

***Interactive comment on “Detailed comparisons of airborne formaldehyde measurements with box models during the 2006 INTEX-B campaign: potential evidence for unmeasured and multi-generation volatile organic carbon oxidation processing” by A. Fried et al.***

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Received and published: 31 October 2011

Responses to Reviewer's Comments and changes to paper

We wish to thank both reviewers for very thoughtful and insightful comments. Accordingly, we have made changes in many cases.

Modifications by Authors

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1. We included Glenn Diskin and Glen Sachse at NASA Langley in the author list since their CO measurements were important in our analysis.
2. We slightly modified our analysis procedure regarding the Mexico City out flow analysis. Rather than compare Master Chemical Mechanism (MCM) results to steady-state results in such plumes as we originally presented, we have incorporated a more direct comparison where MCM runs using complete chemistry and input constraints were compared to other MCM runs using various scenarios. Although the major results and conclusions remain the same, this more direct comparison allowed us to further assess the role of multi-generation hydrocarbon processing.
3. Since the present study was also part of the MILAGRO study we changed the title to include this and we reworded it slightly to emphasize the impacts of our findings related to unmeasured and multi-generation VOC compounds.

Response to Reviewer #1

The shortcoming raised by the reviewer regarding recycling of OH has only been found to be important only under very low NO conditions (typically less than 20 pptv) in the presence of high amounts of hydrocarbons. Under these conditions isomerization of large organicRO<sub>2</sub> radicals like that from isoprene will recycle back to HO<sub>2</sub>, which because of its affect on the HO<sub>x</sub> budget could affect CH<sub>2</sub>O production. In the Mexico City outflow plumes the median NO mixing ratio binned by processing time for the times of prime interest (10-35 hours of processing) was 246 pptv to 70 pptv. Nevertheless, we investigated the effects of such isomerization by including such reactions in the MCM runs, and this resulted in negligible additional CH<sub>2</sub>O production. We added a discussion of this and pertinent references on OH recycling at the end of Section VI.

Specific Comments

1. We have added the information requested in the abstract regarding the geographical study area and the boundary layer focus.

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2. We included a reference to the Stickler et al. 2006 paper in the Introduction.
3. The reviewer's comments (#3,7,8) regarding model uncertainties from erroneous and/or incomplete chemistry on pages 9900, 9918-9919 and 9924 have been addressed by inclusion of appropriate statements on the various pages.
4. We added a statement relating the well-understood part of CH<sub>2</sub>O chemistry due to CH<sub>4</sub> oxidation on page 9901.
5. In Fig. 9 CH<sub>2</sub>O measurements > 6 ppb are already displayed by a single color symbol and comparisons at very high concentrations are shown in Fig. 10, so no changes were added to the manuscript.
6. On page 9917, line 20: Although we agree with the reviewer that the results of this paper suggest problems with lumped mechanisms, we have not really carried out a systematic head-to-head comparison between explicit and lumped mechanisms here and therefore cannot make such definitive statements. Instead, we made the following statement in this section: "Although we have shown the importance of incorporating explicit chemical mechanisms that involve multi-generation hydrocarbon processing and a comprehensive suite of measurements in such complex regimes, results of this study do not directly test differences between explicit and lumped mechanisms, such as employed in the MCM and box model calculations, respectively. Such head-to-head comparisons will be the topic of another paper."

#### Response to Reviewer #2

1. While we agree with the reviewer that the manuscript is a little long, it is not excessively long (only 17 typeset pages of text and 4 typeset pages in the Appendix). This length is inline with many papers published by ACP. Cutting the length would eliminate important information and this would dilute the content too much. This would result in a paper that could not adequately show and discuss the longstanding issues related to boundary layer model CH<sub>2</sub>O underestimations. Therefore, we have not cut the paper

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down in size, but have attempted to address the reviewer's specific concerns regarding organization in many cases. Specific changes are discussed below.

2. I am not sure what the reviewer is referring to in his question regarding "...which of the CH<sub>2</sub>O measurements that have been reported before", and this makes it impossible to address a specific concern. The Introduction on pages 9890 – 9893 provides a very clear and concise discussion of many previous measurements and comparisons with models.
3. I am not clear what the reviewer is referring to in his request to show a representative graph of species evolving with time. Figure 11 already very nicely shows such evolution in the CH<sub>2</sub>O measurement/model ratio discrepancy in the near field within a few hours of the source and Figures 13 and 14 show this behavior in the far field from Mexico City outflow. Although we have not added any additional figures to this end, we have added in Section IV (Measurement-Steady State Box Model Comparisons) a brief summary of the diurnal steady state (DSS) approach. This should address the reviewer's concern regarding the DSS approach right up front.
4. We have added a statement in the summary section that multi-generation oxidation processes identified by the Leeds Master Chemical Mechanism can account for the majority of the discrepancy.
5. We welcome the reviewer's attention to our uncertainty analysis, but disagree with his/her statement that the uncertainties in the Appendix are not in agreement with those used in the measurement/model ratios. The reviewer may be getting confused with the range of model constraint uncertainties presented in the Appendix for different regions with the actual specific model uncertainties used in the calculation for the ratio uncertainty. We have added a sentence in the Appendix to clarify this. Nevertheless, to show that the ratio uncertainties are being calculated correctly, let's take one specific data point. Here we consider the first altitude bin (0.25 km) for the Pacific Ocean ratio plot in Fig. 8., which shows in the plot a range of 0.59 to 1.41 for the combined

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measurement and model ratio (random) uncertainty. The first point in this bin has a  $2\sigma$  measurement precision of 46 pptv for a measured value of 353 pptv and corresponding model values of 55 pptv and 237 pptv. The combined measurement-model uncertainty for the ratio ( $353/237 = 1.49$ ) was calculated from:

$$1.49 * [ (46/353)^2 + (55/237)^2 ]^{1/2} = 0.40$$

The average of all such combined random uncertainties was then calculated for this altitude bin, and resulted in a value of  $\pm 0.41$ . When referenced to a measurement/model ratio of 1.0, this results in limits of 0.59 to 1.41.

