Response to Reviewer #1

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. conducted a comprehensive case study in a coastal region to investigate HONO formation mechanism. The diurnal cycle of HONO is well simulated and successfully explained by the model. Results are convincing and sound. The manuscript reads very clear. I think it in general deserves an ACP publication, while I still have a few comments and some minor text-revising suggestions as below:

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.

Comments:

1. It is interesting to observe the peak HONO at noon. However, if I understand correctly, it is from a monthly average in no-raining days. I am wondering if this diurnal pattern is consistent across individual days, or if multiple distinct patterns exist but are masked by the averaging. From a rough inspection of Fig. 2, the diurnal patterns seem to vary from day to day. I think authors should at least demonstrate that the noon-peak HONO occurred on most days. Even better, they are encouraged to do more analysis to examine 1) if model can capture different diurnal patterns and 2) if the underlying mechanisms can also be explained.

   Response: Thanks for your conducive comments and rigorous attitude to scientific research. We agree with you that averaging can sometimes mask day-to-day variability. In Figure 2, we illustrate the diurnal pattern of HONO concentrations during the entire study period. As you suggested, we have further examined the agreement between observations and simulations on non-rainy and rainy days. As shown in Figure R1, it is revealed that the correlation coefficient (R) between HONO measurements and simulations is 0.75, which is significantly higher than that on rainy days (0.20). The diurnal peak around 14:00 of local time was reasonably captured by the model on most non-rainy days. However, we noticed that the diurnal pattern of HONO concentrations influenced by precipitation shows less variability. Meanwhile, our model overestimated the observed maximum HONO concentration and failed to reproduce the peak hour. This mismatch between observations and simulations on rainy days may be indicative of an underestimated wet removal effect. On the other hand, the simulated daytime NO_2 is in a good agreement with observations under non-raining conditions (Figure R1). But the modelled daytime NO_2 concentration is higher than the observed values on the rainy days, plausibly overpredicting chemical production rate of HONO. To make it clearer, we have rephrased the associated texts in the manuscript as follows.

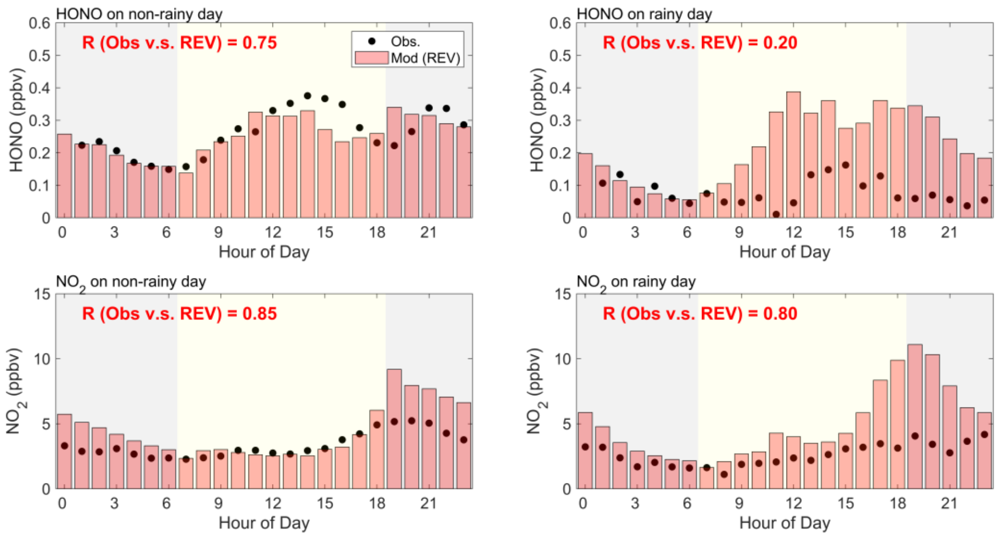

Figure R1. The diurnal variations of the observed and simulated HONO and NO_2 concentrations on rainy days and non-rainy days.

Revisions in Section 3.2:

Figure 3b illustrates that the REV case successfully captured the higher HONO concentrations observed around noon. The Pearson's correlation coefficient (R) between the measurements and simulations increased from 0.657 (BASE) to 0.763 (REV). The REV simulation accurately captured the timing of the observed diurnal peak around 14:00, which the BASE case simulates several hours too early. We further show the comparisons between measurements and simulations in terms of diurnal variations of HONO and NO_2 on rainy and non-rainy days. As shown in Figure S3, the daytime HONO concentrations simulated by REV is in good agreement with observations on non-rainy day. However, the model fails to reproduce the observed low concentration levels and the temporal variations of HONO on rainy days, possibly attributed to an underestimated wet removal caused *by precipitation. Meanwhile, daytime NO_2 concentrations on rainy days also shows an obvious overestimation, further leading to the higher chemical production of HONO.*

2. It might be insufficient to only discuss the HONO chemical production when investigating the impacts of ship emissions on HONO diurnal cycles. I am wondering whether the diurnal cycle of land-sea wind could also play a role in transporting NOx/HONO?

