

**We thank the anonymous referees for reading the paper carefully and providing thoughtful comments, which have resulted in improvements in the revised version of the manuscript. We reply to each comment below in bold text.**

## 5 **Anonymous Referee #1**

10 This paper presents measurements of OH, HO<sub>2</sub> and OH reactivity during the oxidation of 2-methyl-3-butene-2-ol (MBO) in the SAPHIR chamber. Measurements of OH and HO<sub>2</sub> using a Laser-Induced Fluorescence - Fluorescence Assay by Gas Expansion (LIF-FAGE) instrument. While potential interferences with the OH measurements were not measured, the LIF-FAGE measurements were in good agreement with OH measurements by differential optical absorption spectroscopy (DOAS) in the SAPHIR chamber, suggesting that interferences associated with the FAGE technique were minimal. Measurements of HO<sub>2</sub> were done at relatively low HO<sub>2</sub>+NO conversion efficiencies to minimize potential interferences from RO<sub>2</sub> radicals.

15 The authors find that modeled concentrations of OH and HO<sub>2</sub> concentrations during the oxidation of MBO using the latest version of the Master Chemical Mechanism were in good agreement with the measurements. The modeled total OH reactivity was also consistent with measurements of total OH reactivity as well as with measured total OH production, suggesting that the sources and sinks of OH were known and accounted for during the experiments. The modeled HO<sub>2</sub> production rate was also found to be in good agreement with the measured HO<sub>2</sub> loss rate, suggesting that the sources and sinks of this radical were accounted for during the oxidation experiments.

20 The results of these experiments are consistent with ambient measurements of OH and HO<sub>2</sub> in forests where MBO was the dominant biogenic emission, where modeled radical concentrations were found to be in good agreement with the measurements. The results presented here suggest that discrepancies between measurements and models in areas where MBO is not the dominate emission are not due to uncertainties associated with the MBO oxidation mechanism. Rather, the discrepancies may be due to uncertainties in the oxidation of other biogenic emissions such as the oxidation of monoterpenes leading to HO<sub>2</sub> production.

25 The paper is well written and the results suitable for publication in ACP after the authors have addressed the following:

30 1) The authors state that the largest uncertainty associated with the measurement – model agreement is the uncertainty associated with measurements of the OH reactivity during zero-air measurements, but it does not affect the modeled radical concentrations beyond the calibration accuracy of the measurements (pages 5-6). Unfortunately, Figure 2 does not display the model predictions of OH or HO<sub>2</sub> during the zero measurements after the chamber has been opened. The authors state that (page 5) “Because of the unknown chemical nature of the background reactivity that dominates the loss of OH radicals for the zero air phase of the experiment, agreement between measured and modelled radical concentrations cannot be expected during this initial phase. Therefore, no model calculation is shown for this part of the experiment.” However, this unknown background reactivity has been observed previously as referenced in the manuscript (Fuchs et al., 2014; Kaminski et al., 2017) and in these studies the authors were able to demonstrate reasonable agreement of the model with the measurements during the zero-air experiments prior to addition of the reactant of interest. It is unclear why the authors were unable to reproduce the initial OH and HO<sub>2</sub> concentrations in these experiments. Because the OH and HO<sub>2</sub> concentrations depend on radical production from the background production of HONO and HCHO as well as O<sub>3</sub> photolysis, illustrating the ability of the model to reproduce the chamber’s OH and HO<sub>2</sub> production during the zero-air experiments would give more confidence in the ability of the model to reproduce the radical concentrations after addition of MBO. This should be clarified in the revised manuscript.

35 **The authors would like to clarify the challenges in modelling the radical concentrations during the zero-air phase of experiments in the SAPHIR chamber. As the referee correctly underlines, there is production of radical species from HONO, HCHO and O<sub>3</sub> photolysis but not all of the OH radical reactants are known. After accounting for the known OH reactants, a large fraction of the measured OH reactivity during the zero-air phase (~ 70%) remains unexplained. To close the gap between the OH reactivity measurement and the model results in the zero-air phase, CO is chosen as the OH reactant with a direct formation of HO<sub>2</sub> radicals and its concentration is kept constant throughout the experiment. This is of course a simplified approach and its purpose is not to correctly reproduce the chemistry of the radical. Therefore a perfect agreement between radical measurements and model results is not expected. The authors would like to emphasize that after the injection of MBO the oxidation chemistry in the chamber is determined by MBO and its products as even when most of the MBO has reacted away, the unexplained background reactivity contributes to less than a third to the total OH reactivity. The zero-air phase mainly**

serves to check the status of the chamber to identify, for example, if there are any unexpected contaminations. This is now better clarified in the manuscript.

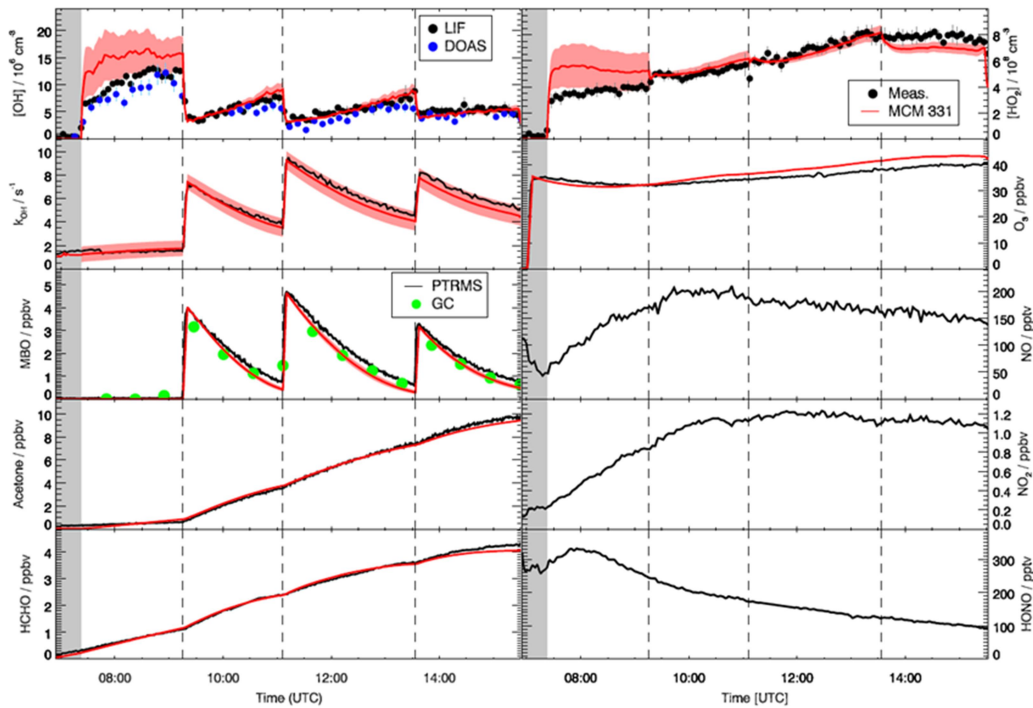


Figure 1. Measured time series including the modelling results during the zero-air phase.

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Model calculations during the zero-air phase for this study have larger uncertainties compared to experiments shown in the past due to an increased uncertainty on the total OH reactivity measurement ( $\pm 0.6 \text{ s}^{-1}$  compared to  $\pm 0.1 \text{ s}^{-1}$  observed in different experiments). As during the zero-air phase this uncertainty is a substantial fraction of the total reactivity, it propagates into a large uncertainty on the OH radical concentration. This effect can be seen in figure 1. The shaded area represents the uncertainty observed when using 0.6 or  $2.0 \text{ s}^{-1}$  as starting OH reactivity in the chamber. For the zero-air phase this results in an uncertainty of  $\sim 30 \%$  which reduces to less than 5% once the MBO is injected and the total OH reactivity reaches  $8 \text{ s}^{-1}$ . The agreement observed in figure 1 between model results and radical measurements in the zero-air phase is comparable to what observed in previous studies (Fuchs et al., 2013; Fuchs et al., 2014; Kaminski et al., 2017). As after the injection of MBO the reactivity of OH and HO<sub>2</sub> radicals is dominated by MBO and its products, the conclusions of this study are not affected by the unknown reactivity during the zero-air phase. However, following the suggestion of both referees figure 4 (see answer to comment #3), which shows model results also for the initial zero-air phase, was added to the supplementary information of the manuscript.

20

2) Similarly, a significant fraction of the modelled HO<sub>2</sub> radical budget appears to be due to the chamber source, which depends on the concentration of OH in the chamber. The authors state that the source is not "atmospherically relevant" (page 7). While I understand that this source is not relevant in the real atmosphere, do the authors mean that it is not a significant source in these chamber experiments, as it accounts for only 30% of the HO<sub>2</sub> production? This could be clarified. What would the budget (and the modeled HO<sub>2</sub> concentrations) look like if this source is removed?

25

The authors would like first to apologize to the referees as the wrong budget figure for the HO<sub>2</sub> radicals was shown in the manuscript. The budget for a reactivity of  $2.0 \text{ s}^{-1}$  during the zero-air phase was shown instead of the average values as shown in figure 1. The figure was modified (Figure 2).

30

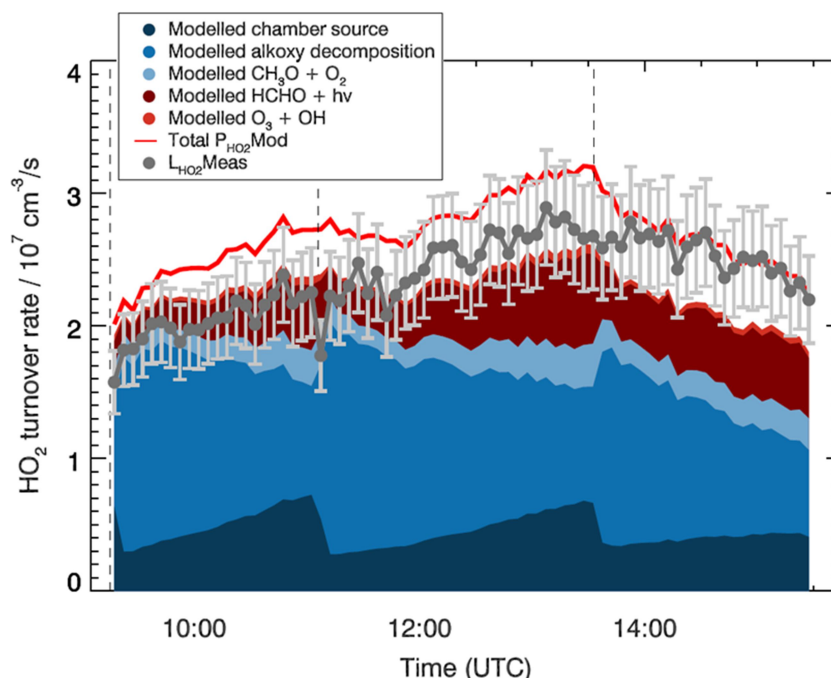


Figure 2. HO<sub>2</sub> budget for the MBO experiment.

- 5 With the comment “not atmospherically relevant” the authors wanted to underline that a certain fraction of HO<sub>2</sub> radicals, between 8 and 30%, on average, depending on the OH reactivity, is produced by the reaction of OH with species Y and therefore is not related to the MBO chemistry but is specific to the SAPHIR chamber. The sentence was rephrased for clarity in the manuscript. Following the suggestion of the referee, this source of HO<sub>2</sub> radicals was removed for a test-run of the
- 10 model (Figure 3).

