

We thank both reviewers for their constructive comments. Below is a detailed answer to their comments.

## Major comments

1. **p.24443, l.1: It would be more straightforward that low NO<sub>x</sub> chemistry is applied to a global model. The issue of the low NO<sub>x</sub> chemistry may need to be addressed in modeling of responses to biogenic sources, although it is noted in p.2448. Please explain why the low NO<sub>x</sub> chemistry was not applied here.**

In the chamber oxidation of IEPOX, formation of HCOOH was observed though the formation mechanism remains unknown. A small yield of HCOOH from the oxidation of IEPOX is thus included in the mechanism implemented in GEOS-Chem. As mentioned by the reviewer, there is considerable uncertainty in isoprene chemistry under low NO<sub>x</sub>. In particular the mechanism proposed by Peeters et al. [4] may dramatically alter the isoprene product distribution in the tropics. However, there is not enough information to properly implement this mechanism and its impact on formic and acetic acid in the GEOS-Chem mechanism. We will emphasize this aspect in the revised version of the manuscript. We also note, that the largest discrepancies between observed and simulated formic acid are concentrated in the polluted regions. This suggests that the major shortcomings of the model are associated with “the high NO<sub>x</sub> regime”.

2. **p.24443, l.25: How did you estimate the yields (15.5%, 7.5%, and 8%)? Please also show yields for other species to complete the reaction equation.**

The complete mechanism used in the study will be included in the supplementary materials. The yields of formic acid from the oxidation of monoterpenes reported in the literature vary widely ( $\sim 7\%$  [3] to  $28\%$  [1]). Our estimate is at the high end of the experimental range, in part to compensate for the lack of secondary chemistry of monoterpene photochemical products in the current GEOS-Chem model. As pointed out in comment 6, the first generation yield is however probably overestimated. Ozone yields are from [2].

3. **p.24450, l.3: Please check tables in previous studies. You need to rephrase this sentence, because absolute differences in direct emissions from biomass and biofuel burning are smaller than those in photochemical production.**

We have corrected the table to incorporate the break down in sources in previous studies (cf. Technical comment 9). The sentence pointed out by the reviewer does indeed need to be rephrased, to point out that, in contrast to FA, biomass burning/biofuel sources do not appear to be a negligible contribution to the overall budget of AA.

4. **p.24459, l.13: It is unclear how the summary #3 is associated with the discussions in the section 3. Please explain it.**

We wanted to emphasize that the discrepancy between observed and simulated formic acid may also stem from an overestimate of its sinks. We agree with the reviewer that this point is not clearly related with the material presented in section 3. We will expand this discussion and move it to the conclusion.

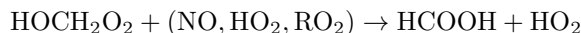
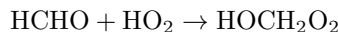
5. **p.24463, l.17: Please show the equation used to estimate the collision of OH with OA. Are the assumed source strengths of FA and AA consistent with the results from the chamber experiments (Paulot et al., 2009)?**

We use the number of collisions between aerosol surfaces and OH assuming an accommodation coefficient of 1, to test the importance of organic aerosols as a source of formic and acetic acids. We will add the equation to the revised manuscript. We will discuss the source of FA/AA from OA in the chamber oxidation of isoprene in the revised manuscript.

6. **The high-NO<sub>x</sub> laboratory yields of formic and acetic acid in the OH-initiated reaction of monoterpenes are actually understood to come from  $\alpha$ -hydroxy peroxy radicals, RCH(OH)O<sub>2</sub>, 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 -hydroxy peroxy radicals decomposition to aldehydes and HO<sub>2</sub> 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.**

We will emphasize this issue in the revised manuscript as well as the lack of secondary photochemistry of monoterpenes, which may result, conversely, in an underestimate of their impact on formic and acetic acids budgets. See also reply to comment 2.

7. **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<sub>x</sub> 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.

