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 1:

HONO is a very important nitrogen-containing reactive species in the atmospheric environment, which has a very great influence on atmospheric oxidability. At present, there are still many unknowns about the formation mechanisms of HONO, and it is very necessary to carry out HONO-related studies.

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.

Major comments:

1. The title of this manuscript emphasizes "marine source", but the discussion of the effects of marine source on the observed HONO only takes up a very small part of this study, which in fact only shows that the large difference between the simulated and observed HONO under the "sea case" conditions is unexplained, while the contribution of the marine source and the mechanisms are not studied.

Response: Thanks for your comment. In this study, we found that although the updated chemical box model performed well in simulating daytime HONO production from non-marine sources (photochemical and dust episodes), however, it failed to reproduce HONO production in "sea case" (up to 0.7 ppbv h^{-1}). Based on correlation analysis, we suggested that the missing marine sources are strongly associated with solar radiation (Figure S7) and assessed the impact of marine sources on atmospheric oxidation capacity and ozone formation using the model. However, determining the precise mechanisms remains challenging based on current observational data. To avoid overemphasizing marine sources, we have revised the title to "**Nitrous Acid Budgets in Coastal Atmosphere: Potential Daytime Marine Sources**" as suggested by the reviewer. The updated title emphasizes our discovery of the presence of marine sources at this site, with the specific mechanisms requiring further research in the future.

2. The accuracy of the model simulations is the key to the discussion in this paper. How can the accuracy of the model simulation be determined in the scenario where there are clearly 2 peaks in HONO during the observation period, but the model can only explain one of them.

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 (May 8), and dust episodes (April 27 and 28). During holiday periods, Mount Lao experiences a significant increase in tourist numbers, coinciding with afternoon spikes in NO levels (Figure R1). 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 R2). We appreciate the reviewer's valuable comments, which has substantially enhanced the reliability and quality of this paper.

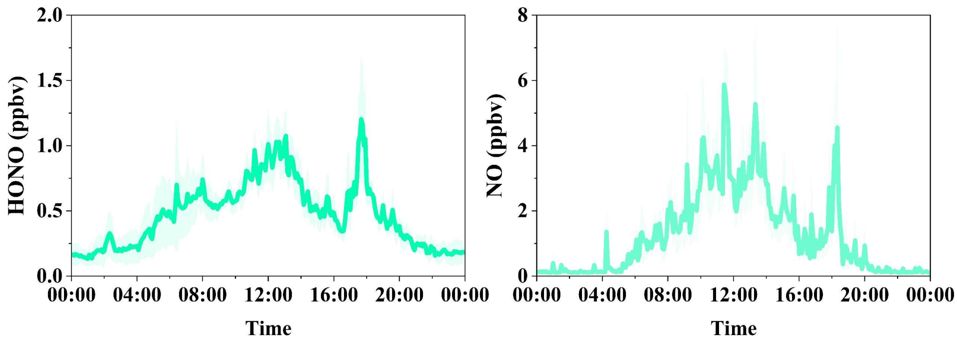

Figure R1. Average diurnal variations of HONO and NO during the International Workers' Day. The shaded area indicates half of the standard deviation.

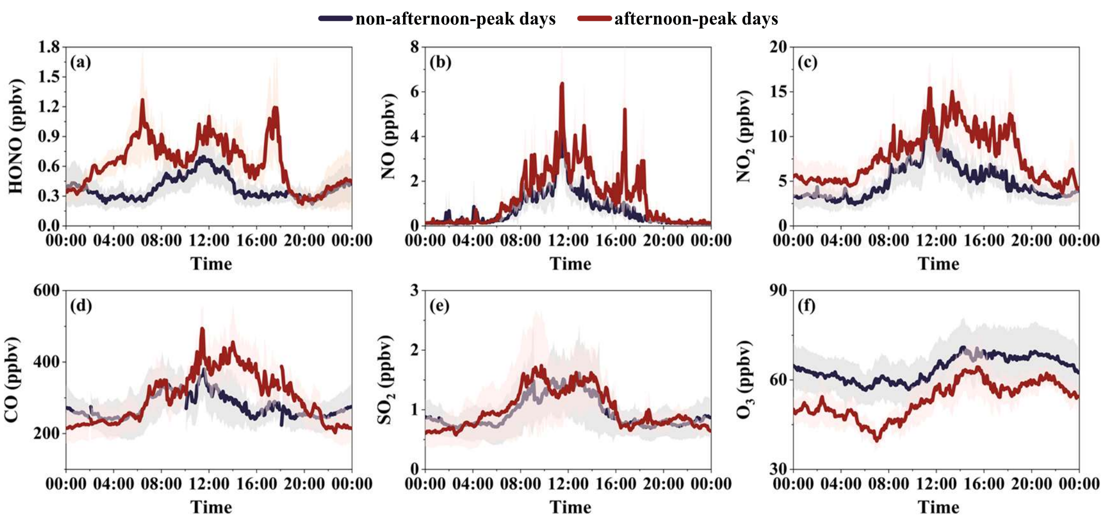

Figure R2. Comparison of diurnal variations of observed parameters in selected days with the afternoon peaks (April 27, 28, May 1, 2, 4, and 8) and overall days excluding the selected afternoon peak days.