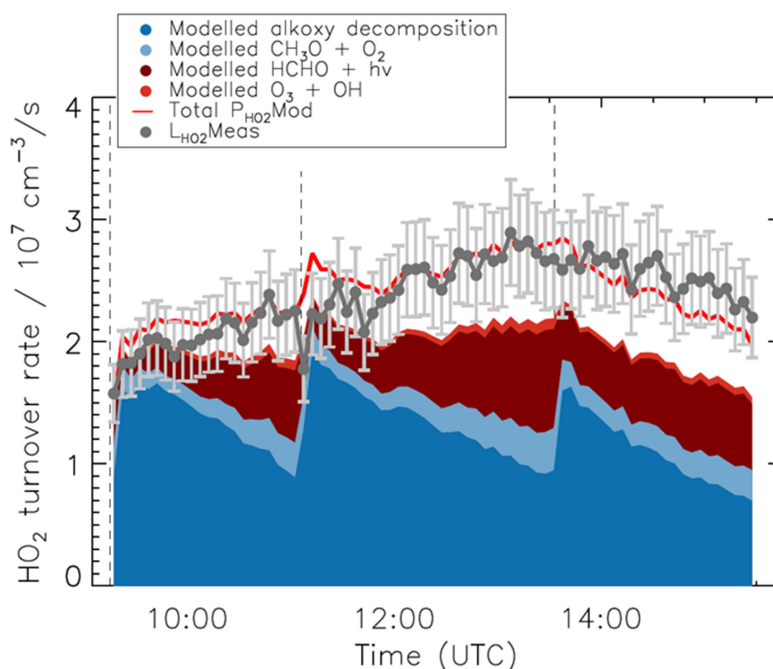


Figure 3. HO<sub>2</sub> budget for the MBO experiment removing the Y source.

- 15 When the chamber source Y is removed from the model, a larger contribution from the other sources to the HO<sub>2</sub> radical production can be observed and the agreement with the measurement is still good (Figure 3). A larger discrepancy would be observed in the agreement between OH and HO<sub>2</sub> radicals in the zero-air phase but after the injection of MBO the observed to model ratio for the HO<sub>2</sub> radicals would be on average  $0.7 \pm 0.2$  which is still reasonable. This is a confirmation that the chemistry observed during the zero-air phase of the experiment has a
- 20 negligible impact once MBO is injected in the chamber.

3) Related to this, the authors assume that the chamber source acts similarly to the OH + CO reaction and propagates OH directly to HO<sub>2</sub>. Have the authors done a sensitivity test where they assume the unknown OH reactivity leads to either RO<sub>2</sub> production or to OH radical termination instead of propagation directly to HO<sub>2</sub>? While the resulting modeled HO<sub>2</sub> concentrations appear relatively insensitive to the uncertainty associated with the OH reactivity measurement, it is not clear whether the modeled HO<sub>2</sub> concentrations and budget are sensitive to the assumption of the nature of the missing OH reactivity in the chamber. A missing reactivity mechanism that does not directly convert OH to HO<sub>2</sub> may lead to a model underestimation of the measured HO<sub>2</sub> concentrations, suggesting a missing HO<sub>2</sub> source similar to that found in the ambient measurements discussed in section 3.4. Again, demonstrating that the model can reproduce the observed OH and HO<sub>2</sub> during the zero-air experiments would provide some justification for their assumption of the nature of the missing OH reactivity in the chamber, but a sensitivity study that shows that the modeled HO<sub>2</sub> concentrations were relatively insensitive to the nature of the missing OH reactivity would also give confidence in their conclusion that the chemistry of OH and HO<sub>2</sub> is “well described our current understanding of the MBO OH-initiated degradation processes.”

15 **Following the suggestion of the referee, a test-run of the model using CH<sub>4</sub> as species Y instead of CO was performed. Figure 4 contains on the left panels a comparison for OH and HO<sub>2</sub> radicals, OH reactivity and MBO between model results and measurements when CO is used as species Y and on the right panels when using CH<sub>4</sub> as species Y instead. CO and CH<sub>4</sub> are used as they represent two extremes for the HO<sub>2</sub> formation after the reaction with OH. In the CO case the formation of HO<sub>2</sub> radicals is immediate, while with CH<sub>4</sub> there are several steps in between.**

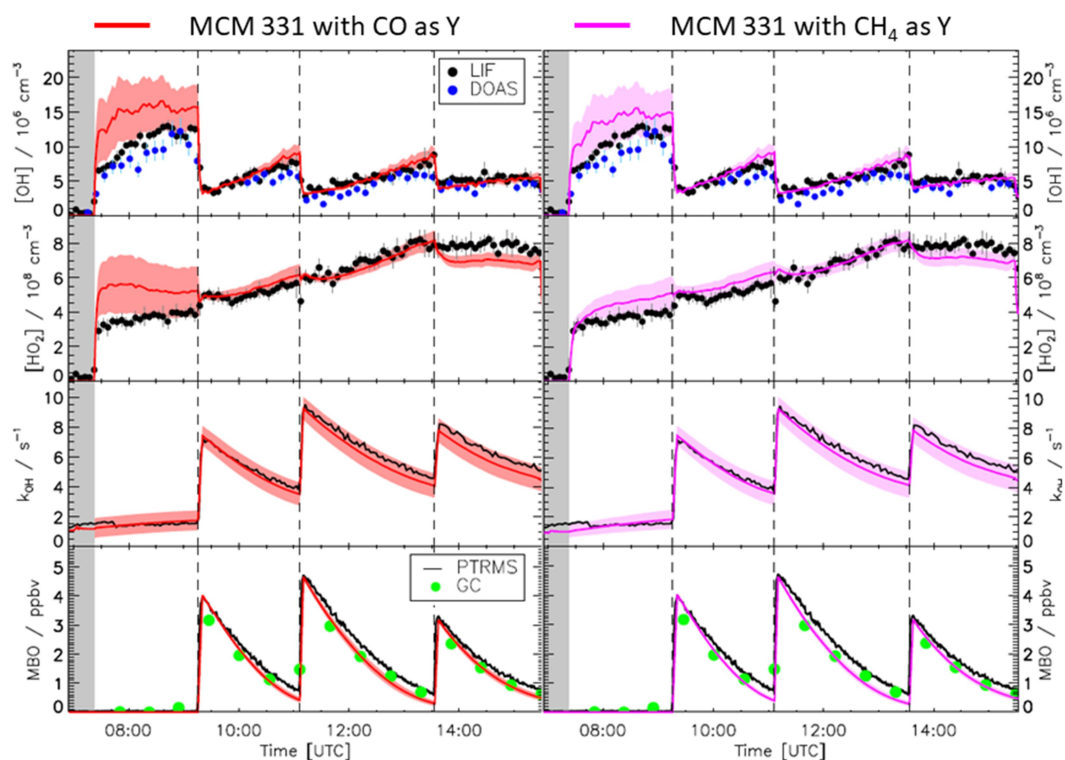


Figure 4. Measured time series including the modelling results during the zero-air phase using CO (left panels) or CH<sub>4</sub> (right panels) as Y species.

25 **When CH<sub>4</sub> is used as species Y there is a slight improvement during the zero-air phase in the agreement between model results and measured OH radicals. An even larger improvement can be observed, during the zero-air phase, for the HO<sub>2</sub> radicals. Nevertheless, after the injection of MBO there is a negligible difference for all species. This shows that after the injection of MBO, the radical concentrations are pretty**

30 **insensitive to the species Y confirming that the chemistry of OH and HO<sub>2</sub> radicals is well described by the current understanding of the MBO OH-initiated degradation processes. Figure 4 was added to the supplementary information of the manuscript.**

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5 This paper describes the data and analysis from a chamber experiment in which MBO was oxidized in the presence of NO<sub>x</sub>. Measurements of HO<sub>x</sub> radicals, oxides of nitrogen, ozone and organic compounds were made as functions of time during the experiment that included three additions of MBO spaced about two hours apart. The observations were compared with calculations using the Master Chemical Mechanism model modified to include hydrogen shift reactions of peroxy radicals. From the comparisons, it is concluded that oxidation of MBO is well-represented by MCM, and that observed levels of OH and HO<sub>2</sub> in two studies that exceeded calculated amounts cannot be explained by radical recycling in the oxidation of MBO.

10 General comments.

15 While the agreement between observations and the MCM model is impressive, this reviewer is concerned that a single experiment may not cover a sufficient range of conditions (e.g. NO, O<sub>3</sub> and MBO levels, *j*-values) to fully test the MCM MBO oxidation mechanism. Because of this, it is premature to conclude that MBO oxidation chemistry is fully understood. It is important to conduct experiments at very low NO levels, so that the other peroxy radical chemistry can compete with oxidation by NO.

20 **A total of three experiments were performed at very similar conditions as the one analyzed in this work but two of them were affected by instrumental failures and are therefore not included in this study. However, the good agreement between modelled and measured radical and trace gases found in the experiment shown in this work and also the results from theoretical work, from which no effect from additional radical chemistry is expected (Knap et al., 2016), led us to the decision that there was no need to perform more MBO chamber experiments, which require a high effort compared to typical laboratory experiments. The purpose of this work was to investigate the chemistry of MBO under conditions expected in a rural environment. The values of ozone and NO used during this experiment are comparable with what was observed in the two MBO field campaigns compared with this study (~50 ppbv of ozone and 150 pptv of NO). Therefore it is reasonable to say that, at typical atmospheric conditions in which MBO was previously measured in forests, this work shows that the MBO oxidation chemistry is fully understood.**

30 The background chamber chemistry, while having been characterized and discussed in the literature, is also of concern. Since the nature of the OH reactivity is not fully understood, one is left to wonder whether the specie(s) contributing are also impacting the types and chemistry of peroxy radicals produced in the chamber. A measurement of RO<sub>2</sub> would help clarify the radical chemistry. Also, presentation of attempts to model the background chemistry (that were not shown because of “the unknown chemical nature of the background reactivity”) would give the reader an indication of its cause and behavior, obviously without repeating everything in previous papers on this topic.

40 **Please refer to the answers 1 and 3 provided to referee #1**

This reviewer is willing to accept the paper (with revisions) based just on the one experiment, but the conclusions would be much stronger with additional chamber runs. Suggest the authors consider more experiments before publication.

45 Specific comments.

Abstract. In reading the first half of the abstract, this review was confused whether the discussion was related to the present study. Suggest adding something like “Several previous field studies” to indicate that this text is background information for the present study.

**Changed as suggested.**

50 Page 1, line 17. Suggest “...studies have reported unexpectedly large...”

**Changed as suggested.**

55 Page 1, line 18. Suggest “...mechanisms that largely...” or just eliminate “...which largely underestimated the observations”, since unexpectedly large observations and model underestimations are essentially the same thing.

**Changed as suggested.**

Page 1, line 22. Suggest “...radical concentrations showed...”

