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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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Review of "Detailed comparisons of airborne formaldehyde measurements with box models during the 2006 INTEX-B campaign: potential evidence for unmeasured and multi-generational volatile organic carbon oxidation processing" by Fried et al for ACP

note: some quotes are modified to avoid symbols that can't be pasted in.

The main objective of this manuscript is compare HCHO observations with a diurnal steady state box model and show how model – observation differences are intrinsic

features of using a steady state calculation for a compound that is not in steady state. Further insight into the prediction of HCHO is gained with a Master Mechanism Lagrangian model that contains more HCHO precursors. With a stated uncertainty of plus or minus 13%, the HCHO measurements are a significant accomplishment. The idea of examining box model results for non-steady state effects is excellent.

This article is long. Organization needs improvement. On several occasions in this Review, I will say the authors should have specified this, that, or the other thing. And maybe they did, multiple pages ago in a place that is not obvious. Reading the paper in one sitting would have helped, but as I said, the manuscript is long. I anticipate that other readers will have similar problems. Another organizational problem is that material needed to understand a discussion is presented pages later.

I do not know which of the HCHO measurements have been reported before. This may be a case of me not going back and searching the text.

The manuscript needs a clear description of how species evolve with time (a graph of a representative case would help), how this evolution is mis-represented in the box model calculations (including a description of what a DDS calculation is), and what the effect on calculated HCHO is. I think that this could be accomplished in a shorter article by careful editing.

At the end of the article, I can see that the authors have found model deficiencies. But I have a hard time putting it into perspective considering the Conclusion material on Page 9919, line 2 – 4. (which I may not be interpreting correctly) "Approximately one-third of these discrepancies can be accounted for using an analysis where Lagrangian outflow model calculations, employing typical VOC mixing ratios observed over Mexico City, are sampled by the steady-state box model." This leaves open the questions as to where the majority of the discrepancy comes from.

Many items are not clearly presented to the extent that I do not know what the authors intentions are. I am, more or less, the intended audience and will not apologize for my

lack of knowledge as I have read many similar articles without difficulty (and some with more difficulty).

My recommendation is that this article have major revisions to improve the presentation and to provide justification for the stringent uncertainty bounds used to judge model performance.

1. Uncertainty analysis

Uncertainties that are presented in Appendix A are not in agreement with those used in the analysis of the ratio of modeled to observed HCHO. The model uncertainty (2 sigma) due to measurement of constrained species is 8-35% over the continental U.S. and Mexico. I don't know how this is related to the 24% model random uncertainty from Frost et al (2002) on page 9896 line 6. Also, I'm not sure what set of circumstances would result in measurement errors producing only an 8% error in calculated HCHO. I would think that uncertainties in just actinic flux would be greater. Uncertainty due to model kinetics is either 50 – 62% or 34 – 68% depending on sampling region. I guess that the model kinetic term includes uncertainties that lead to errors in OH. OH appears on the formation and destruction side of HCHO, so errors in these terms offset each other but they do not cancel. page 9923 line 26-29 "A total systematic error (2 sigma level) of 13% was estimated from the quadrature addition of various individual uncertainties involving flow and flow dilution uncertainties, and uncertainties in the HCHO permeation rate and calibration factors over the course of the mission."

I don't know how to reconcile the above uncertainties (with allowance for translating 2 sigma in to upper quartile) with the value cited on Page 9901, line 24-26. "It is useful to keep in mind that the upper quartile value for the combined estimated measurement-model ratio uncertainty in the boundary layer is 1.18, and thus many of the averaged ratios over these domains are systematically high.

Or the uncertainty cited on Page 9902, line 23 – 26. "The gray shaded region represents the median for the combined measurement (random uncertainty) and model

constraint uncertainty at the 2 sigma limits in the HCHO ratio for the boundary layer (plus or minus 13%).

In Fig. 10, The HCHO observed to calculated ratio is presented in relation to a gray shaded region that represents "the median for the combined measurement and model 2 sigma uncertainty limits (plus or minus 13%) in the boundary layer.

