Interactive comment on “A large and ubiquitous source of atmospheric formic acid” by D. B. Millet et al.

Anonymous Referee #1

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The paper “A large and ubiquitous source of atmospheric formic acid” by Millet et al. presents a detailed study of the formic acid budget in the southeast of the US. It analyzed the available experimental data from three major field campaigns: SENEX, SOAS and SLAQRS and compares by comparing it with model calculations using GEOS-Chem model. The paper gives a good overview in the introduction on current knowledge of sources and sinks of HCOOH and comes to the conclusion that there is a major gap in our understanding of the HCOOH budget.

In the first part, the possible sources and sinks of HCOOH and their current knowledge are detailed and the values used for the model calculations are derived and motivated. In the second part of the paper, the output of the model is compared to the available data from the different field campaigns. By careful comparison of the evolution of the C995
HCOOH concentration with time, heights as well as the ratio its concentration with that of tracer molecules they consolidate the suspicion, already announced in other recent papers and well discussed in the introduction, that major gaps in the understanding of the HCOOH budget exists.

The paper is well written, draws clear conclusions from their study and is certainly worth to be published in ACP. I have only a few minor comments:

Page 4546: there is a very new paper on the rate of Criegee with H2O (Chao, W.; Hsieh, J.-T.; Chang, C.-H.; Lin, J. J.-M. Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor. Science 2015, 347, 751-754.) which confirms that the reaction takes place with the water dimer. Even though this doesn’t change any conclusion of the current paper, it would be good to include this reference in the discussion.

Page 4547, line 3: you say hot formic acid might decompose to peroxyacyl radicals, that subsequently could react with HO2 to form HCOOH. I can’t follow this: I would think that hot formic acid would decompose to OH and the acyl radical, and the acyl radical would under atmospheric conditions always react to HO2 and CO. Could you be more precise in this point?

Page 4551, line 13: the absorption cross section has not been measured by Boscolasco et al, but by Faragó, E. P.; Viskolcz, B.; SchoeMaeker, C.; Fittschen, C. Absorption Spectrum and Absolute Absorption Cross Sections of CH3O2 Radicals and CH3I Molecules in the Wavelength Range 7473–7497 cm−1. The Journal of Physical Chemistry A 2013, 117, 12802-12811. In the same paragraph at the end you say that the rate constant would be fast enough to represent an important CH3O2 sink and you cite the same three papers as for the absorption cross section: it would be more appropriate to cite: Fittschen, C.; Whalley, L. K.; Heard, D. E. The Reaction of CH3O2 Radicals with OH Radicals: A Neglected Sink for CH3O2 in the Remote Atmosphere. Environ. Sci. Technol. 2014, 118, 7700–7701.
Page 4563, line 25: does your model contain already the new, fast rate constant for the Criegee + SO2, such as published by Welz et al? I’m not sure if MCMv3.2 has already been updated?

Page 4566, discussion on the influence of CH3O2 + OH: I understand that you have removed all experimental data showing high NOx concentration before comparing with the model? However, a possible bias to the reaction CH3O2 + OH would be probably detected if the NOx dependence would be observed: the reaction of CH3O2 + OH becomes much less important with increasing NOx. So if a sizeable fraction of HCOOH would originate from CH3O2 + OH, the model should perform better at higher NOx concentrations: do you see any trend in the bias of the model with NOx concentration? Concerning the rate constant of CH3O2 + OH, did you test a lower rate constant to see if the CH3OOH results would be less degraded while still adding to the missing HCOOH budget? Recent measurements of the rate constant for C2H5O2 + OH using different precursors find a lower value of 1.2e-10 (Faragó, E. P.; Schoemaecker, C.; Viskolcz, B.; Fittschen, C. Experimental determination of the rate constant of the reaction between C2H5O2 and OH radicals. Chem. Phys. Lett. 2015, 619, 196-200.).

A very recent work on the reaction of CH3O2 + BrO (Shallcross, D. E.; Leather, K. E.; Bacak, A.; Xiao, P.; Lee, E. P. F.; Ng, M.; Mok, D. K. W.; Dyke, J. M.; Hossaini, R.; Chipperfield, M. P.et al. The Reaction between CH3O2 and BrO Radicals: a New Source of Upper Troposphere Lower Stratosphere Hydroxyl Radicals. The Journal of Physical Chemistry A 2015, doi:10.1021/jp5108203.) finds the Criegee intermediate to be the major reaction product. You could cite this work as an analogous reaction to CH3O2 + OH, nex to the reaction CH3O2 + Cl.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 4537, 2015.