**Changed as suggested.**

60 Page 1, line 28. Suggest “...trace gases agreed well...”

**Changed as suggested.**

- Page 1, line 30. Suggest "...cannot contribute in reconciling the unexplained..."  
**Changed as suggested.**
- 5 Page 2, line 17. Suggest "...radical concentrations measured..."  
**Changed as suggested.**
- Page 2, line 40. Suggest "...within the Western US..."  
**Changed as suggested.**
- 10 Page 3, line 26. Suggest "...synthetic air until..."  
**Changed as suggested.**
- Page 3, line 30. The statement about ozone duplicates what was stated in lines 27-28. Suggest consolidating.  
**Changed as suggested.**
- 15 Page 4, line 7. Suggest "...agreement between these two instruments..."  
**Changed as suggested.**
- Page 4, lines 23-25. Is it possible to obtain concentrations of other hydrocarbon products that are expected (e.g. glycoaldehyde, HMPR, and others)? Also, do the PTR mass spectra offer any insight into the missing OH reactivity? A statement as to why certain species are observed and others are not would be instructive for the reader.  
**The PTRMS was only calibrated for the species shown in the figures and as such concentrations of other products are not available.**
- 25 Page 5, Line 9. This reviewer does not agree that agreement between measured and modeled concentrations cannot be expected during the initial phase (before MBO) addition. It is possible to constrain the nature of the OH reactant(s) by including a "CO-like" reactant and a "hydrocarbon-like" reactant. Suggest including the modeling results from the initial phase.
- 30 **Please refer to the answers to the first and third point of the referee #1. Following the comments of both referees a figure including the model results during the zero-air phase for both a CO and a hydrocarbon-like reactants was added to the supplementary information.**
- Page 5, line 30. Suggest "...more of the MBO that reacted..."  
**Changed as suggested.**
- 35 Page 5, line 35. Suggest "...although poorer than OH, was still satisfactory..."  
**Changed as suggested.**
- 40 Page 6, line 18. Suggest "...of any intermediates."  
**Changed as suggested.**
- Page 6, line 28. Suggest "...missing OH sources, assuming the correctness..."  
**Changed as suggested.**
- 45 Page 7, line 1-2. Suggest removing "where  $y$  is the fraction of O(1D) reacting with water vapour multiplied with the OH yield of the O(1D) + H<sub>2</sub>O reaction." This is given in page 6, lines 38-39.  
**Changed as suggested.**
- 50 Page 7, line 6. Suggest "...deviation becomes insignificant."  
**Changed as suggested.**
- Page 7, line 18. Suggest "Here, different from the..."  
**Changed as suggested.**
- 55 Page 7, line 22. Suggest more description of what is meant by decomposition of alkoxy radicals, perhaps showing a sample reaction.  
**The sentence in the manuscript was changed as it was not accurate and a direct reference to the reaction schematic (Figure 1 of the manuscript) was added.**
- 60 Page 7, line 26. Yes, the alkoxy radicals were not measured, but their abundance can be inferred from the rates of reaction of OH with hydrocarbons. This review suggests that a production of HO<sub>2</sub> can be calculated using steady-state assumptions for alkoxy radicals. Also, modeling exercises described earlier can help better constrain the background reactivity.

The authors prefer to keep the budget for the HO<sub>2</sub> radicals as is since the calculation of a steady-state concentration of alkoxy radicals would have to rely heavily on the results from the model result and would not add additional insights.

5 Page 7, line 36-37. Suggest "...when including the LHO2, meas..."  
**L<sub>HO2</sub> Meas is used as one word to be easily identified in the legend of figure 3.**

10 Page 8, lines 1-20. When discussing BEARPEX and BEACHON-ROCS measure-model comparisons, it is important to identify whether the models used the same mechanisms as that used in this study. Suggest adding one or sentences to clarify this.  
**A sentence to clarify was added.**

15 Page 8, line 32. Suggest "...state-of-the-art..."  
**Changed as suggested.**

Page 8, line 33-34. Suggest "...firstly, average observed to modeled ratios of 1.0 ± 0.2 and 0.9 ± 0.1 are found..."  
**Changed as suggested.**

20 Page 8, line 34-35. The observed to modeled MBO being near 1.0 does not mean the observed and modeled decays are in agreement. A fit of the ratios versus time for the observations and model would be better. Alternatively, a comparison of lifetimes for each of the decays could be instructive.  
**As can be seen from the time series plot in Fig. 2, the modelled MBO decays a little bit faster than the MBO measured by the PTRMS. This ratio becomes the highest (~ 1.5) at the very end of the experiment. The authors do not think it is necessary to add an additional plot showing the time dependency of the ratio.**

Page 8, line 38. Suggest "...do not have significant impacts on the model..."  
**Although we appreciate the suggestion of the referee, we prefer the current wording.**

30 Page 9, line 4. Suggest "...photo-oxidation as good agreement..."  
**Changed as suggested.**

Page 9, line 5. Suggest "As large discrepancies were also observed..."  
**Changed as suggested.**

35 Page 10. Suggest a note in the table to indicate that accuracy estimates are for concentrations well above the detection limit (which is three times the precision? Or ?). Also, suggest a note to indicate the PTR precision and accuracy values vary with compound. Could give a range of values rather than > and < values.  
**For this experiment, accuracy and precision for the species measured by the PTRMS (MBO and acetone) were the same.**

Page 15, References. Suggest using hanging paragraph indent, as it is difficult to find a specific reference with the current format.  
**Changed as suggested.**

45

## References

50 Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H. P., Haseler, R., Holland, F., Kaminski, M., Li, X., Lu, K., Nehr, S., Tillmann, R., Wegener, R., and Wahner, A.: Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, *Nat Geosci*, 6, 1023-1026, doi:10.1038/Ngeo1964, 2013.

55 Fuchs, H., Acir, I. H., Bohn, B., Brauers, T., Dorn, H. P., Häseler, R., Hofzumahaus, A., Holland, F., Kaminski, M., Li, X., Lu, K., Lutz, A., Nehr, S., Rohrer, F., Tillmann, R., Wegener, R., and Wahner, A.: OH regeneration from methacrolein oxidation investigated in the atmosphere simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 14, 7895-7908, doi:10.5194/acp-14-7895-2014, 2014.

60 Kaminski, M., Fuchs, H., Acir, I. H., Bohn, B., Brauers, T., Dorn, H. P., Häseler, R., Hofzumahaus, A., Li, X., Lutz, A., Nehr, S., Rohrer, F., Tillmann, R., Vereecken, L., Wegener, R., and Wahner, A.: Investigation of the β-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 17, 6631-6650, doi:10.5194/acp-17-6631-2017, 2017.

Knap, H. C., Schmidt, J. A., and Jorgensen, S.: Hydrogen shift reactions in four methyl-buten-ol (MBO) peroxy radicals and their impact on the atmosphere, *Atmos. Environ.*, 147, 79-87, doi:10.1016/j.atmosenv.2016.09.064, 2016.

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# Evaluation of OH and HO<sub>2</sub> concentrations and their budgets during photo-oxidation of 2-methyl-3-butene-2-ol (MBO) in the atmospheric simulation chamber SAPHIR

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**Abstract.** Several previous field studies have reported unexpectedly large concentrations of hydroxyl and hydroperoxyl radicals (OH and HO<sub>2</sub>, respectively) in forested environments that could not be explained by the traditional oxidation mechanisms which–that largely underestimated the observations. These environments were characterized by large concentrations of biogenic volatile organic compounds (BVOC) and low nitrogen oxide concentration. In isoprene-dominated environments, models developed to simulate atmospheric photochemistry generally underestimated the observed OH radical concentrations. In contrast, HO<sub>2</sub> radical concentration showed large discrepancies with model simulations mainly in non-isoprene dominated forested environments. An abundant BVOC emitted by lodgepole and ponderosa pines is 2-methyl-3-butene-2-ol (MBO), observed in large concentrations for studies where the HO<sub>2</sub> concentration was poorly described by model simulations. In this work, the photooxidation of MBO by OH was investigated for NO concentrations lower than 200 pptv in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich. Measurements of OH and HO<sub>2</sub> radicals, OH reactivity ( $k_{\text{OH}}$ ), MBO, OH precursors and organic products (acetone and formaldehyde) were used to test our current understanding of the OH-oxidation mechanisms for MBO by comparing measurements with model calculations. All the measured trace gases agree–agreed well with the model results (within 15%) indicating a well understood mechanism for the MBO oxidation by OH. Therefore, the oxidation of MBO cannot contribute to–reconcile reconciling the unexplained high OH and HO<sub>2</sub> radical concentrations found in previous field studies.

## 1 Introduction

The hydroxyl radical (OH) is the most important daytime oxidant in the troposphere and its concentration affects the fate of many pollutants thus having a direct impact on the formation of ozone (O<sub>3</sub>), oxygenated volatile organic compounds (OVOCs) and as such, influencing particle formation and climate. Understanding the OH radical formation and destruction paths is therefore critical.

Measurements of OH radicals in environments characterized by low NO concentrations, pristine conditions and isoprene being the most abundant measured BVOC (Carslaw et al., 2001; Tan et al., 2001; Lelieveld et al., 2008; Whalley et al., 2011; Wolfe et al., 2011a), as well as in environments characterized by mixed emissions from biogenic and anthropogenic sources (Hofzumahaus et al., 2009; Lu et al., 2012; Lu et al., 2013; Tan et al., 2017), have shown a significant underestimation of observed OH concentrations by state-of-the-art models. In addition, the analysis of the OH budget using only measured species obtained by comparing all known OH radical sources together with the OH radical loss rate has demonstrated that



the discrepancy with model simulations is due to a large missing OH radical source (Rohrer et al., 2014). Theoretical studies have proposed new OH recycling paths which, contrary to traditional mechanisms, do not require NO for the regeneration of HO<sub>x</sub> from RO<sub>2</sub> radicals. The proposed mechanism involves unimolecular reactions of specific isoprene peroxy radicals (RO<sub>2</sub>) (Dibble, 2004; Peeters et al., 2009; Nguyen et al., 2010; Peeters and Müller, 2010; Silva et al., 2010; Peeters and Nguyen, 2012; Peeters et al., 2014). Laboratory (Crounse et al., 2011) and chamber studies (Fuchs et al., 2013) have confirmed this mechanism and have helped constraining its atmospheric impact. Contemporary, other trace gases have been investigated as the results from the isoprene studies show that OH recycling through isoprene-RO<sub>2</sub>, alone, is not sufficient to explain the OH concentrations observed in the field. Chamber and laboratory studies on methacrolein (MACR) (Crounse et al., 2012; Fuchs et al., 2014), methyl vinyl ketone (MVK) (Praske et al., 2015), isoprene hydroxy hydroperoxide (D'Ambro et al., 2017) and glyoxal (Feierabend et al., 2008; Lockhart et al., 2013), important products from the oxidation of isoprene by OH, also have shown new OH recycling paths as predicted by theory (Peeters et al., 2009; da Silva, 2010; Setokuchi, 2011; da Silva, 2012). Further laboratory studies also have discovered OH radical recycling in the bimolecular reaction of HO<sub>2</sub> with acyl peroxy radicals which was previously considered to be a radical termination reaction only (Dillon and Crowley, 2008; Groß et al., 2014; Praske et al., 2015). These results underline the need to carefully investigate the OH radical budget, at least for the most abundant volatile organic compounds, to test our current knowledge.

