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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_xComp field campaign" *by* Y. Kanaya et al.

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We thank the reviewer very much for reading our paper carefully and giving us valuable comments. Detailed responses to the comments are given below.

Major comments: The reviewer requested a more in-depth justification and description with respect to the consideration of isoprene chemistry for a short duration (12 min) in the model.

Question: "Is there any evidence to suggest that air masses coming to the site from

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the local isoprene source do not also contain aged air and isoprene oxidation products in addition to the fresh isoprene emissions?"

Answer: As mentioned in a separate author's comment, the measurement site was located on the campus of Forschungszentrum Jülich, which lies in a mixed deciduous forest. The extension of the forest around the campus is about 1-2 km in all geographic directions. In north, upwind direction for the three days analyzed in this paper, outside the forest, the air had passed for more than 20 km over agricultural land (growing mostly wheat, corn, sugar beets), outskirts of Jülich and a few small villages, before reaching the forest at the Forschungszentrum. The plants are known as low-isoprene emitter (e.g., Evans et al., 1982) and thus the distant isoprene source is not likely influential. It should be noted that the aim here to include the isoprene chemistry only for 12 min is only to calculate adequate concentrations of HALD5152 (a species representing unmeasured and unspecified products from isoprene chemistry), which cannot be constrained by observations. (MACR and MVK concentrations are constrained by observations in the full simulations.) Even if distant sources are present, the production of MACR and MVK to the observed concentration levels is just allocated to distant areas rather than the nearby forest, and we do not expect large differences in the concentrations of HALD5152 and thereby in the HOx concentrations and OH reactivity.

Comment: "The justification for the model approach is given only in terms of the modeled concentrations of MVK and MACR. The manuscript also states that there were measurements of HCHO at the site, which is also an oxidation product of isoprene. If the model is not constrained to HCHO, how do simulations of HCHO concentrations compare with observations when isoprene chemistry is considered during the full 5 days of integration and when isoprene chemistry is considered only in the last 12 minutes of integration?"

Answer: HCHO was overestimated by factors of 1.5âĂŠ4 when full 5 days of integration was made, consistent with our analysis for MACR and MVK in the pre-runs. Because HCHO is formed from hydrocarbons other than isoprene, we estimated the contribu-

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tion from isoprene by calculating difference from two model runs, with isoprene concentrations constrained to observations and assumed to be 0. For the case of 12-min integration, adequate evaluation was not possible because the background concentration of HCHO produced from hydrocarbons other than isoprene (as estimated from the above-mentioned 5-day integration model run without isoprene) is almost comparable to the observed level and the increment from isoprene chemistry was small.

Question: How are the modeled HOx concentrations and OH reactivity impacted by the treatment of isoprene chemistry? What are the modeled concentrations and reactivity when isoprene chemistry is considered during the full integration period? The authors make several statements throughout the manuscript regarding model discrepancies for OH in previous field campaigns in high VOC and low NOx conditions, and state that the measurements during HOxComp are in good agreement with the model approach used in this study and are thus in contrast to previous studies. Please provide some discussion as to how the modeled HOx concentrations and OH reactivity are impacted by the use of the 12 min integration period for isoprene chemistry as opposed to the approach taken in previous studies where isoprene chemistry is considered during the full integration period.

Answer: OH and HO2 are only 3% lower and 6% higher when the 5-day integration with isoprene was employed in comparison to the base case (12-min integration) here. The OH reactivity is increased by 0.85 s**-1 (about 10%) as an average for daytime (6:00âĂŠ18:00 UTC) over the three days. This is related to the lowered OH concentration mentioned above. The increased OH reactivity agreed better with the observations. However, the 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 HOx concentrations is small and will not affect the conclusion here, which is different

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from other recent studies. This will be mentioned in the revised manuscript.

Minor comments 1. Page 28855, line 6: The referencing of other work is somewhat incomplete, for example work done in areas impacted by higher levels of isoprene, for example measurements in forested regions in Greece and the USA and aircraft measurements over Borneo and Africa.

We will include Stone et al. (2011), Carslaw et al. (2001), and Tan et al. (2001) in the revised manuscript. Aircraft-borne OH measurements over Africa will not be mentioned here because instrumental issues were possible (Stone et al., 2010).

2. Page 28856, line 13: Has the Elshorbany et al. (2011) paper been published yet? I was unable to find it in the literature. Please update the date to 2012 if not.

Elshorbany et al. is in press in JGR and thus will be mentioned accordingly.

3. Page 28859, line 9: Do the authors mean MCM v3.2? As far as I am aware v3.1 did not include epoxide formation in isoprene oxidation.

We will mention that the base mechanism adopts the isoprene chemistry from MCM ver. 3.1 (http://mcm.leeds.ac.uk/MCM/) and is further updated with the recently discovered epoxide formation mechanism (Paulot et al., 2009).

4. Page 28860, line 25: Please see above comments and include a more detailed description and justification of the treatment of isoprene chemistry, particularly regarding the effects on modeled concentrations of HCHO, HOx and OH reactivity.

We will include the above answers in the revised manuscript.

5. Page 28863, line 15: Please include some discussion of the differences in treatment of isoprene chemistry between the present study and previous studies.

We will mention that the differences cannot be attributable to the short oxidation duration (12 min) of isoprene.

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6. Page 28863, line 21: Please provide a more detailed comparison between the isoprene and NOx conditions experienced during HOxComp to those encountered in other field campaigns. The sensitivity of modeled HOx concentrations was investigated using aircraft measurements over Africa in the AMMA campaign. How does the current work compare with this work?

We will rephrase the sentence to "Under conditions with similar mixing ratios of isoprene and NO, observed OH was underpredicted by a box model by up to a factor of 8 in PRD (Hofzumahaus et al., 2009; Lu et al., 2011)." Stone et al. (2010) investigated HO2 sensitivity on isoprene and NOx and did not study OH sensitivity. Because we explore OH analysis here, direct comparison was not possible.

7. Page 28863, line 26: I am not sure that the statement 'apparently, such processes do not seem to play an important role for HOxComp ...' is justified without a more in-depth justification of the model approach used in this work.

We hope that the statement is justified given the additional information regarding the model's sensitivity to the oxidation duration of isoprene.

8. Page 28864, line 17: Is there any explanation for the difference between the MPI observations and those from the other instruments?

It is beyond the scope of this paper to identify the instrumental differences responsible for the different results. As also requested by reviewer #2, however, several features of the instruments which might be related to the different behaviors are briefly mentioned in the Experimental section.

A tandem chamber with multi-pass for laser excitation was employed for the MPI instrument, 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).

9. Page 28866: Please provide some quantification of the relative importance of the

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processes controlling HOx and radical concentrations in the text.

Percentage contributions of major processes will be mentioned in the revised text.

10. Page 28867-8: What is the sensitivity of the modeled OH reactivity to the time period for which isoprene chemistry is included in the model? How do improvements to the modeled reactivity affect modeled concentrations of OH and HO2?

A longer time period allows buildup of unmeasured secondary products from isoprene chemistry and thus the OH reactivity is increased. However, the increase in OH reactivity is only ∼10% even when we allow their buildup to quasi steady state levels by including isoprene for 5 model days. Therefore the time period is not a sensitive parameter. The modeled concentrations of OH and HO2 after adjusting the reactivity by introducing unmeasured hydrocarbons have been discussed in these pages and the results are listed in Table 3.

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

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