photochemical heterogeneous HONO formation, which is the surface-catalyzed photolysis of HNO₃ ($\text{HNO}_3 + h\nu \rightarrow \text{HONO}$) (R7), following the work by Lee et al. (2016). Our model accessed this photolysis at a rate 100 times faster than the gas-phase HNO₃ photolysis ($\text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2$). To access the assumption of this photolysis for aerosol nitrate and other aqueous surfaces and adsorbed HNO₃ on ground surfaces, we conducted three sole simulations for (R7). The first run (namely JANO3-A) is for ground surfaces only, applying (R7) for the first vertical layer. The second and third runs (JANO3-B and JANO3-C) are for surfaces of grounds and all-kind aerosols, addressing (R7) for the model grid cells of particular surface area density ranges. Fortunately, the JANO3-B and JANO3-C cases successfully produce HONO at daytime for the height 0 ~ 2000 m during EMERGe flights, although their effects in increasing NO₂ and O₃ worsened the model bias for these species. We tried to amend this problem by the combined cases of JANO3-B and JANO3-C with another promising case (maxST), in which the uptake coefficient of aerosol-uptakes of NO₂ was raised to 0.1, resulting in more HONO during EMERGe, but the reductions for NO₂ and O₃ were enhanced. The combined cases succeed in closing the gaps for HONO, NO₂, and O₃ levels with EMERGe's measurement. The additional discussions of these extra simulations regarding the model's NO_x-recycle issue, global HONO distribution and burden, and the effects to global oxidizing capacity were also added in the new version, highlighted in yellow.

Referee#1 comment:

As for the quantitative choice of uptake coefficients of heterogeneous processes, it is suggestive to parameterize them to reproduce the observational HONO concentration in the field. The sensitivity of uptake coefficient of the heterogeneous formation processes would be high in the boundary layer in polluted areas, validation in urban areas should be performed at first by the global model comparing with the results of regional models. Then, validation for vertical profiles by aircraft measurements of EMERGe and Atom1 should be made before the discussion of the effect of HONO chemistry in the lower troposphere in general.

Author comment:

We made rearrangements for the manuscript order as per your suggestion. Please find the new construction in our updated version in section 3.2 in the evaluation and verification order as for EMERGe → Atom → Mirai → EANET/EMEP. In addition, the comparison for TCO with OMI was moved to before the discussion on global impacts, as TCO changes could be seen as a global effect on ozone.

Referee#1 comment:

Although the present paper refers limited laboratory studies on the heterogeneous dark reactions of HONO formation and loss on specific aerosol such as soot, the uncertainties are more than an order of magnitude, and it is not appropriate to select particular values for the "standard" run as in Table 2. Considering the large uncertainty of the uptake coefficients at this stage, the empirical approach mentioned above is suggested to be followed in the future paper.

over

Author comment:

We are sorry for the large uncertainties in the particular values of uptake coefficients used in the "standard" run. It is the first try to perform HONO chemistry in our model. We simplified the related configurations at the least computational cost, using the averaged uptake coefficients and the most basic pathways of gaseous, heterogeneous reactions of HONO and direct emission. This manuscript tells the first results of this approach to HONO chemistry, although we tried various sensitivity simulations for amplifying the existing mechanisms. Adding the new mechanisms such as photochemical heterogeneous processes is complex; thus, we did not conduct any before this response. In the revised manuscript version, we sincerely thank you for checking again our new results, which resulted from adding the heterogeneous photolysis of HNO₃, one of your valuable suggestions.

We hope this version can share the current knowledge of global HONO chemistry.

Response to Anonymous Referee #2's comment,

Referee#2's comment: A review report for manuscript entitled "Implementation of HONO into the chemistry-climate model CHASER (V4.0): roles in tropospheric chemistry" by Phuc et al., 2021.

The study investigates the impacts of including HONO three formation paths (gas phase, heterogeneous, and emissions sources) on the levels of PM_{2.5}, SO₄²⁻, HNO₃, CO, O₃, in the model compared to measurements from different platforms. However, the study does not account for major HONO sources via night and daytime heterogeneous NO₂ conversion on-ground sources, and nitrate photolysis. In addition, the study presents the results of comparison but without a sufficient or reasonable explanation of these differences. This is a major issue, and the authors should carefully review the article and provide adequate clarifications accounting for HONO impact on each species beyond increase or decrease in species concentrations.

Author's comment: We sincerely thank the referee for your time and devotion to pointing out our manuscript's shortcomings. To improve the manuscript, we will specifically clarify each point.

Referee#2's comment: Specifics

Abstract: remove "for the first time" since HONO has been parameterized in several previous studies (e.g., Elshorbany et al., 2012; Zhang et al., 2021).

