

Interactive comment on “Technical Note Formal blind intercomparison of OH measurements: results from the international campaign HOxComp” by E. Schlosser et al.

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We thank referee #2 for the positive evaluation and for the suggestions made. We address all comments in the following. Reviewer comments are given in italics and author responses are in plain text; changes to the manuscript text are in bold text.

... Although the basic technique for LIF measurements is similar for all instruments, there are differences that may have an impact on potential interferences, such as number of passes, laser power, repetition rate, inlet diameter, internal pressure, etc. Although some of this information is provided in the text describing the individual instruments, the details are not consistent. For example, while the laser power typically

C4872

used for the FZJ-LIF-SAPHIR system is given, the typical laser powers used by the FRCGC-LIF or the MPI-LIF instrument are not. Although this information may be included in separate publications, the paper would benefit from a description of some of the specific operating parameters used in this campaign for each LIF instrument.

All instruments were operated in their standard configuration optimized for field deployment with the exception of the CIMS instrument which used a modified inlet system customized to meet the sampling conditions in the SAPHIR chamber. We minimized the instrumental description to avoid redundancy because a detailed technical description of the contributing instruments is given in the cited references. Following the suggestion of the referee we now completed the instrumental description of the LIF instruments by specifying the laser power actually used in the intercomparison campaign: FRCGC-LIF: 5 – 9 mW; MPI-LIF: 2 – 20 mW)

The paper describes a significant dark background interference for the MPI-LIF instrument, resulting in non-daylight measurements being submitted as not valid. However, the paper does not describe the level of this interference and whether this background was present during daylight measurements. Were tests performed to insure that this background was negligible during the day? The paper would benefit from an expanded discussion of this interference, including the level of the interference and potential reasons why the MPI-LIF is the only one affected, which may be related to the different operating parameters described above.

Data of non-daylight measurements was marked as not valid because previous experiments with the MPI-LIF indicated the existence of a variable interference for non-daylight measurements. Measurements of the MPI-LIF without daylight are therefore not included in the data set of the HOxComp intercomparison campaign. As mentioned in the manuscript, the reason for the observed variable background signal of the MPI instrument during measurements without daylight is not yet understood. Investigations were not conclusive and further discussion of this interference at this time would therefore be highly speculative. The detailed analysis of the interference and its

C4873

causes is still under way because additional experiments both in the lab and in ambient air are required. In the reply to the comments of the first referee, we have added to the concluding remarks of the manuscript that the investigation of the HO_x chemistry at nighttime and/or with high VOC load should be addressed in a future instrument intercomparison campaign.

We did not observe such an interference for daylight measurements of the MPI-LIF. This assessment is supported by the analysis of HO_xComp data presented in the paper. No offset is found comparing the MPI-LIF OH data to the data from other instruments as could be expected if this interference would have been present. All comparisons performed during HO_xComp, and especially the comparison in ambient air shown in Figure 6, are linear correlations with no significant offset when the MPI-LIF data are plotted versus the data of any of the other instruments. Also the correlation with the CIMS instrument is very high. Thus the intercomparison campaign proves the absence of significant interferences in the presence of daylight under the conditions tested.

We propose to amend the last paragraph of Section 2.1.2 accordingly:

In contrast to OH measurements at daylight a significant and variable OH background signal was often observed at periods without daylight during experiments previous to HO_xCOMP. Therefore all OH measurements by the MPI-LIF at times without daylight were submitted to the referee as not valid. The reason of this effect is not yet understood. Studies have verified though that the interference is not due to laser-induced OH generation.

The paper also describes an interference for the MPI-LIF instrument when CO was added to the chamber, which decreased the OH concentration to near zero and increased the HO₂ concentration to approximately 6E8 cm⁻³. The authors suggest that back-diffusion of NO from the HO₂ detection axis could lead to the conversion of HO₂ in the OH axis, leading to the observed OH concentration of approximately 7E5 cm⁻³.

C4874

For a HO₂/OH ratio of approximately 100 this interference would only be approximately 10% of the ambient OH concentration. However, mean ratios greater than 180 have been reported in the boundary layer over a tropical forest. . .). Under similar conditions, this interference could be more significant.

Back-diffusion of NO from the HO₂ detection axis is a likely explanation for the OH signal observed with the MPI-LIF when 500 ppm CO was added to the chamber in order to suppress OH below the detection limit thereby leading to exceptionally high HO₂/OH ratios in the chamber air. If traces of the added NO reach the OH detection axis, some HO₂ is converted to OH, causing an interference. Assuming this was the case in this phase of the experiment, the observed fraction of OH converted from HO₂ corresponds to about 0.1%. For a HO₂/OH ratio of 100, this conversion would lead to 10% interference for OH, for HO₂/OH ratios of 200 it translates into 20% interference.

Usually a check for NO back-flow into the OH detection axis is routinely performed during field and chamber measurements by switching off the NO flow in the HO₂ channel. During these tests a significant change of the OH signal while the NO was switched off compared to when it was on was never observed. However, during the one hour measurement period when very high amounts of CO were added to the chamber (see Figure 5), the OH signal was close to the detection limit and this test was not made.

Although there was very good agreement between the measurements under the controlled environment of the chamber, the measurements in ambient air do not show the same level of agreement. In particular, it appears that there is a systematic difference between the LIF instruments and the CIMS instrument... The authors suggest that an error associated with the calibration of the instruments is primarily responsible, given the high correlation of the measurements especially between the MPI-LIF and the CIMS instruments. However, could some unknown interference associated with ambient air also contribute to the difference between the techniques, perhaps similar to the unknown offset affecting the MPI-LIF nighttime measurements? The manuscript would benefit from an expanded discussion of potential interferences in the ambient

C4875

measurements not accounted for in the chamber measurements.

Any interference would have to be proportional to OH or identical in both techniques in order not to disrupt the high linear correlation found between the LIF and the CIMS instruments (or the LIF and DOAS instruments inside the chamber). The excellent correlation is therefore a good indicator for the absence of significant interferences in ambient air under the conditions encountered during the intercomparison campaign. The systematic deviation observed between the LIF and CIMS instruments is a constant factor, thus pointing to a calibration issue.

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C4876