

## Author's comments to anonymous referee #2

First of all, thank you for your valuable comments and suggestions. In the revised manuscript, we attempt to improve the manuscript based on your comments and suggestions. Major changes made in the manuscript are as follows:

- (1) We re-drew Figs. 2 through 6.
- (2) We added Fig. 8.
- (3) We split original Fig. 3 into Figs. 3 and 4, in order to more clearly show two separate issues: the changes in the ship-plume HCHO concentrations (Fig. 3) and the source budget of the ship-plume HCHO concentrations (Fig. 4).
- (4) We removed the simulation results from neutral MBL condition for the ITCT 2K2 ship-plume case, in order to more consistently show the results from Fig. 3 to Fig. 9. In Fig. 6, we added the simulation results from stable MBL condition.
- (5) We decided to show the results for only six ship-plume transects in Figs. 5 and 6, in order to more succinctly present our simulation results.
- (6) We inserted color-codes into Fig. 6.
- (7) We re-constructed Sect. 2.3. Now, Sect. 2.3 has three subsections: (1) Estimation of the emission rates; (2) Model simulation for base case; and (3) Model simulation for constructed cases.
- (8) We re-constructed Table 3.
- (9) We shrank down many parts of the text.

Other added/modified parts in the manuscript are painted in a red color in the revised manuscript. Here, we would like to reply to some specific questions raised by you below:

### *General comments*

1. *“Kim et al., which is the companion study of this paper, claim that the presented ship plume chemistry model should be used to model the changes in ship-plume chemical compositions and to better evaluate the atmospheric impact of ocean-going ship emissions. While the model adequately simulates some aspects, a caveat should be mentioned, that the presented model simulations will always be limited to specific case studies for certain regions; one weakness of the case study simulations is the background which is often not very well known and initialized from a variety of different sources (CTMs, observations, etc.); this could cause inconsistencies or the neglect of seasonal variations in the background as done here. Therefore a full assessment of the global impact of ship emissions will in addition require global model studies and observations. The paper could therefore do more in establishing ties between global models and the model studies presented here. Overall, I can recommend publication of the paper in ACP once my comments below have been adequately*

addressed.”

- Obviously, the model has such limitations. We added some paragraphs into the text (refer to pp.7:21-8:5; pp.12:2-pp.12:8; pp.22:9-pp.22:10; pp.27:1-pp.27:3). Also, we attempted to establish a connection between this modeling work and 3-D global CTM studies (see pp.5:4-pp.5:11; pp.27:9-pp.27:17).

#### *Specific comments*

1. *“Abstract: the one main conclusions of the manuscript is that CH<sub>4</sub> oxidation by elevated levels of in-plume OH radicals was found to be the main factor responsible for the elevated levels of HCHO in the ship corridors. The authors should clarify that this conclusion refers to (it seems) a single ship under a certain meteorological condition. Similarly, the second main conclusion of enhanced HCHO levels in different regions seems to be based on case studies carried out under 10:30 am local time. While this is fine, the abstract (and summary) should avoid generalization of these statements that are not justified by the manuscript.”*
  - You are right! We modified the abstract and main text to reflect your comment. Please, check out pp.2:10-pp.2:16, pp.6:6-pp.6:8, and pp.27:1-pp.27:3
2. *“Pg 15444, line 14-25: This paragraph does not appropriately summarize the main conclusions of Marbach et al. Rather Marbach et al. already point to several of the key conclusions that are found here, so this study in many ways confirms some of the Marbach et al conclusions or indications. This should be made clearer. For example, Marbach et al find differences between the observations of NO<sub>2</sub> and HCHO and conclude that these differences have important implications for the source of the enhanced HCHO concentrations. From the differences between the simultaneously observed tropospheric column NO<sub>2</sub> values over the shipping route to those of HCHO they conclude that direct emissions of HCHO (source 1 of elevated HCHO in this study) or degradation of emitted NMHC (source 2 of elevated HCHO in this study) cannot explain the observed enhanced HCHO values and point to increased CH<sub>4</sub> degradation due to enhanced OH concentrations related to the ship emissions (source 3 of elevated HCHO in this study) Again on the same point, Marbach et al. conclude that ‘the CH<sub>4</sub> oxidation source is probably too weak to fully explain the observed values’. The authors should clarify their results in light of this statement. Do they disagree with it also in the context of global model simulations? If yes, why? Since the authors also exclude source 1 and 2, could other factors as speculated by Marbach et al. play a role? Then this should be brought forward to the abstract.”*
  - Our original intention was to discuss some points raised by reviewers and authors of

Marbach et al. (2009) on acpd and acp. But, it appears that the discussions would be complicated to readers and reviewers. Now, we tried to revise the text to clarify the points throughout the manuscript. Please, check out the red-painted parts of the revised manuscript.

