Response to the comments from referee #1:

We thank the reviewer for the helpful comments

Comment: My main comment is that from the way the data in figure 4 is presented the measured OH, at least by LIF, seems noticeably higher than the one modelled using "RO2 isom. B", especially in the last segment of the experiments. I very strongly suggest showing the data in the top right of figure 4, specifically LIF-OH, DOAS-OH, MCM OH and RO2 isom. B OH as ratio of measured to model. It is likely that due to the way the data is shown the measured LIF values lie behind the other traces, which gives rise to the impression I describe. I realize that Figure 5 shows something related for DOAS OH, but figure 4 does not look very similar and I think this needs to be clarified.

Response: The OH data in Figure 4 are from the experiment on 11 August 2011. On this particular day, the LIF data were indeed higher than the DOAS data by on average 0.5×10^6 cm^{-3} (determined from the intercept of a linear regression; Fuchs et al., 2012). Such a difference was not observed during other MACR oxidation experiments, leading to the conclusion that the OH measurements are not subject to a significant interference from MACR (Fuchs et al., 2012). In the present paper, we show data from the 11 August (Figs. 1, 2, 4, 5), because on this day the number of supporting measurements such as PAN, MPAN and HONO were available in contrast to the other two experiments. For the quantitative analysis in Figs. 2 and 5, we used the DOAS data because DOAS is regarded to be a reference technique. In Fig. 3, all data (LIF, DOAS) from all experiments were used to determine the OH yield of the missing OH source. The OH yield (slope of the regression line) has only a small sensitivity to the offset between DOAS and LIF. In fact, the offset has little impact on the results and conclusions of the present study. If we had used LIF data only, the result of the experiment would be still the same. All MACRO2 needs to produce OH from isomerization reactions, in order to explain the OH measurements. In order to address the referee's point, we will add the following explanations in the revised paper:

We will add a statement on p.5201 l.26: "On 11 August 2011 OH production rates from photolysis were highest and a large number of instruments was available. Therefore, time series and model calculations from this experiment are shown here. Experiments on the other two days give similar results and are included in the analysis of the OH budget."

We will add a statement on p.5202 l.28: "During the experiment on 11 August 2011, the correlation between OH measurements by DOAS and LIF shows a small intercept of 0.5×10^6 cm^{-3}, which was not observed in other experiments investigating MACR oxidation (Fuchs et al., 2012). For the analysis of data from 11 August 2011 in Fig. 2 and 5, we chose the DOAS data, which is regarded to be an absolute measurement reference."

We will add a statement on p.5211 l.22: "This result is independent of the choice of OH data from either the DOAS or the LIF instrument, because the lower limit is determined by the slightly smaller OH concentrations measured by DOAS compared to LIF (see above)."

Comment: Could the authors comment on the model under-prediction of HO2 observed in Figure 4 (it probably is not statistically significant?). Is the "unknown factor related to water vapor" (Fuchs et al. ACP 10, 12233-12250, 2010, doi:10.5194/acp-10-12233- 2010) of relevance for the work presented here?

Response: The reviewer is correct. The HO2 is described by all model modifications reasonably well within the accuracy of measurements considering the uncertainty of the calibration (except maybe the isomerization case A, which is not considered as a good description of the experiment). The reason for difference between measurements of three LIF instruments depending on water vapor observed during HOxCOMP is still not clear. We do not think that this is an issue for the work here, because differences between instruments during HOxCOMP were largest for small water concentrations, but

reasonably well agreed for higher water concentrations like in this study.

Comment: It could be useful to have a figure that shows the fractional contribution to sources of OH, as well as the (source) and sink of HO2. The reason is that although this is a regime in which HO2 is likely well coupled to OH via NO, HO2+NO cannot explain the OH, as the RO2 isomerization is so fast. This is quite interesting as it highlights that isomerizations have to be considered even outside of what is often considered strictly low NOx conditions.

Response: We fully agree with the reviewer that the fast isomerization reaction makes this reaction important for regimes with relatively high NO concentrations. We already tried to highlight this point and will strengthen it in the revised version (see also response to reviewer 1). Fig. 2, which shows the source and sinks of OH on an absolute scale, demonstrates the importance of the additional OH source, which is required to balance the OH destruction. A similar figure with fractional contributions would be redundant without new information. The values of the fraction of RO2 radicals that would isomerize for conditions of these experiments are given in the text (p.5211 l.6-9, l.22-24).