Line 272: It is important to note that both HONO and NO_x exhibit a second daytime peak in the late afternoon, which is primarily caused by specific days with primary emissions or transport events. After excluding these days, the diurnal variation of HONO aligns more closely with observations in clean regions (Jiang et al., 2022). We have included the diurnal variation of HONO after removing days with afternoon peaks in the supporting information. Since their impact is largely confined to specific days, it does not significantly affect our subsequent analysis, particularly the "sea case" analysis.

3. The authors only set the HONO concentration to zero in the "without HONO" scenario, which in fact still has the effect of HONO in the model. I think that the HONO-related reactions should be turned off instead of just setting HONO concentration to zero.

Response: Thanks for the reviewer's insightful suggestions. In the revised manuscript, we simulated the "without HONO" scenario by setting the HONO concentration to zero and turning off the HONO-related reactions. Since we used 5-minute temporal resolution input constraints in the previous manuscript, the impact of the change is relatively minor. The modified results are as follows:

Line 425: In contrast, in the "without HONO" scenario, we turn off seven HONO production pathways summarized in Table 1 and set the input HONO concentrations to zero.
Line 435: Specifically, the absence of HONO resulted in a decrease in the net O_3 production rate and OH radical primary production rate in the "overall case" from 7.39 ppbv h^{-1} and 1.44×10^7 molecules cm^{-3} s^{-1} to 3.41 ppbv h^{-1} (a 54% reduction) and 2.81×10^6 molecules cm^{-3} s^{-1} (an 81% reduction), respectively. Regarding concentration, the absence of HONO chemistry resulted in a reduction in the average OH radical concentration from 3.6×10^6 molecules cm^{-3} to 1.9×10^6 molecules cm^{-3}, and the peak OH concentration from 5.2×10^6 molecules cm^{-3} to 2.7×10^6 molecules cm^{-3}. Similarly, in the marine air masses, the production rates of O_3 and OH decreased from 6.22 ppbv h^{-1} and 7.69×10^6 molecules cm^{-3} s^{-1} to 3.33 ppbv h^{-1} (a 46% reduction) and 2.14×10^6 molecules cm^{-3} s^{-1} (a 72% reduction), respectively without HONO chemistry.
Line 449: Specifically, missing marine HONO sources contributed 36% to the peak net O_3 production rate（from 9.24 ppbv h^{-1} to 5.90 ppbv h^{-1}）and 28% to peak OH concentration (from 3.4×10^6 molecules cm^{-3} to 2.4×10^6 molecules cm^{-3}).

Minor comments:

1. Additional studies on marine source need to be added in the introduction section.

Response: Thanks for the suggestion. We have added additional studies on marine HONO sources into the introduction section of the revised manuscript.

Line 71: The marine boundary layer (MBL) with a large air/water interface, where the ocean and atmosphere exchange trace gases, heat, and aerosol particles (Wurl et al., 2016), and the interfacial photochemistry processes often occur (Bruggemann et al., 2018), is utterly different from inland environments. The opposite diurnal variations of HONO with a peak concentration at noon at marine sites implied the different predominant HONO processes compared with polluted inland areas (Jiang et al., 2022). Furthermore, recent observations of HONO in coastal and marine regions indicate the existence of marine HONO sources (Jiang et al., 2022; Crilley et al., 2021; Ye et al., 2016a; Yang et al., 2021a). The observed accelerated NO_2-to-HONO conversion in marine air masses suggests that air-marine interactions enhance HONO production (Zha et al., 2014; Yang et al., 2021a). However, the heterogeneous conversion of NO_2 on vast air/water interface, a potential source of marine HONO, remains uncertain (Wojtal et al., 2011; Zhu et al., 2022; Yu et al., 2021). Crilley et al. (2021) obtained a factor of 5 lower ocean-surface NO_2-to-HONO conversion than previous studies; there was still a debate on the importance of ocean-surface-mediated conversion of NO_2 into HONO. Nitrate Photolysis is believed to contribute to marine HONO sources (Ye et al., 2016a; Andersen et al., 2023), but significant controversy persists (Romer et al., 2018; Shi et al., 2021). The specific influencing factors remain unclear (Zhang et al., 2020; Andersen et al., 2023), with some studies suggesting other factors may be responsible (Yang et al., 2021a; Wojtal et al., 2011). Accordingly, Jiang et al. (2023) highlighted the contribution of the dust-surface-photocatalytic conversion of reactive nitrogen compounds to HONO formation and the important role of halogen chemistry in HONO simulation in CVAO. However, most existing studies still rely on steady-state analysis, and there is a lack of quantitative research determining if current HONO mechanisms can adequately explain observed marine daytime HONO concentrations.

