Response to comments by referees

We thank the referee for the helpful comments and suggestions. Below are the detailed responses. The referee's comments are in *italic*; our responses are in red.

Reviewer #1

This paper presents a modeling study on the impact of HONO and $ClNO_2$ chemistry on RO_x budgets and pollutant formation in marine and coastal environments. The WRF-Chem model, with an updated chemical mechanism, is used to determine how ship emissions and added HONO and Cl chemistry affect RO_x, O_3, and $PM_{2.5}$ levels. The results of the study are clear, and the paper is publishable, however the comments below should be addressed before publication.

1. In the model setting section (2.1), more thorough descriptions of the model updates are needed to assess this study. A list of the HONO reactions and their reaction rates would be helpful to readers. The rate should especially be included for the HONO formation from particle nitrate photolysis since this is not included in Zhang et al., 2017, so it is unclear what values are used here.

Response: Thank you for your suggestion. We updated the model with the additional source of HONO from the photolysis of particular nitrate. The reaction and the photolysis rate of particular nitrate in were added section 2.1, and is also shown below:

"For this study, an additional HONO source from the photolysis of particulate nitrate ($PNO_3 \rightarrow 0.67HONO + 0.33\ NO_2$) was updated into our model. The photolysis rate constant of PNO_3 (J_{PNO3}) followed the reported value used in Fu et al., (2019) ($J_{PNO3} = (8.3\times10^{-5}/7\times10^{-7}) \times J_{HNO3\text{-}WRF\text{-}Chem}$; $J_{HNO3-WRF\text{-}Chem}$ is the photolysis rate of gaseous HNO_3 calculated online in the WRF-Chem model)".

2. In the emissions section, please cite the land-based HONO/NO_x emission ratios used. It would be useful to give an approximate range of ship-based NO_x emission rates as well since this plays a large role in HONO and $ClNO_2$ chemistry.

Response: Thank you for your suggestion. We added two citations (Kurtenbach et al., 2001, Gutzwiller et al., 2002) to describe the land-based HONO/NO_x emission ratios used in this study. For the ship-based NO_x emission rates, we showed a spatial distribution of the NO_x emission fluxes from shipping emission inventories (see Figure 1a in the manuscript). Also shown below:

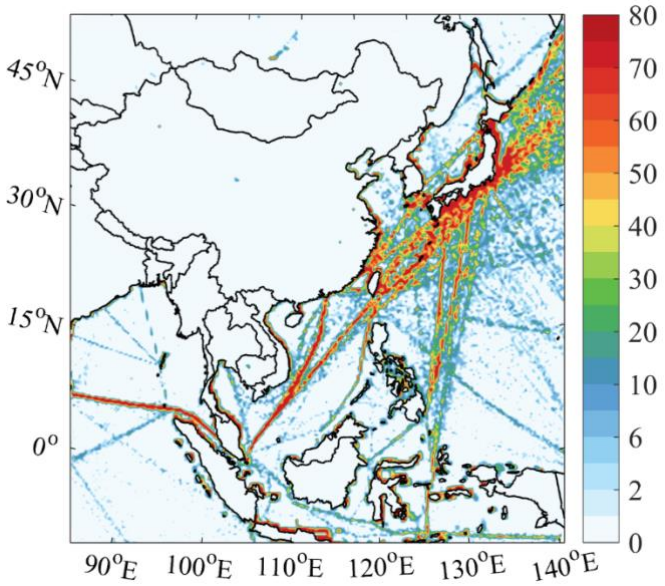

Figure 1: NO_x emission fluxes from ships (Unit: g m^{-2} $month^{-1}$) in July 2017.

3. In the model validation section (2.4), please clarify what data is being used to validate model performance and which model run is being compared. Are the values listed in Table S2 daytime hourly averages and is this averaged over the entire observational region? Is the SIM values listed for the BASE model case? Similar clarification is needed for Table S3 and the subscript description is incorrect in this table.

