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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical Note: Formal blind intercomparison of HO_2 measurements in the atmosphere simulation chamber SAPHIR during the HOxComp campaign" *by* H. Fuchs et al.

Anonymous Referee #2

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This paper presents a comparison of HO2 measurements made in ambient air and within the SAPHIR large simulation chamber by three different instruments operated by different research groups. The manuscript describes the campaign approach, experiments performed and compares the measurements obtained using each system; the intercomparison was performed in a formal blind manner. The paper is closely related to Schlosser et al., ACP, 2009, which described the intercomparison of OH measurements performed in the same campaign.

HOx radical measurements are technically challenging, and formal blind intercomparison exercises such as these are essential to the confidence of the community in related

ambient observations. The manuscript should make a substantial contribution to our understanding of the reliability of atmospheric HOx measurements performed using the LIF approach.

The topic of the paper is suitable for publication in ACP. The paper is generally well written, and I recommend publication, after the comments below are satisfactorily addressed.

-As no absolute HO2 measurement was available, the analysis is necessarily restricted to comparing the relative HO2 values obtained by the different instruments. As the basic approach used was the same in each case (LIF detection of OH following HO2 conversion through addition of NO) concern may remain that the absolute accuracy of HO2 measurements has not been tested. This is noted in the manuscript, and is unavoidable given the experimental issues with MIESR, but should be more clearly flagged in the abstract and conclusions.

-Nighttime data. The ambient measurements (e.g. Fig 2) seem to agree better during the day than during the night; in the manuscript (p. 21204 line 16) it is stated that "...the nighttime data are discussed separately", but this discussion does not appear to be present. The nighttime data should be explicitly considered in the paper, and the correlations / regression between the instruments during the night included in tables 3 and 4 (either collectively as all ambient data, or distinguished by day/night).

-Instrument calibration details: Table 1 presents a summary of the instrument parameters, but it might be useful to include the typical laser fluence used in each system (which would directly relate to any interference effect), and to specify the NO used (supplier, purity etc) in each case. The estimated accuracy of each instrument is also given in table 1, and the regression slopes between the instruments are compared with these values in the text. This is fine but I wonder if some of the systematic uncertainties in the estimated accuracy values will be common to some of the instruments – e.g. water vapour absorption cross sections – and so slightly better agreement might be expected than these values (in isolation) indicate ?

The calibration approaches used differ in that some systems used added excess CO while others use the increase in HOx signal upon addition of NO. For the instruments which used both, did the calibration constants for HO2 derived from added excess CO agree with those obtained from the (increase in) HOx signal when NO was added to the sampled air ? One might expect a difference, if calibration tube and/or inlet losses of OH and HO2 differ, which might then feed into the measurement difference (as OH, HO2 are typically present at comparable levels during calibration, but HO2 » OH in ambient air).

p. 21213 line 18 mentions that different calibration constants were used for the ambient and chamber measurements – how different ? Is this indicative of calibration drift which might influence the comparisons (relating to discussion on p. 21208) or were the instrument configurations simply slightly different. P.21214 line 16 states that the same calibration factors were applied ?

Ozone interference – What humidity is the 0.07 ppt interference per 50 ppb O3 determined for (p. 21198) in the FZJ instrument, and how does this compare with the humidity levels experienced during the campaign ? Considering the laser fluence (see above) would a larger or smaller interference be expected for the other systems ?

Humidity dependence of calibration. Some (other) LIF systems are known to show a greater than expected (from quenching alone) sensitivity dependence upon H2O, which has previously been attributed (rather loosely) to HO2.H2O cluster formation in the expansion. The observed humidity-dependence to the HO2 data (e.g. Fig 11) is interesting and suggests that this effect, or possibly some interaction between HO2, H2O and NO, may be occurring in some of the systems – this would then explain the difference in humidity-dependence agreement for HO2, not observed for OH. It may be useful to compare the humidity dependence of the HO2 observations reported here with that observed for OH in Schlosser et al.

Diurnal profiles, figure 2: The morning HO2 rise (on 9/7/05) seems to be more closely correlated with the rise in O3 than the fall in NO, as stated in the text. May indicate NO-driven cycling of RO2-HO2-OH rather than simply NO acting as an HO2 sink.

Figure 8, why are there so few datapoints, esp. for the third panel – the ambient timeseries (e.g. Fig 6) seems to include many more data points.

p.21206 lines14+ - it is unclear here which data are included – all ambient or daytime only ? First night or both nights ?

p.21209 line 24 The O3 levels are actually somewhat different between the time periods mentioned (10 vs 40-50 ppb).

p.21213 last line – the ambient OH data shown in Schlosser et al. seem to be in fairly consistent relationship between instruments. One might expect OH, with a shorter chemical lifetime, to show a stronger dependence upon inhomogeneous mixing than HO2.

Conclusions – related to the point above, the nighttime data differ substantially between instruments. I would like to see a slightly more critical consideration of these data included in the concluding remarks that there was “good correlation between ambient air data”.

Other points

-Please give dates of the HOxCOMP campaign

-define SAPHIR where first used

-Ascarite – give IUPAC name

-Table 3, 4 the distinction between the SAPHIR and SAPHIR* results could be clearer

Typos

p.21196 line 25 needs rewording

A number of the references seem to have extra numbers after the publication year.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 21189, 2010.