Response to Editors and Reviewers

We gratefully thank the reviewers for their constructive comments and suggestions to improve the manuscript. As detailed below, the reviewers' comments are shown in *black italic*; our response to the comments is in blue. New or modified text is in red.

Referee 2:

General comments:

HONO is an important source of OH radicals in the atmosphere. Elucidating the characteristics and formation mechanisms of HONO is vital to understand the OH budget of OH. By combining modeling and field studies, Zhong et al provide evidence of a significant unidentified daytime marine source of HONO. Further, this missing HONO source is likely photochemical induced. This work has important implications for atmospheric chemistry in coastal and marine areas and will motivate further work on this topic in due course. This manuscript is well written and ACP is an appropriate venue. I would recommend the paper for publication after the following issues are addressed.

Response: Thanks for the reviewer's comments and suggestions. We have addressed the specific comments and revised the manuscript accordingly. For clarity, the reviewer's comments are listed below in *black italic*, while our responses and changes in the manuscript are shown in blue and red, respectively.

Specific comments:

1. Line 1: Should it be "the presence of a daytime marine source"?

Response: Thanks for the reviewer's suggestion. According to the suggestions of reviewer 1 and reviewer 2, we have revised the title to "**Nitrous Acid Budgets in Coastal Atmosphere: Potential Daytime Marine Sources**" to emphasize our discovery of the presence of marine sources in the coastal atmosphere.

2. Line 53: It would be helpful to introduce the missing source of daytime HONO.

Response: Thanks for the reviewer's suggestion. We have added the introduction about the missing source of daytime HONO in the revised manuscript.

Line 52: Despite its short daytime atmospheric lifetime, HONO is frequently observed at high concentrations at noon (Ye et al., 2016; Yang et al., 2021; Jiang et al., 2023). Traditional mechanisms cannot fully explain these observed daytime HONO peaks, indicating the presence of additional daytime HONO sources (missing sources of daytime HONO). Over recent decades, researchers have extensively investigated the missing sources of daytime HONO in various environments (Kleffmann, 2007; Lee et al., 2016; Jiang et al., 2022; Zhang et al., 2022).

3. Lines 137-138: Would the data averaging procedure introduce uncertainties to the subsequent analysis considering that different period of time was chosen for different days?

Response: Thanks for the reviewer's comment. To confirm the reliability of our conclusions, we conducted simulation comparisons using a case study on May 10, which was primarily influenced by marine air masses for almost an entire day. The simulation results show that even with the updated model, the simulated daytime HONO concentration is still significantly lower than the observed value (0.09 ppbv versus 0.29 ppbv). The missing HONO production rate is up to 0.51 ppbv h^{-1}, similar to the average case. Therefore, the data averaging procedure does not affect our conclusions. However, as the reviewer noted, averaging with limited data introduces uncertainties. Future research should continue with a larger dataset.

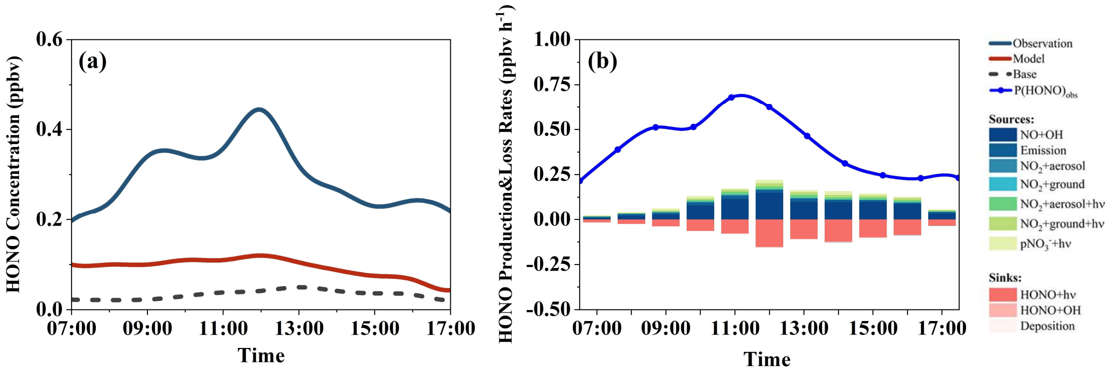

Figure R1. Comparison of observed and modeled daytime (7:00–17:00) HONO concentrations and modeled HONO budgets on May 10th, primarily influenced by marine air masses for almost an entire day.