I am dwelling on these uncertainty estimates because the central theme of the paper is to explain seemingly small model to observation ratios. i.e., Page 9904. 13-19 "However, a closer look shows that for the highest bin, the model slightly overpredicts the observations by up to 18%, and this suggests that very close to large sources of NMHCs (primarily ethene), the model's diurnal steady state assumption is inadequate, resulting in significant overpredictions of HCHO generated from ethene."

On page 9900, lines 4-6, I think the authors address the large discrepancy between the error estimate that they are using to diagnose model performance (13% ?) and the actual error estimate, almost all of which is on the calculation side. The text reads: "Although these discrepancies do fall within the combined systematic error estimates (not shown), which include instrumental systematic error estimates and model kinetic uncertainty estimates (see Appendix A)" This off-hand comment does not give any indication as to the difference in magnitude between error estimates. Nor does it give a rationale as to why the smaller error estimate was used.

2. Model calculations The box model used in examining the ratio of calculated to observed HCHO is not defined until Appendix A. Results are presented before the reader is alerted that the box model does not just calculate the HCHO that is in steady state with long lived species measured at the same time. Problems with the calculations are discussed before one finds out that the model's diurnal steady state assumption is inadequate. the key word being "diurnal". In order to follow the discussion, one has to skip ahead to the Appendix or know beforehand the modeling products used by these groups.

First reference to calculation: There is reference to “standard steady state modeling assumptions” in the Abstract.

An example of use of the model before it is adequately defined: Page 9891 near line 25 “The modeling studies listed above have used a steady-state modeling approach that is constrained by in-situ measurements of precursor species. This approach does not include direct CH2O emission sources and is limited to instantaneous measurements of non-methane hydrocarbons and other precursors, so in the vicinity of large and relatively fresh emissions, this approach may underestimate the recent history of photochemical production of CH2O from very short-lived hydrocarbons during rapid decay just prior to the point of measurement.”

I believe this is the first place where diurnal steady state is mentioned. Not everyone will understand term. Page 9904, line 16 the model’s diurnal steady state assumption is inadequate, resulting in significant overpredictions of CH2O generated from ethene.

A brief description of diurnal steady state that needs to be presented before discussing problems with calculations: Page 9922, Appendix A “As discussed in Fried et al. (2008a), the model calculates for each set of measurements the associated self-consistent diurnal profile of radical and other computed species determined from the constraint of long-lived precursors to measured concentrations.

Lagrangian Calculations I could not integrate the information on the Lagrangian calculations with results presented in Fig. 11a. I do not know which Lagrangian calculation is considered better.

3. Other Comments

Page 9895, line 8. The reader does not learn what the duration of an HC sample is until pages after the effects of a calculations time greater than the 1s HCHO measurements are discussed.

p 9896 line 19 “for which can be found” usage

p 9903 line 19 – 22 “It is thus apparent that the higher altitude binned data out of the boundary layer reflects entirely different behavior than within the boundary layer, indicating that the measurement of HCHO mixing ratio is not the primary factor affecting the agreement.” Is the basis for this statement a demonstrated linear response and the absence of interference, except for methyl alcohol?

Page 9906 Sec 5 Temporal behavior of CH2O in fresh boundary layer plumes

I found this section very hard to follow. Line 17 – 18 “The DSS assumption constrains values of ethene to the instantaneous observed value throughout the model day, resulting in model overestimates of CH2O” I don’t know what “instantaneous observed values throughout the day means”.

p9906 line 23 “The later effect is another permutation of non-steady state conditions”

What was the other permutation?

p9908, line 29 “largest 6 bins

should this be highest concentration 6 bins?

page 9909, line 11 the additional 5 points of Fig. 11b

I don’t know where these 6 points are.

page 9916 line 11-12 “where the Model Input Designations changed with transport time.”

I do not understand. Perhaps an example would help.

p 9924, line 6-8. “The box model was run 11 times for every data point; each time one of the 11 constraints considered was increased by its given one sigma measurement uncertainty.”

I don’t understand

Figure 10. What are the bar and whiskers? Median and some percentile of HCHO

ratio? I see that data points are not on median line. Are data points average values?

Figure 11. I don't understand what the inset is. Although, it is microscopic in the pdf version, I can see that the x-axis values are an order of magnitude larger than in the main graph.

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