**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.

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

1. "The model also had some modest success in simulating the plume spatial distribu-

tion of NOx, NOy, O3, HNO3, and H2SO4. The estimated correlation coefficients with the observations ranged from 0.66 to 0.85. ..... Potentially this model can be useful in terms of devising parameterized schemes to help the global and/or regional models to better deal with sub-grid processes, if the model is capable of accurately representing the plume chemical and dynamical processes."

Reply: Although there remain several uncertainties in the ship-plume dynamic/chemistry modeling (these issues are discussed further in the revised text), we would assert that our model predictions agreed greatly with the observations. In actuality, it has been shown to be extremely difficult to accurately predict the plume chemical composition using plume chemistry/dynamic models (e.g., refer to Karamchandani et al., 2000; Sillman, 2000). If one compares the works between the above-mentioned modeling efforts and ours, it can be demonstrated that our modeling work was in much better agreement with the observed concentrations, not only in terms of "correlation coefficients", but also in terms of "errors and biases", shown in Table 3.

2. "The comparisons displayed in Fig 4 though 8 raised some serious concerns about the model performance. For example, the largest model biases in NOx are seen in the four plume transects closest to the ship, where the chemistry is believed to be most intense and highly sensitive to absolute NOx level (Chen et al., 2005). This model bias is likely to have influenced the OH prediction and propagated to other comparisons, e.g., H2SO4 and HNO3."

Reply: Relating to Reply 1, there are some discrepancies that occurred between the model-predicted and measured NOx and NOy concentrations, primarily at the first three transects from A to C. In the revised manuscript, we discuss further the possible causes of the discrepancies: (i) influences from the other emission sources (the most likely); (ii) uncertainties in the ship emissions and stability class of the MBL; and (ii) turbulence effects induced by aircraft during the measurements. Regarding the error propagation in the OH concentrations, it is expected that there should be discrepancies in the OH concentrations at transects A to C due to the different levels in NOx, and thus

be also in the HNO3 and H2SO4 concentrations. We discuss this further in modified Figs. 4 and 5 and improved Sect. 3.3. Please, check them out.

3. "In addition, the authors should explore to what extent the different NOx lifetimes from the previous study can be explained by NOx prediction bias. The authors should test if the model bias resulted from the incompleteness or inaccuracy in model chemistry or if the Gaussian dispersion scheme is overly simplified for the plume dispersion process. One cannot help wondering how accurate the actual atmospheric plume dilution processes can be represented by the Gaussian scheme which is based on discrete satiability classes."

Reply: Basically, you are right! We conduct several model sensitivity runs, and have added some further discussions regarding the variability in NOx lifetimes into the revised text. With regard to the accuracy of the chemical and dynamic components incorporated in our study, it is difficult to assess the accuracy of both the components. (We also think that this type of study might be slightly beyond the scope of this work, partly because for the purpose of testing the accuracy of the chemical and dynamic components of the model we may require more sophisticatedly-designed plume composition data with more homogeneous background concentrations and perfect information on the meteorological conditions and point source data). Again, although the NOAA ITCT 2K2 ship-plume observation data might be the best one currently available, there are still many unknown and uncertain factors to completely test the accuracy of the both components (also, including possibly varying stability classes of the MBL). Some more reasons will also be mentioned in Reply 4.

4. "The author's explanation of influence by other sources appears to be inconsistent with the fact that the more diluted plume transects agreed better with model."

Reply: The influence of the other ships (or other sources) was previously addressed by Chen et al. (2005). This was inferred by the fact that the background NOy (mostly, NOx) concentrations close to the ship location (particularly, transects A to C) were

higher than those in the downwind areas (say, transects D to H). The effects of the high background concentrations are accounted for in our modeling framework, i.e., the background concentrations varying along the plume travel direction from transects A to H (also, refer to Reply 1) below). However, further difficulties are presented by the fact that the background volumes entrained into the plume volume do not evidence uniform background concentrations (rather have spotted elevations), for example, of NOx and NOy, particularly around the location close to the ship, owing to the influences of other ships (or other sources). You may be able to see some multi-peaks in panels (a), (b), and (c) of Figs. 4 and 5. Such peaks appear to be influenced by the entrainment of the spotted background elevations. We cannot consider these situations in our current model framework (nor can other models), and this may, therefore, be considered an obvious limitation of the current study.

5. "It is interesting that the HNO3 assessment resulted in an HNO3 reaction probability of less than 10-3, which is about 100 times smaller than the estimated by Chen et al, (2005).". ... "The estimated reaction probability would be much higher in the authors compared only with the directly measured HNO3. The author should have commented on the assessment by Chen et al. (2005) on the consistency between NOy and HNO3 measurements."

