**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Comparisons of observed and modeled OH and HO$_2$ concentrations during the ambient measurement period of the HO$_x$Comp field campaign" *by* Y. Kanaya et al.

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Reply to reviewer #2

We appreciate the comments given by reviewer #2 after careful reading of our manuscript.

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).

Answer: In the revised manuscript, we will show the HO2(*) comparison from the beginning. We will show the original HO2 comparison only as reference to show the degree of RO2 interference and also to assist comparisons to past studies.

2. Recent measurement of OH are generally not well reproduced by models, especially under high biogenic low NOx loadings. In this study the authors report a much smaller discrepancy (under higher NOx 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 NOx.

Answer: Instrument intercomparison for OH was studied in detail in Schlosser et al. (2009); the systematically lower CIMS results could also be attributed to calibration issues (as mentioned in line 27, page 28855). Unfortunately each instrument was calibrated only by its own system and crosscheck was not made. It is beyond the scope of this paper to identify the instrumental differences responsible for the different results. As also requested by reviewer #1, however, several features of the instruments which might be related to the different behavior are briefly mentioned in the Experimental section:

A tandem chamber with multi-pass for laser excitation was employed for the MPI in-

strument, while a dual chamber with single-pass for laser excitation was used for the FZJ instrument. The FRCGC instrument employed a single chamber with single-pass for laser excitation. For more details, see Schlosser et al. (2009).

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 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).

Answer: Additional information published in the separate author's comment will be included in the revised manuscript. We agree that the isoprene-active period should be determined from time to time for precise simulation. However, for HOxComp this optimization is limited by the sporadic MACR and MVK observations and their uncertainty. The impact of this limitation on the modeled HOx concentrations is small, because the isoprene oxidation time influences only the concentration of isoprene oxidation products other than MACR and MVK (the latter were constrained to observations in the actual base and S-type runs presented in the paper). For example, employing an oxidation time of 20 min instead of 12 min in the S1 pre-run at 12:30 UTC on 10 July increases MACR+MVK concentrations from 0.15 to 0.25 ppb, in better agreement with the interpolated observation value (0.28 ppb). However, the impact of using 20 min instead of 12 min in the S1 run was small; it increased OH and HO2 only slightly by 9% and 7%, respectively. For the base-type chemistry model, we made an additional sensitivity run where the isoprene chemistry is considered continuously for five days, while the MACR and MVK concentrations are constrained to observations. The sensitivity

run yielded OH and HO2 concentrations only 3% lower and 6% higher in comparison to the base run (with 12-min integration).

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.

Answer: We agree that the missing hydrocarbon is possibly biogenic and that the unmeasured HC8 is not likely present at that high concentration. We will rephrase the conclusion sentence at the end of section 4.4.

"Addition of HC8 at large amounts explaining the missing OH reactivity was the only scenario in which the ensemble of OH observations was reproduced with the chemical mechanism including the isomerization. This scenario is not likely because the missing reactivity was small on 9 July, when the influence from anthropogenic hydrocarbons was strong, but was large on 10 and 11 July, when biogenic hydrocarbons were relatively important. In summary, isomerization of isoprene peroxy radicals at the rates proposed by Peeters and Müller (2010) would be unlikely, even when additional hydrocarbons explaining the missing OH reactivities are taken into account."

(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.

Answer: The added hydrocarbon concentrations were calculated from missing reactivity with a time resolution of 10 min. This will be included in the revised manuscript.

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).

Answer: The missing hydrocarbons are taken into account at steady state (i.e., included from the first step of five-day simulation). If added only for 12 min similar to isoprene, the impact will become smaller. Here we intend to estimate maximum impact of hydrocarbon addition, and thus we chose including them for a long period. The 12-min period is justified only for isoprene (from air transport time and MACR/MVK concentrations) and is not justified for any other types of additional hydrocarbons.

iii. what is the sensitivity of the simulated reactivity to the assumed oxidation time for isoprene ?

Answer: When isoprene was taken into account fully from the five-day simulation, the simulated OH reactivity is increased by 0.85 s**-1 (about 10%) as an average for daytime (6:00âĂŠ18:00 UTC) over the three days. The increased OH reactivity agreed better with the observations. However, this increment in OH reactivity is provided by the unmeasured and unconstrained secondary products from isoprene chemistry whose concentrations were unreasonably estimated from the viewpoint of the observed MACR and MVK concentrations levels. Therefore we employed the 12-min period in

this study. Anyway, the influence of the choice of the time period in which isoprene chemistry is effective on the reactivity is small.

Technical comments 1. p28857 line 20 Could the authors provide some justification for the different day/night OH threshold

Answer: It is a threshold for the HO2/OH ratios to be used for analysis. (i.e., it was not applied for screening OH concentration data.) This helped to eliminate data with low accuracy. For the following discussion only daytime threshold is important.