3. *“As mentioned above, the paper could do more in comparing the results to previous global model simulations and conclusions, which would also make the paper more useful in a broader context. How would the results change if the emissions were instantaneously emitted on to a large grid box? Is it possible to assess this with the model presented here? If so this would be a valuable extension which could at least be mentioned in the outlook if it is beyond the scope for this study.”*
  - This issue was explored and discussed previously by Song et al. (2003a) and von Glasow et al. (2003). However, as you said, in order to make this manuscript more useful in a broader context, we put some more discussions on this issue into the text. Please, see pp. 5:2-pp.5:11 and pp.27:9-pp.27:17.
4. *“Pg 15445, line 14-21: rather than explaining the different options this model has, some more details (even if they repeat Kim et al.) on the model as used in the setup here would be helpful. The paragraph as it stands is not sufficient to understand the model simulations from this paper. Please extend. I would recommend to introduce a separate subsection ‘2.1 Model description’ and rename the current headline with e.g. ‘2. Model characteristics, evaluation and simulations’.”*
  - As mentioned above, we re-constructed Sect. 2. Also, Sect. 2.3 has three subsections: (1) Estimation of the emission rates; (2) Model simulation for base case; and (3) Model simulation for constructed cases. In addition, we put some more explanations about the model setups. Please, check out pp.7:15-pp.8:6.
5. *“Pg 15445, line 23 - Pg 15446, line 12: This paragraph should be moved from ‘2.2 Model validation’ to ‘2.1 Model description’.*
  - We moved this paragraph from Sect. 2.2 to 2.1.
6. *“Figure 2: The figure caption says that the NO<sub>x</sub> emission rates have been varied from 2.6-13.3gs<sup>-1</sup>, but it is not clear in the figure which lines or shaded areas correspond to this range. Also there are quite some discrepancies between observed and modeled values in particular for HNO<sub>3</sub> which should be discussed.”*
  - As mentioned above, we re-drew Fig. 2. Also, we put some discussions into Sect. 2.2 about the discrepancies, but many discussions about the discrepancies had already been made in

the previous publication (Kim et al., 2009). Please, check out pp.9:4-pp.9:10.

7. *“Pg 15448, line 10: I would recommend dividing the section on ‘Model simulation’ into two subsections, ‘2.2.1’ on the base-case (as it stands now) and ‘2.2.2 Constructed model simulations’ (i.e., move the model description from Section 3.2 but not the results to Section 2.2.2). In this way all model simulations are introduced in Section 2.2. which gives the reader more guidance to understand the results that are described in Section 3.”*
  - Thank you for your suggestions! As mentioned above, we re-constructed Sect. 2.3, reflecting your comments. Please, see Sect. 2.3.
8. *“Pg 15447, line 11 – Pg 15448, line 5: How do these values compare to the most up-to-date study on ship emissions by the International Maritime Organization (IMO)? The Second IMO GHG study provided an update of emission factors and total emissions separated into various ship types and species: Buhaug, Ø., J. J. Corbett, Ø. Endresen, V. Eyring, J. Faber, S. Hanayama, D. S. Lee, D. Lee, H. Lindstad, A.Z. Markowska, A. Mjelde, D. Nelissen, J. Nilsen, C. Pålsson, J. J. Winebrake, W.-Q. Wu, and K. Yoshida, Second IMO GHG study 2009; International Maritime Organization (IMO) London, UK, March 2009, see <http://www.imo.org/Environment/> The assumptions here should be put into context of these results, e.g. the NMVOC emission factor was given as 2.4 kg of NMVOC per tonne of fuel and NO<sub>x</sub> for Slow-speed diesel engines 90-85 and for Medium-speed diesel engines 60 to 51 kg per tonne of fuel. The IMO study therefore indicates that the NO<sub>x</sub>:NMVOC ratio varies for different ship types which should be considered for the constructed cases. It should also be made clear in summary and abstract that the base-case study is valid only for a certain ship.”*
  - Ship emission factors are highly uncertain. We tried to add information into the text. Please, see pp.10:7-pp.10:11. As you pointed out, the ratios of NO<sub>x</sub> to NMVOC range between 35.4 and 37.5 and between 21.2 and 25.0 for slow-speed and medium-speed diesel engines, respectively. Our ratios appear to fall in-between.
9. *“Pg 15450, line 10-12: this seems incorrect.”*
  - We corrected it. Primary reactions of O(<sup>1</sup>D) are with N<sub>2</sub> and O<sub>2</sub> (quenching reactions). Please, check out pp.13:16-13:18.
10. *“Pg 15450, line 1-28: a lot of this is repetition of issues that have already been discussed in the introduction, so should be removed here. Rather this section would be more readable if it started with the actual results before they are discussed (i.e. directly start this section*

