

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 #1

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General

This is an interesting and thorough study of formaldehyde measurements, mostly in the plume of Mexico City and contrasted with several cleaner locations. It uses systematic comparisons of measurements with chemical box modeling results to investigate our understanding of tropospheric formaldehyde chemistry, emissions and modeling assumptions. Excellent model-measurement agreement is obtained for background

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conditions over the Pacific Ocean, while especially in the polluted boundary layer significant discrepancies are found. The study provides important insight in the limitations of steady state assumptions for the modeling of pollution plumes, even up to plume processing times of several days.

There is one shortcoming which I would like to see addressed in some detail. In the recent literature about unsaturated hydrocarbon chemistry it has been found that the recycling of hydroxyl radicals is generally underestimated. I recommend testing this assumption for polluted conditions and discussing its importance for the Mexico City plume and CH₂O chemistry. Further it would be good to revisit the definition of model uncertainty (see below). And I suggest the minor revisions indicated below.

Specific comments

p.9889, l.4: The abstract should provide some information about the geographical study area and mention the focus on BL outflow from Mexico City.

p.9890, l.19: You could also refer to A. Stickler et al., JGR, 2006.

p.9900, l.6: Please mention that chemical mechanism model uncertainties are not only “kinetic” uncertainties, but also include uncertainties associated with wrong and/or incomplete chemistry. This needs to be corrected throughout the manuscript (see also remarks below).

p.9901, l.5: Please add that the well-understood part of CH₂O chemistry is related to CH₄ oxidation.

p.9901, l.16: Is it possible to include CH₂O measurements >6ppb by a single color symbol (i.e. for all measurements between 6 and 28 ppbv)? It would be interesting to see the model-measurement discrepancies for very high CH₂O conditions.

p.9917, l.20: The inference that lumped mechanisms are not adequate to describe the complex hydrocarbon chemistry of the Mexico City plume corroborates that higher generation reaction intermediates are important, including underestimated OH recy-

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cling and influencing CH₂O production/destruction rates. Please discuss that such mechanisms are generally optimized to reproduce ozone levels under photochemical smog conditions, and to some degree ignore relevant details of the second and higher generation reaction products.

p.9918-9919 (summary): Please discuss the role of errors in the chemical scheme (in addition to kinetic uncertainty) and the potential role of underestimated OH recycling (see above).

p.9924, I.1-5: "The uncertainty in box model predictions of CH₂O and other radicals include a component due to uncertainties in the measurement of constrained species (model constraint uncertainty), and a component due to uncertainties in kinetic and photolytic rates (model kinetic uncertainty)." Please add that uncertainties also include a component of erroneous and/or incomplete chemistry, in particular wrt higher generation reaction intermediates. Note that most of the reaction intermediates in chemical mechanisms, including the MCM, have not been measured but calculated based on theoretical chemistry approaches. It is obvious that this is associated with uncertainty.

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