

Interactive comment on “Importance of secondary sources in the atmospheric budgets of formic and acetic acids” by F. Paulot et al.

Anonymous Referee #2

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General Comment

The manuscript presents a global model study on the budget of two important organic long-lived acids in the atmosphere. The authors make use of GEOS-Chem whose standard chemical mechanism does not include formic acid. In comparison to other sources and sinks, these extensions to the mechanism are superficially described in a section and no list of reactions is shown. This makes difficult to evaluate the quality of the model used and the list of organic reactions used should be added in the supplement. Besides that, the manuscript fall well with the scope of the journal. It adds some new insights to the understanding of atmospheric formic acid that deserve publication. I recommend publication after the comments are properly answered and the necessary changes made.

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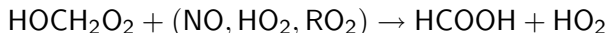
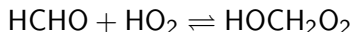
Interactive Discussion

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Major Comments

1) The high-NO_x laboratory yields of formic and acetic acid in the OH-initiated reaction of monoterpenes are actually understood to come from α-hydroxy peroxy radicals, RCH(OH)O₂, that react with NO (see Atkinson et al., EST, 1995; Orlando et al., JGR, 2000; Larsen et al., JAC, 2001). The theory also support this view (Peeters et al., PCCP, 2001 and see Sect. 2.3 of Capouet et al., ACP, 2004). However, it adds that α-hydroxy peroxy radicals decomposition to aldehydes and HO₂ is competitive with reaction with NO under lab conditions but not under atmospheric conditions. Therefore the OH-initiated oxidation of monoterpenes should not be considered as formic acid source. The authors do not need to re-do any simulation but they should clearly mention that the contribution of monoterpene oxidation to formic acid production is likely overestimated because of the reasons mentioned above.

2) The authors also neglect the following chemistry



by Veyret et al., JPC 1989 and Jenkin et al., PCCP 2007 that has been estimated to produce 174 Gmol/yr of formic acid (14% of the total sources as shown in Table 3) in the UTLS region (Hermans et al., JPC A 2005). This would lead to a substantial overestimation of formic acid in the UTLS. This may be due to less hydroxyacetone and glycolaldehyde getting to the UTLS region. This in turn may be due to a rather different low-NO_x isoprene chemistry that, compared to what is in GEOS-Chem, would result in either lower yields of hydroxyacetone and glycolaldehyde or higher boundary layer OH concentrations in the tropics (Lelieveld et al., Nature 2008). Such problems should be discussed.

3) The underestimation of formic acid in the Northern Hemisphere, where O₃ is higher, may be well due to either the representation of terminal alkene ozonolysis or missing unsaturated compounds. However, this is difficult to judge without a table with the list

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of reactions of the modified mechanism used in GEOS-Chem.

Technical corrections

- page 24462 line 23 typo after the word "scale"

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24435, 2010.

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