4. *Lines 152: What are the unconstrained species?*

Response: Thanks for the reviewer's comment. The unconstrained species refers to species included in the MCM model (over 6900 species) that were not constrained with input from observed data. These primarily include atmospheric radicals and some secondary VOCs.

5. *Lines 161-164: What is the HONO/NOx value used in this study?*

Response: Thanks for the reviewer's comment. In this study, a commonly used HONO/NO_x ratio of 0.8% (Czader et al., 2012; Lee et al., 2016; Xue et al., 2020) was employed for modeling scenarios, and sensitivity simulations were conducted using ratios of 0.4% and 1.6% to assess the impact of parameter selection uncertainty on the results. We have made the following modifications to the manuscript:

Line 185: In this study, we employed the widely used ratio of 0.8% for modeling scenarios and sensitivity simulations using ratios of 0.4% and 1.6%.

6. *Lines 250-252: There is another peak of HONO at around 18:00. What are the potential reasons?*

Response: Thanks for the reviewer's constructive and insightful comments. Upon careful examination, we have found that the late afternoon HONO peak around 18:00 is primarily attributed to specific days with relatively high primary emissions. These emissions are notably associated with International Workers' Day (May 1, 2, and 4), a residential fire incident on May 8, and dust episodes on April 27 and 28. During holiday periods, Mount Lao experiences a significant increase in tourist numbers, coinciding with afternoon spikes in NO levels (Figure R2). Additionally, it is worth noting that transport-related influences likely contribute to afternoon peaks during dust episodes. When excluding the data from the above-selected afternoon peak days, only a noon peak of HONO is observed during the overall observation period, consistent with previous observations in clean areas (Jiang et al., 2022). Importantly, in the "sea case" we selected, there were no significant afternoon peaks in HONO concentrations (Figure 5). In the revised manuscript, we provided further clarification and included a figure illustrating the diurnal variations of HONO and other pollutants after excluding data from days affected by direct emissions in the supporting information (Figure R3). We appreciate the reviewer's valuable comment, which has substantially enhanced the reliability and quality of our paper.

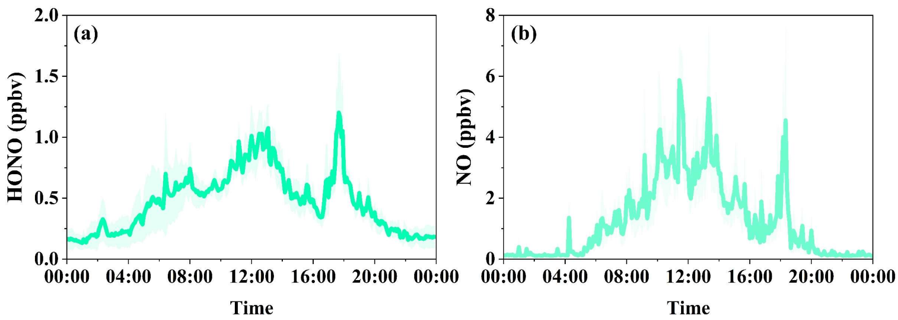

Figure R2. Average diurnal variations of HONO and NO during the International Workers' Day. The shaded area indicates half of the standard deviation.