Including the reaction of HCHO with HO<sub>2</sub> indeed leads to a great overestimate of formic acid in the upper troposphere, where it is the dominant source. We will present the results of a simulation where all HOCH<sub>2</sub>OO (at equilibrium with HCHO) reacts to make HCOOH. We will also test the sensitivity to the temperature dependence of this equilibrium and the importance of hydroxyacetone and glycolaldehyde at high altitude.

8. **The underestimation of formic acid in the Northern Hemisphere, where O<sub>3</sub> 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 of reactions of the modified mechanism used in GEOS-Chem.**

This is an excellent point. Small alkenes are treated in the GEOS-Chem mechanism but their ozonolysis does not appear to yield much formic acid. In the current mechanism, we only included formation of FA and AA from propene and ethene. Formation of formic acid from acetylene is also included. Of great interest is the fate of OVOC, particularly aldehydes, which are known to be emitted by agricultural activities and whose photooxidation could represent a large source of both carboxylic acids (for instance in the California Central Valley). This source is not well represented in the model, as only primary emissions of HCOOH/CH<sub>3</sub>COOH from farming are included. We will emphasize these issues in the revised version of the manuscript.

## Technical corrections

1. **Technical corrections - page 24462 line 23 typo after the word "scale"**  
corrected
2. **p.24439, l.18: Define i. Present the unit for E.**  
wrote "i" under the summation sign, such that it's clear that "i" is just a summation indice
3. **p.24439, l.25: Define T. p.24440**  
done. T is the current leaf temperature
4. **p.24440 l.5 and l.7: Rephrase "CO" emission, because you cannot calculate FA and AA emissions from CO emissions using the**

**emission factors in Table1.**

Corrected

5. **p.24441, l.21: T is the “soil” temperature. p.24452**  
corrected
6. **l.10: Fig. S8 should be corrected to “Fig. S7”. p.24453**  
corrected
7. **l.10: Fig. S6 should be corrected to “Fig. S8”.**  
corrected
8. **Table 1: Present the references for the emission factors.**  
These estimates were provided by R.J. Yokelson. Akagi et al. recently published these updated emission factors ([www.atmos-chem-phys-discuss.net/10/27523/2010/](http://www.atmos-chem-phys-discuss.net/10/27523/2010/)). These new estimates differ from the ones communicated by R.J. Yokelson earlier. Namely,
 

	This study	Akagi et al.
FA from tropical forests	0.42	0.27
FA from boreal forests	0.80	0.57
AA from boreal forests	4.05	4.41

 These differences are relatively minor, given the small importance of biomass burning in the budget. We will highlight these differences that highlight the great uncertainty in the estimate of emissions factors.
9. **Table 2: Present previous estimates for direct emissions of acetic acid (see Table 3 in von Kuhlmann et al., 2003 and Table 2 in Ito et al., 2007) and add them to total sources in parentheses.**  
added
10. **Fig.4 caption: Correct “20042008 model range”.**  
corrected
11. **Supplement, p.2: Remove “from the” in the first sentence.**  
replace by “The photooxidation of glycolaldehyde yields FA”

## References

- [1] B.R. Larsen, D. Di Bella, M. Glasius, R. Winterhalter, N.R. Jensen, and J. Hjorth. Gas-phase OH oxidation of monoterpenes: Gaseous and particulate products. *J. Atmos. Chem.*, 38(3):231–276, 2001.
- [2] A. Lee, A. H. Goldstein, M. D. Keywood, S. Gao, V. Varutbangkul, R. Bahreini, N. L. Ng, R. C. Flagan, and J. H. Seinfeld. Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes. *J. Geophys. Res.*, 111:D07302, 2006.

- [3] J. J. Orlando, B. Nozière, G. S. Tyndall, G. E. Orzechowska, S. E. Paulson, and Y. Rudich. Product studies of the OH- and ozone-initiated oxidation of some monoterpenes. *J. Geophys. Res.*, 105:11561–11572, 2000.
- [4] J. Peeters, TL Nguyen, and L. Vereecken. HO<sub>x</sub> radical regeneration in the oxidation of isoprene. *Phys. Chem. Chem. Phys.*, 11(28):5935–5939, 2009.