   Response: Thank you for this valuable comment. We agree with your point regarding the important role of sea-land breeze circulation in pollutant transport within coastal regions (Huang et al., 2025; Liu et al., 2025; Shen et al., 2021). The sea-land breeze (SLB) is defined as a unique wind pattern in coastal areas where the wind direction reverses between daytime and nighttime due to the differential heating of land and sea. We have identified SLB events during the study period following the criteria used by Liu et al. (2025). Specifically, an effective SLB cycle includes the land breeze phase (01:00-08:00), the sea breeze phase (13:00-20:00), and transition periods in between. In the coastal regions of Fujian, sea breezes are winds from 50° to 220° and land breezes from 240° to 40°. In addition, the sea breeze or land breeze phase should last at least 4 hours, with the opposing breeze lasting no more than 2 hours during these phases. Meanwhile, the wind speed throughout the SLB cycle should be less than 10 m s^{-1}. As illustrated in Figure R2a, our analysis based on the wind field data in Figure 2 reveals that a typical sea-land breeze event occurred on only one day during the entire one-month study period (i.e. 30^{th} of May). A further analysis of atmospheric circulation indicates the coastal region of Fujian was dominated by a persistent northeasterly wind (Figure R2b) for most time, suppressing the formation of local, thermally-driven sea-land circulations, thus limiting their overall role in transport. Overall, the three-dimensional numerical model (WRF-Chem) is capable of simulating atmospheric transport processes. Therefore, the net effect of both the dominant synoptic winds and local circulations have been accounted for in our simulation results. To include the discussion about the potential effect of sea-land breeze, we have revised the relevant texts in the manuscript as follows. We would like to express our gratitude to the insightful suggestion from the reviewer again.

