

Response to Reviewer #3

Dear Editor and Reviewer:

We greatly appreciate your consideration and the reviewer's insightful and constructive comments on the manuscript "**HONO Formation Mechanisms and Impacts on Ambient Oxidants in Coastal Regions of Fujian, China**" (egusphere-2025-2630). We have carefully revised the manuscript to address all the comments described below. Reviewer comments are shown in black. Our responses are shown in blue. The revised texts are shown in red.

Zhang et al. present a comprehensive analysis of the production and loss mechanisms of HONO, incorporating the updated mechanism into the WRF-Chem model over the coastal region of Fujian, southeastern China. Their measurements, supported by modeling, quantify unusually elevated daytime HONO levels. Through a series of sensitivity simulations, the study further examines the impact of shipping emissions on HONO, as well as the contributions of HONO to OH radical production and O₃ formation. Overall, the manuscript is well written and recommended for publication in ACP. Some specific comments are:

Response: We thank you for the comments. Based on your helpful and insightful comments, we have revised our manuscript, and the point-by-point responses to the specific comments were given subsequently. We sincerely hope these revisions could address your concerns.

1. Lines 16-18: Briefly mention why HONO concentration is lowest around noon.

Response: Thank you. We have rephased this sentence as you suggested.

Revisions in Abstract:

Previous studies have mainly focused on investigating the chemical fate of HONO in polluted urban areas of China and found a general diurnal variation featuring the minimum concentration around noon due to the fast self-photodissociation.

2. In Introduction discuss HONO patterns outside China and cite studies reporting any unusual trends elsewhere as well.

Response: Thank you for this insightful suggestion. We acknowledge that the current introduction mainly focuses on studies within China. To provide a broader international context, we have revised the introduction to include a discussion on diurnal pattern of HONO concentrations from other regions worldwide.

Revisions in Section 1:

Observational studies conducted in polluted urban areas of China indicated that lower concentrations of HONO typically occurred around noon (Fu et al., 2019; Song et al., 2023; Wang et al., 2025; Zhang et al., 2021). The similar diurnal pattern of HONO concentrations was also reported by measurements in urban areas of Italy, South Korea, Japan, and the United States (Acker et al., 2006; Kim et al., 2024; Nakashima et al., 2017; Stutz et al., 2010).

However, several in-situ observations in typical coastal regions such as Cyprus and Cape Verde revealed an inverse diurnal variation of HONO with higher concentrations occurring at noon (Crilley et al., 2021; Jiang et al., 2023; Meusel et al., 2016). In China, Zhong et al. (2023) reported that their measurement campaign in Qingdao, a coastal city adjacent to the Yellow Sea, identified an unexpected diurnal peak in HONO concentrations at 12:00 local time (UTC+8).

3. Lines 37-39: It will be informative to include reaction rates/photolysis coefficients with references for all reactions discussed in the manuscript.

Response: Thanks for your constructive comment. The gaseous and photolysis reactions listed in the manuscript are fundamental atmospheric reactions that are part of the standard SAPRC99 mechanism used in our simulations. To maintain the draft's focus and brevity, we did not list these standard rate constants individually. The rate constants of HONO from multi-phase reactions are shown in Table 2. In the revised manuscript, we have explicitly stated that these rates are standard within the SAPRC99 mechanism and provide a clear reference to the original work for readers seeking detailed information.

Revisions in Section 1:

Concurrently, RO_2 can react with NO to produce NO_2 (R11), a reaction that reduces ozone (O_3) titration (R12) while providing NO_2 for the subsequent formation of O_3 through reactions R13 and R14. The associated reactive rate constants of these listed gaseous and photolysis reactions are well documented in Carter et al. (2000).

4. Line 39: In reaction R3, replace ν by Greek letter ν , if possible.

Response: Thanks for your careful reminder. We have corrected all photolysis symbols " $h\nu$ " to " $h\nu$ " throughout the revised manuscript.

5. Line 44: Probably authors meant Additionally and not Adaptationally?

Response: Thanks for your careful reminder. Yes, it is a typo and has been corrected as follows.

Revisions in Section 1:

Additionally, OH radicals can degrade volatile organic compounds (VOCs), ...