with p. 15451, l. 5).”

- We shrank down some parts. Please, check out pp.13:9-pp.13:20.
11. *“Figure 3: It is hard to understand this figure with the limited explanation that is given. Please expand and maybe draw the readers’ attention specifically to some of the lines shown in the plot (e.g. compare line X with line Y at the end of the sentence in line 13). Maybe this figure should also be better split into two figures that show the first two rows and the second two rows in separate figures.”*
- As mentioned in the beginning, we split original Fig. 3 into Figs. 3 and 4, and also expanded the sizes of Figs. 3 and 4.
12. *“Pg 15453, line 9-29: as for Figure 3, the description of this figure has to be improved to give the reader a bit more guidance in understanding the results. Some of the panels are really small (I can hardly see any differences in Figure 4a between the cases).”*
- Again, we attempted to improve Fig. 3 (splitting into two and expanding the sizes of Figs.). Also, we put some more descriptions on Fig. 3 into the text. Please, check out pp.13:21-pp.13:23 and pp.14:3-pp.14:7.
13. *“ Figure 5: now the figure caption refers to (a) OH etc whereas in Figure 4 (a), (b) etc was referring to the individual rows. A similar format would help; also write in figure caption OH red line, methane lifetime blue and HCHO production rate green line (same in Fig. 4).”*
- As mentioned in the beginning, to show the simulation results more consistently, we removed the results from neutral MBL conditions from Fig. 3 to 8, and newly added the results from stable MBL condition into Fig. 6. Also, we changed the caption for Fig. 6.
14. *“Pg 15454, line 5: while equations 1 and 2 are clear from the reactions given in Table 2, this is not clear for equation 3. Provide details that confirm this equation is correct; the given text is rather confusing.”*
- Eq. (3) is a conceptual expression for the HCHO formation rate. Actual equation we used in this study was the following one:

$$\begin{aligned}
F_{HCHO} = & k_{CH_3O_2+CH_3O_2}[CH_3O_2]^2 + k_{CH_3OOH+OH}[CH_3OOH][OH] + k_{CH_3O+O_2}[CH_3O][O_2] \\
& + k_{CH_2OH+O_2}[CH_2OH][O_2] + k_{RAN1+NO}[RAN1][NO] + 0.5k_{ISOP+O_3}[ISOP][O_3] \\
& + 0.9k_{RIO2+NO}[RIO2][NO] + k_{INO2+NO}[INO_2][NO] + 0.5k_{MVK+O_3}[MVK][O_3] \\
& + 0.3k_{VRO2+NO}[VRO2][NO] + k_{MVN2+NO}[MVN2][NO] + 0.65k_{MVCR+O_3}[MVCR][O_3] \\
& + k_{MAN2+NO}[MAN2][NO] + k_{ETHE+O_3}[ETHE][O_3] + 2k_{EO2+NO}[EO2][NO] \\
& + 2.4k_{EO2+EO_2}[EO_2]^2 + 0.525k_{ALKE+O_3}[ALKE][O_3] + k_{PO2+NO}[PO2][NO] \\
& + k_{PRN1+NO}[PRN1][NO] + k_{CHO_2+NO}[CHO_2][NO] + k_{CHO_2+NO_2}[CHO_2][NO_2] \\
& + k_{CHO_2+SO_2}[CHO_2][SO_2] + k_{MCO_3+CH_3O_2}[MCO_3][CH_3O_2] + k_{MCO_3+CH_3O_2}[MCO_3][CH_3O_2] \\
& + J_{MCP}[MCP] + 0.5k_{MCP+OH}[MCP][OH] + k_{EP+OH}[EP][OH] + 2J_{EP}[EP] \\
& + k_{HACO+NO}[HACO][NO] + k_{HEP+OH}[HEP][OH] + 2J_{HEP}[HEP]
\end{aligned}$$