2. *What are the definition criteria for daytime time ranges (7:00-17:00) in this study? The light intensity is already so low at 18:00 that the photolysis reaction has stopped?*

Response: Thanks for the reviewer's comment. Our choice of the daytime range from 7:00–17:00 is primarily based on two considerations. Although photolysis reactions continue at 18:00, the light intensity is relatively low, approximately one order of magnitude lower than at noon (Figure R3). Given our focus on investigating the missing daytime HONO sources, we restrict our analysis to 7:00–17:00 to minimize potential simulation errors associated with lower light intensity. Additionally, the choice of the time range is to synchronize with other observational data. Specifically, the filter sample collection started at 7:00, while carbonyl samples ended at 17:00. This ensures the consistency of our data. Overall, this choice would not alter the major conclusions of this study.

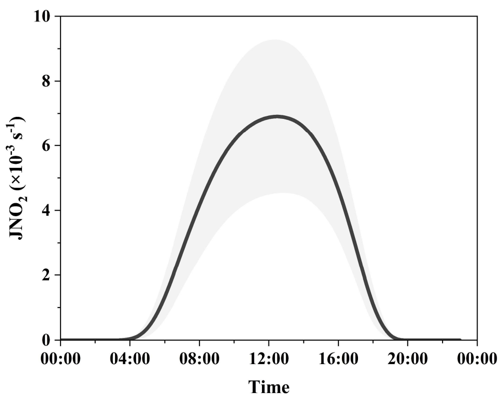

Figure R1. Average diurnal variation of JNO_2 during the observation period. The shaded area indicates the range of the standard deviation.

3. Line 167: How are the contribution of vehicle emissions to HONO adjusted based on the environment and traffic density?

Response: Thanks for the reviewer's comment. We apologize for the misleading description in the previous manuscript. In this study, we did not adjust HONO emissions based on the environment and traffic density. 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. From the results shown in Figures S2, S3, and S4, the simulated HONO concentrations in all model cases remained unchanged with changes in HONO/NO_x. 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%.

4. Line212：The dry deposition of the other components is not considered?

Response: Thanks for the reviewer's comment. We also considered the dry deposition of other components, including ozone, peroxides, carbonyls, and organic acids, in the OBM model, as described in our previous study (Xue et al., 2014). We have included this clarification in the revised manuscript.

Line 231: The dry deposition of HONO, ozone, and other species, including peroxides, carbonyls, and organic acids, are also considered in the OBM model (Xue et al., 2014).

5. Can the authors explain the reason for the second HONO peak in the late afternoon?

Response: Thanks for the reviewer's constructive and insightful comments. As explained above, the HONO peak in the late afternoon, around 18:00, is primarily due to direct vehicle emissions during International Workers' Day (May 1, 2, and 4) and a fire incident on May 8. During holiday periods, Mount Lao experiences a notable surge in tourist numbers. We also observed afternoon spikes at NO levels during these times. It is worth noting that there are also noticeable afternoon peaks during dust episodes (April 27 and 28), which may be due to transport-related influences. 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). We have added clarification in the revised manuscript and included a figure depicting the diurnal variations of HONO and other pollutants after removing the data from days affected by direct emissions in the supporting information. We thank the reviewer again for the comments to improve our paper's reliability and quality.

6. How the VOC data is used in the model, since the VOC measurements have such a low time resolution?

Response: Thanks for the reviewer's comment. In this study, the daytime VOCs were linearly interpolated to a time resolution of one hour for model constraints, whereas the nighttime VOCs were calculated according to their linear regressions with other species. Specifically, the nighttime VOCs were interpolated to one-hour time resolution using their linear regression with CO concentration. We have made the following revisions to the manuscript:

Line 159: The observed data of HONO, O_3, NO, NO_2, SO_2, CO, VOCs, pNO_3^-, Sa, temperature, RH, and pressure were averaged or interpolated to a time resolution of 5 minutes, except for VOCs and pNO_3^-, which were linearly interpolated to a time resolution of 1 hour to constrain the model (Yang et al., 2018).

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