6. Lines 59-60: Mention the major reactions contributing to lower HONO concentrations in the noon time in polluted urban environments, as discussed in the previous studies.

Response: Thank you for this comment. We have rephased the related texts as you suggested in the revised manuscript.

Revisions in Section 1:

Observational studies conducted in polluted urban areas of China indicated that lower concentrations of HONO typically occurred around noon (Fu et al., 2019; Song et al., 2023; Wang et al., 2025; Zhang et al., 2021). The similar diurnal pattern of HONO concentrations was also reported by measurements in urban areas of Italy, South Korea, Japan, and the United States (Acker et al., 2006; Kim et al., 2024; Nakashima et al., 2017; Stutz et al., 2010). These lower HONO concentrations could be attributed to the fast photo-dissociation at noon.

7. Lines 60-61: Please add the reference for the study reporting inverse HONO diurnal variation; if it is Zhong et al. (2023), cite it here as well.

Response: Thank you for your careful reminder. We have added the necessary citations regarding the inverse diurnal pattern of coastal HONO concentrations as you suggested.

Revisions in Section 1:

However, several in-situ observations in typical coastal regions such as Cyprus and Cape Verde revealed an inverse diurnal variation of HONO with higher concentrations occurring at noon (Crilley et al., 2021; Jiang et al., 2023; Meusel et al., 2016). In China, Zhong et al. (2023) reported that their measurement campaign in Qingdao, a coastal city adjacent to the Yellow Sea, identified an unexpected diurnal peak in HONO concentrations at 12:00 local time (UTC+8).

8. Lines 61-65: Discuss Zhong et al.'s suggested reasons for the unexpected HONO diurnal peak.

Response: Thank you for this comment. We have rephrased the relevant texts in the revised manuscript as you suggested.

Revisions in Section 1:

In China, Zhong et al. (2023) reported that their measurement campaign in Qingdao, a coastal city adjacent to the Yellow Sea, identified an unexpected diurnal peak in HONO concentrations at 12:00 local time (UTC+8). Using the observation-based model (OBM), their study suggested that the higher HONO concentrations at noon was likely attributed to an unidentified marine source.

9. Lines 64-65: It would be worth discussing in conclusions - the key differences in HONO formation and loss mechanisms between coastal and urban polluted regions.

Response: Thank you for this constructive suggestion. In Section 3.3.1, we have made some comparisons in chemical fate of HONO between coastal areas and inland regions. We agree with you that systematically summarize and contrast the key HONO formation and loss mechanisms between our coastal study and those typically found in polluted inland urban regions in the conclusion section will strengthen the paper. We have revised the related texts as follows.

Revisions in Section 4:

Our study highlights that while the primary daytime loss mechanism for HONO is self-photodissociation in both coastal and highly polluted inland urban areas, their formation mechanisms exhibit significant discrepancies. Previous studies in inland areas often identify the heterogeneous uptake of NO₂ on ground surfaces as the dominant source with the maximum contribution up to 86% (Zhang et al., 2024). Our findings in coastal Fujian reveal that the heterogeneous uptake on the ground surface and photo-oxidation of NO_x were found to be equally crucial contributors. Furthermore, the contribution from heterogeneous uptake of NO₂ on aerosol surfaces, which can be significant in a typical urban environment, was found to be negligible (1-2%) in coastal areas due to much lower aerosol concentrations.

10. Lines 68-69: Please mention the typical number / quantitative of HONO emissions from shipping activities.

Response: Thanks for your careful reminder. We have added the reported ratio of HONO to NO_x emissions measured by Sun et al. (2020) in the revised manuscript as follows.

Revisions in Section 1:

Furthermore, HONO emissions have been acknowledged as a result of shipping activities (Ke et al., 2025; Sun et al., 2020). Sun et al. (2020) estimated that the ratio of HONO to NO_x emissions was 0.51% based on specific measurements for ship plumes.

11. Lines 85-86: Do the authors consider this unusual daytime high HONO pattern in coastal regions to be seasonal, or the results valid across all seasons? Additionally, please discuss the applicability of these findings to other coastal regions worldwide in the conclusions.

