

Interactive comment on “Investigation of ship-plume chemistry using a newly-developed photochemical ship-plume model” by H. S. Kim et al.

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First of all, thank you so much for your helpful comments and suggestions. In the revised manuscript (which will be submitted after the response phase), we will have improved the text, tables, and figures based on your comments and suggestions by eliminating, modifying, and adding several parts from/into the original manuscript. (The added/modified parts are shown in red in the revised manuscript). Prior to submitting the revised manuscript, we would like to reply to some of the questions raised by you below:

1. “The model is called a photochemical model in the title throughout the
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text, but it would be better described as a dynamics/photochemistry or metrological/photochemical model.”

Reply: We have changed this throughout the entire text.

2. “In particular, the distinction between this model and other box models needs to be made more clear. . . .The difference in NO_x lifetimes between this model and a box model are large, but these differences are minimized and confused (end of Section 5) by including comparison with power plants and the lack of importance for analyzing satellite data.”

Reply: The largest distinction between this work and other box models would be that in this work ship-plume NO_x lifetime was evaluated throughout the “entire ship-plume volume”, not simply on parts of a ship plume such as the ship-plume centerlines (Song et al., 2003a; von Glasow et al., 2003) or ship-plume transects by aircraft (Chen et al., 2005). Secondly, the developed ship plume chemistry/dynamic model has now been rendered more realistic. For example, in the previous studies (Song et al., 2003a,b; von Glasow et al., 2003; Chen et al., 2005), the models did not take into account the varying concentrations of background chemical species. In this study, we consider such effects by running a more box in the background (refer to Fig 1 and added Sect. 2.3 in the revised manuscript). The time-variant and location-variant background species concentrations are entrained into the ship-plume volume via the dilution process. The above-mentioned factors can affect the ship-plume NO_x lifetimes. We clarify these points further in the revised manuscript. Thirdly, as we mentioned in the text, we put a parameterization for the HNO₃ partitioning into sea-salt particles. Based on this, we can approximate the magnitude of reaction probability of HNO₃ into sea-salt particles. Regarding the differences in NO_x lifetime between this model and other model can also be explained in this context. At the end of Section 5, we put more discussions about the differences in NO_x lifetimes, and eliminated some discussions on analyzing satellite data.

3. "NO_x lifetimes are important for determining the effects of ship NO_x on O₃ levels over the oceans. A more useful discussion would explain why the lifetimes are different between the 2 models and the observations. Will this model, with a longer NO_x lifetime, predict different O₃ levels over the oceans?"

Reply: As mentioned at Reply 2, in this study ship-plume NO_x lifetime was evaluated throughout the "entire ship volume" (including the early ship-plume development stages, particularly between the ship location and transect A). In this regard, the NO_x lifetime should differ from those suggested by other modeling studies or observations. The longer NO_x lifetimes will certainly affect the ozone concentrations in the MBL. We have added some discussion regarding the influences of the varying NO_x lifetimes on the ship-plume ozone concentrations into the revised manuscript.

4. "Additionally, I am confused how the NO_x lifetime varies with atmospheric stability. NO_x concentrations are predicted to change with stability class, but the variations of lifetime with stability are not discussed. Also, are the stability classes observed here representative of many oceanic regions?"

Reply: This is an important point! The ship-plume NO_x lifetimes are a function of the stability class of the MBL, e.g.: (i) 3.67 hrs at the neutral stability class; (ii) 2.86 hrs at the moderately stable stability class; and (iii) 2.64 hrs at the stable stability class for the ship-plume we are currently analyzing. We have added this analysis into the revised manuscript. Actually, the most common (or likely) stability class in the remote MBL of world ocean would be neutral (in regard to this point, refer to Song et al., 2003a).

5. "The interpretation of the observations is confusing and sometimes inaccurate. For instance, the background SO₂ levels are listed as 400 pptv and the SO₂ data are described as too scattered to distinguish plume shapes. Both of these statements could be clarified by noting that the SO₂ values were usually below instrument detection limits (stated as 350 pptv in Brock et al, JGR 2004). As such, the background values and many (but not all) of the ship-plume enhancements cannot be interpreted without aver-

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aging and some discussion. Similarly, the PAN measurements were said to "generate little available data in the ship plumes" (pg 11715). This is confusing and misleading. A more accurate statement would be that PAN data were acquired once every 90s or longer, and few measurements were obtained in ship plume encounters that were often less than 60s in duration."