In a similar way, the HO<sub>2</sub> radical ~~concentration~~ concentrations measured in several field campaigns performed in forested areas have shown discrepancy of measurements with model calculations highlighting an incomplete understanding of the chemistry involving formation and loss paths of HO<sub>2</sub> radicals. In some environments, the model tends to overestimate the measured HO<sub>2</sub> concentration (Stone et al., 2011) while in others there is the tendency to underestimate the measurements (Kubistin et al., 2010; Wolfe et al., 2011b; Hens et al., 2014; Wolfe et al., 2014). It has been recently shown that HO<sub>2</sub> radical measurements performed by laser induced fluorescence (LIF) via conversion of HO<sub>2</sub> into OH after reaction with nitrogen oxide (NO) are likely affected by an interference that originates from organic peroxy radicals (Fuchs et al., 2011; Nehr et al., 2011; Whalley et al., 2013; Lew et al., 2018). Therefore some of the discrepancies observed in previous studies may be partly caused by inaccurate HO<sub>2</sub> radical measurements. Nevertheless, recent studies where this peroxy radical interference is accounted for still showed discrepancy with model calculations (Griffith et al., 2013; Hens et al., 2014; Wolfe et al., 2014). These recent studies, performed in environments where isoprene was not the dominant measured BVOC, were all characterized by poor agreement between modelled and measured results for both OH and HO<sub>2</sub> concentrations, with the measurements being up to a factor of 3 higher than the model results. Good agreement was observed between modelled and measured OH radicals when the model is constrained to the HO<sub>2</sub> radical measurements. These studies have concluded that there is a missing HO<sub>2</sub> source for environments where the dominant measured BVOC are monoterpenes and 2-methyl-3-butene-2-ol (MBO) (Hens et al., 2014; Wolfe et al., 2014). Corresponding photo-oxidation studies have been performed for β-pinene in the SAPHIR chamber at Forschungszentrum Jülich. Consistent with field studies, a significant (up to a factor of 2) model under-prediction of both OH and HO<sub>2</sub> concentrations was observed when β-pinene was oxidized by OH under low-NO conditions (< 300 pptv) (Kaminski et al., 2017). The observed discrepancies in the chamber could be explained by additional HO<sub>2</sub> production, for which Kaminski et al. (2017) proposed a mechanism involving unimolecular radical reactions and photolysis of oxygenated products.

MBO is the dominant emission from lodgepole (*Pinus Contorta*) and ponderosa (*Pinus Ponderosa*) pines (Goldan et al., 1993; Harley et al., 1998). Its global emission is lower than that of isoprene (Guenther et al., 2012), but in forested areas within the West-US Western US, MBO is the most abundant BVOC measured contributing most of the measured OH reactivity (Nakashima et al., 2014; Ortega et al., 2014). In the atmosphere, MBO reacts primarily with OH forming two peroxy radicals that yield acetone, glycolaldehyde, 2-hydroxy-2-methylpropanal (HMPR) and formaldehyde after reaction with NO (Fantechi et al., 1998; Ferronato et al., 1998; Carrasco et al., 2006) (Fig. 1). The reaction of the peroxy radicals with HO<sub>2</sub> yields two different dihydroxy hydroperoxides (MBOAOOH and MBOBOOH, Fig. 1). Recent theoretical studies have

described a mechanism that involves additional hydrogen shift reactions for the RO<sub>2</sub> that reforms OH and produces HO<sub>2</sub> (Knap et al., 2015; Knap et al., 2016). As the predicted unimolecular reaction rate following the hydrogen shift is, at most, 1.1 x 10<sup>-3</sup> s<sup>-1</sup> (at 298 K and 1013 hPa) the study by Knap et al. (2016) concludes that in environments where the NO concentration is high (> 1 ppbv), the reaction between RO<sub>2</sub> and NO will be the dominant loss path for RO<sub>2</sub> radicals, and in  
5 forested areas, where the NO concentration is lower than 0.2 ppbv, reactions with HO<sub>2</sub> and RO<sub>2</sub> will dominate the RO<sub>2</sub> fate. In this study, the photo-oxidation of MBO initiated by OH radicals is investigated in the atmospheric simulation chamber SAPHIR in the presence of approximately 200 pptv of NO. The OH and HO<sub>2</sub> budget are analysed and a comparison with an up-to-date model is performed to test the current understanding of the oxidation processes of this important BVOC.

## 10 2 Methods

### 1.1 Atmospheric simulation chamber SAPHIR

The experiment performed in this study was conducted in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany. The chamber allows for the investigation of oxidation processes and mechanisms of organic compounds at atmospheric conditions in a controlled environment. The SAPHIR chamber has a cylindrical shape  
15 with a volume of 270 m<sup>3</sup> and is made of a double-wall Teflon (FEP) film that is inert and has a high transmittance for solar radiation (Bohn and Zilken, 2005). It is equipped with a shutter system that is opened during photolysis experiments allowing the natural solar radiation to penetrate the chamber. The air provided to the chamber is mixed from ultra-pure nitrogen and oxygen (Linde, > 99.99990 %). A fan in the chamber ensures a complete mixing of trace gases within two minutes. The pressure in the chamber is slightly higher than ambient pressure (~ 30 Pa) to avoid external air penetrating the  
20 chamber. Due to small leakages and air consumption by instruments, a dilution rate of ~ 4 % h<sup>-1</sup> was required during this study. More details regarding the chamber can be found elsewhere (Rohrer et al., 2005; Poppe et al., 2007; Schlosser et al., 2007).

### 1.2 Experimental procedure

At the beginning of the experiment, only synthetic air was present after flushing during the night. Evaporated Milli-Q<sup>®</sup> water  
25 was first introduced into the dark chamber by a carrier flow of synthetic air ~~containing~~ until a concentration of ~ 5 x 10<sup>17</sup> cm<sup>-3</sup> of water vapour was reached. Ozone produced by a silent discharge ozonizer (O3onia) was subsequently added to reach 40 ppbv in the chamber ~~and was used to keep the concentration of NO within a few hundreds of pptv~~. This initial phase is defined as the dark phase. After opening the shutter system of the chamber, nitrous acid (HONO) was photochemically formed on the Teflon surface and released into the chamber. Its subsequent photolysis produced OH radicals and NO  
30 (Rohrer et al., 2005) during this so-called zero-air phase. ~~Ozone (~ 40 ppbv) was injected to keep the concentration of NO within a few hundreds of pptv~~. Afterwards, the MBO was injected three times at intervals of about two hours using a high-concentration gas mixture of MBO (~ 600 ppm, 98% from Merck) pre-mixed in a Silcosteel Canister (Restek) to reach ~ 4 ppbv of MBO in the chamber after each injection.

### 1.3 Instrumentation

35 Table 1 summarizes the instruments available during the experiment quoting time resolution, 1σ accuracy, and precision for each instrument. The concentrations of OH and HO<sub>2</sub> radicals were measured with the laser induced fluorescence (LIF) instrument permanently in use at the SAPHIR chamber and described previously (Holland et al., 2003; Fuchs et al., 2011). Recent studies have shown the possibility of interferences on the OH signal measured by LIF instruments that depend both on the chemical conditions of the sampled air and on the geometry of the different instruments (Mao et al., 2012; Novelli et

al., 2014; Rickly and Stevens, 2018). A laboratory study performed with this LIF instrument (Fuchs et al., 2016) showed only interferences for high ozone concentrations (300 ppbv – 900 ppbv) together with BVOC concentrations ranging 1 to 450 ppbv which are far beyond any condition encountered in this study. Therefore, the OH radical concentration measured by the LIF instrument in this study is considered free from interferences. In addition, OH was measured by differential optical absorption spectroscopy (DOAS) (Dorn et al., 1995). Numerous intercomparisons between the LIF and the DOAS instrument in the SAPHIR chamber (Schlosser et al., 2007; Schlosser et al., 2009; Fuchs et al., 2012) showed very good agreement amid-between these two instruments giving high reliability to the OH radical measurements performed in the chamber. OH concentration measurements by DOAS in this study were on average 14% lower than those by LIF. This difference was well within the combined accuracies of measurements and was taken into account as additional uncertainty of OH concentration measurements in the analysis of this study, for which mainly OH data from the LIF instrument was used. Several studies have proven that RO<sub>2</sub> radicals can cause an interference signal in the HO<sub>2</sub> radicals measured by conversion to OH after reaction with an excess of NO (Fuchs et al., 2011; Hornbrook et al., 2011; Whalley et al., 2013; Lew et al., 2017). It was shown that a reasonable approach for avoiding the interference is to lower the concentration of NO reacting with the sampled air inside the instrument. During this study, the NO concentration ( $\sim 2.5 \times 10^{13} \text{ cm}^{-3}$ ) was thus adjusted to lower the interference to a minimum as described in Fuchs et al. (2011). As during the investigation of the interference from RO<sub>2</sub> originating from the oxidation of different VOCs, MBO was not tested, the amount of interference that arises from its oxidation products is not known (Fuchs et al., 2011; Whalley et al., 2013; Lew et al., 2017). An upper limit could be estimated from experiments with isoprene peroxy radicals at similar operational conditions of the instrument. The relative detection sensitivity for RO<sub>2</sub> radicals originated from isoprene, compared to the HO<sub>2</sub> signal, was among the largest of the studied peroxy radical species, with a value of 20% under the conditions of the present work (Fuchs et al., 2011). This value is considered to be a reasonable estimate bias in the HO<sub>2</sub> radical measurements and will be considered later in the discussion. The OH reactivity ( $k_{OH}$ ), the inverse lifetime of OH, was measured by a pump and probe technique coupled with a time-resolved detection of OH by LIF (Lou et al., 2010; Fuchs et al., 2017). MBO was measured by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, (Lindinger et al., 1998; Jordan et al., 2009)) and a gas chromatography system (GC, (Wegener et al., 2007)) with a PTR-TOF-MS to GC ratio of  $1.1 \pm 0.1$ , and acetone by PTR-TOF-MS. Formaldehyde (HCHO) was detected with a Hantzsch monitor (Kelly and Fortune, 1994), HONO with a long-path absorption photometry (LOPAP (Li et al., 2014)), carbon monoxide (CO) with a reduction gas analysis instrument (RGA, (Wegener et al., 2007)), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), water vapor by an instrument applying cavity ring-down spectroscopy (CRDS, Picarro), NO, nitrogen dioxide (NO<sub>2</sub>) with chemiluminescence (CL, (Ridley et al., 1992)) and O<sub>3</sub> by UV absorption (Ansyco). Photolysis frequencies were calculated from measurements of solar actinic radiation by a spectroradiometer (Bohn et al., 2005; Bohn and Zilken, 2005).

#### 1.4 Model calculations

A zero-dimensional box model using chemical mechanistic information from the Master Chemical Mechanism, MCM version 3.3.1 (Jenkin et al., 1997; Saunders et al., 2003) downloaded via website: <http://mcm.leeds.ac.uk/MCM> was used to calculate radical and trace gas concentrations. The model was implemented with specific chamber-related properties. First, a dilution rate was applied to all the trace gases present in the model to account for the dilution from the replenishing flow. The background production of HONO, HCHO and acetone known to occur in the sunlit chamber (Rohrer et al., 2005; Karl et al., 2006), was parametrized by an empirical function that depends on temperature, relative humidity and solar radiation. Source strengths were adjusted to match the time series of HCHO and acetone during the zero-air phase, when the chamber was the only source for these species ( $\sim 0.3 \text{ ppbv h}^{-1}$ ). These chamber sources also impacted the OH reactivity measured during the zero-air phase. Ideally, after accurately accounting for the chamber sources, the OH reactivity should be well

represented by the model, but it is commonly the case that there is still the need for an OH reactant equivalent to  $\sim 1.0 \text{ s}^{-1}$  of OH reactivity. This unexplained reactivity is parametrized with a co-reactant Y added to the model, which converts OH to HO<sub>2</sub> in the same way as CO does (Fuchs et al., 2012; Fuchs et al., 2014; Kaminski et al., 2017). The concentration of Y was adjusted to match the observed OH reactivity during the zero-air phase of the experiment and was kept constant throughout the experiment. The uncertainty of the OH reactivity in this experiment was  $\pm 0.6 \text{ s}^{-1}$  determined by the uncertainty in the instrumental zero ( $1.5 \text{ s}^{-1}$ ) of the OH reactivity instrument. This uncertainty was applied in sensitivity runs of the model, but had a minor effect on the results discussed here.