6. The reviewer raises the question how the 8-35% model uncertainty over the continental U.S. and Mexico during the spring of 2006 in the present study relates to the 24% uncertainty published by Frost et al., which covers the North Atlantic Ocean during September 1997. The Frost model random model uncertainty estimate ( $2\sigma$ ) of 24% was an estimate based upon the random input uncertainties from the measurements on the NOAA P3 at that time and an overall median value was presented. The model uncertainties in the present paper are different from Frost et al. for a number of reasons: 1) the model input uncertainties for each important measurement are better characterized; 2) the instruments have improved performance since the 1997 Frost study; 3) the spatial coverage and time of year are different between the two studies; and most importantly 4) individual point-by-point model uncertainties were calculated and used rather than a single median value. This is a good question and we have added the above text in the Appendix to explain such differences.

7. The 8% model constraint uncertainty occurs in the boundary over the U.S. and Mexico. Although the reviewer is correct in asserting that the total photolysis rate uncertainties (which includes model constrained uncertainty plus model kinetic uncertainty) should be larger than this, we are only considering here the model constraint uncertainty. This is the model input uncertainty due to the total actinic flux measurements, which ranges between 4 and 5.8%. As stated at the beginning of this paragraph, the

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photolytic rate uncertainties, which includes the uncertainty in the molecular parameters, are only included in the model kinetic uncertainty. A few sentences were added in this section to further clarify this. We are not sure what the reviewer is asking regarding OH errors, but yes the calculated OH does respond to the kinetic uncertainties.

8. The reviewer questions how the various uncertainties presented relates to the combined model ratio uncertainty of 1.18 for the upper quartile of all the boundary layer measurements. By prefacing this with our systematic measurement uncertainty, the reviewer appears to confuse our systematic estimates with the combined imprecision estimates from both the measurement and model, which is what we are trying to state here. To clarify this, we have changed the wording in the text in Section IV to the following:

It is useful to keep in mind that the median value for the combined estimated measurement-model ratio uncertainty in the boundary layer is  $\pm 0.13$ , and thus many of the averaged ratios over these domains are systematically high. As discussed in Appendix A, the combined measurement-model uncertainty (measurement precision combined with the model constraint uncertainty) for both the differences and ratios are calculated for every comparison point on the hydrocarbon time base.

We have adopted the median value here instead of the upper quartile (75 percentile value) to be more consistent with other discussions. We have also added a sentence in the Appendix in the uncertainty section to further clarify this. This should thus also clarify the reviewer's next concern related to the median value of 13%.

9. The reviewer raises an excellent point regarding our mention of combined systematic error estimates without the rationale for using the smaller imprecision error estimates. We added some sentences on page 9900 to justify this and added a brief discussion in the Introduction to re-emphasize that we are trying to identify sampling regimes where the combined measurement and model imprecisions cannot explain the measurement-model differences (i.e., we are trying to identify the presence of systematic differences).

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10. The reviewer's concern regarding the introduction of diurnal steady state has been addressed in relation to item 3 above at the beginning of Section IV.

11. The points in Fig. 11b, which refer to those in Fig. 11a, are very easy to discern by their ethene production percentage and their photochemical processing times and thus we are not clear about the point of confusion. For example, the maximum in the measured and modeled CH<sub>2</sub>O mixing ratios in Fig. 11a clearly refers to the point on the 1:1 line in Fig. 11b at a processing time of 2.2 hours. Also from the text, we do not attempt to pinpoint which Lagrangian calculation is better since the NO<sub>x</sub> history is variable and we really don't have this true history from the point of emission to the time sampled. The point we are making is that the spread in Lagrangian to box model spans the measured/box model ratios. No changes were made here.

12. We added the duration of the HC time base on page 9895.

13. We corrected the wording on page 9896 line 19.

14. Page 9903, line 19-22: What we are referring to is our past studies that showed an increasing discrepancy with CH<sub>2</sub>O mixing ratio but this was not discussed here. What we are trying to say here is that the air mass origin plays a role in the discrepancy and we therefore cut out the discussion related to CH<sub>2</sub>O mixing ratio and the discrepancy.

15. We addressed the reviewer's concerns regarding the wording of the page 9906, lines 17-18.

16. Page 9906, line 23: We changed the wording "permutation" to "perturbation due to".

17. Page 9908, line 29: We reworded to "for the largest 6 model bins of Fig. 10 . . ."

18. Page 9909, line 11: We addressed the reviewer's question regarding the nature of the 5 points in the text.

19. The reviewer's question regarding the change in model input designator with trans-

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port time on page 9916, line 11-12 is no longer operative since the steady-state calculations were no longer used in the MCM comparisons.

20. Page 9924, line 6-8: We are not sure what the reviewer doesn't understand here regarding the model uncertainty determinations since this was clearly worded. The Frost et al. study also utilizes this approach. We have not made any changes to the text.

21. We added in the Fig. 10 caption the meaning of the bar and whiskers for the plot.

22. The explanation of the inset in Fig. 11b is given in the figure caption.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 9887, 2011.

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