Author's comment: We removed the ambiguous phrase in the revised manuscript as suggested (**line 12**).

Referee#2's comment: Page 1, line 24: the 51% contribution of heterogeneous NO₂ to HONO formation on aerosol, and emissions sources are very high compared to current literature (e.g., Zhang et al., 2021).

Author's comment: Zhang et al. (2021) implemented in the CMAQv5.3 3D-model six homogeneous reactions and five distinct heterogeneous reactions for day and nighttime. They included HONO emissions from vehicles and not from soil. Their simulations resulted in dominant contribution of heterogeneous production from NO₂ adsorbed on the ground (~75 %) of the total HONO production for the haze days in Beijing (China). However, they also found that the second dominant contributor to HONO production is heterogeneous production from NO₂ adsorbed on aerosol surfaces. Our study did not include NO₂ conversion on ground surfaces, while HONO emission from vehicles, combustion, and soils are all considered. That is why the contributing portions of NO₂'s aerosol-uptakes and HONO emission are higher in our study than in Zhang's calculation.

Referee#2's comment: Page 1, line 30: Why does reducing NO_x (NO₂+NO) reduce the atmospheric oxidation capacity? For instance, reducing NO₂ would increase OH in high NO_x conditions. Please clarify.

Author's comment: for high NO_x conditions (e.g. China), reducing NO₂ increases regional OH and O₃ levels (Fig. 12, first and third rows). However, for the larger part of the globe (non-polluted regions, higher altitudes), the NO_x-deficit environments caused by NO₂ uptakes on clouds/aerosols (mainly on clouds) restricts O₃ formation and OH radical formation (via O₃ photolysis or via HO₂+NO→NO₂+OH reaction) at these environments (explanation is given in **lines 742-745** in the new version). Therefore, we added an explanation at **line 32** as well.

Referee#2's comment: Page 6, line 169: I don't see the value of the OLD simulations which assumed no HONO chemistry since all models have at least gas-phase HONO chemistry (OH+NO=HONO;HONO=OH+NO; and HONO+OH).

Author's comment: we added a description for the OLD case, highlighted in **lines 141-143** and **207-209**. In the OLD case, the model excludes HONO species and HONO chemistry, and there are no gas-phase HONO reactions in the OLD case (Table 1). Results for the OLD are also exhibited in sub-sections in 3.1 (Figures 2 to 8).

Referee#2's comment: Page 6, table 2: How is the heterogeneous loss of HONO (R6) leads to NO?

Author's comment: The loss process of HONO occurs on surfaces of ice, liquid and aqueous sulfate aerosols via the reaction $\text{HONO} + \text{H}_2\text{O} \rightarrow \text{NO} + \text{H}_3\text{O}^+$, since HONO uptake by liquid water probably involves hydrolysis (Revised manuscript, **line 80-81**). Our model simplified this hydrolysis as $\text{HONO} \rightarrow \text{NO}$ (R6). NO will be converted to NO₂ in a few hours in the atmosphere. We have checked this reaction with (R6) being $\text{HONO} \rightarrow \text{NO}_2$ and there is no big difference in the results.

Referee#2's comment: Page 7, line 175: I suggest you differentiate NO from NO₂ in model calculations throughout the paper.

Author's comment: Line 214. This line is about the equation Eq.(1) to determine the effects of each mechanism on atmospheric species (OH, O₃, NO_x, CO). We agree that, for HONO chemistry, NO₂ is an important precursor of HONO that should be separately investigated from NO. Compared with ATom and EMERG data, NO₂ measurement is available, so simulated NO₂ data is used in these parts. However, only NO_x data is available for other comparisons (EANET, EMEP). Therefore, we use simulated NO_x data to compare measurements at EANET and EMEP stations. Also, NO_x is used to calculate global effects, as NO_x can better represent an important tropospheric species than NO₂ solely.

Referee#2's comment: Page 9, line 230: Please report the calculated surface aerosol density for each aerosol type.

Author's comment: Line 275-284. We added the calculated SAD values for each aerosol type per your suggestion.

Referee#2's comment: Page 10, lines 238-247: Please elaborate on "O₃-reducing effects of HONO chemistry". The authors should explain how HONO would reduce O₃ when its photolysis is a source of OH, supposedly increasing the oxidation capacity?