Reply: Again, thank you for raising good points. We revise the manuscript, reflecting your comments on the SO₂ and PAN measurements. However, in the case of the PAN measurements, the number of PAN measurement data points inside the ship-plume was quite small. For example, in the NOAA data archive, the reported time resolution of the PAN measurements is approximately 90 sec - 270 sec, whereas the ship-plume traverse times by WP-3D flights were ~20 sec at transect A with a plume width of ~2 km and ~120 sec at transect H, with a plume width of ~ 12km.

6. "The background NO_x and CO₂ (pg 11710) differ from that listed in Chen et al, JGR 2005, but data are said to be the same. Why is there a difference?"

Reply: In accordance with your suggestion, we began an account at the NOAA data archive and downloaded the official dataset. We determined that both the data (data from NOAA and data from the Iowa FTP server) were the same, with the exception of a few data points. We detected small differences in the NO_x and CO₂ concentrations, and have changed them in the revised manuscript.

7. "The interpretation that the HNO₃ data did not follow plume shapes is incorrect, and estimating HNO₃ from a difference of many measured and modeled species does not constrain HNO₃. . . The estimate of HNO₃ from NO_y-NO_x-PAN-NO₃-organic radicals contains so many unjustified assumptions and approximations that it cannot be used. . . . Lastly, the discussion HNO₃ estimated and HNO₃ measured is extremely confusing, as the 2 quantities are often called former and latter and it is hard to tell which is which.

Reply: The HNO₃ concentrations along the eight ship-plume transects do not have "very clear" plume or Gaussian shapes (Now, you can check those values in Figs. 7

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& 10 in the revised manuscript). This led us to use estimated HNO₃ concentrations in the original manuscript, since they showed better Gaussian plume shapes. However, as you mentioned, this also caused many uncertainties and was based on several unjustified assumptions (and thus could raise many troubles in the analysis). In the revised manuscript, we use the HNO₃ concentrations measured directly by the CIMS instrument on the WP-3D aircraft, and then again attempted to evaluate the reaction probability of HNO₃ onto sea-salt particles. The estimated magnitude of reaction probability appears to range between 0.5x10⁻¹ and 10⁻¹, which is consistent with what Chen et al. (2005) determined (check out the modified Fig. 10 and the relevant text).

8. "It isn't clear in Fig 13 which HNO₃ is plotted."

Reply: As mentioned in Reply 7, we now utilize only one type of HNO₃ concentration—directly measured HNO₃ concentrations.

9. "Most of these problems with data interpretation could have been eased considerably by consultations with those who obtained the measurements. In the acknowledgements, it was noted that the data were obtained from the FTP server at the University of Iowa. This is not the official or primary source for these data. . . . Access to the data is provided readily and eagerly, and acquiring the data from the official archive may help strengthen scientific analysis by ensuring that the data from these special research campaigns are used appropriately. Often times, the researchers who collected the data can provide additional insights into the measurement capabilities and limitations for these newly developed instruments."

Reply: As mentioned at Reply 6, we have established an account at NOAA and downloaded the official dataset from the NOAA ITCT 2K2 data archive. Additionally, while revising the manuscript, we will invite the instrument PIs to be co-authors of the manuscript, asking them for their counsel regarding the detailed data interpretations.

Minor comments:

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1) "The figures are very difficult to read. I recommend expanding the scales and enlarging the figures."

Reply: The fonts, scales, and symbols have been enlarged in the revised manuscript.

2) "Quotation marks are used in nearly every paragraph, and I'm not sure what they mean."

Reply: In the revised manuscript, we have tried to use quotation marks only where necessary (i.e., we have tried to minimize the use of quotation marks).

3) "O₃ and ozone used-pick on and use throughout"

Reply: Yes, we have now used "ozone" throughout the entire text.

4) "Pg 11701, line 26: replace MLB with MBL"

Reply: We changed this.

5) "Pg 11702, line 3: replace while with with".

Reply: We changed this.

6) "Pg 11702, line 17: replace absence with failure to account for"

Reply: We replaced this.

7) "Pg, 11703, line 10: replace "hotly-debated issue" with an issue of considerable scientific interest"

Reply: We replaced this.

8) "Pg, 11704, eqn 2: the collision rate for molecules with a surface is attributed to Schwartz 1986, but it is far older than that"

Reply: To the best of our knowledge, Schwartz's theoretical analysis was published in 1981 at Atmos. Environ. He was then awarded the Haggen-Smit prize with the 1981 publication in 1983 (we would think that this paper would be the most famous

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one). Therefore, we used this publication in our reference section (check out the new reference).

9) "Pg 11706, line 12: replace capped by "inversion height". . . with boundary layer is capped by temperature inversion at height h."