In contrast to the OH budget, it is not possible to deduce the HO2 budget from measurements alone. The main source of HO2 is the reaction of RO2 with NO, so that specified RO2 measurements would be required, in order to determine the correct HO2 production rate. The measurement of the sum of RO2 alone as done here, however, is not sufficient to determine the fraction of RO2 that would isomerize instead of reacting with NO. Similarly, one contribution to the HO2 loss rate would be the reaction of HO2 with RO2, which again would require specified RO2 measurement. Therefore, we do no think that a plot of the HO2 budget from measurements performed during these experiments would help, but would require a lengthy explanation of the limitations of such a plot.

Comment: P. 5214: "therefore substantial MACR" only if the conditions are not low NO(x). The MCM v3.2 being used in this work should have low MACR production from isoprene under low NO(x) (only via RO2+RO2).

Response: This statement refers to the reference Kubistin et al. 2010, where measured isoprene and MVK+MACR are given. For the case with the largest difference between measured and modelled OH concentrations 1.6ppbv MVK+MACR was measured in the presence of 4.3ppbv isoprene. We will change the first two sentences to: "... isoprene was the dominant OH reactant. Measurements of the sum of MVK and MACR also indicate substantial amounts of MACR (Kubistin et al., 2010)."

Comment: P. 5201 Line 20: Milli-q water is defined via conductivity, but organic species could be present that are not conductive (e.g., carbonyls). Were total organic carbon measurements conducted for these or previous experiments?

Response: The total carbon content of the water is monitored during the purification process. It was always less than 10ppbv in the liquid water before evaporation. Only small traces of organic compounds are typically found in the chamber after humidification of the chamber air (measured by GC).

Comment: P. 5205 Line 16: "unstable" or "labile"

Response: Done.

Comment: P. 5206: Line 6: Perhaps "blank experiment" or something similar would be clearer than "initial phase"

Response: We will change the text to: "...during the part of the experiment before OH reactants are injected into the chamber..."

Comment: Figure 1: Please clarify whether the shown measured and modelled HO2 includes the RO2 contribution or not.

Response: We will add to the legend of Fig. 1: "HO2 measurements and calculations include a small

interference from specific RO2 (see text for details)."

Comment: Figure 3: "has elapsed"

Response: Done.

Response to the comments from referee #2:

We thank the reviewer for the helpful comments.

Comment: One subtlety that almost gets lost in the detail is that even in the presence of 90 ppt NO (or $\approx$1 ppb NOx), the isomerization reaction still dominates. Maybe this could be stated more forcibly.

Response: We agree. We will add a sentence at the end of the abstract: "The isomerization reaction would be the dominant reaction pathway for this specific RO2 radical in forested regions, where NO mixing ratios are typically much smaller." We will change the text on p.5213 l.22-23 to: "Thus, the 1,4-H-shift reaction would be competitive to the reaction of MACRO2 with 150 pptv NO or even higher NO mixing ratios.

Comment: The measured loss of methacrolein is larger than that predicted by MCM. However, the MPAN concentration is modeled quite well. Why is this the case?

Response: The calculated MPAN mixing ratio depends on the yield of MACO3 in the reaction of methacrolein and OH, the calculated NO2 concentration, temperature and the thermal equilibrium constant. Only few studies exist investigating the MACO3 yield and the thermal equilibrium of MPAN. Therefore, calculated MPAN mixing ratios are considered to have a large uncertainty. The measurements of MPAN have a larger uncertainty (20%) than stated in the original manuscript. The value has been corrected in the revised version (Tab. 2), because the sensitivity of the GC for MPAN was deduced from the measured sensitivity for PAN with a correction taken from literature (Flocke et al., J. Atom. Chem., 2005). As seen in Fig. 4 calculated MPAN mixing ratios do not change more than 30% between the model runs. Adjustment of the MACO3 yield in the reaction between methacrolein and OH and/or the thermal equilibrium constant within their uncertainties can easily change calculated MPAN mixing ratios for a perfect match with observations. Therefore, we do not regard the apparently better agreement of calculated MPAN mixing ratios compared to the agreement of methacrolein in the MCM model run as a hint for an inconsistent description.

Comment: Could you comment on the MPAN profiles? Do they roll off because of loss by OH + MPAN, or because of decreased production efficiency?

Response: The shape of the MPAN profile is eventually determined by the production of MACO3 radicals. MACO3 production decreases after each methacrolein injection due to the consumption of MACR. Therefore, MPAN production decreases, but also the loss of MPAN due to its thermal equilibrium with MACO3 increases. The loss rate of MPAN due to its reaction with OH is at least four times smaller for conditions of this experiment. We will add on p.5206 l.3: "The shape of the temporal behavior of MPAN mixing ratios is determined by the thermal equilibrium between MPAN and MACO3, forcing the fast built up of MPAN after each methacrolein injection. At later times, the MPAN reservoir starts to deplete, when MACO3 concentrations are decreasing with the decreasing production from the reaction of MACR with OH."

