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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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This paper presents results of the first formal blind intercomparison of several instruments designed to measure ambient OH. The campaign included both an intercomparison of ambient measurements as well as an intercomparison of measurements made inside the SAPHIR chamber. The results are significant and provide additional information and confidence in the ability of these techniques to accurately measure OH radical concentrations in the atmosphere, although it is clear from the paper that not all interferences have been eliminated. The agreement of the chamber measurements between the different techniques, including the DOAS measurements, is particularly important as it suggests that under relatively simple chemical conditions the instruments appear to be free from interferences. The agreement between the instruments

for the ambient measurements is also reasonable although not as good as the chamber results. I recommend publication after the authors have addressed the following minor comments.

The intercomparison involved several LIF –based instruments. 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 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.

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.

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 HO_2 concentration to approximately 6×10^8 cm^{-3}. The authors suggest that backdiffusion of NO from the HO_2 detection axis could lead to the conversion of HO_2 in the OH axis, leading to the observed OH concentration of approximately 7×10^5 cm^{-3}. For a HO_2/OH ratio of approximately 100 this interference would only be approximately 10% of the ambient OH concentration. However, mean ratios greater

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than 180 have been reported in the boundary layer over a tropical forest (Lelieveld et al., 2008). Under similar conditions, this interference could be more significant.

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, with the LIF instruments measurements systematically higher than the CIMS. Unfortunately there are no measurements from the CIMS instrument inside the chamber to help to identify the source of the error. This result could have important implications regarding nighttime measurements by these techniques. 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 measurements not accounted for in the chamber measurements.

References:

Lelieveld, J. et al., Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452(7188), 737-740, doi:10.1038/nature06870, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 14081, 2009.