Reply: We replaced this.

10) "Section 3.1. It would be helpful to give a brief description of the location of the measurement (i.e. –off the coast of CA, 100 m above sea level)"

Reply: In the revised manuscript, we have added some descriptions of the location of the aircraft measurements.

11) "Pg 11708, line 10-15: I don't understand. The measurements were made with the same resolution inside outside plumes."

Reply: What we attempted to convey in this section was that when one uses photo-stationary state approximation to obtain adequate solutions for atmospheric species inside the ship plume, the input concentrations measured by many different instruments in the aircraft should be obtained at exactly the same time point. However, in reality, each instrument was independently operated (even if they were housed in the same aircraft), and would have different time resolution. Additionally, due to the detection limit of each observation technique and the temporary malfunction of some instruments, the measured species concentrations were not all available at exactly the same point of time of interest. Therefore, one should (or would) utilize an interpolation technique to obtain the input concentrations at exactly the same time point of interest. However, due to the non-linear (or non-Gaussian) nature of ship-plume chemistry, the interpolation can result in incorrect ship-plume concentrations. In the revised manuscript, we have attempted to express this point more clearly.

12) "Pg 11708, line 24: Times are unclear throughout the text. I believe noon means 12:00 local time or Pacific Daylight Saving Time (not standard time). Time should be

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clarified at first use, and then used the same throughout text."

Reply: The ship-plume experiment was conducted from 17:40 to 21:30 GMT. We clarified this in the revised manuscript.

13) "Pg 11709, line 11: include Chen et al. Delete last sentence."

Reply: We have deleted this.

14) "Pg 11709, lines 25-29. Why do the WP3 and NCEP lapse rate differ? Is the difference important. Also, Chen et al called the conditions "between neutral and unstable", which contradicts the moderately stable to stable conditions reported here. There should be a comment as to why the stability differs between the 2 studies, and also consequences of this."

Reply: We first evaluated stability class using the meteorological data measured by WP-3D aircraft in the MBL, where the ship-plume had developed. Although the temperature data were very scattered, it appeared that the stability classes would be "between moderately stable and stable". In the revised manuscript (Fig. 3), we selected the temperature-altitude data more carefully over the locations, and then attempted to again determine the stability class. The conclusion remains the same: it would be "between moderately stable and stable". As this result differs from the one reported by Chen et al. (2005), we wish to once more confirm our results using the NCEP data (an independent meteorological dataset). Again, the stability classes are "between moderately stable and stable". The different lapse rates are the consequence of different locations and different retrieval time of the NCEP data.

15) "Pg 11710, line 14-15: delete sentence beginning w/Again (redundant)"

Reply: We have deleted this.

16) "pg 11712, line 8-10: Replace "the volume of in plume data . . ." with each plume crossing occurred in approximately 1 min"

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Reply: We have replaced this.

17) "Pg 11714, line 23: Reference incorrect, as it describes a different instrument with differ ion chemistry. The ion chemistry is described Huey et al. Int. J. Mass Spectromm Ion Proc, 1996, and the instrument is described in Neuman et al, JGR, 2002."

Reply: Thank you for this correction. We have replaced this reference.

18) "Pg 11716, line 25: replace get improved with improve"

Reply: We have replaced this.

19) "Pg 11718, line 23: Chen et al estimated uptake coefficient"

Reply: We removed this sentence.

20) "Pg 11722: I am confused. How is OH determined? Earlier, you state that OH was not compared."

Reply: Here, all the OH concentrations are model-generated values.

21) "Pg 11722, line 18-19: remove #"

Reply: We have removed this.

22) "Pg 11723, line 11-12: remove sentence beginning with again (redundant)"

Reply: We have removed this.

23) "Pg 11725, last paragraph: I think is a key finding and one that distinguished this work from previous box modeling efforts. . . ."

Reply: We added some discussions into the revised manuscript regarding the general implications of this study.

24) Pg 11727: last paragraph is confusing. This appears to be a new discussion about the possible utility of the model. A stand-alone discussion section could be useful. This paragraph could be moved to the discussion section and introduced with "This

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dynamics/photochemistry model may be valuable for understanding the influences of ship emissions on aerosol and cloud formation. For instance, Russell et al. . . ."

Reply: We moved the last paragraph of the conclusion to new discussion section (Sect. 6).

25) "References: Instead of Brock et al 2000, 2003, the Brock et al JGR 2005 paper should be used, since it describes the instruments as they were used during this study."

Reply: Thank you for this correction. Brock et al., 2005 may be Brock et al., JGR 2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 11699, 2009.

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