2. p28859 line 15. I believe you mean that MVK is treated separately from MACR. If so, please rephrase as this is not clear.

Answer: The original RACM includes MVK in the category of OLT and we do not necessarily mean the separation from MACR. In the revised text, we will mention that "MVK is taken into account as a separate species."

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.

Answer: Elshorbany et al. is in press in JGR and thus will be mentioned accordingly. Correction to Paulot et al. 2009 is made.

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.

Answer: Karl et al. studied deposition to the in-canopy forest and might not necessarily represent the HOxComp upwind condition (agriculture field, small villages and nearby forest). On the other extreme end, default setting of the MCM box model even omits deposition of carbonyl species (other than HCHO and CH3CHO). We did not agree with the deposition velocity of zero and thus tried to incorporate mild velocities (0.5 cm

s**-1, in reference to Zhang et al.). The MACR/MVK deposition velocity is important to determine the isoprene-active time period in the pre-run. However, the aim of determining the time period is to adequately estimate the concentrations of unmeasured secondary species produced from isoprene oxidation (other than MACR and MVK, HALD5152 in the base run for example) and thus the influence of deposition would be canceled out when the deposition velocity is similar for the MACR/MVK and for the unmeasured organic species. Besides, the deposition velocity is also important for other unmeasured organic species produced from hydrocarbon other than isoprene. However, our model simulations are well constrained by ancillary observations (including HCHO, CH3CHO, MACR, and MVK) and the influence of unmeasured organic species to HOx chemistry is limited. This has been shown in the very small difference between (A) and (C) in Fig. 6, where the sum reactivity in the base model run is mainly contributed by reactions with observed species (including methane), rather than those with unmeasured secondary species calculated in the model. From this, it is easily inferred that increasing deposition velocity by a factor of 2 for example will have limited impact on our calculations.

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.

Answer: We will shorten this part and explain the additional model simulations later.

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.

Answer: The slopes used in this study are model/observations. We will clearly mention

C14228

this in the revised text.

7. p28865 line 10, it would be interesting to carry out a sensitivity simulation with reduced isomerization rate (following Crounse 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).

Answer: Upon this suggestion, we made a sensitivity model run where the isomerization rates are reduced by a factor of 50 and found that both OH and HO2 concentrations were reduced to levels similar to those in the base run (only 2% higher than those of the base run). The fraction of isoprene peroxy radicals that undergo isomerization was high (71-76%) during 12:00-15:00 UTC on 10 July when NO mixing ratio was low, but was lower (7-53%) for the other midday (9:00-15:00 UTC) period in the S-type runs. When the isomerization rates were decreased by a factor of 50, the fractions were reduced to 5-7% during 12:00-15:00 UTC on 10 July and 0.2-2.5% for the other midday (9:00-15:00 UTC) period.

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.

Answer: As suggested, the model budget analysis part will be rearranged in the revised manuscript. The breakdown of the modeled OH reactivity will be discussed together with its comparison to observations.

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.

C14229

Answer: We will delete Fig. 1 as suggested.

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.

Answer: We had no specific reason and just employed the rate constant used by Paulot et al. (2009) for IEPOXO2 + HO2. Our results are not sensitive to the rate coefficient.

(b) the reaction of MAHP with OH does not seem correct. There should be significant abstraction of the peroxide group and abstraction of the aldehydic H (MACR) that would all prevent return to MACP (and hence artificial removal of HOx)

Answer: We agree with the reviewer. However the degradation of MACR has minor impact on HOx in all cases in this study and thus we tentatively retained the mechanism and avoided producing new species for brevity.

(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.

Answer: An additional model run assuming a reduced MPAN yield (0.25) had negligible impact on HOx concentrations.

(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.

Answer: Although ISOPEO2 in the base mechanism represented δ-hydroxy peroxy radicals, ISOPEO2 in the S-type mechanism represent "other minor peroxy radicals where the OH is attached to internal carbons" (Stavrakou et al., 2010). Because δ-hydroxy peroxy radicals are less stable than the β-hydroxy peroxy radicals, δ-hydroxy

C14230

peroxy radicals are not treated in the S-type mechanism (following Stavrakou et al., 2010). We will use separate notation in the revised manuscript (ISOPACO2 for δ-hydroxy peroxy radicals and ISOEO2 for minor peroxy radicals). Considering the fast interconversion between peroxy radicals, ISOPBO2 and ISOPDO2 could be considered to virtually undergo 1,5- and 1,6-shift, as combination of the processes, which are parameterized by Peeters and Müller (2010) and Stavrakou (2010) and are used here.

We thank the reviewer for their comments helping us to improve our manuscript.

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C14231

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