

***Interactive comment on “Comparisons of
observed and modeled OH and HO₂
concentrations during the ambient measurement
period of the HO_xComp field campaign” by
Y. Kanaya et al.***

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Comment by J.-F. Müller & J. Peeters

Kanaya *et al.* presents box model simulations using either a “standard” mechanism based on MCMv3.1 or a mechanism modified to include unimolecular reactions of the LIM0 mechanism, following Peeters and Müller (2010). Two versions of the LIM0 mechanism are tested, differing by the number of OH radicals generated in the photolysis of the HPALDs: $m=3$ (run S1) or $m=1$ (S2). Because the major isoprene source in-

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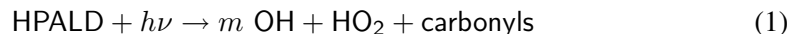
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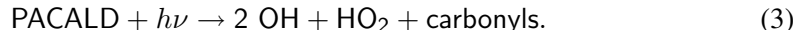


fluencing the site is limited to a relatively small area in the upwind direction, isoprene is introduced only during the last 12 minutes of each 24-hour simulation. The 12-min duration was optimised by Kanaya *et al.* in order to match the measured average MVK+MACR concentration in the base run. We have two major comments regarding this modeling exercise:

- The combined reaction



with value $m=3$ was proposed in Peeters and Müller (2010) in order to account for the production of OH in the subsequent photolysis of peroxy-acid-aldehydes (PACALDs) generated in the photolysis of the HPALDs:



However, in the present situation, the HPALDs and PACALDs can photolyse only for a minor fraction over the 10–20 min period. The value $m=3$ is therefore inappropriate, since the photochemical state for the PACALDs is very far from established in that short period. This also explains the relatively small difference between the effects calculated in simulations S1 and S2. Also, it rationalizes why the LIM0 chemistry leads to minor HOx regeneration in the given conditions but to major OH recycling in extended areas with high isoprene levels such as the Amazon basin. We therefore recommend the explicit implementation of PACALD formation and photolysis in the model simulations, i.e. adopting the two separate reactions above. The results should be close to those of simulations S2. The modeled [OH] and [HO₂] in this S2 run, from about 9 am to 5 pm on the 10th and 11th July, differ by only about 20 to 35% from the Base run results, which is actually less than the difference between the highest and lowest measurements.

- A crucial quantity for the model results is the time the isoprene chemistry is active; it is determined by the wind speed and direction and should in reality not remain constant over the 3-day period. Moreover, the 12-min duration deduced from the base run cannot be appropriate for the S simulations which include the isomerisations of hydroxyperoxy radicals, since these reactions lead to substantially reduced yields of MVK+MACR in the oxidation of isoprene by OH. Even taking into account that [OH] is enhanced by about ~20–40% in simulations S1 and S2, compared to the base run (Fig. 2 and Table 3), the production of MVK+MACR should on average be about a factor of 1.5 lower in simulations S1–S2, and therefore isoprene chemistry should be introduced for a longer period. Evidence for the strongly reduced MVK+MACR yields in run S1 is provided in Fig. 5: on July 10, the concentrations of ISOPBO2 and ISOPDO2 (the direct precursors of MVK and MACR) are more than a factor of 2 lower in run S1, compared to the base run. For proper comparison with the base run, the time interval during which isoprene chemistry is activated in the S runs should be estimated day by day such that the predicted MVK+MACR concentrations match those of the Base run - which were shown in Fig. S2 to reproduce the observations. This should lead to about twice longer isoprene activation times on July 10, compared to the base run, and therefore to larger OH losses and lower OH concentrations, thus further reducing the difference between the S and Base runs.

Minor comments:

- In Table S1, the same notation ISOPEO2 is used for the δ -hydroxyperoxy radicals in the standard mechanism and for the hydroxyperoxy radicals resulting from OH addition to the central carbons of the isoprene molecules, in the alternative mechanism. These radicals are different and should have different reactions. For example, ISOPEOOH+OH should lead to IEPOX formation in the standard mechanism. And ISOPEO2+NO cannot form the hydroxy-aldehydes (HALD5152) in

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the alternative mechanism.

- The MCMv3.1 rate constant for the $\text{NO}_2 + \text{OH}$ reaction is adopted from IUPAC. Its value at 298 K is about 12% higher than the JPL recommendation, and 30% higher than the latest determination (Mollner et al., 2010) which is also considered the most accurate (Donahue, 2011).

References

Donahue, N. *Nature Chem.* 3, 98–99, 2011.

Mollner, A. K. *et al. Science* **330**, 646–649, 2011.

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