Response: Thank you for this comment. This is a very valuable point. Our study was conducted in May 2024, a period with strong solar radiation in the late spring. We speculate that this photochemically-driven daytime peak pattern would be similarly prominent in summer but may be less pronounced in winter due to weaker solar radiation. More observational evidence should be collected for further investigation in the future. On the other hand, we agree that our findings could be applicable to other mid-latitude coastal regions with similar NO_x sources and meteorological conditions. We have added a discussion to the conclusion section on the potential seasonality of our findings and their broader applicability to other coastal regions worldwide.

Revisions in Section 4:

This study identifies photochemical-driven processes as the dominant driver of the midday HONO peak in May, a late spring period characterized by abundant solar radiation. Given a more intense solar radiation in summer, it is possible that the daytime HONO formation would be even more pronounced. Whereas in winter, the contribution from these photochemical pathways would likely diminish, potentially leading to a less distinct diurnal pattern where other sources, such as direct emissions, could become relatively more important. Furthermore, the mechanisms discussed in this study might be applicable to other mid-latitude coastal regions worldwide that have similar conditions including NO_x precursor sources from shipping emissions and abundant solar radiation. Coastal areas such as the Mediterranean region, the coast of California, and monsoon zones in East Asia may therefore experience similar HONO diurnal variations. To shed more light on coastal HONO chemistry, future long-term, multi-seasonal measurement campaigns in a wider variety of coastal environments are still in need.

12. Lines 102-103: It would be helpful if the authors could further elaborate the statement that the simulation was conducted in a seven-day loop to avoid systemic biases.

Response: Thank you for pointing this out. The seven-day loop cycle we used is refer to manually restarting the WRF-Chem model every seven days. The objective this process is to reduce the long time accumulation of biases of numerical computation. To clarify this point, we have revised the associated texts as follows.

Revisions in Section 2.2:

The entire WRF-Chem simulation was manually restarted every seven days to reduce the influence of the accumulation of biases from the numerical computation.

13. Lines 135-137: Are the daytime gamma values assumed or based on reported studies? Please provide relevant citations.

Response: Thank you for your careful reminder. The maximum uptake coefficient γ was chosen based on previous modeling studies. We have revised the related texts to attach the source reference.

Revisions in Section 2.3:

The base nighttime uptake coefficients of NO_2 were set to 8×10^{-6} for the ground surface and 4×10^{-6} for aerosol surfaces. During the daytime, these values were dynamically increased with solar radiation using a linear equation, reaching their maximums of 6×10^{-5} and 1×10^{-3} , respectively (Liu et al., 2019).

14. Lines 174-176: It would be nice to mention the modelled HONO concentrations as well for Beijing to assess how well they match observations.

Response: Thanks for your insightful comment. We would like to clarify this point. The mention of Beijing on lines 174-176 in the original manuscript was intended to provide context by comparing the observed HONO levels at coastal site in Fujian with observed levels from a heavily polluted region in China. However, the modeling domain for this study was focused on southeastern China and did not include Beijing. Therefore, we do not have any simulated HONO concentrations for Beijing from this study to compare with previous observations. We would like to express our gratitude to your constructive suggestion again.

15. Line 185-186: Are the definitions of non-rainy and rainy days based on a specific metric?

Response: Thank you for pointing out the need for a precise definition. In our analysis, rainy periods (shaded areas in Fig. 2) were defined as any hour during which the regional meteorological station in Putian recorded non-zero precipitation. We have added this specific metric to the manuscript for clarity as you suggested.

