Atmos. Chem. Phys. Discuss., 9, C2423–C2427, 2009
www.atmos-chem-phys-discuss.net/9/C2423/2009/

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 #2

Received and published: 2 July 2009

Major comments:

This manuscript presented a modeling study of the evolution of a ship plume observed during the NOAA ITCT-2K2 airborne field campaign. This study used an emission based box model with detailed chemistry and Gaussian dispersion schemes, which is quite similar to that described in Song et al. (2003a, b). The modeling results were assessed through comparisons with the in-situ observations. The modeling results again demonstrated that the ship emitted NOx can be effectively and rapidly removed by the plume photochemical process. The model also had some modest success in simulating the plume spatial distribution of NOx, NOy, O3, HNO3, and H2SO4. The estimated

correlation coefficients with the observations ranged from 0.66 to 0.85. Furthermore, the authors attempted to address the loss mechanism for HNO3 as formed through oxidation of the ship emitted NOx. Through the comparison with the observed and the "estimated" HNO3, the authors derived the reaction probability of HNO3 onto sea-salt particles to be less than 10-3. Although the manuscript is generally well written and model calculations are rigorous, the analysis and interpretation of the comparison between the observations and the model prediction are less than convincing. Therefore, this reviewer cannot recommend this manuscript be published unless several critical issues are adequately addressed.

The "photochemical ship-plume model" that the authors developed contains both photochemistry and dilution process driven by a Gaussian dispersion scheme, which allows simulation/prediction made from emissions. 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. The authors made an argument that their model "showed good agreement" with the observations. The comparisons displayed in Figure 4 through 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 NOx bias is likely to have influenced the OH prediction and propagated to other comparisons, e.g., H2SO4 and HNO3. In addition, the authors should explore to what extent the different NOx lifetimes from the previous study can be explained by the 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. These critical issues will determine if this "photochemical ship-plume model" can be used for quantitative assessment of

ship plume evolutions. 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.

It is a generally accepted notion that the in-plume photochemical destruction can effectively shorten the NOx lifetime. There is, however, a significant uncertainty in the loss processes of the HNO3 formed within the plume (Chen et al., 2005). It is commendable that the authors attempted to further assess the HNO3 loss mechanism. 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 estimate by Chen et al. (2005). The author should have discussed and contrasted these assessments and provided plausible explanations. This reviewer believes that there are a number of factors, including the difference in OH and NOx levels between conditions for this study and those for the Chen et al. study. Equation (2) may be inadequate for assessment of the HNO3 scavenging rate and may lead to significant overestimates for the sea-salt cases. Of even more serious concerns, the authors opted to choose an alternative standard for HNO3 comparisons. As shown in Figure 10, the authors compared the model predicted HNO3 with the direct HNO3 observation and with HNO3 derived from NOy. The estimated reaction probability would be much higher if the authors compared only with the directly measured HNO3. The authors should have commented on the assessment by Chen et al. (2005) on the consistency between NOy and HNO3 measurements. It is rather puzzling that the authors stated (started in line 26, page 11714) that the directly measured HNO3 was used only as reference data, "since they did not show plume shapes (presumably Gaussian) along the plume cross sections". Direct measurements of HNO3 indicate that it is a small component of NOy. As such, a significant uncertainty is inherent in the derivation of HNO3 by differencing NOy and the individual NOy species. Another point worth noting is that the authors did not provide an assessment for the validity of model estimated particle nitrate content. Finally, the comparison between model predicted and observed NOy showed very significant differences, especially for the plume transects closer to the ship. All these points argue

against use of the so called "estimated HNO3". Furthermore, there is a large difference between the "estimated HNO3" and the directly measured HNO3. Thus, they cannot be both valid. The authors should consult with the instrument PI as which of them is better suited for model comparison and evaluation of the HNO3 reaction probability.

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.

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. Chen et al. (2005) intended to use model constrained by the actual observed ship plume conditions to evaluate the early hypothesis proposed by (Song et al., 2003a, b) that plume NOx lifetimes can be significantly shorter than those in MBL. In that case, the use of observations to constrain the model enabled the authors to bypass the complicated mixing processes. Both time dependent and steady-state models were used by Chen et al. (2005). The major model difference here is that the current study incorporates a Gaussian dispersion scheme into the model to represent the plume dilution processes. 2. As the authors tend to emphasize, this study was based on a newly developed model. 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 authors should discuss the implications of these differences to their modeling results. 3. In the H2SO4 comparison, the authors stated in line 26, page 11716 that "Although the observed and model-predicted SO2 and OH concentrations were not compared in this study, the H2SO4 comparisons suggest that our ship-plume photochemical model reproduces both the ship-plume SO2 and OH concentrations reasonably well". This reviewer believes that this statement lacks scientific rigor. This reviewer believes that

this statement needs to be supported by independent comparisons of SO2 and OH.

Please also note the Supplement to this comment.

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