The unknown chemical nature of the background reactivity that dominates the loss of OH radicals for the zero-air phase of the experiment strongly limits the ability of the simple model used during this phase in reproducing the measured radical concentrations. Additional parameters such as, for example, a loss path for HO<sub>2</sub> radicals could improve the agreement with the model results but would hinder the concept of using a simple model. A test-run of the model using CH<sub>4</sub> as species Y instead of CO was performed and the results are shown in Figure 1 from the supplementary information. It can be clearly seen that using CH<sub>4</sub> as species Y instead of CO does increase the agreement between measured and modelled HO<sub>2</sub> radicals during the zero air-phase, but has a negligible impact on the agreement observed once the MBO is injected. This underlines how the radical concentrations are insensitive to the nature of the Y species once the MBO is present in the chamber. As the zero-air phase serves to check the status of the chamber to identify, for example, unexpected contamination and has no impact on the chemistry once MBO dominates the OH reactivity, no model calculation is shown for this part of the experiment in the following.

Because of the unknown chemical nature of the background reactivity that dominates the loss of OH radicals for the zero air phase of the experiment, agreement between measured and modelled radical concentrations cannot be expected during this initial phase. Therefore, no model calculation is shown for this part of the experiment.

Photolysis frequencies (j values) for O<sub>3</sub>, NO<sub>2</sub>, HONO, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and formaldehyde were constrained to the measurements. All the other photolysis frequencies present in the model were first calculated for clear sky conditions according to the MCM 3.3.1 and then scaled by the ratio of measured to calculated j(NO<sub>2</sub>) to account for clouds and transmission of the chamber film. The model was constrained to measured water vapour, chamber pressure (= ambient pressure), and temperature, NO, NO<sub>2</sub> and HONO. Values were re-initiated every minute. MBO and O<sub>3</sub> injections were implemented in the model by applying a source just active for the time of the injection. The O<sub>3</sub> source was adjusted to match the concentration measured at the injection and the MBO source to match the change in OH reactivity at the injection time. For completeness, the model included the reaction of MBO with O<sub>3</sub> although this reaction contributed on average 3% to the reactivity of MBO which was dominated by the reaction with OH radicals.

### 3 Results and discussion

#### 3.1 Model comparison

Figure 2 shows the times series for the trace gases measured during the MBO experiment compared to the model including the sensitivity runs for the uncertainty introduced by the zero OH-reactivity value. At the beginning of the experiment, during the dark phase, formation of radicals was not expected as the roof was closed and only water vapour and ozone were added. The reactivity of  $1.7 \text{ s}^{-1}$  observed during this phase was due to desorption of trace gases from the walls of the chamber that could be observed during the humidification process. Some of these trace gases are HONO, HCHO and acetone as seen from their slow but steady increase. Immediately after opening of the roof, there was production of OH, HO<sub>2</sub> radicals and NO<sub>x</sub> from the photolysis of HONO and HCHO. After the injection of MBO, the OH reactivity was dominated by the reaction with MBO ( $\sim 70\%$  for all three MBO injections) and its oxidation products contributed significantly to the OH reactivity, up to 40%, once most of the more of the MBO had reacted away. Good agreement between modelled and measured

concentrations, well within the accuracy of the different instruments, could be observed for the majority of the species when MBO was oxidized by OH in this experiment. Formation of both measured major products from the oxidation of MBO, formaldehyde and acetone, was well reproduced by the model (averaged measurement to model ratio of  $1.00 \pm 0.02$  for both). The modelled OH fitted the observation with an average measurement to model ratio of  $1.0 \pm 0.2$  and the agreement between modelled and measured HO<sub>2</sub> ~~was~~, although less good compared to the OH, was still satisfying ( $0.9 \pm 0.1$ ). The MBO decays due to its reaction with OH radicals were slightly over-predicted by the model (average observed to model ratio of  $1.3 \pm 0.2$ ) in accordance with the measured decline of OH reactivity. This is in agreement with the PTR-TOF-MS measurement. However, results did not change significantly if the model was constrained to measured MBO concentrations. The major uncertainties in this measurements-model comparison are introduced by the uncertainty of the zero measurement of the OH reactivity data and by the possible interference of RO<sub>2</sub> radicals in the measured HO<sub>2</sub> signal. The first mostly affects the agreement between measured and modelled results for the OH reactivity itself. Modelled OH and HO<sub>2</sub> radicals are also partially affected but the uncertainty introduced is lower than the accuracy of radical measurements while the remaining modelled species are not influenced. As mentioned in the instrumental description section, 20% is the upper limit for the interference from RO<sub>2</sub> radicals that could be expected from MBO on the HO<sub>2</sub> signal, based on the experiments performed with isoprene (Fuchs et al., 2011), for the conditions the instrument was run. The HO<sub>2</sub> concentration obtained from the model when accounting for this RO<sub>2</sub> interference would be, on average, only 8% larger ( $\sim 5.5 \times 10^7 \text{ cm}^{-3}$ ) than the HO<sub>2</sub> concentration without any RO<sub>2</sub> interference for the periods in the experiment where the MBO was present in the chamber. This value is lower than the accuracy of the HO<sub>2</sub> measurement itself and has an insignificant impact on the other trace gases.

### 3.2 Model comparison including hydrogen shift reactions

In a recent theoretical work from Knap et al. (2016), hydrogen shift reactions (H-shift) in the peroxy radicals originated after photooxidation of four different methyl-buten-ol isomers were investigated. The 1,4, 1,5 and 1,6 H-shift reactions were studied and the rate coefficients at ambient temperature and pressure were given. For the photooxidation of the MBO isomer under investigation in this study, predicted products are OH and HO<sub>2</sub> radicals, 2-hydroxy-2-methylpropanal (HMPP), acetone, and glycolaldehyde (Fig. 1). Also  $\beta$ - and  $\delta$ -epoxides are proposed as possible products although, due to their extremely slow unimolecular rate coefficients (Fig. 1), they are insignificant. As a sensitivity study, the three H-shift reactions, excluding the branching towards the epoxides, were included in the MCM 3.3.1 model as shown in Fig. 1, using the upper limit rate coefficients at 1013 hPa and 298 K as calculated by Knap et al. (2016). In the model, the H-shift reactions proceed directly to the final stable products ~~with no formation~~without formation of any intermediates. As expected from the low reaction rates for these reactions, their addition to the MBO degradation scheme has a very small impact with a change of less than 1% on any of the trace gases modelled in our chamber study bringing no improvement in the already good agreement between measurements and model calculations. This is consistent with the study by Knap et al. (2016) where they concluded that H-shift reactions are not relevant for the oxidation scheme of MBO even for low NO conditions ( $< 50 \text{ pptv}$ ) where the reaction with HO<sub>2</sub> remains the dominant loss process for the MBO-RO<sub>2</sub> radicals. This is also expected as MBO contains only one double bond and the fast H-shift reactions observed for isoprene and methacrolein are favoured by the formation of conjugated double bonds in the stable radical co-products (Peeters and Nguyen, 2012).

### 3.3 OH and HO<sub>2</sub> radicals budget analysis

The calculation of the experimental OH budget helps identifying possible missing OH sources, ~~trusting~~assuming on the correctness of the measured OH concentration and OH reactivity. The total experimental OH loss rate,  $L_{\text{OH}}$ , is given by the product of the OH concentration and the OH reactivity and, as the OH radical is assumed to be in steady-state, it should be

equal to the total OH production rate ( $P_{OH}$ ) (Eq. 1).  $P_{OH}$  includes the OH production rate from known sources,  $P_{OHMeas}$  (Eq. 2), plus other possible sources.  $L_{OH}$  can be compared with  $P_{OHMeas}$ , which can be calculated from the measured data.

$$L_{OH} = k_{OH} \times [OH] \approx P_{OH} = P_{OHMeas} + \text{other sources} \quad \text{Eq. 1}$$

$$P_{OHMeas} = ([HO_2] \times [NO] \times k_{HO_2+NO}) + ([HONO] \times j(HONO)) + ([O_3] \times j(O^1D) \times y) + ([HO_2] \times [O_3] \times k_{HO_2+O_3})$$

Eq. 2

Here  $[OH]$ ,  $[HO_2]$ ,  $[NO]$ ,  $[HONO]$ , and  $[O_3]$  represent the measured concentrations of the trace gases,  $k_{HO_2+NO}$  and  $k_{HO_2+O_3}$  the rate coefficient of  $HO_2$  with  $NO$  and ozone, respectively,  $j(HONO)$  and  $j(O^1D)$  the photolysis rates of  $HONO$  and  $O_3$ , respectively, and  $y$  is the fraction of  $O(^1D)$  reacting with water vapour multiplied with the OH yield of the  $O(^1D) + H_2O$  reaction. If all the sources contributing to the OH production are included in the calculation, then  $P_{OHMeas} \approx P_{OH}$ . In

10 this study, the known OH sources considered are: reaction of  $NO$  and  $HO_2$ ; reaction of  $O_3$  and  $HO_2$ ; photolysis of  $HONO$ ; photolysis of  $O_3$ , ~~where  $y$  is the fraction of  $O(^1D)$  reacting with water vapour multiplied with the OH yield of the  $O(^1D) + H_2O$  reaction.~~ The formation of OH from ozonolysis of MBO is not included as it does not contribute noticeably.

Figure 3 shows the comparison between  $P_{OHMeas}$  and the total experimental OH loss,  $L_{OH}$ . The averaged ratio between  $P_{OHMeas}$  and  $L_{OH}$  is  $0.9 \pm 0.1$  ( $1\sigma$ ). A small deviation from unity, which would indicate a missing OH source contributing at  
15 most 20% to the total OH production, is obtained. Nevertheless, if the errors of the different measurements are taken into account, this deviation becomes ~~not significant~~ insignificant. For example, the total error of the total experimental OH loss is ~~~ 2517%~~ to which the errors of the measured traces gases, mainly of the  $HO_2$  radicals (16%) and of the rate coefficients (~10%) used to calculate the  $P_{OHMeas}$ , should be added. From these considerations, the experimental OH budget can be considered closed and no additional OH sources aside the ones considered in Equation 2 is needed to explain the OH radicals  
20 loss.

Figure 3 also depicts the total modelled OH production  $P_{OHMod}$ . This is included in the analysis of the experimental OH radical budget to understand how well the OH-formation paths in the model can describe the measurements. The averaged ratio between  $P_{OHMod}$  and  $L_{OH}$  provides a value of  $1.0 \pm 0.1$  ( $1\sigma$ ). The good agreement observed between  $P_{OHMod}$  and  $L_{OH}$  indicates that the model is able to correctly represent the OH radical sources. The averaged difference between  $P_{OHMod}$  and  
25  $P_{OHMeas}$  is  $(2.3 \pm 1.9) \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ . A large part of the difference,  $\sim 1.5 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ , is due to additional OH radical sources included in the model and not considered in the experimental OH production, e.g.  $RO_2$  ( $CH_3CO_3$  and  $HOCH_2CO_3$ ) reacting with  $HO_2$  forming OH. The additional small discrepancy ( $\sim 0.8 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ ) is due to the differences observed for  $HO_2$  and ozone between measurements and model calculations.