Although this is the true expression we used in this study, we felt that showing the entire equation in the manuscript appears to be clumsy. That was why we used a rather conceptual expression of Eq. (3). Now, Eq. (3) is modified. Please, check out Eqs. (3), (3-1) and (3-2). Also, see pp.17:14-18:3.

15. "Pg 15458, line 17-21: it seems that the background conditions are chosen to be the same for all seasons. This is obviously a significant weakness and caveats should be mentioned."
  - As mentioned in the previous replies, we discussed the weakness and caveats of the current modeling studies throughout the revised manuscript. Please, check out pp.7:21-8:5; pp.12:2-pp.12:8; pp.22:9-pp.22:10; pp.27:1-pp.27:3.
16. "Pg 15463, line 1: the first sentence sounds like this is a result from this paper. Make clear that this is a result from previous studies."
  - We modified the sentence. Please, see pp. 26:16-pp.26:18.
17. "Pg 15463, line 1-16: The majority of the results are derived from the base case which is examined for a certain ship and a certain meteorological situation. Additional sensitivity simulations are carried out for 10:30am local time. It should be made clearer in the summary and abstract which results are derived from the base case and which for the extended set. All figures are shown only for the base case, and the detailed analysis that is presented under Section 3.1 is not repeated for all sensitivity scenarios; rather for those only the HCHO enhancement is studied. This needs to be much better summarized and a generalization of statements avoided."
  - Again, as mentioned in the previous replies, we tried to put some discussions on such limitations of the current modeling study. Please, refer to pp.7:21-8:5; pp.12:2-pp.12:8; pp.22:9-pp.22:10; pp.27:1-pp.27:3.

18. *"Pg 15463, line 17 - Pg 15464, line 11: This is all rather speculative and shouldn't make up half of the summary."*

- We shrank down some parts of the text.

#### *Minor comments*

1. *"Pg 15442, line 4: 'predicted by global 3-D chemistry-transport models' should be replaced with 'simulated by global 3-D chemistry-transport models (similar replace or remove predicted in the context of model simulations throughout the manuscript)."*

- We replaced them throughout the manuscript.

2. *"Pg 15443, line 20: 'vertical columns' should be replaced with 'tropospheric columns'"*

- Thank you for your correction. We replaced it. See pp.4:15.

3. *"Pg 15443, line 24: The sentence 'Moreover, if the main...' should be rewritten."*

- We re-wrote the sentence.

4. *"Pg 15444, line 6-8: The Corbett and Koehler, 2003 reference is on ship emissions, while in the context of this sentence it reads like this paper is on CH<sub>4</sub> destruction in the MBL."*

- We agree with the point. Please, see pp. 5:1-pp.5:2.

5. *"Pg 15444, line 9: TBL?"*

- We replaced it with PBL and MBL. Please, check out pp.5:3-pp.5:4.

6. *"Pg 15444, line 9-13: The paragraph on the Hoor et al paper is confusing. Global models consider non-linearity and chemistry-climate interactions, but so far do not include a parameterization or modeling of subgrid scale processes in ship plumes. This should be clarified."*

- We tried to clarify this point. Please, refer to pp. 5:4-pp.5:11.

7. *"Pg 15444, line 20: 'Considering....': for readability, start new paragraph."*

- We separated the paragraph.

8. *"Pg 15460, line 6: 'observed' should be 'simulated'"*

- We replaced it.