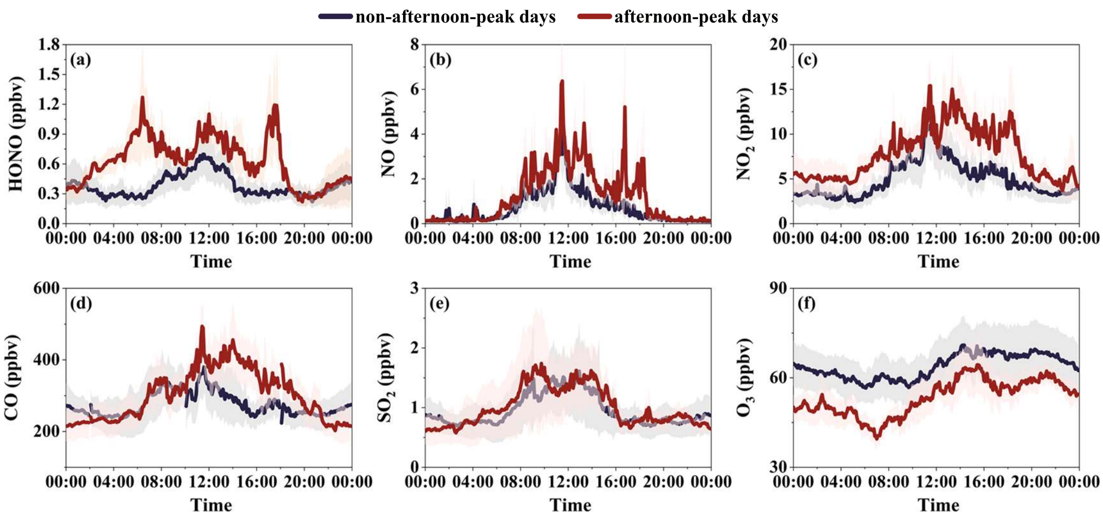

Figure R3. Comparison of diurnal variations of observed parameters in days with the selected afternoon peaks (April 27, 28, May 1, 2, 4, and 8) and overall days excluding the selected afternoon peak days. We have also included this figure in the supporting information.

7. Lines 268-270: I am curious about the performance of the updated OBM on non-polluted periods. Do the model results of HONO agree well with the observations?

Response: Thanks for the reviewer's constructive comment and suggestion. Similar to photochemical and dust episodes, the updated model with revised parameters performs well in simulating daytime HONO budgets during non-polluted periods (excluding the influence of marine air masses). Figure R4 compares the observed and simulated daytime (7:00–17:00) HONO concentrations during the non-polluted period. The simulated average HONO concentration is 0.59 ppbv, close to the observed value (0.67 ppbv). The index of agreement (IOA) value during the non-polluted period is 0.79, indicating that the updated OBM effectively reproduces the observation of HONO. This result suggests that the model performs relatively well in simulating non-marine sources at the observation site.

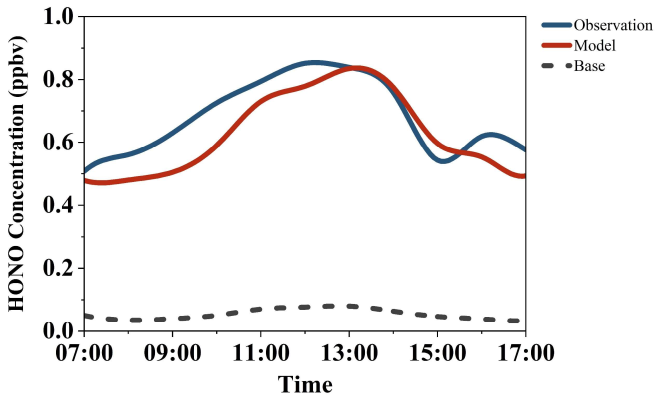

Figure R4. Comparison of observed and modeled daytime (7:00–17:00) HONO concentrations in the non-polluted period.

8. Lines 340-342: Though the authors focus on the sources of HONO during the daytime, the nighttime observations may constrain the non-photochemical sources of HONO. Could the model capture the high nighttime HONO/NO_2 ratio in the "sea case"?

Response: Thanks for the reviewer's comment. We observed high HONO/NO_2 ratios during the nighttime in the "sea case" (0.12 ± 0.11), which suggests potentially significant roles of the heterogeneous NO_2 conversion or other sources without the involvement of NO_2. After incorporating updated mechanisms into our model, the simulated HONO concentrations significantly increased and maintained relatively high nighttime HONO levels. However, the simulated values still fell below the observed values (Figure R5). The simulated HONO/NO_x ratio reached 0.07 ± 0.01, lower than the observed value. This indicates that there may be other sources of HONO during nighttime, such as microbial activity or soil emissions (Oswald et al., 2013; Song et al., 2022), or potentially higher efficiency in the conversion of NO_2 in marine air masses (Yang et al., 2021; Yabushita et al., 2009). However, compared to daytime, the nighttime simulations showed relatively better agreement with observations, and daytime HONO has a more significant impact on atmospheric oxidation and ozone formation. Therefore, in this paper, we primarily focused our discussion on daytime HONO.

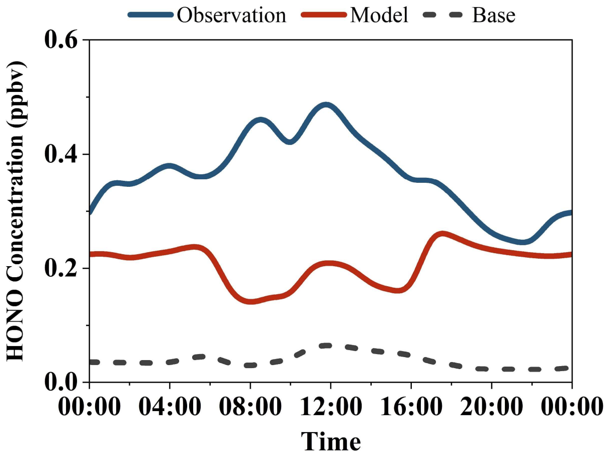

Figure R5. Comparison of the observed and modeled HONO concentrations in the "sea case".