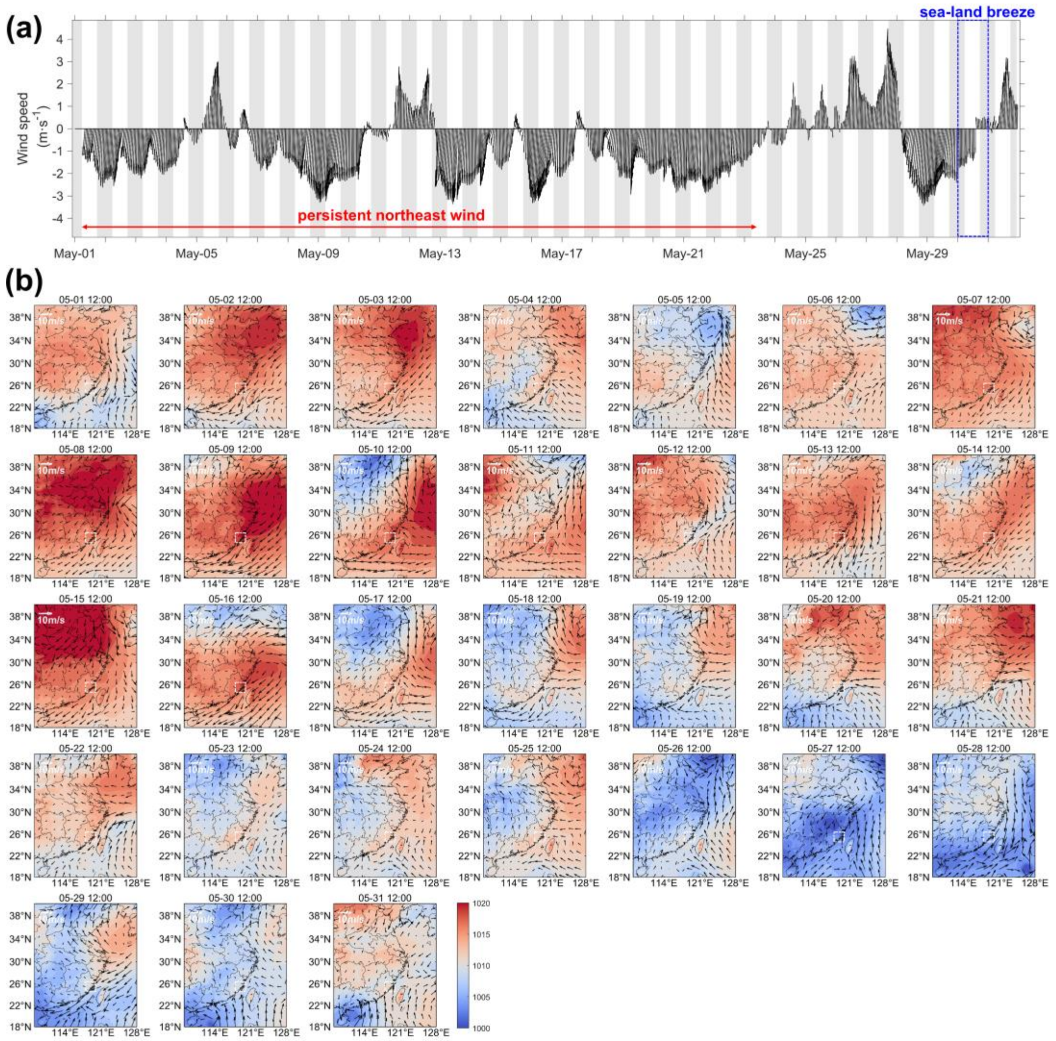

Figure R2. Wind fields during the study period. Panel (a) shows the temporal variations of wind vectors at the site DZSK. The shaded areas represent the nighttime (19:00 to 6:00). Panel (b) illustrates the spatial pattern of the sea level pressure (hPa) and the surface wind field at 12:00 on each day in May 2024.

Revisions in Section 3.3.2:

The impact of the shipping emissions is based on the atmospheric transport of air pollutants from the upstream region. Specifically, the regional transport is driven by both background circulation and local circulations such as sea-land breeze (SLB). Following the criteria of SLB given by Liu et al. (2025), we identified SLB events over the study region based on the local wind field data exhibited in Figure 2. The further analysis of wind fields demonstrates that the study area is less affected by the SLB. The impact of shipping emissions on HONO formation was mainly attributed to the transport effect of regional persistent northeasterly wind.

Minor suggestions:

1. Line 20: please specify the model name in the abstract

Response: Thank you for pointing this out. We have specified the full name of the numerical model in the revised manuscript.

Revisions in Abstract:

Using an updated Weather Research and Forecasting coupled with Chemistry (WRF-Chem) model, we captured the magnitude and temporal variation of HONO concentrations observed in coastal areas, and improved the model performance on diurnal patterns of the NO_2 and O_3.

2. Lines 39-40 and Lines 48-49: The new reactions of the photo- and dark-oxidation of NOx should also be listed. In the reactions of HONO removal, the HONO oxidized by OH should also be included, as it is used in the following analyse (Fig. 5a).

   Response: Thanks for your reminder. We have added the missing reactions and rephased the related texts in the manuscript.

   Revisions in Section 1:

   In addition, a recent laboratory study also reported that the photo- and dark-oxidation of nitrogen oxides (NO_x) could significantly contribute to HONO formation (R4-R5) (Song et al., 2023).

   In the presence of sunlight, HONO can rapidly undergo photodissociation (R6) to yield NO and OH radicals (Seinfeld and Pandis, 2016). Meanwhile, HONO can be slightly consumed by OH oxidation (R7).

   $HNO_3 + NO \rightarrow HONO + NO_2$ (R4)

   $NO_3 + NO \rightarrow 1.98\ NO_2 + 0.02\ HONO$ (R5)

   $HONO \rightarrow OH + NO$ (R6)

   $HONO + OH \rightarrow NO_2 + H_2O$ (R7)

3. Lines 56-58: what are the associated conclusions of this previous study?

   Response: Thank you for pointing this out. A new description has been rephrased in the relevant paragraph.

   Revisions in Section 1:

   Our previous study focused on the Yangtze River Delta (YRD) region indicates that HONO contributed to a 22% and 28% increase in concentrations of fine particulate matter and O_3 during a short-term compound air pollution case in March of 2019 (Zhang et al., 2024b).

4. Lines 102-103: It is not clear what is the 'seven-day loop cycle'? What 'systemic

biases' authors want to avoid?

Response: Thanks for this comment. The seven-day loop cycle we used refers to manually restarting the WRF-Chem model every seven days. The objective of this process is to reduce the long time accumulation of biases of numerical computation. To clarify this point, we have revised the associated texts in the manuscript 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.

5. Table 2. Please clarify that the 120 is from the ratio between measured NO_3^- photolysis rates and the default HNO_3 photolysis rate.

Response: Thanks for your kind reminder. We have corrected this point as you suggested.