Comment: Do the formaldehyde measurements provide any constraint on the chemistry, and in particular the extent of cycling?

Response: Formaldehyde is not thought to be a co-product of hydroxyacetone, the product species, whose concentrations is affected most by the additional OH cycling processes. It is mostly determined here by the processing of acetaldehyde, PAN, and MPAN. Because we have a small source of acetaldehyde and also formaldehyde in the chamber, the contribution of formaldehyde from MPAN is too small for a better constraint of MPAN (and therefore the production of MACO3 as a product of the MACR+OH reaction) for conditions of these experiments.

Comment: I presume that the RO2 instrument is mainly measuring "MACRO2" radicals. If so, a short, specific statement as to their detection efficiency, and their contribution to the HO2 measure-

ment, would be useful.

Response: Only model calculations allow concentrations of specific RO2 to be estimated. Here, a larger part of the total RO2 was also methyl-peroxy radicals for conditions of these experiments. However, the fractional contribution changes over the course of the experiment and strongly depends on the model that is applied. For example, application of the model modification that includes the fast isomerization predicts that the majority of RO2 radicals is CH3O2 due to the short lifetime of MACRO2 in this case.

For these reasons, also the contribution to HO2 measurements can only be estimated using model calculations as stated on p.5204 l.20-22. We will add two more specific statements:

p.5204 l.20-22: "... the contribution of this interference to the entire HO2 detection was less than 5%, most of which is caused by RO2 from MACR."

p.5202 l.22: "The detection efficiency for MACR derived RO2 which are efficiently converted is similar to that of methyl-peroxy radicals."

Comment: 5199-18. "products yields" should be "product yields"

Response: Done.

Comment: 5201-25. It looks like 3 injections of about 7 ppb MACR were made. This might be a more useful statement, rather than "maximum mixing ratio up to 14 ppb".

Response: We will change the statement accordingly: "The initial phase ("ZA") with zero air, water vapour, and ozone had a total duration of 2 hours. Thereafter, MACR was injected several times increasing the mixing ratio by 7 ppbv each time. The maximum mixing ratio was 14 ppbv."

Comment: 5205-16. "instable" should be "unstable".

Response: Done.

Comment: 5208, (R8) and (R9): The products in Table 4 are different from those in the text.

Response: We will correct the typo in the table.

Comment: Figs 4 and 5. The red and pink colors are a little hard to distinguish.

Response: We will change colors.

Comment: 5210, bottom. MACROHO2 can actually undergo two 1,5 H-shifts, both leading to the same products. Please state explicitly that it is the shift of the aldehyde H you are talking about.

Response: We will change the text on p.5210 l.26 to: "The 1,5-H-shift of the aldehyde H-atom in MACROHO2 would produce hydroperoxyacetone..."

Comment: 5211-3. "According to this study" Please specify which (Crounse or the present one).

Response: We will change the text on p.5211 l.3 to: "According to the study by Crounse et al. ..."

Comment: 5212-1. I still think it is a little glib to say that the yield 0.47 is consistent with 0.77 +/- 0.3.

Response: The error of 0.3 of the slope in our correlation analysis results from the 1-σ accuracy of several measurements. Moreover, also the yield of MACROHO2 (8 %) needs to be added, if the mechanism by Crounse is applicable, because also MACROHO2 would exclusively isomerize for conditions of this experiment. We will change the text on p.5212 l.1 to: "Our OH yield of 0.77 for each OH radical consumed by MACR (Fig. 3) is larger than the yield of 0.55 predicted by the model calculation, if MACRO2 and MACROHO2 is completely converted to OH in the isomerization reaction. This is, however, no contradiction considering the relative large uncertainty of ± 0.3 (1-σ) of our experimental value and the uncertainty of the model. Thus, our SAPHIR experiments presented

in this work do not allow to determine an upper limit of the 1,4-H-shift isomerization rate constant."

Comment: Overall, this is an excellent study. The analysis understandably focuses on the radical budget, but this means that some details, such as the MPAN and NO/NOx profiles, get overlooked. The authors should consider whether the inclusion of any of these other results could help to reduce the uncertainties in their measurements.

Response: The reviewer is correct that the focus of this study was on the radical budget. We certainly looked into the budget for nitrogen oxides. However, the longer lifetime of nitrogen oxide species compared to HOx radicals makes an analysis more complicated, because chamber sources (HONO) and reservoir species (see response above) have to be known with high accuracy. This was beyond the scope of this study. Regarding the OH cycling, nitrogen oxide species would not give a better constraint than determined from the OH budget. Especially MPAN is formed from the RO2 species (MACO3), which is not thought to produce OH from an H-shift reaction. Therefore, MPAN would only be useful to better constrain the yield of the different RO2 species.