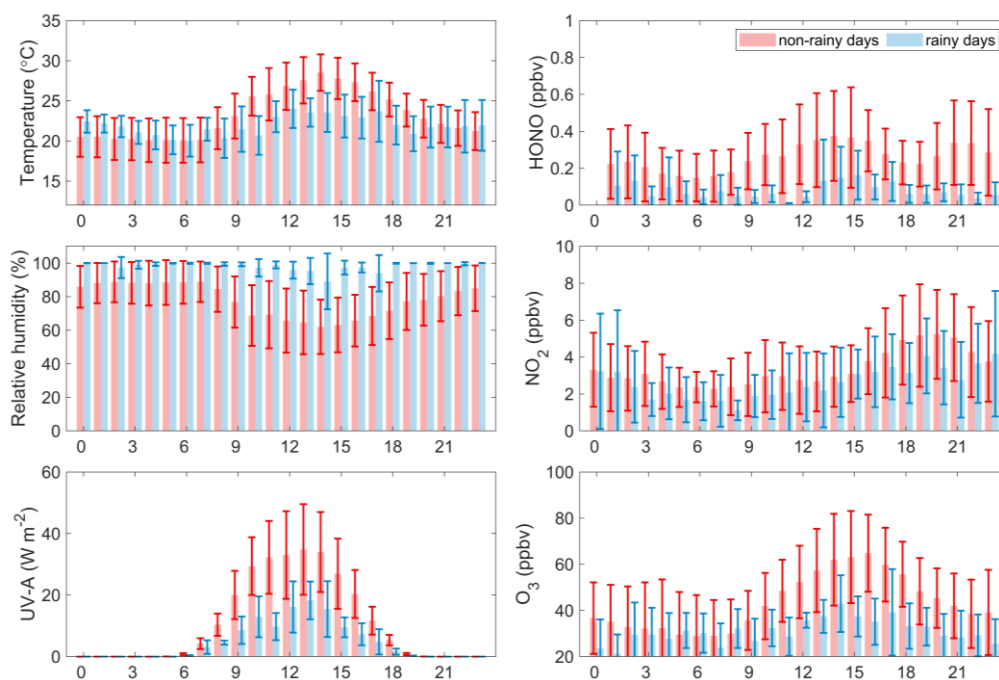
Revisions in Section 3.1:

Figure S2 exhibits the diurnal variations of gaseous air pollutants and meteorological parameters. Based on observations of the regional meteorological station in Putian, we categorized any hour with non-zero recorded precipitation into rainy days.

16. Lines 190-191: It would be informative to include standard deviations in Fig. S2, particularly for the HONO, NO₂, and O₃ plots.

Response: Thanks for this valuable comment. We have adjusted Figure S2 as you suggested to include plots of standard deviations for meteorological parameters and air pollutants.

Revisions in Figure S2:



17. Lines 193-194: Discuss the possible reasons for high O₃ at 4 pm despite low meteorological parameters?

Response: Thank you for pointing this out. The lag between the peak in solar radiation around 14:00 and the peak in O₃ concentration at 16:00 could be attributed to the favorable atmospheric oxidizing capacity resulting from the

simultaneous high HONO levels. O_3 is a secondary pollutant whose formation from the photochemical oxidation of VOCs and NO_x is a cumulative process that takes several hours. The chemical production rate of O_3 remains high even as solar radiation begins to decline, leading to the O_3 peak occurring later in the afternoon. We have added this discussion to the revised manuscript.

Revisions in Section 3.1:

Despite the decrease in air temperature and radiation after 14:00, the O_3 concentration increased until it reached a daily maximum of 64.8 ppbv at 16:00. The lag of O_3 peak concentration could be attributed to the strengthened AOC conditions resulting from the simultaneous high HONO levels. The chemical production of O_3 is a cumulative process that takes several hours so that O_3 levels could remain high even as solar radiation begins to decline, leading to the O_3 peak occurring later in the afternoon.

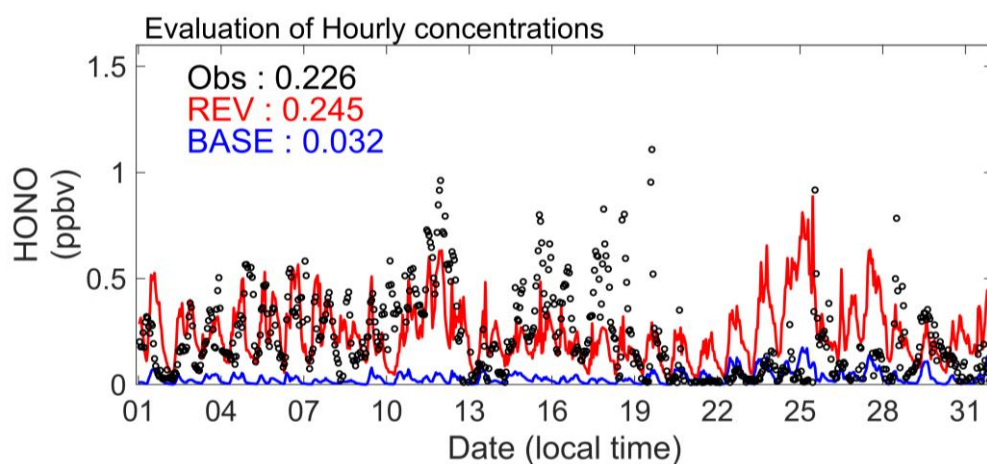
18. Lines 215-216: Please mention correct figure number.