Author's comment: Although HONO photolysis (R1) is a source of OH, the calculation in STD case shows the OH and O₃ increases only occur at the surface of polluted sites. For remote regions, the NO₂ conversion to HONO and HNO₃ (R4) becomes a removal pathway for NO_x, thus restricting the formation of O₃ and OH for the larger part of the troposphere via lacking oxygen atom from NO₂ photolysis. We added elaboration on "O₃-reducing effects of HONO chemistry" from **line 679-681**~ (revised manuscript)

Referee#2's comment: Page 11, line 262-264: The authors are advised to explain the causal factors leading to increase or decrease in the impacted species (PM2.5, SO4²⁻, HNO₃, O₃..etc) rather than stating the numbers.

Author's comment: Line 549-556. We added the explanation for increase or decrease in HNO₃, NO₃, PM2.5, SO4²⁻, and referred to the statistical values in Table 7 along with the explanation.

Referee#2's comment: Page 11, line 285: Again, an explanation of causal factors is missing.

Author's comment: Line 569. We added the explanation highlighted in yellow.

Referee#2's comment: Page 14, line 344: Again, the authors should explain how the inclusion of gas-phase HONO sources led to increased CO in some regions but decreased CO in other regions...

Author's comment: Lines 491-497. We added the explanation and Figure S14 (supplement) to support the understanding of O₃-CO chemistry during *Mirai* observation.

Referee#2's comment: Page 17, line 382 and Figure 7: Figure 7 does not show the vertical profiles of simulated HONO. I also don't think that HONO will have any impacts at 200 hPa??

Author's comment: Line 417. We don't have the available HONO measurement from ATom, so Figure 5 (Figure 7 in the revised version) does not show the simulated vertical HONO level, instead of showing only model biases and changes in NO₂, O₃, OH, HO₂, CO, induced by HONO chemistry. We changed the text to clarify this. Note that in the revised manuscript, we added comparison for ATom's HO₂ concentration to strengthen the model bias reduction against ATom flight regarding HO_x radicals. Also, we agree that HONO chemistry's impacts mainly stay in the lower and middle troposphere (Figure 12 (i-p)).

Referee#2's comment: Page 21, lines 445: HONO values at these heights are extremely high. HONO values of 70 ppt at 2000m are almost impossible given its ground-based sources and its fast photolysis. Authors should show some evidence that these numbers are reasonable.

Author's comment: Lines 334-338. These values (mean 70 ppt HONO at 2000m) is from the EMERGe measurement (Andrés Hernández et al., 2021). Our simulation in the STD case also can not reproduce this high level of HONO. Yes, we agree that the measured HONO level measured in EMERGe for height 2,000 m ± 500 m (10-115 ppt) is surprisingly high. Wang et al. (2019) reported vertical HONO profile measured by a MAX-DOAS instrument at a station in the North China Plain and presented only < 100 ppt of measured HONO in May 2016 and averaged of < 30 ppt HONO during April to June 2016 at this height. We added a statement and reference for this issue in the revised manuscript.

References used by author's comments:

- Andrés Hernández, M. D., Hilboll, A., Ziereis, H., Förster, E., Krüger, O. O., Kaiser, K., Schneider, J., Barnaba, F., Vrekoussis, M., Schmidt, J., Huntrieser, H., Blechschmidt, A.-M., George, M., Nenakhov, V., Klausner, T., Holanda, B. A., Wolf, J., Eirenschmalz, L., Krebsbach, M., Pöhlker, M. L., Hedegaard, A. B., Mei, L., Pfeilsticker, K., Liu, Y., Koppmann, R., Schlager, H., Bohn, B., Schumann, U., Richter, A., Schreiner, B., Sauer, D., Baumann, R., Mertens, M., Jöckel, P., Kilian, M., Stratmann, G., Pöhlker, C., Campanelli, M., Pandolfi, M., Sicard, M., Gomez-Amo, J. L., Pujadas, M., Bigge, K., Kluge, F., Schwarz, A., Daskalakis, N., Walter, D., Zahn, A., Pöschl, U., Bönisch, H., Borrmann, S., Platt, U., and Burrows, J. P.: Overview: On the transport and transformation of pollutants in the outflow of major population centres – observational data from the EMERGe European intensive operational period in summer 2017, *Atmos. Chem. Phys. Discuss.* [preprint], doi: 10.5194/acp-2021-500, in review, 2021.
- Lee, J. D., Whalley, L. K., Heard, D. E., Stone, D., Dunmore, R. E., Hamilton, J. F., Young, D. E., Allan, J. D., Laufs, S., Kleffmann, J.: Detailed budget analysis of HONO in central London reveals a missing daytime source. *Atmos. Chem. Phys.*, 16, 2747–2764. doi: 10.5194/acp-16-2747-2016, 2016.

Sincerely,

On behalf of all co-authors,

Phuc T. M. Ha.