Revisions in Table 2:

Table 2. *Chemical parameterizations of HONO sources in the revised WRF-Chem model.*

Pathway	*Parametrization*	*Descriptions*
Photolysis of nitrate aerosols	$J_{NO3-} = 120 \times J_{HNO3}$	*J_{NO3-} and J_{HNO3} are the photolysis frequencies of nitrate aerosols and gaseous HNO_3 (Fu et al., 2019). The ratio of 120 is estimated between the measured NO_3^- photolysis rate and the default HNO_3 photolysis rate.*

6. Line 215. Figure 3b? Meanwhile, it looks like the BASE experiment also shows noon-peak HONO. Could you explain why it is? Could it be possible to imply that the diurnal emissions/transport also contribute to the noon-peak HONO?

Response: Thank you for your careful comment. The typo of the figure number has been corrected in our revised manuscript. The BASE scenario refers to the default WRF-Chem model which only takes the homogeneous reaction between NO and OH into account. The direct emission of HONO is turned off in BASE so that direct emissions and transport from upstream regions could not contribute to local HONO formation. In BASE scenario, we believe that the noon-peak of HONO concentrations is attributed to the higher production rate of the reaction NO + OH (Figure R3). Both concentrations and production rates of HONO reach their peaks at 11:00 of local time. The NO + OH reaction rate is highest at noon because

OH radical concentrations, driven by photochemistry, peak at this time. This explains the timing of the noon-peak in the BASE case. However, only considering the reaction between NO and OH fails to capture well the chemical production fate of HONO during the daytime that the daily maximum concentration of HONO in BASE is significantly lower than the observed value.

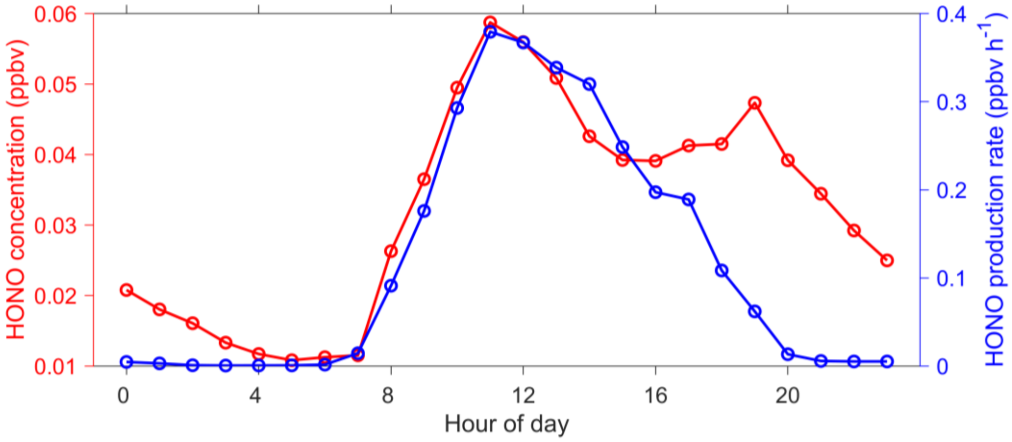

Figure R3. The simulated concentrations and production rates of HONO in BASE scenario which only considers homogenous reaction between NO and OH.

7. Lines 314-316. Which one is daytime and which one should be nighttime?

Response: Thank you for your careful comment. This typo has been corrected as follows.

Revisions in Section 3.3.2:

However, due to the self-photolysis of HONO, the overall increase in coastal HONO concentrations caused by shipping emissions during the daytime (0.19 ppbv) was close to nighttime levels (0.20 ppbv).

8. Lines 422-423. Please specify the ratio of HONO to NOx of mobile sources are supposed to be higher or lower?

Response: Thanks for your insightful suggestion. According to the recent report by Ke et al. (2025), the ratio of HONO to NO_x of mobile sources are expected to be higher. For aircraft, this ratio ranges from 0.82% to 6%. For offroad mobile machinery, this ratio can reach 2.3%. To specify this point, we have rephrased the related texts in the manuscript as you suggested.

Revisions in Section 3.5:

However, Ke et al. (2025) have pointed out that the same ratio of HONO to NO_x may not be applicable to mobile sources, including mobile machinery, ships, and aircraft. The ratios of HONO to NO_x were examined to be 0.8~6.0% and 2.3% for *aircraft and offroad mobile machinery, respectively.*

9. The uncertainty of soil HONO emissions should also be discussed, especially there are large cropland areas in the study domain.

   Response: Thank you for pointing this out. We indeed agree with you that the uncertainty of direct emissions from soils should be discussed. We have incorporated the related discussions in the manuscript.

   Revisions in Section 3.5:

   In addition to mobile emissions for HONO from combustion processes, the soil volatilization could be another important contributor to ambient HONO (Tan et al., 2023; Wu et al., 2022), especially when there are large areas of cropland and agricultural activities. The neglect of soil HONO emissions may introduce some uncertainties in the HONO simulation in this study.

References

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