Response: Thanks for your kind reminder. The typo has been corrected.

19. Figure 3: To avoid confusion, it would be better to label the legends as REV and BASE, respectively, instead of ‘Mean model’ for both.

Response: Thanks for your careful comment. We have adjusted the legends of Figure 3a as you suggested for clarity as follows.

Revisions in Figure 3a:



20. Line 224: In Figure 4, NO_2 values for BASE and REV appear very similar and closer to each other than to the observations. Does this mean the updates have little

effect on NO₂ concentrations? Notably, the 24-hour mean NO₂ for BASE seems slightly closer to observations than REV. Please clarify.

Response: Thanks for your conducive comments and rigorous attitude to scientific research. You are correct that, as shown in Figure 4, the updates to the HONO chemistry in the REV simulation resulted in little net change to the simulated NO₂ concentrations compared to the BASE case. The 24-hour mean NO₂ in the REV case is even slightly further from the observations. This phenomenon occurs because the updated HONO chemistry can enhance the atmospheric oxidizing capacity, which has a more direct and significant impact on the formation of secondary pollutants like O₃. In contrast, the net effect on NO₂ is more complicated and multifaceted, resulting from several competing chemical pathways: while the new HONO sources act as a sink for NO₂, the concurrently enhanced OH radical concentrations can also promote the conversion of NO to NO₂, and the changes in O₃ concentration also influence NO₂ levels via the titration effect. These competing processes result in only a small net change in the overall NO₂ concentration. Thus, the slight increase in the model bias for NO₂ in REV is a reasonable trade-off for the substantial improvements achieved in the simulations of HONO and O₃, which were the major objectives of our model updates. To make this point clearer, we have incorporated an additional in the revised manuscript as follows.

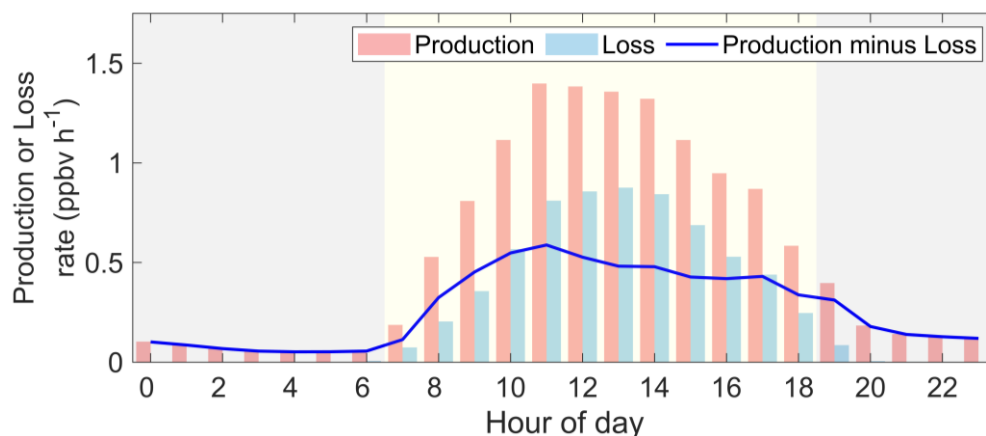
Revisions in Section 3.2:

The updated HONO chemistry had a limited net impact on NO₂ concentrations due to several competing chemical pathways. Specifically, the consumption of NO₂ by the newly added HONO formation reactions was largely offset by enhanced NO-to-NO₂ conversion from increased OH radicals and altered O₃ titration, resulting in only a minor change in the overall NO₂ budget.

21. Lines 240-242: It would be helpful to include a supplementary plot of the net production rate (Production – Loss) to show when production dominates.

Response: Thanks for this insightful comment. We have added the curve of net HONO production rate (using production rate minus loss rate) in Figure S4 to clearly show the temporal variation of net HONO chemical production as you suggested.

