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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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This manuscript demonstrates the utility of incorporating both turbulent dispersion and photochemistry in a model of the evolution of ship plumes over the ocean. The model results are compared to measurements from an aircraft that sampled a ship plume transported over the ocean. The comparison shows that this model captures the full spatial and temporal evolution of plumes. This work provides a valuable new tool for precisely determining changes to atmospheric composition and chemistry caused by emissions from ships. The paper is well-written and the description of the model is thoroughly detailed.

This work will be valuable to the research community once several omissions and in-

accuracies are addressed. The model could address many important questions and hold a greater appeal if the important findings were better emphasized, discussed, and put into a broader context. In particular, the distinction between this model and other box models needs to be made more clear. The model is called a photochemical model in the title and throughout the text, but it would be better described as a dynamics/photochemistry or meteorological/photochemical model. The difference in NOx lifetimes between this model and a box model are large, but these differences are minimized and confused (end of section 5) by including comparisons with power plants and stating the lack of importance for analyzing satellite data. NOx lifetimes are important for determining the effects of ship NOx 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 NOx lifetime, predict different O3 levels over the oceans? Additionally, I am confused how the NOx lifetime varies with atmospheric stability. NOx 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?

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

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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 HNO3 levels were low in the ship plumes (10s of pptv, Chen et al, JGR 2005) and near the instrument precision of 25 pptv for 1 s data. Averaging the data to 5 or 10 s clearly shows HNO3 formation in ship plumes, and HNO3 appears to have the same plume shape as NOx and NOy, contradicting the statement on pg 11714. The estimate of HNO3 from NOY-NOx – PAN – NO3 – organic radicals contains so many unjustified assumptions and approximations that it cannot be used. This difference calculation assumes that the NOy instrument samples and measures particulate nitrate quantitatively. This has never been demonstrated. It also assumes PAN concentrations in the plume that were never measured. And lastly, it assumes that all these measurements and model determinations are without significant bias or uncertainties, even at these low levels. The Nowak at al paper (JGR, 2004) that used the same data set showed that the sum of the individually measured reactive nitrogen compounds was less than NOy, and that the combined uncertainties were approximately 100 pptv at 350 pptv of NOy. Thus, this difference estimate of HNO3 is not useful at these low levels. Indeed, the very large difference between estimated HNO3 and modeled HNO3 in Fig 13 d in the freshest plumes is simply an artifact of the measurement uncertainties. Large differences arise when both NOy and NOx are large. Lastly, the discussion of 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. It isn't clear in Fig 13 which HNO3 is plotted.

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. Data should be obtained from the proper archive to guarantee that the data are the most current and to ensure that professional courtesy is maintained. The archive for the data is at the NOAA Earth System Research Lab (ESRL) Chemical Sciences Division (CSD) at

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www.esrl.noaa.gov/csd/tropchem. There, the data are carefully archived, regularly updated, and generally available. Also, it is worth noting the data policy on that archive, which states that use of the data "requires users to collaborate with the relevant instrument PIs during analysis, and presumes coauthorship will be offered on any scientific publications using 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.

Smaller points and typos: 1) The figures are very difficult to read. I recommend expanding the scales and enlarging the figures.

2) Quotation marks are used in nearly every paragraph, and I'm not sure what they mean. Sometimes I believe it is to indicate a word is used loosely, and sometimes for emphasis. Whatever the case, all quotation marks should be removed, and where they were used to represent a word that was ill-defined, then the word should be clearly defined.

3) O3 and ozone used – pick one and use throughout

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

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

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

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

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

9) Pg 11706, line 12: replace capped by the "inversion height"... with boundary layer

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is capped by a temperature inversion at height h.

10) Pg 11708, line 2: what does diluted completely mean?

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

12) Pg 11708, lines 10-15: I don't understand. The measurements were made with the same resolution inside and outside of plumes.

13) Pg 11708, line 24: Times are unclear throughout the text. I believe noon means 12:00 local time or Pacific Daylight Savings Time (not standard time). Time should be clarified at first use, and then used the same throughout text.

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

15) Pg 11709, lines 25-29. Why do the WP3 and NCEP lapse rates 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 the consequences of this.

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

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

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

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

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

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

22) Pg 11722, lines 18-19: remove #

23) Pg 11723, lines 11-12: remove sentence beginning with again (redundant)

24) pg 11725, last paragraph: I think is a key finding and one that distinguishes this work from previous box modeling efforts. More discussion is needed here. Is the stability likely to differ with location or season? Cold this info be useful to improve estimations of ship emissions contributions to background continental O3? Also, the observed NOx lifetime of 109 min is never discussed here as it is in Chen et al. What does it mean that the dynamics/photochemistry model disagrees with the observed NOx lifetimes even more than the box model? Is this a problem with the model, or with the interpretation of the observed NOx lifetimes?

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

26) 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.

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