9. Lines 374-376: The interfacial chemistry may lead to a high uptake coefficient of NO_2 on aerosol. Previous laboratory studies have found that the uptake coefficient of NO_2 on the aerosol surface can reach 2×10^{-4} (see Liu and Abbatt (2021); Yabushita et al. (2009) and references therein).

Response: Thanks for the reviewer's comments and recommended references. The measured NO_2 uptake coefficient of 2×10^{-4} by Liu and Abbatt (2021) represents a relatively high value observed in laboratory studies. However, upon carefully comparing their experimental conditions with our field observations, we find it challenging to achieve such values under field conditions. Firstly, their laboratory experiments involved a high SO_2 concentration of 280 ppbv, which can enhance NO_2 uptake, whereas the SO_2 level during our observation was around 1 ppbv. Furthermore, Liu and Abbatt (2021) reported that at pH levels below 4, the pathway for NO_2 uptake becomes negligible, suggesting that the NO_2 uptake coefficients should be considerably lower under these conditions. Our thermodynamic model estimated an aerosol pH of 3.1 during the observation. Therefore, we consider it challenging to achieve NO_2 uptake coefficients of this magnitude during our observations, and even the value of 2×10^{-4} is still twice less than the required NO_2 uptake coefficients. For the study of Yabushita et al. (2009), they measured initial-state (1 ms) uptake coefficients, and the equilibrium-state NO_2 uptake coefficients would likely be considerably lower (Yu et al., 2021). However, it should be noted that their study mentioned that the presence of halogens could enhance NO_2 uptake, which may contribute to the relatively high conversion of NO_2 to HONO in marine environments. We have cited and discussed these two papers in our manuscript. Once again, we thank the reviewer's comments.

Line 401: Although NO_2 uptake coefficients on the order of 10^{-4} have been measured in laboratory experiments under conditions of high SO_2 concentration (280 ppbv) and moderate acidity (pH = 5) (Liu and Abbatt, 2021), our observational site features lower

SO_2 concentrations (~ 1ppbv) and slightly acidic aerosols (pH = 3.1). These conditions suggest that the uptake coefficients should be considerably lower than the laboratory-measured 2×10^{-4}. It is worth noting that previous research has indicated that the presence of halogens can enhance NO_2 uptake, which could potentially explain the higher NO_2 to HONO conversion ratios in marine environments (Yabushita et al., 2009). However, further research is needed to explore this possibility. Overall, the observed missing HONO source in the "sea case" cannot be explained by the current photochemical processes.

10. Figure 4: Do the blue lines in Figure 4c, d represent the observed HONO production rate?

Response: The blue lines in Figures 4c and 4d represent the observed HONO production rate. We have modified the legends of Figures 4 and 6 by changing "$HONO_{obs}$" to "$P(HONO)_{obs}$" accordingly.

