

Comparisons of observed and modeled OH and HO₂ concentrations during the ambient measurement period of the HO_xComp field campaign

Kanaya et al.

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This paper presents the results of a modeling study to investigate our understanding of OH and HO₂ concentrations measured by several instruments and OH reactivity measurements during the ambient period of the HO_xComp field campaign in Germany in 2005. The authors describe the model framework, based on the RACM, and describe a number of sensitivity tests conducted to investigate the impacts of recent work regarding the oxidation of isoprene under low NO_x conditions. The authors also consider potential impacts of RO₂ interferences in LIF measurements of HO₂. The paper is generally well written and is within the scope of this journal. I have a few comments which the authors should consider in their revision of the manuscript.

Major comment

The authors describe a box model that is integrated over a 5 day period to calculate OH and HO₂ concentrations, but with isoprene chemistry only considered in the last 12 minutes of the model run to account for differences in modeled concentrations of the isoprene oxidation products MVK and methacrolein (MACR) with observations. The authors propose that consideration of isoprene chemistry in just the last 12 minutes of the model run (optimized to provide model success for MVK and MACR) represents the view that the site is impacted only by fresh emissions of isoprene and that isoprene chemistry is not active for sufficient time for isoprene oxidation products to reach steady state concentrations. While some evidence is proposed to explain the 12 minute period in terms of the time taken for an air mass to arrive at the site from the nearest significant isoprene source, this model approach requires a more in-depth justification and description.

Is there any evidence to suggest that air masses coming to the site from the local isoprene source do not also contain aged air and isoprene oxidation products in addition to the fresh isoprene emissions?

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?

How are the modeled HO_x 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 NO_x conditions, and state that the measurements during HO_xComp 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 HO_x 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.

Minor comments

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.

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.

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.

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, HO_x and OH reactivity.

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

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

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

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

Page 28866: Please provide some quantification of the relative importance of the processes controlling HO_x and radical concentrations in the text.

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?