

Response to Anonymous Referee #1

We would like to thank the reviewers for their efforts in reviewing this manuscript, and we feel that the manuscript is much stronger with the suggested changes. Below are detailed responses to their comments, which are highlighted in italics.

This paper focuses on the characterization of the RO₂-originated interference in the HO₂ signal measured with the LIF-FAGE instrument from the Indiana University. This interference was shown to affect LIF-FAGE instruments from several groups (Fuchs et al., 2011; Whalley et al., 2013) in a different amount connected to the geometry of the detection cell, the methodology of the NO injection and the sample flow. These together determine the concentration and the mixing of the NO in the cell and affect the conversion of RO₂ into HO₂. In this study, several VOCs, relevant for the different campaigns in which the instrument was deployed, were tested and the impact on the MCMA-2006 campaign was evaluated.

The paper is well written and the results are well presented. Publication is recommended after the authors address the following points:

1- It is not clear why it was not possible to replicate the exact same NO flow observed during the MCMA-2006 campaign. The authors say that the flow of NO during the test was kept at 1 sccm as this was the flow during all the campaigns (page 8 and 9) although saying that in reality the flow during the MCMA-2006 campaign was changed and a larger flow of NO could (reasonably) explain the discrepancy in the HO₂ to OH conversion efficiency observed. Is it not possible to actually operate at the NO flow used during the MCMA-2006 campaign? How different was the NO flow? As this discussion focus on the MCMA-2006 campaign a better characterization of the interference impact for this campaign would be beneficial.

The NO flow of 1 sccm used in these experiments is the same NO flow reportedly used during the MCMA 2006 campaign. However, the measured HO₂-to-OH conversion efficiency at this NO flow in these experiments was found to be approximately 20% lower than the HO₂-to-OH conversion efficiency measured during the MCMA 2006 campaign, and the reason for this discrepancy is unclear. As discussed in the manuscript, potential explanations include the possibility that the NO flow during MCMA-2006 was actually greater than the 1 sccm that was measured, or it may indicate problems in accurately recreating the overall detection cell flow and mixing conditions during this campaign in these laboratory experiments. Since it is not known whether the flow was greater than the 1 sccm that was measured, or whether the flow conditions led to more efficient mixing, we chose to conduct the experiments using the measured 1 sccm flow rate, with the caveat that the conversion efficiencies may represent a lower limit to the actual conversion efficiencies during MCMA-2006. We have clarified this in the revised manuscript.

2- The use of RACM to compare with previous results is interesting although, as there is now the availability of RACM2 (which should be an improved version of RACM) and as the authors do mention that the discrepancy between the model results and the measured HO₂ could be due to the different treatment of dycarbonyl species, a model run using the more update RACM2 should be performed. It would be an interesting add up to this work and could help understanding the reasons of the discrepancy between model results and measured data.*

We chose to compare the measurements to the model results using the RACM mechanism so that they could be compared to the RACM results originally published in Dusanter et al. (2009b). We agree that a comparison of the measurements with the updated RACM2 mechanism would be valuable, and we are planning to do this in a subsequent publication that also examines photochemical production rates of ozone during the campaign.

Minor comments:

Page 4, lines 16 and 20. The laser was changed between the campaigns and the laboratory tests although the name given for the new laser model is the same as for the old laser model. What is the difference then?

Although the pump lasers are identical, the original laser system operated at 5 kHz repetition rate and pumped a Lambda Physik dye laser. Preliminary measurements of the conversion efficiencies were done with this laser, which was the same model used during the MCMA-2006 campaign. The new laser operates at 10 kHz and pumps a different dye laser (Sirah Credo). The conversion efficiencies measured by the two laser systems were similar. This has been clarified in the revised manuscript.

Page 5, line 4. Is there any improvement in injecting NO so far from the detection cell? As far as the reviewer is aware most of the other LIF-FAGE instrument inject the NO immediately on the top of the detection cell also to reduce the losses of OH radicals.

The longer inlet was originally used to increase the reaction time for the conversion of HO₂ to OH. This inlet length does have the advantage of raising the inlet farther above the detection cell to avoid any possible surface effects from the environmental cover over the detection cell. However, it does lead to increased wall loss of OH which results in somewhat lower sensitivity to ambient OH.

Page 7, line 15. It could be helpful to rename COH+VOC in COH→RO₂ for consistency with all the other conversion efficiency.

This has been renamed as suggested.

Page 9, line 16. Please, state in the summary table 2 the number of experiments performed for each VOC.

The number of experiments performed for each VOC is given by the number in parenthesis after the conversion efficiency in Table 2.

Page 10, lines 10 to 16. It is interesting to observe such a different result from what observed previously by Fuchs et al. (2011). It would be beneficial to extend the discussion a little bit. Why the authors think there is this discrepancy? Is the same type of mercury lamp used by both groups? Could it be possible that the signal observed arises from impurities present in the VOC samples? How much is the HO₂ signal due to the photolysis of the VOC?

We have expanded the discussion as suggested, as differences in the mercury lamp flux or impurities in the VOC samples could have led to the production of both OH and HO₂ radicals from the photolysis of these VOCs. We have added tables to the Supplementary Information that describes the purity of the VOCs used in these experiments.

Page 10, lines 24 to 31. Also here it could be beneficial to extend the discussion. Do the authors have any hypothesis of what could be impacting the conversion of RO₂ to HO₂ in addition to the points already mentioned?

As suggested, we have expanded the discussion of the mechanism of peroxy radical decomposition to HO₂ from the OH-initiated oxidation of MVK and MACR. As pointed out by Fuchs et al. (2011) the fates of the peroxy radicals produced by the OH initiated oxidation of MVK and MACR are not well known and likely involve multiple channels with different reaction times, resulting in a more complex dependence on reaction time compared to the mechanism of HO₂ production from other alkenes.

Page 13, line 15 to 16. The term contrast in this case is misleading. As the authors underling later in the text, the two campaigns are characterized by different VOCs load (one is a forest environment, the other is a city) therefore it is not unexpected to observe a different amount of interference. The sentence should be rephrased. A small paragraph underlying the main chemical conditions for the three campaigns discussed in this work should be add to help the reader understanding similarity and differences between the environments.

We have rephrased this sentence as suggested, focusing on how the different environments lead to different contributions of the various peroxy radicals to the overall interference during each campaign. As part of this rephrasing, we have added information on the relative contribution of individual peroxy radicals to the overall interference for each campaign, providing additional information on the similarity and differences between these environments.

Page 22, Table 1. Use Pascal instead of Torr. Remove the inches unit.

This has been changed as suggested.

Page 27, Figure 4. I suggest grouping the RO2 and use of a more easily understandable labels.

We chose to include the RACM category labels for each peroxy radical in this plot to illustrate the contribution of each RACM peroxy radical category to the total modeled peroxy radical concentration. The RACM labels are defined in Section 4.2 (page 13 of the revised manuscript), and we have revised the caption to help clarify these points.

Page 28, Figure 5. The colors of the plot are not easy to separate, I suggest changing the colors.

We have changed the colors of the plot as suggested.