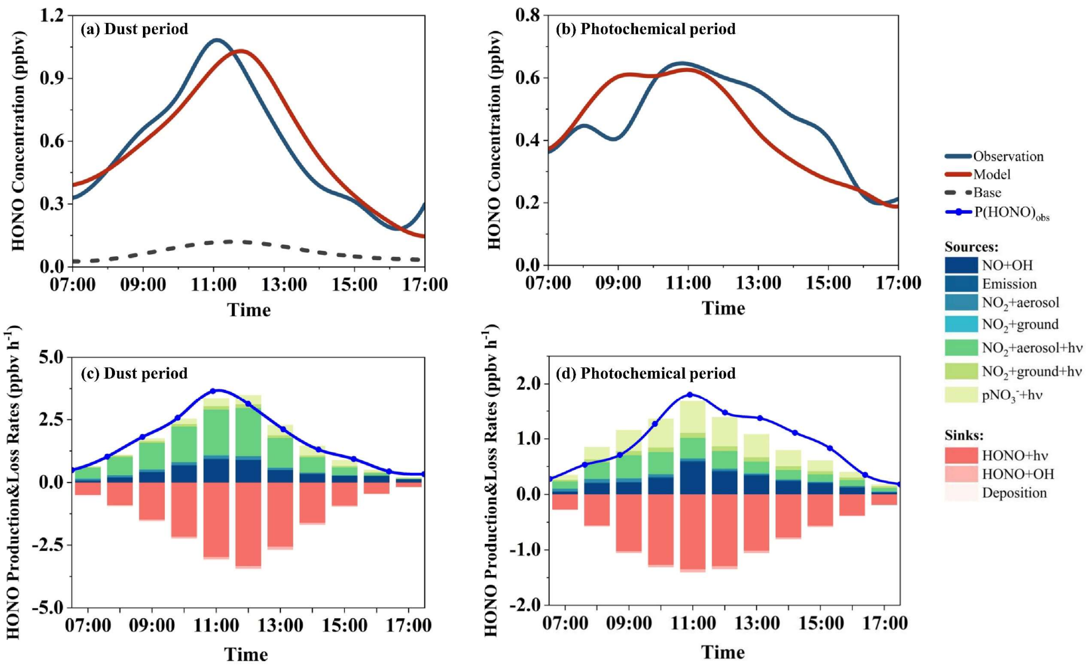

Figure 4. Daytime HONO budgets in dust (a, c) and (b, d) photochemical period at Mount Lao. The base case only considered the homogeneous reaction of NO + OH, and the model case considered the updated HONO sources described in this study.

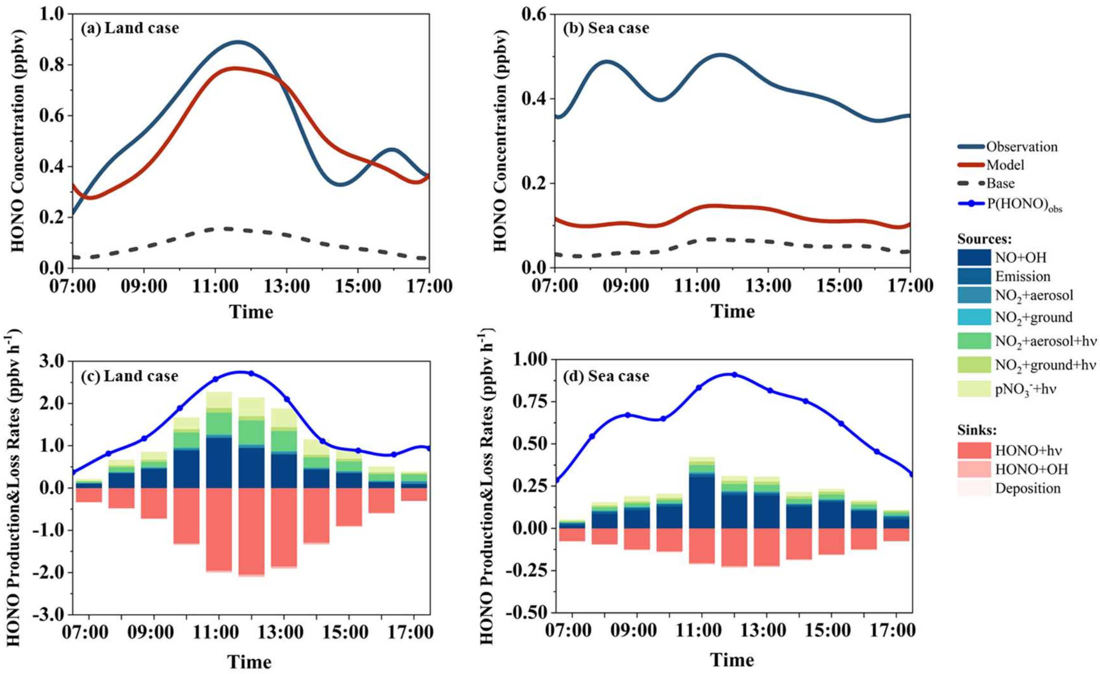

Figure 6. Comparison of the observed and modeled daytime (7:00–17:00) HONO concentrations and modeled HONO budgets in the "land case" (a, c) and the "sea case" (b, d).

Technical comments:

1. *Line 116: Give the full words of VOC in the first appearance.*

Response: We have corrected it accordingly.

Line 130: During the field campaign, fifty-seven VOC (volatile organic compound) canister samples were collected at 2-hour intervals from 9:00–19:00 local time on pollution episode days and at 6-hour intervals from 9:00–21:00 on non-episode days.