Revisions in Figure S4:



22. Line 347: Along with OH production rates, it would be informative to show OH loss rates too, since NO_y, HO_y, CO, CH₄, and VOCs significantly consume OH.

Response: Thank you for this constructive suggestion. We agree that incorporating the various chemical sink pathways for OH radicals would make our analysis more informative. The source-oriented method (SOM) employed in this study is designed for source apportionment by diagnosing the rate changes from different reactive pathways. While the WRF-Chem model already uses a lumped approach to reduce the number of VOC variables, applying the SOM to also diagnose the vast number of OH sink reactions, particularly with the numerous VOC species, would introduce a substantial additional computational and storage burden. Considering that the primary objective of Section 3.4.1 was to quantify the contribution of HONO to primary sources of OH radicals, the utility of rerunning our computationally intensive simulations to calculate OH sinks may be limited in the context of this specific goal. Nevertheless, we believe your suggestion is highly valuable as it motivates us to further investigate the broader importance of the enhanced atmospheric oxidative capacity driven by HONO. For future studies, we will develop targeted modifications to our SOM approach to improve the efficiency of calculating OH sinks, and we intend to incorporate this investigation into our future work. Thank you again for this valuable suggestion.

References

- Acker, K., Febo, A., Trick, S., Perrino, C., Bruno, P., Wiesen, P., Möller, D., Wieprecht, W., Auel, R., Giusto, M., Geyer, A., Platt, U., and Allegrini, I.: Nitrous acid in the urban area of Rome, *Atmos. Environ.*, 40, 3123–3133, <https://doi.org/10.1016/j.atmosenv.2006.01.028>, 2006.
- Carter, W. P. L.: “Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment,” Report to the California Air resources Board, Contracts

- 92-329 and 95-308, 2000.
- Crilley, L. R., Kramer, L. J., Pope, F. D., Reed, C., Lee, J. D., Carpenter, L. J., Hollis, L. D. J., Ball, S. M., and Bloss, W. J.: Is the ocean surface a source of nitrous acid (HONO) in the marine boundary layer?, *Atmospheric Chem. Phys.*, 21, 18213–18225, <https://doi.org/10.5194/acp-21-18213-2021>, 2021.
- Fu, X., Wang, T., Zhang, L., Li, Q., Wang, Z., Xia, M., Yun, H., Wang, W., Yu, C., Yue, D., Zhou, Y., Zheng, J., and Han, R.: The significant contribution of HONO to secondary pollutants during a severe winter pollution event in southern China, *Atmospheric Chem. Phys.*, 19, 1–14, <https://doi.org/10.5194/acp-19-1-2019>, 2019.
- Jiang, Y., Hoffmann, E. H., Tilgner, A., Aiyuk, M. B. E., Andersen, S. T., Wen, L., van Pinxteren, M., Shen, H., Xue, L., Wang, W., and Herrmann, H.: Insights Into NO_x and HONO Chemistry in the Tropical Marine Boundary Layer at Cape Verde During the MarParCloud Campaign, *J. Geophys. Res. Atmospheres*, 128, e2023JD038865, <https://doi.org/10.1029/2023JD038865>, 2023.
- Ke, J., Yang, X., Lu, K., Fu, M., Wang, Y., Yin, H., and Ding, Y.: Overlooked Underestimation of Mobile Sources Posing a Pronounced Imbalance in the HONO Budget, *Environ. Sci. Technol.*, 59, 5875–5877, <https://doi.org/10.1021/acs.est.5c02684>, 2025.
- Kim, K., Han, K. M., Song, C. H., Lee, H., Beardsley, R., Yu, J., Yarwood, G., Koo, B., Madalipay, J., Woo, J.-H., and Cho, S.: An investigation into atmospheric nitrous acid (HONO) processes in South Korea, *Atmospheric Chem. Phys.*, 24, 12575–12593, <https://doi.org/10.5194/acp-24-12575-2024>, 2024.
- Liu, Y., Lu, K., Li, X., Dong, H., Tan, Z., Wang, H., Zou, Q., Wu, Y., Zeng, L., Hu, M., Min, K.-E., Kecorius, S., Wiedensohler, A., and Zhang, Y.: A Comprehensive Model Test of the HONO Sources Constrained to Field Measurements at Rural North China Plain, *Environ. Sci. Technol.*, 53, 3517–3525, <https://doi.org/10.1021/acs.est.8b06367>, 2019.
- Meusel, H., Kuhn, U., Reiffs, A., Mallik, C., Harder, H., Martinez, M., Schuladen, J., Bohn, B., Parchatka, U., Crowley, J. N., Fischer, H., Tomsche, L., Novelli, A., Hoffmann, T., Janssen, R. H. H., Hartogensis, O., Pikridas, M., Vrekoussis, M., Bourtsoukidis, E., Weber, B., Lelieveld, J., Williams, J., Pöschl, U., Cheng, Y., and Su, H.: Daytime formation of nitrous acid at a coastal remote site in Cyprus indicating a common ground source of atmospheric HONO and NO, *Atmospheric Chem. Phys.*, 16, 14475–14493, <https://doi.org/10.5194/acp-16-14475-2016>, 2016.
- Nakashima, Y., Sadanaga, Y., Saito, S., Hoshi, J., and Ueno, H.: Contributions of vehicular emissions and secondary formation to nitrous acid concentrations in ambient urban air in Tokyo in the winter, *Sci. Total Environ.*, 592, 178–186, <https://doi.org/10.1016/j.scitotenv.2017.03.122>, 2017.
- Song, M., Zhao, X., Liu, P., Mu, J., He, G., Zhang, C., Tong, S., Xue, C., Zhao, X., Ge, M., and Mu, Y.: Atmospheric NO_x oxidation as major sources for nitrous acid (HONO), *Npj Clim. Atmospheric Sci.*, 6, 30, <https://doi.org/10.1038/s41612-023-00357-8>, 2023.
- Stutz, J., Oh, H.-J., Whitlow, S. I., Anderson, C., Dibb, J. E., Flynn, J. H., Rappenglück, B., and Lefer, B.: Simultaneous DOAS and mist-chamber IC measurements of