The analysis of the  $HO_2$  budget is shown in Fig. 4. Here, ~~different~~ from the OH budget, the measured  $HO_2$  loss rate,  $L_{HO_2}$ ,  
30 is compared to the total modelled  $HO_2$  production rate,  $P_{HO_2Mod}$ . This comparison provides information on the completeness in the understanding of the  $HO_2$  production and loss processes for the MBO photooxidation mechanism.

Within the model, the fifteen most important  $HO_2$  production paths are explicitly considered and depicted in Fig. 4. ~~The largest contribution to the  $HO_2$  production comes from decomposition of alkoxy radicals with a subsequent reaction with oxygen (51%, see, as an example, reaction of MBOAO from Fig. 1), followed by the conversion of OH by species Y (20%) which is specific to the SAPHIR chamber and therefore not atmospherically relevant.~~ The largest contribution to the  $HO_2$   
35 ~~production comes from the decomposition of alkoxy radicals (46%), followed by the conversion of OH by the unknown background reactivity Y in the chamber (30%, not atmospherically relevant).~~ Smaller contributions originate from formaldehyde photolysis (~~1518%~~), and H-abstraction reaction by oxygen from the methoxy radical ( $CH_3O$ , ~~78%~~). As most of the relevant species contributing to the  $HO_2$  production rate such as the alkoxy radicals were not measured and the  
40 background reactivity Y cannot be specified, it is not possible to calculate the production rate of  $HO_2$  only from measured species as it was done for the OH radical budget.

The  $HO_2$  radical is expected to be lost mainly via its reaction with  $NO$  accounting for  $\sim 90\%$  of the total loss rate calculated from the model. Additional losses are  $HO_2+HO_2$  self-reaction, reaction with ozone and reaction with the first generation  $RO_2$

produced from the MBO oxidation (MBOAO2 and MBOBO2, Fig. 1). Therefore, the majority of the HO<sub>2</sub> loss rate can be obtained from measured NO, HO<sub>2</sub> and ozone concentrations (Eq. 3).

$$L_{HO_2} Meas = ([HO_2] \times [NO] \times k_{HO_2+NO}) + ([HO_2] \times [HO_2] \times k_{HO_2+HO_2}) + ([HO_2] \times [O_3] \times k_{HO_2+O_3}) \quad \text{Eq. 3}$$

Here [HO<sub>2</sub>], [NO], and [O<sub>3</sub>] represent the measured concentrations of the trace gases,  $k_{HO_2+N}$ ,  $k_{HO_2+HO_2}$  and  $k_{HO_2+O_3}$  the rate coefficient of HO<sub>2</sub> with NO, itself and O<sub>3</sub>, respectively. The measured HO<sub>2</sub> loss rate,  $L_{HO_2} Meas$ , is in good agreement with the total modelled HO<sub>2</sub> production rate with an average ratio of measured to modelled rates of  $0.8 \pm 0.1$ . The agreement with the total modelled HO<sub>2</sub> production increases (average ratio of measured to modelled rates of  $0.9 \pm 0.1$ ) when including in the  $L_{HO_2} Meas$  the modelled loss rate by the reaction of HO<sub>2</sub> with modelled RO<sub>2</sub> radicals. The largest discrepancies are observed during the first injection of MBO, because the calculated HO<sub>2</sub> production rate is smaller than what is obtained from the model. The main reason is the lower measured HO<sub>2</sub> concentration (13%) compared to the model during this period. With the increasing agreement between modelled and measured HO<sub>2</sub> radical also the agreement in the HO<sub>2</sub> budget increases. The good agreement observed in the HO<sub>2</sub> budget, although partly relying on modelled species concentrations, indicates that the HO<sub>2</sub> production, within this chamber experiment, can be explained by alkoxy radical decomposition, photolysis of formaldehyde, and the chamber specific Y source.

### 3.4 Comparison with previous studies

MBO was the major BVOC measured in two field campaigns which included measurements of OH and HO<sub>2</sub> radicals and a comparison with model calculations. The Biosphere Effects on Aerosols and Photochemistry Experiment II (BEARPEX09) campaign was performed near the Blodgett Forest Research Station in the California Sierra Nevada Mountains (Mao et al., 2012). This campaign was characterized by large MBO concentrations (daily average ~ 3000 pptv), followed by isoprene (daily average ~ 1700 pptv) and monoterpenes ( $\alpha$ -pinene, daily average 100 pptv and  $\beta$ -pinene, daily average 70 pptv). Both measured OH and HO<sub>2</sub> radicals compared reasonably well with modelled calculations, in agreement with the results observed in this chamber study.

The 2010 Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H<sub>2</sub>O, Organic and Nitrogen – Rocky Mountain Organic Carbon study (BEACHON-ROCS) was performed in the Manitou Experimental Forest in the Front range of the Colorado Rocky Mountains (Ortega et al., 2014). Here the dominant measured BVOC was MBO (daily average ~ 1600 pptv) followed by monoterpenes (daily average ~ 500 pptv) (Kim et al., 2013). As observed for the OH radical budget within this study, during the BEACHON-ROCS campaign the calculated OH concentration from ozone photolysis and from the recycling via HO<sub>2</sub> plus NO reaction, divided by the measured OH reactivity, agreed with the measured OH concentration (Kim et al., 2013). No additional OH recycling paths were necessary to close the OH budget. Nevertheless, during the BEACHON-ROCS campaign, the model was able to reproduce the OH radical concentration only when constrained to the HO<sub>2</sub> radical measurements as the model underestimated the measured HO<sub>2</sub> radicals up to a factor of 3 (Kim et al., 2013; Wolfe et al., 2014). This is different from what was observed in the chamber experiment discussed in this study where a good agreement ~~can be~~ was found between modelled and measured HO<sub>2</sub> concentration. The base models used during both campaigns contained the same MBO-oxidation scheme as tested in this study and as described in the MCM 3.3.1.

One difference between the two field studies is the BVOC compositions. During the BEARPEX09 campaign the concentration of the measured monoterpenes relative to the concentration of MBO during daytime was smaller (6%) compared to what observed during the BEACHON-ROCS campaign (31%). Two recent studies in environment with large concentrations of monoterpenes (Hens et al., 2014; Kaminski et al., 2017) also showed model calculations largely underestimating HO<sub>2</sub> radical measurement. Both studies concluded that the unaccounted HO<sub>2</sub> source seems to originate from monoterpene-oxidation products. The results collected by Hens et al. (2014) and by Kaminski et al. (2017) together with what is observed in this chamber study support that model-measurement discrepancies for HO<sub>2</sub> radicals in the BEACHON-

ROCS campaign are not related to the MBO and its oxidation products but rather to the presence of monoterpenes and, as they were present in smaller concentrations, they would need to constitute a very efficient source of HO<sub>2</sub> radicals.

#### 4 Summary and conclusions

A photooxidation experiment on 2-methyl-3-butene-2-ol (MBO), an important BVOC emitted by lodgepole and ponderosa pines, was performed in the atmospheric simulation chamber SAPHIR. Measurements of OH and HO<sub>2</sub> radicals and OH reactivity together with other important trace gases were compared to results from a state-of-the-art chemical mechanistic model (MCM v3.3.1). The overall agreement is very good: firstly, an average observed to model ratio of  $1.0 \pm 0.2$  and  $0.9 \pm 0.1$  is found for OH and HO<sub>2</sub> radicals, respectively. Also the MBO decay caused by reaction with OH radicals fits the expected decay from the model (average observed to model ratio of MBO concentration  $1.3 \pm 0.2$ ) and is consistent with the measured OH reactivity. Moreover, the major measured products, acetone and formaldehyde, both match the model calculation with an average ratio of  $1.00 \pm 0.02$ . Addition of H-shift reactions from RO<sub>2</sub> radicals to the kinetic model as suggested in the literature (Knap et al., 2016) does not have a significant impact on the model results as expected from the small reaction rates ( $< 1.1 \times 10^{-3} \text{ s}^{-1}$ ). The observed closure for both OH and HO<sub>2</sub> radical budgets indicates that their chemistry is well described by our current understanding of the MBO OH-initiated degradation processes.

The good agreement within the experimental OH budget is consistent with what was observed in previous field campaigns where MBO was the dominant BVOC measured (Mao et al., 2012; Kim et al., 2013). However there was no closure for the HO<sub>2</sub> budget or agreement between measurements and model results when a larger concentration of monoterpenes was also observed (Wolfe et al., 2014). This discrepancy cannot be explained by MBO photo-oxidation as a good agreement between measured and calculated concentration of HO<sub>2</sub> is found in this chamber study. As a large discrepancy ~~were~~ was also observed for chamber studies with  $\beta$ -pinene (Kaminski et al., 2017) and in environments with large monoterpene concentrations (Hens et al., 2014), it is reasonable to assume that field observation for HO<sub>2</sub> radicals could be explained by an additional HO<sub>2</sub> radical source from monoterpenes-oxidation products, as proposed by Kaminski et al. (2017).

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Table 1 Instrumentation for radical and trace-gas quantification during the MBO oxidation experiment.

	Technique	Time resolution	1 $\sigma$ precision	1 $\sigma$ accuracy
<b>OH</b>	LIF	47 s	0.3 x 10 <sup>6</sup> cm <sup>-3</sup>	13%
<b>OH</b>	DOAS	200 s	0.8 x 10 <sup>6</sup> cm <sup>-3</sup>	6.5%
<b>HO<sub>2</sub></b>	LIF	47 s	1.5 x 10 <sup>7</sup> cm <sup>-3</sup>	16%
<b>k<sub>OH</sub></b>	Laser-photolysis + LIF	180 s	0.3 s <sup>-1</sup>	10%
<b>NO</b>	Chemiluminescence	180 s	4 pptv	5%
<b>NO<sub>2</sub></b>	Chemiluminescence	180 s	2 pptv	5%
<b>HONO</b>	LOPAP	300 s	1.3 pptv	12%
<b>O<sub>3</sub></b>	UV-absorption	10 s	1 ppbv	5%
<b>VOCs</b>	PTR-TOF-MS	30 s	> 15 pptv	< 14%
<b>MBO</b>	GC	30 min	4 – 8 %	5%
<b>HCHO</b>	Hantzsch monitor	120 s	20 pptv	5%