Reference:

Czader, B. H., Rappenglück, B., Percell, P., Byun, D. W., Ngan, F., and Kim, S.: Modeling nitrous acid and its impact on ozone and hydroxyl radical during the Texas Air Quality Study 2006, Atmos. Chem. Phys., 12, 6939-6951, 10.5194/acp-12-6939-2012, 2012.

Jiang, Y., Xue, L., Shen, H., Dong, C., Xiao, Z., and Wang, W.: Dominant Processes of HONO Derived from Multiple Field Observations in Contrasting Environments, Environ. Sci. Technol. Lett., 9, 258-264, 10.1021/acs.estlett.2c00004, 2022.

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 NOx and HONO chemistry in the tropical marine boundary layer at Cape Verde during the MarParCloud campaign, Journal of Geophysical Research: Atmospheres, 10.1029/2023jd038865, 2023.

Kleffmann, J.: Daytime sources of nitrous acid (HONO) in the atmospheric boundary layer, Chemphyschem, 8, 1137-1144, 10.1002/cphc.200700016, 2007.

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., and Kleffmann, J.: Detailed budget analysis of HONO in central London reveals a missing daytime source, Atmos. Chem. Phys., 16, 2747-2764, 10.5194/acp-16-2747-2016, 2016.

Liu, T. and Abbatt, J. P. D.: Oxidation of sulfur dioxide by nitrogen dioxide accelerated at the interface of deliquesced aerosol particles, Nat Chem, 13, 1173-1177, 10.1038/s41557-021-00777-0, 2021.

Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., and Delon, C.: HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen, Science, 341, 1233-1235, 2013.

Song, W., Liu, X. Y., Houlton, B. Z., and Liu, C. Q.: Isotopic constraints confirm the significant role of microbial nitrogen oxides emissions from the land and ocean environment, Natl Sci Rev, 9, nwac106, 10.1093/nsr/nwac106, 2022.

Xue, C., Zhang, C., Ye, C., Liu, P., Catoire, V., Krysztofiak, G., Chen, H., Ren, Y., Zhao, X., Wang, J., Zhang, F., Zhang, C., Zhang, J., An, J., Wang, T., Chen, J., Kleffmann, J., Mellouki, A., and Mu, Y.: HONO Budget and Its Role in Nitrate Formation in the Rural North China Plain, Environ Sci Technol, 54, 11048-11057, 10.1021/acs.est.0c01832, 2020.

Yabushita, A., Enami, S., Sakamoto, Y., Kawasaki, M., Hoffmann, M., and Colussi, A.: Anion-catalyzed dissolution of NO2 on aqueous microdroplets, The Journal of Physical Chemistry A, 113, 4844-4848, 2009.

Yang, J., Shen, H., Guo, M.-Z., Zhao, M., Jiang, Y., Chen, T., Liu, Y., Li, H., Zhu, Y., Meng, H., Wang, W., and Xue, L.: Strong marine-derived nitrous acid (HONO) production observed in the coastal atmosphere of northern China, Atmos. Environ., 244, 10.1016/j.atmosenv.2020.117948, 2021.

Ye, C., Zhou, X., Pu, D., Stutz, J., Festa, J., Spolaor, M., Tsai, C., Cantrell, C., Mauldin, R. L., 3rd, Campos, T., Weinheimer, A., Hornbrook, R. S., Apel, E. C., Guenther, A., Kaser, L., Yuan, B., Karl, T., Haggerty, J., Hall, S., Ullmann, K., Smith, J. N., Ortega, J., and Knote, C.: Rapid cycling of reactive nitrogen in the marine boundary layer, Nature, 532, 489-491, 10.1038/nature17195, 2016.

Yu, C., Wang, Z., Ma, Q., Xue, L., George, C., and Wang, T.: Measurement of heterogeneous uptake of NO2 on inorganic particles, sea water and urban grime, J Environ Sci (China), 106, 124-135, 10.1016/j.jes.2021.01.018, 2021.

Zhang, X., Tong, S., Jia, C., Zhang, W., Li, J., Wang, W., Sun, Y., Wang, X., Wang, L., Ji, D., Wang, L., Zhao, P., Tang, G., Xin, J., Li, A., and Ge, M.: The Levels and Sources of Nitrous Acid (HONO) in Winter of Beijing and Sanmenxia, Journal of Geophysical Research: Atmospheres, 127, 10.1029/2021jd036278, 2022.