- HONO in Houston, TX, *Atmos. Environ.*, 44, 4090–4098, <https://doi.org/10.1016/j.atmosenv.2009.02.003>, 2010.
- Sun, L., Chen, T., Jiang, Y., Zhou, Y., Sheng, L., Lin, J., Li, J., Dong, C., Wang, C., Wang, X., Zhang, Q., Wang, W., and Xue, L.: Ship emission of nitrous acid (HONO) and its impacts on the marine atmospheric oxidation chemistry, *Sci. Total Environ.*, 735, 139355, <https://doi.org/10.1016/j.scitotenv.2020.139355>, 2020.
- Wang, L., Chai, J., Gaubert, B., and Huang, Y.: A review of measurements and model simulations of atmospheric nitrous acid, *Atmos. Environ.*, 347, 121094, <https://doi.org/10.1016/j.atmosenv.2025.121094>, 2025.
- Zhang, H., Ren, C., Zhou, X., Tang, K., Liu, Y., Liu, T., Wang, J., Chi, X., Li, M., Li, N., Huang, X., and Ding, A.: Improving HONO Simulations and Evaluating Its Impacts on Secondary Pollution in the Yangtze River Delta Region, China, *J. Geophys. Res. Atmospheres*, 129, e2024JD041052, <https://doi.org/10.1029/2024JD041052>, 2024.
- Zhang, S., Sarwar, G., Xing, J., Chu, B., Xue, C., Sarav, A., Ding, D., Zheng, H., Mu, Y., Duan, F., Ma, T., and He, H.: Improving the representation of HONO chemistry in CMAQ and examining its impact on haze over China, *Atmospheric Chem. Phys.*, 21, 15809–15826, <https://doi.org/10.5194/acp-21-15809-2021>, 2021.
- Zhong, X., Shen, H., Zhao, M., Zhang, J., Sun, Y., Liu, Y., Zhang, Y., Shan, Y., Li, H., Mu, J., Yang, Y., Nie, Y., Tang, J., Dong, C., Wang, X., Zhu, Y., Guo, M., Wang, W., and Xue, L.: Nitrous acid budgets in the coastal atmosphere: potential daytime marine sources, *Atmospheric Chem. Phys.*, 23, 14761–14778, <https://doi.org/10.5194/acp-23-14761-2023>, 2023.