

Interactive comment on “Source identification and budget analysis on elevated levels of formaldehyde within ship plumes: a photochemical/dynamic model analysis” by C. H. Song et al.

Anonymous Referee #1

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This manuscript reports a modeling study of the impact of ship emissions on the marine boundary layer CH₂O levels. This study utilized a photochemical box model with an implemented Gaussian dispersion scheme that has been used in several previous ship plume studies. The authors conducted simulations to investigate the relative importance of three CH₂O sources, i.e., CH₄ oxidation, ship emission, and oxidation of ship emitted NMVOC. These simulations were designed to represent various atmospheric conditions at various latitudes and under different atmospheric stabilities. In

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conclusion, the authors suggested that the enhanced shipping corridor CH₂O level can mostly be attributed the CH₄ oxidation by elevated OH levels, which is, in turn, a direct result of ship emissions of NO_x. The manuscript is generally well organized and the research method appears to be reasonable. This reviewer, however, has a serious concern about the major conclusion. The authors should re-examine their work and provide better explanations before the final publication of this manuscript.

The authors have stated the emission ratios for various NMVOC species in Table 1. The C₄ Alkane species have the highest values. It would be very helpful for the readers to know the magnitude of the ship emission impact on various NMVOC species, i.e., the simulated mixing ratios for each NMVOC species. Based on the levels given in Table 3, the rate of NMVOC reaction with OH would be a significant fraction of the CH₄ oxidation rate. The reaction rate coefficients are 3 – 4 orders of magnitudes higher for the NMVOC reactions than that for CH₄. The CH₂O yield (mostly through Acetaldehyde) can be significantly higher than unity. Thus, it is not easy to understand why the difference between case I and II is not observable in Figures 3 and 4. In addition, freshly emitted CH₂O can be a net source of HO_x. It is desirable for the authors to show the OH values for all three cases. As for the NMVOC contribution, the authors should conduct a detailed budget analysis for CH₂O, including a budget for CH₃O₂ and CH₃OOH to show the relative contributions from NMVOC and CH₄ and direct CH₂O formation throughout the NMVOC degradation steps. Based on the background mid-latitude conditions given in Table 3, a quick box-model calculation gives NMVOC contribution in the order of 10%. The equation (3) cited in the manuscript is neither rigorous nor practical (see details in specific comments). The term Φ is rather difficult to determine as it is a function of chemical conditions. Finally, the authors should also consider the background Acetone and Ketone in the analysis, since oxidation of these species can be a non-negligible source of CH₂O.

Specific Comments:

Page 4, line 22: “the removal of CH₄ can also . . .”, is this an over-simplified statement?

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Page 5, paragraph 2: This paragraph really casts doubts on if there is a CH₂O enhancement in the ship traffic corridor. The authors should re-organize this paragraph and clarify their points.

Page 7, line 16/17: OPE is not a direct observation.

Page 8, paragraph 1: The authors should provide more detailed discussions on the comparison between model and observations, shown in Figure 2. It should be pointed out that the level of agreement is different for different species and ship plume transects.

Page 11, line 8: "O(1D) radicals mainly react with the more ..." This is not correct, the main losses for O(1D) are the reactions with O₂ and N₂.

Page 16, equation (3): This equation is incorrect since there are important feedback reactions after CH₃O₂ + HO₂ and CH₃O₂ + CH₃O₂, which will produce CH₂O. The authors should have some discussion on the values of the CH₂O yield from the key NMVOC species from ship emissions. This equation should be revised or deleted. A better definition of NMVOC contributions is needed for the manuscript. The authors should trace sources of CH₃O₂ and CH₃OOH in terms of relative contribution from NMVOC and CH₄ oxidations.

Page 37, Table 3: The CO levels appear to be very high for the tropical case! The authors are referred to check NASA PEM-Tropics A and B observations. The other CO values are more consistent with the polluted regions. This reviewer questions if the authors should show the ship emission impact in polluted environments?

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 15441, 2010.