Reply: In the original manuscript, we determined that the HNO3 concentration profiles along the eight ship-plume transects by WP-3D aircraft did not evidence very clear plume or Gaussian shapes (they are very noisy!). This compelled us to use "estimated HNO3 concentrations". However, this analysis is also subject to many uncertainties (and thus can cause many troubles in analysis), as pointed out by both reviewers. In the revised manuscript, we utilize the HNO3 concentrations measured directly by the CIMS instrument on WP-3D aircraft, although they evidenced very scattered (and not very clear Gaussian) distributions. We then attempted again to evaluate the reaction probability of HNO3 on sea-salt particles. The estimated reaction probability appears to range between 0.5x10-1 and 10-1, which are consistent with what was found by

Chen et al. (2005). Currently, we have added the modified figures (Figs, 7 and 10) and relevant discussions into the revised text.

6. "Equation (2) may be inadequate for assessment of the HNO3 scavenging rate and may lead to significant overestimates for the sea-salt cases."

Reply: We do not understand precisely what the reviewer has pointed out here. The reviewer's point would be, we guess, that Schwartz kinetics usually generates larger mass transfer coefficients than do other kinetics (e.g., Fuchs-Sutugin kinetics). If this is the reviewer's point, then yes, it is perfectly true! Rigorously, the heterogeneous mass transfer rates between gas and particles are proportional to the "second moment" for the kinetic regime particles (say, Kn>10), whereas they are proportional to the "first moment" for the continuum regime particles (Kn<0.1) (Song and Carmichael, 2001). Sea-salt particles are in transitional regime, but could be closer to continuous regime particles. Were aerosol size distributions for "sea-salt particles" available, we could go with more rigorous kinetics. However, in cases in which only aerosol surface areas for sea-salt particles were available (90 um2/cm3) (in other words, it was impossible to separate sea-salt size-distributions from the aerosol size measurements), Schwartz kinetics would be the only option. The difference between the two approaches would be 2- or 3-fold, not an order of magnitude. As we mentioned in the original text, our intention is to approximate the magnitude of reaction probability of HNO3 into sea-salt particles.

7. "Another point worth noting in that the author did not provide and assessment for the validity of model estimated particle nitrate content. Furthermore, there is a large difference between the "estimated HNO3" and the directly measured HNO3."

Reply: As we mentioned in Reply 5, these could be examples of the troubles we might encounter, should we have stuck to the analytical method presented in the original manuscript. Again, in the revised manuscript, we utilize only one type of HNO3 concentration – namely, HNO3 concentrations measured directly by the CIMS instrument.

8. "In the acknowledge section, the authors indicated that the observational data was obtained from University of Iowa, instead of the official NOAA data site. This raises serious concerns that if the data used in this analysis is the final data and if the NOAA data protocol was followed."

Reply: In the course of revising the manuscript, we started an account at NOAA and downloaded the official dataset from the data archive. We found that both the data (data from NOAA and data from a web site at the University of Iowa) were nearly identical, with the exception of a few data points. Additionally, while revising the manuscript, we will invite the instrument PIs to be co-authors of the manuscript, asking them for some counsel regarding the data interpretations in detail.

Minor comments:

1) "In the introduction section, the authors attempted to address the difference between this study and that by Chen et al. (2005). The authors should state that these two studies have/had different objectives. As such, the authors should highlight the difference between this new model and those used in Song et al. (2003a, b) in terms of the chemistry and plume dispersion scheme.... The major model difference here is that the current study incorporates a Gaussian dispersion scheme into the model to represent the plume dilution processes..... the authors should highlight the difference between this new model and those used in Song et al. (2003a, b) in terms of the chemistry and plume dispersion scheme. The authors should discuss the implications of these differences to their modeling results."

Reply: Actually, the new model features several different aspects. The most salient difference would be that the new model can consider the ship-plume chemical/physical aging over the "entire ship-plume volume", and thus can evaluate, for example, NOx lifetimes over 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 eight ship-plume transects by aircraft (Chen et al., 2005). Secondly, the model now becomes

more realistic. For example, in the previous modeling studies (Song et al., 2003a,b; von Glasow et al., 2003; Chen et al., 2005), the models did not consider the variations in the background chemical species concentrations. In this study, we have considered such effects by running another box in the background (i.e., outside the ship-plume; refer to Fig 1 (c) and relevant text in the revised manuscript). The time-variant and location-variant background species concentrations are entrained into the ship-plume volume via the dilution process in the modeling. We clarify these points further in the revised manuscript. Thirdly, as we mentioned in the text, we put a parameterization for the HNO_3 partitioning into sea-salt particles. Based on this, we can approximate the magnitude of reaction probability of HNO_3 into sea-salt particles.

2) "In the H_2SO_4 comparisons, the author stated in line 26, page 11716 that "Although the observed and model-predicated SO_2 and OH concentrations were not compared in this study, the H_2SO_4 comparisons suggest that our ship-plume photochemical model reproduces both the ship-plume SO_2 and OH concentration reasonably well". This reviewer believes that this statement lacks scientific rigor. This reviewer believes that this statement needs to be supported by independent comparison of SO_2 and OH."

Reply: Basically, this is correct. This part has now been removed from the original manuscript.

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