Response: We used the meteorological data, including wind speed, relative humidity, and temperature, from NOAA's National Climatic Data Center and the air pollutants data, including NO_2, $PM_{2.5}$, and O_3, from China's Ministry of Ecology and Environment to validate the model performance. The simulated data from the BASE case is compared. The values listed in Table 2S are the hourly averages of the available observational data over entire China for the model validation. SIM represents the simulated data from the BASE case. We have revised the table caption in Table S2 and Table S3 as below:

"OBS represents the hourly averages for the available observational data (over the entire regions for the meteorological parameters and over mainland China for the air pollutants). SIM represents the simulations from the BASE case."

4. In the results section, clarification is again needed about the data that is shown in the figures. Is average HONO referring to daytime averages or 24-hour daily? The values seem quite high if nighttime data is included in the averages.

Response: the average HONO in the manuscript is the 24-hour daily average. We have clarified this. With the consideration of heterogeneous conversion from NO_x to HONO, the nighttime value of HONO is higher than the value during daytime. For this reason, the relatively high value of HONO in our study is reasonable.

5. Check the order of your subsections – section 3.2 is missing.

Response: Thanks for pointing out this problem. It has been corrected.

6. In line 279, you discuss the switch between NO_x and VOC-sensitive regimes, stating that increased HONO provides an additional source of NO_x. The increase in RO_x will also increase the back reaction from NO to HONO. Can you comment on the balance between these two reactions?

Response: I think the photolysis of HONO is the main reaction in this balance. The back reaction from NO and RO_x to HONO relies on the level of NO and oxidants, and the reaction rate of the photolysis of HONO is faster than that of the back reaction from NO to HONO.

7. In section 2.4, you state that the model under predicts NO_2 and over predicts $PM_{2.5}$. I think this should be discussed in the results/discussion as well as to how this impacts your conclusions about the importance of HONO and Cl chemistry.

Response: Thank you for your comment. We added a statement in discussion to point out this impact on the importance of HONO and Cl chemistry. And also showed below:

"In our simulation, the under predicted NO_2 may lead to the underestimation in HONO, and the over predicted $PM_{2.5}$ can also result in the underestimated uptake of N_2O5 and overestimated conversion to HONO. These results may contribute to a further increase in the contribution to average ozone formation and a decrease to average $PM_{2.5}$."

8. In line 196, you state that HONO spatial distribution is consistent with NO_2 due to the homogeneous and heterogeneous conversion. Are you referring to the HO_2+NO_2 as the homogeneous conversion? It's my understanding that this is a relatively unimportant HONO source compared to others. A comparison of the default to base run should provide more information since HO_2+NO_2 is included in the default mechanism. Perhaps you should discuss if direct emissions of HONO from ships is relevant here.

Response: Thank you for your comment. We agree that the homogeneous conversion of NO_x and HO_x is a relatively unimportant HONO source and direct emission from ships is relevant. We have changed the statement to "The distribution of HONO was consistent with that of NO_2 due to the heterogeneous conversion of NO_2 to form HONO and direct HONO emission by ships".

9. In line 340, the conclusions would be clearer if you presented values for coastal versus oceanic regions rather than just giving the total range of RO_x, O_3, and $PM_{2.5}$ increases.

Response: Thanks for the suggestion. We have added the value for coastal and oceanic regions and changed the statement to "The results show that photolysis of the two compounds releases OH and Cl radicals, recycles NO_x, and increases conventional hydroxyl and organic peroxy radicals (RO_x = OH + HO_2 + RO_2) by 0.8% to 21.4% (0.8-7.7% over coast and 2.6-21.4% over ocean), O_3 by 5.9% to 16.6% (6.9-14.6% over coast and 5.9-16.6% over ocean), and $PM_{2.5}$ by -1.2% to 8.6% (-1.2-6% over coast and 3.2-8.6% over ocean) at the surface in coastal and Western Pacific regions.".