

Review for “Comparisons of observed and modeled OH and HO₂ concentrations during the ambient measurement period of the HO_xComp field campaign” by Kanaya et al.

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In this study, Kanaya et al. use HO_x observations collected in Jülich during the HO_xComp campaign to investigate the model’s ability to capture OH, HO₂, OH reactivity under a variety of VOC and NO_x concentrations. Though many studies have tackled this issue in a similar fashion in the past, the use of multiple OH measurement techniques combined with measurement of OH reactivity should make this paper worthy of publication in ACP. However, there are a number of important issues that need to be carefully addressed before I can support publication.

Major comments

1. This authors argue on page 28862 line 25 that the model captures HO₂ quite well. Yet, this does not account for the significant interference by RO₂ that the authors discuss in section 4.5. Since this interference has been characterized for one of the instrument (FZJ) and reported for another (MPI), the authors should only use the corrected HO₂ (even if that means excluding the MPI and possibly the FRCGC) in their analysis. This is especially important since their conclusions regarding model/observation agreement are different depending on whether or not the correction is used (Fig. 8)
2. Recent measurement of OH are generally not well reproduced by models, especially under high biogenic low NO_x loadings. In this study the authors report a much smaller discrepancy (under higher NO_x conditions), with the notable exception of the MPI instrument that was used in the Lelieveld study. This needs to be discussed in greater depth (e.g. at the end of p28863).
 - (a) Could the authors elaborate some more on the differences between instruments ? In particular the CIMS instrument seems systematically lower than the LIF instruments.
 - (b) The MPI instrument seems systematically higher than other LIF. It seems important to comment on it since the results from this instrument spurred considerable work on the oxidation of isoprene under low NO_x [4].
3. The model description in the manuscript is incomplete and does not allow the reader to understand what the authors really did. This major concern is mostly addressed by the authors’ short comment requested by the editor. The authors argue that the use of a single oxidation time is justified by the “steady” wind experienced during the the experiment. They use their model to optimize the oxidation time. Looking at Fig. S2, it seems the fit is rather poor with many high or near zero MVK+MACR observations, not captured by the model in particular on Day 1 and on Day 3. This seems to contradict the authors’ hypothesis that the oxidation time of isoprene is constant. A possible remedy would be to optimize the oxidation time for every MVK+MACR observations and every chemistry (as pointed out by Dr. J-F Müller).
4. Similar to the description of the model, the reader is left guessing how the authors carried out their “added” reactivity simulations (section 4.4).
 - (a) The justification for adding reactivity is the discrepancy between model and measured reactivity. However this discrepancy is much too rapidly analyzed (cf. also short comment 9). The discrepancy is significantly larger on Day 2 and 3 of the experiment, when isoprene accounts for a greater share of the reactivity. Hence it seems reasonable to assume the discrepancy is related to missing biogenics or errors in the representation of their chemistry. Thus, the authors’ conclusions that “the isomerization of isoprene

peroxy radicals at the rates proposed by Peeters and Müller (2010) could not be fully rejected because of the possible presence of unmeasured hydrocarbons (such as HC8) that could impede HOx radical propagation.” is not convincing. Indeed the only way to reconcile this mechanism with the authors’ observations is to assume a very unlikely elevated level of unmeasured HC8, i.e. anthropogenic VOC, which seems inconsistent with the observations

- (b) how is the additional chemical compound added ? The authors only give the daily mean addition
- i. is the concentration of the compound assumed constant throughout the day and from day to day ?
I am guessing it is since one would expect overestimates on day 1 to lower the underestimate on day 2 and 3. Except if there is compelling evidence for variations in anthropogenic precursors between day 1 and 2 (not shown), this does not seem an appropriate sensitivity study, e.g., for HC8.
 - ii. are the products of the oxidation of this compound assumed to be at steady state ?
I am assuming so since the authors mention that photochemical products play an important role. But shouldn’t the authors treat short-lived compounds like they do for isoprene (i.e. assume a short oxidation time in particular for APIN).
 - iii. what is the sensitivity of the simulated reactivity to the assumed oxidation time for isoprene ?

Technical comments

1. p28857 line 20
Could the authors provide some justification for the different day/night OH threshold
2. p228859 line 15.
I believe you mean that MVK is treated separately from MACR. If so, please rephrase as this is not clear.
3. A couple of references are missing or wrong, e.g., Elshorbany et al. is missing, Paulot et al. 2008 -> Paulot et al. 2009. Please check.
4. Have the authors tested their sensitivities to deposition ? This is unlikely to make much of a difference but Karl et al. ([3]) recently showed that the deposition of OVOC (including MVK, MACR) was significantly faster than is generally assumed. Given the very simple, parameterization used by the authors, the reference to Zhang et al. ([8]) does not seem justified.
5. p28861-28862 I suggest the authors rephrase the introduction to the model simulations. A roadmap is useful but the authors already give so many details that the main points are a little lost.
For instance, introducing every single sensitivity simulations with their associated acronyms is probably not necessary. It might be more useful to describe them in detail at the beginning of section 4.4, so that the reader does not have to constantly switch back and forth to understand what the authors did.
6. p28863 line 11, please specify what slope you are referring to: model vs observation or observation vs model. This can be inferred from the tables but it would be useful to include it in the text as well.
7. p28865 line 10, it would be interesting to carry out a sensitivity simulation with reduced isomerization rate (following Crouse et al. [2] for instance) to determine the extend to which isomerization occurs under those conditions (i.e. what’s the fraction of peroxy radical undergoing isomerization in the different scenarios investigated here).
8. Section 4.3 does not fit well in the paper because it solely focuses on the modeling results. I suggest the authors replace this section with a detailed comparison between measured and modeled OH reactivity. This can be readily accomplished by combining the study of OH reactivity in section 4.3 with its measurement (beginning of section 4.4). This would help justify why the authors decide to add chemical compounds to match the measured reactivity.
9. Fig 1 does not provide much information that cannot be found elsewhere or in the supplementary table. Given the lack of sensitivity to secondary isoprene chemistry (as far as OH reactivity is concerned), I would suggest removing this figure.
10. The authors may or may not consider the comments (a)-(c) regarding Table S1.

- (a) Based on the parameterization used in MCM, one would expect the same rate to be used for IEPOXO2 + HO2 and ISOPOO + HO2 that both have 5 carbons. Could the authors comment on the reason why they did not use the same reaction rate coefficient.
- (b) the reaction of MAHP with OH does not seem correct. There should be significant abstraction α of the peroxide group and abstraction of the aldehydic H (MACR) that would all prevent return to MACP (and hence artificial removal of HOx)
- (c) is the formation of MPAN scaled down to account for the fact that only ~50% of MACP (from MACR) and 0% of MACP (from MVK) can actually yield MPAN.
- (d) I am surprised by the representation of the isomerization of ISOPO2. Shouldn't ISOPEO2 undergo 1,6 isomerization, while ISOPBO2 and ISOPDO2 only undergo 1,5 isomerization. The authors assume ISOPBO2 and ISOPDO2 undergo both 1,5 and 1,6 isomerization while ISOPEO2 does not undergo any isomerization. This does not seem to be consistent with the description of this set of reactions (cf. [1, 5, 6, 7])

References

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- [3] T. Karl, P. Harley, L. Emmons, B. Thornton, A. Guenther, C. Basu, A. Turnipseed, and K. Jardine. Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation. *Science*, 330(6005):816–819, 2010.
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