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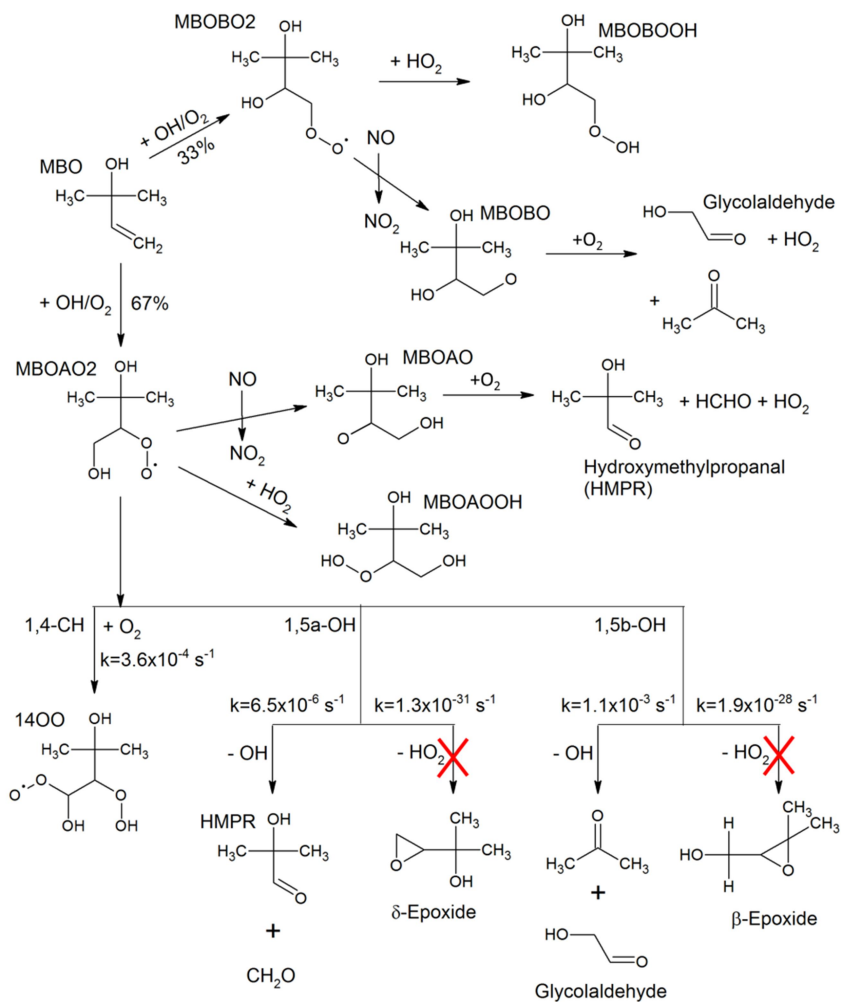


Figure 1: Simplified MBO OH-oxidation reaction scheme as described in the MCM version 3.3.1, including 1,4 and 1,5 H-shift reactions and their rate coefficient at 1013 hPa and 298 K as suggested by Knap et al. (2016). These H-shift reactions were added to the MCM version 3.3.1 kinetic model for a sensitivity test excluding the ones forming the epoxides (marked with the red cross).

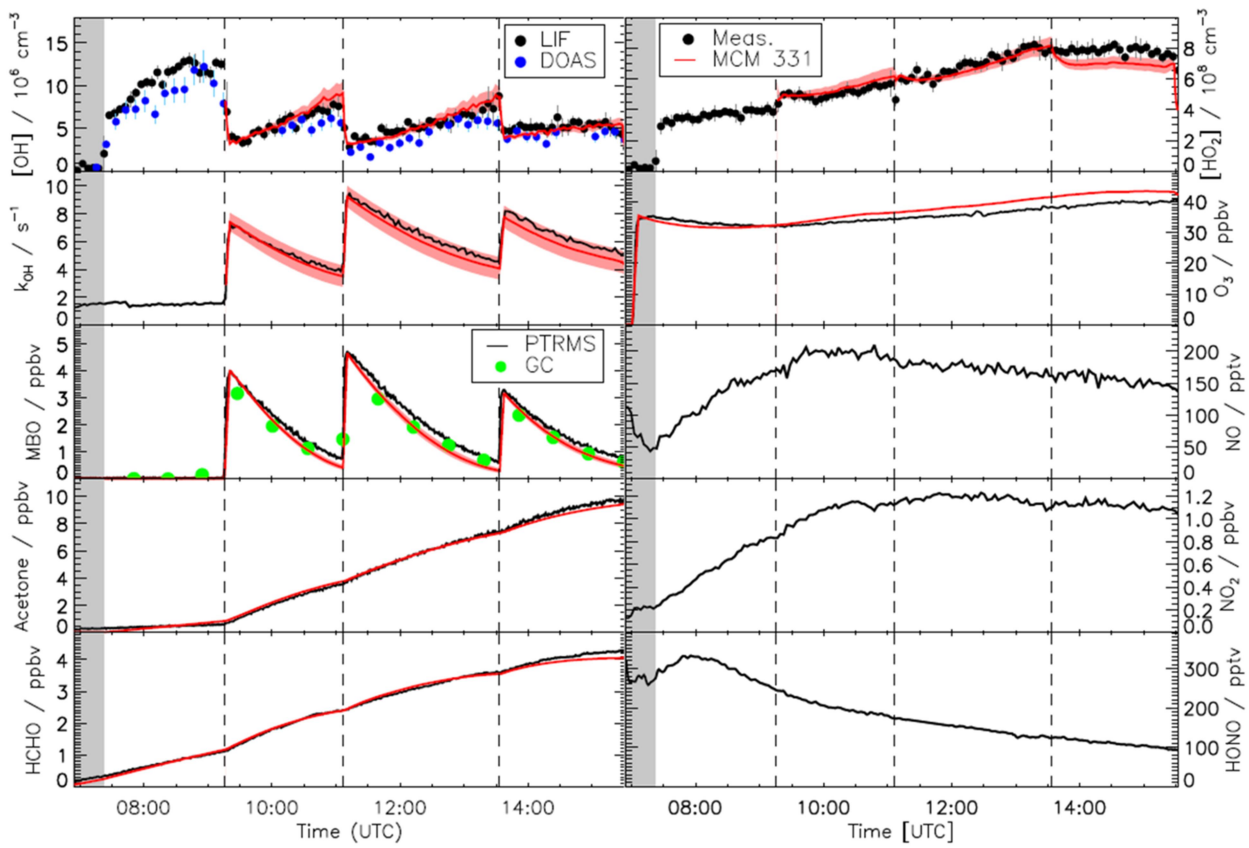


Figure 2: Measured time series of OH, HO<sub>2</sub>, MBO, acetone, formaldehyde, O<sub>3</sub>, trace gases and OH reactivity compared to results obtained from modelling using the MCM version 3.3.1. There are no model results for NO, NO<sub>2</sub>, and HONO as the model was constrained to the measurements. The red shaded areas represent the uncertainty of the model due to the uncertainties on the zero of the OH reactivity measurements (see text for details). Grey shaded areas indicate the times before opening the chamber roof and vertical dashed lines indicate the times when MBO was injected.

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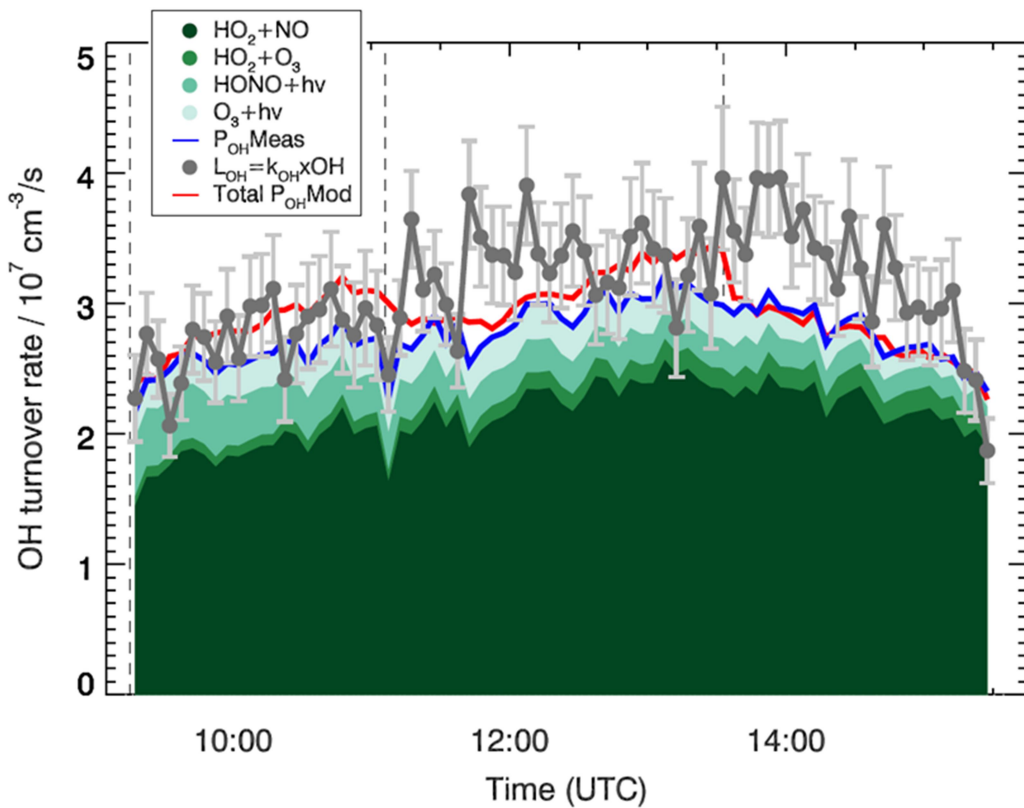
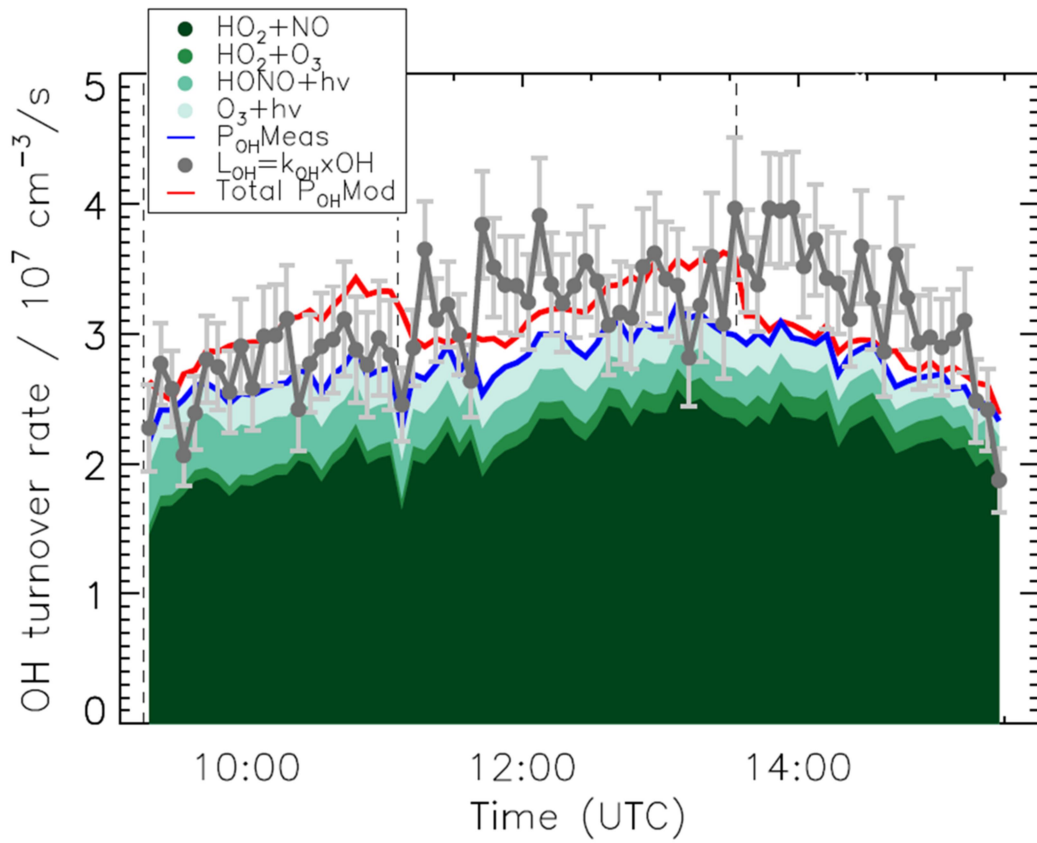
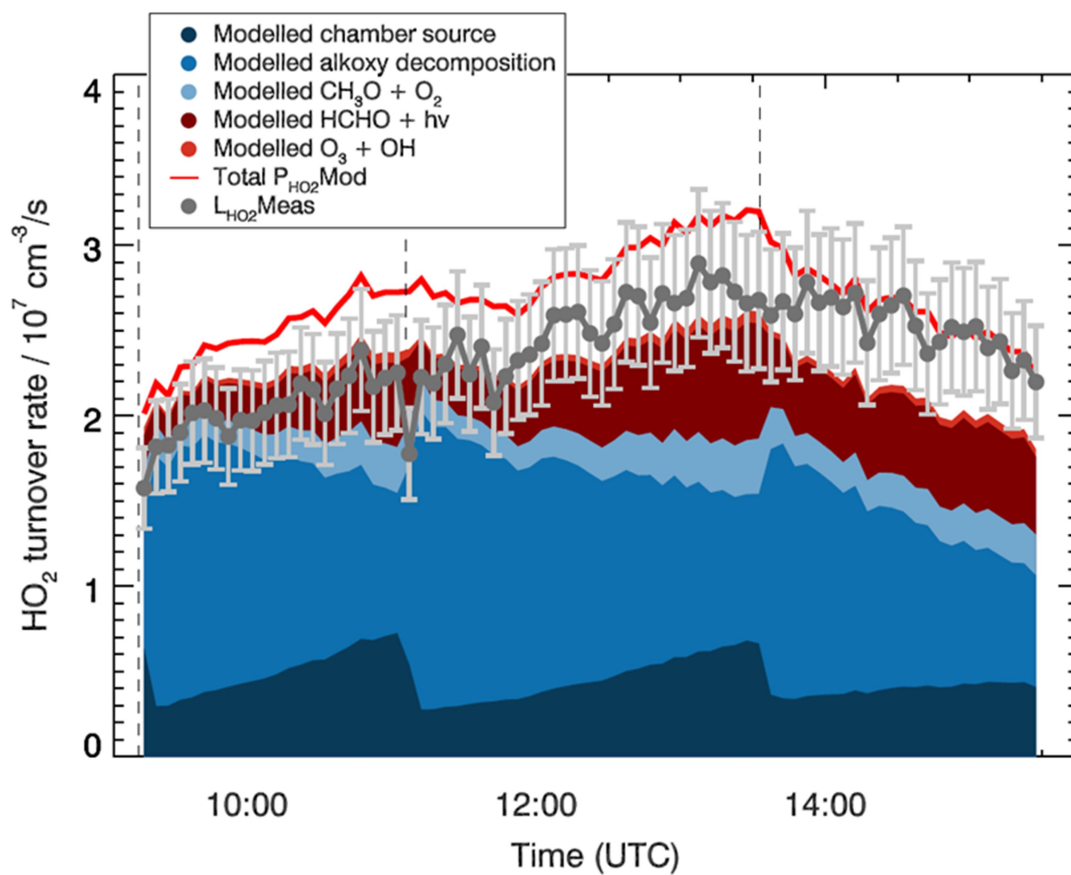
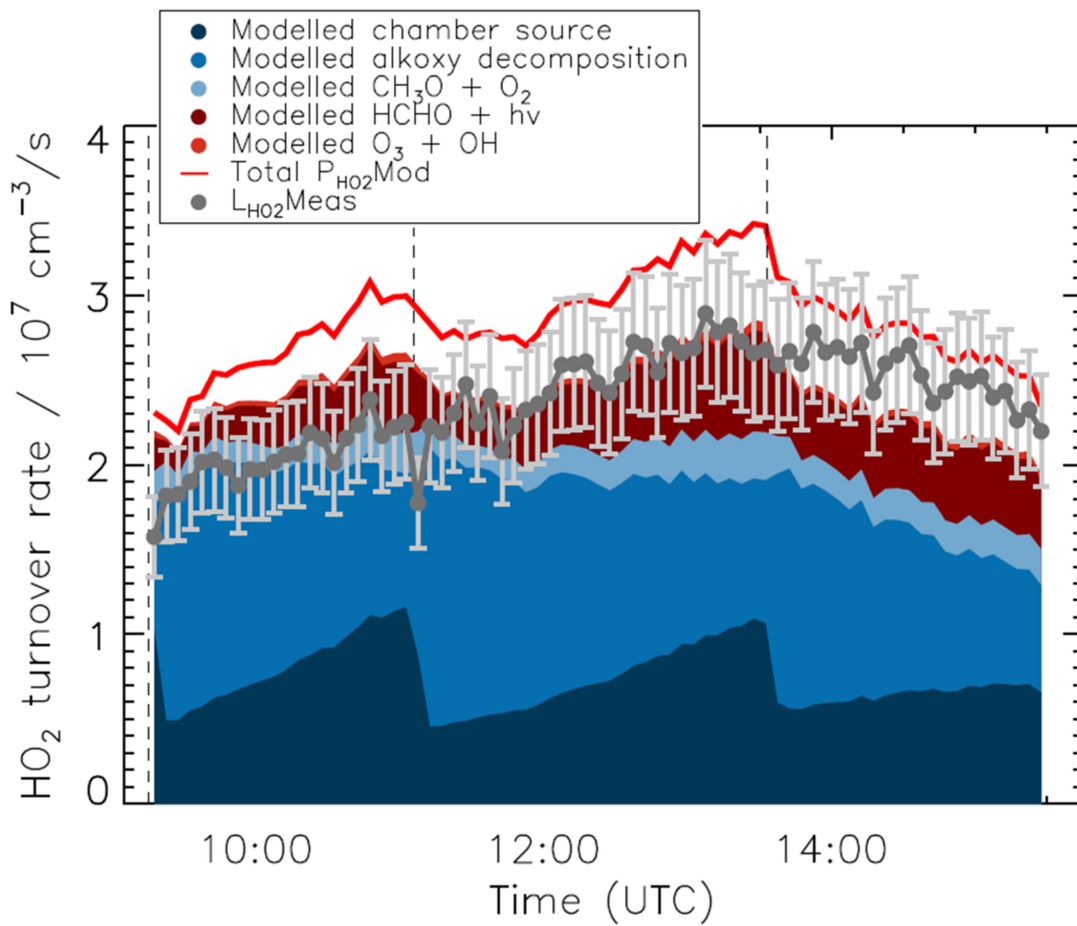


Figure 3: OH budget for the MBO experiment. The experimentally determined total OH loss rate,  $L_{OH}$ , and individual production terms are shown. For comparison, the red line indicates the total modelled OH production,  $P_{OH}Mod$ , which equals the modelled loss rate. Vertical dashed lines indicate the times when MBO was injected. Error bars ( $1\sigma$ ) for  $L_{OH}$  include the accuracy of measurements.



5 Figure 4: HO<sub>2</sub> budget for the MBO experiment. The loss rate of HO<sub>2</sub> calculated from measured NO, ozone and HO<sub>2</sub> concentrations, L<sub>HO<sub>2</sub></sub>Meas, and individual modelled production terms are shown. For comparison, the red line indicates the total

modelled HO<sub>2</sub> production, P<sub>HO<sub>2</sub></sub> Mod, which equals the total modelled loss rate. Vertical dashed lines indicate the times when MBO was injected. Error bars (1σ) for L<sub>HO<sub>2</sub></sub> Meas include the accuracy of HO<sub>2</sub> measurements.

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## Supplementary information

### Evaluation of OH and HO<sub>2</sub> concentrations and their budgets during photo-oxidation of 2-methyl-3-butene-2-ol (MBO) in the atmospheric simulation chamber SAPHIR

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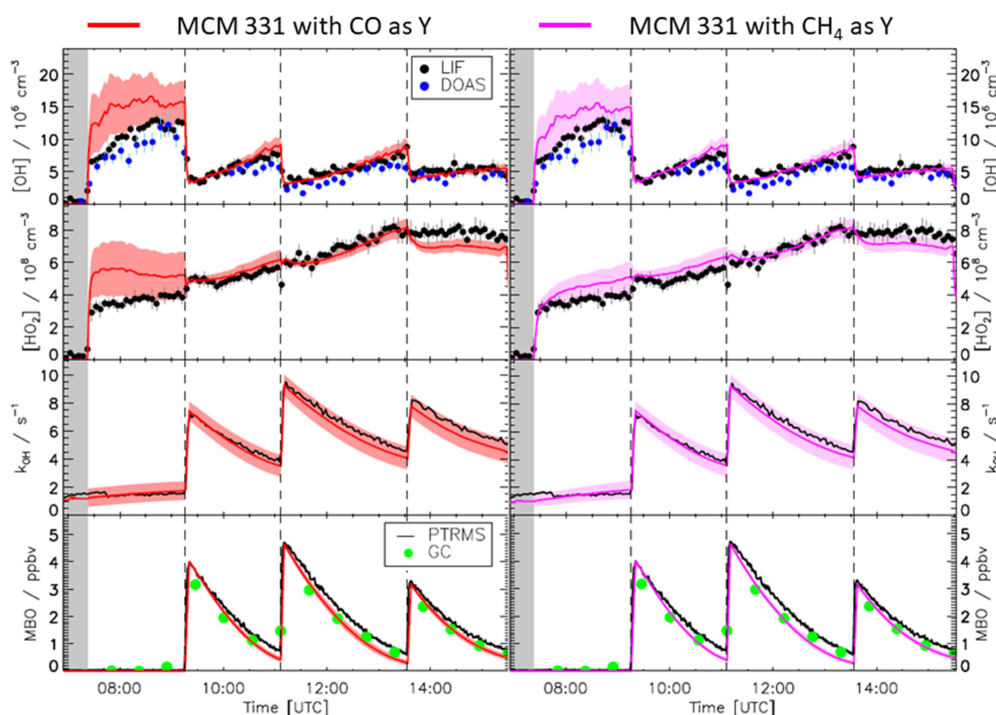
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#### Zero-air phase model results



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Figure S1: Measured time series of OH and HO<sub>2</sub> radical concentrations, OH reactivity and MBO concentrations compared to results obtained from modelling using the MCM version 3.3.1. On the left hand panels a hypothetical species Y that behaves like CO was introduced in the model to explain the background reactivity before addition of MBO. In the right hand panels Y is assumed to behave like CH<sub>4</sub> instead with a delayed secondary formation of HO<sub>2</sub> radicals. The red and pink shaded areas represent the uncertainty of the model caused by the uncertainties of the OH reactivity measurements (see text for details). Grey shaded areas indicate the times before opening the chamber roof and vertical dashed lines indicate the times when MBO was injected. Note that the model results after the injection of MBO do not differ significantly, i.e. the nature of the background reactivity in the chamber is secondary for the main part of the experiment. In Fig. 1 of the main manuscript the modelling results for the period before MBO injection were therefore omitted for clarity.

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