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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.

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We thank referee #2 for her/his positive comment. In the following we give a step by step answer to the comments.

COMMENT: As no absolute HO_2 measurement was available, the analysis is necessarily restricted to comparing the relative HO_2 values obtained by the different instruments. As the basic approach used was the same in each case (LIF detection of OH following HO_2 conversion through addition of NO) concern may remain that the absolute accuracy of HO_2 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

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flagged in the abstract and conclusions.

RESPONSE: We added on p. 21191 l. 5: ”All instruments were based on the same detection scheme; no absolute reference was available.” and p. 21214 l.6: ”Because measurements by a MIESR instrument failed during the campaign, no absolute reference measurement was available, so that the accuracy of individual instruments could not be addressed.”

COMMENT: 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).

RESPONSE: We added ambient nighttime data in tables 3 and 4 and extended our discussion on p. 21206 after l. 19: ”FRCGC-LIF was only operated during the second night. These data behaved systematically different from the daytime data (see color distinction in Figure 8 and nighttime data were therefore treated separately (Table 3 and 4). Linear regression results in slopes of 2.95 for FRCGC-LIF versus MPI-LIF, 0.75 for MPI-LIF versus FZJ-LIF and 0.46 for FZJ-LIF versus FRCGC-LIF. During the second night the FZJ-LIF was operated with the additional ROx converter. Although during the following day when measurements between FZJ-LIF and FRCGC-LIF were in good agreement like the days before, nighttime measurements by FZJ-LIF may have suffered from interferences related to the additional ROx converter.” and on p. 21213 after l. 12: ”During the second night, MPI-LIF show significantly higher values than FRCGC-LIF than during day. This compares to the interference as observed in the dark chamber. During the first night FRCGC-LIF was not operated. FZJ-LIF was operated in two different configurations (with and without an additional converter for the detection of ROx during the first and second night. Without the reactor (first night), the relationship

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between FZJ-LIF and MPI-LIF was similar to daytime, but FZJ-LIF and MPI-LIF agreed better during the second night, when FZJ-LIF was operated with the additional reactor, compared to their agreement during the day. The limited number of nighttime data which are available to compare instruments with identical configuration and the diverse relationship observed during the two nights do not allow drawing a definite conclusion from ambient nighttime data from this campaign."

COMMENT: 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?

RESPONSE: Parameters which determine the laser fluence are now given in Table 1. For this campaign NO was supplied by the FZJ for all instruments. Each instrument got one bottle from Linde (purity 99.5%). We added this point on p. 21196 l. 29: "During this campaign all instruments used pure NO supplied by Linde (purity 2.5)." Only one parameter in the calibration, the water vapor cross section, is common for all instruments, other parameters, even the effective oxygen absorption cross section has to be determined individually for each calibration system. However, the uncertainty of the water vapor cross section is small compared to the uncertainty of the other parameters. We added this point on p. 21199 l. 16: "The accuracy of HO_2 measurements is determined by the uncertainty in the calibration (Table 1). Although the calibration scheme is similar for all instruments, accuracies are nearly independent, because the major contribution to the uncertainty is from the determination of specific parameters of the radical sources (mainly the irradiation parameters of the 185nm light). This is

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accomplished with different methods as described above."

COMMENT: 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 HO_2 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 HO_2 differ, which might then feed into the measurement difference (as OH, HO_2 are typically present at comparable levels during calibration, but HO_2 » OH in ambient air).

RESPONSE: Only FRCG-LIF uses both methods, but only the calibration mode when CO is added is used to determine the HO_2 sensitivity. Nevertheless, both measurements give the same calibration factor. One does not expect errors from different inlet losses. If CO is added the measured signal gives the calibration factor directly including potential inlet losses for HO_2. If switching NO is used to determine the instrument sensitivity, two measurements are required. Nevertheless, the calibration source delivers OH and HO_2 during both measurements constantly with the same concentration. If NO is off, only OH is detected, so that the signal relates to the OH sensitivity of the instrument including the specific OH inlet loss. If NO is on, OH and HO_2 are detected with their specific sensitivity both of which include the specific OH and HO_2 inlet loss. The signals add up to the entire signal, so that subtraction of the first measurement gives the same HO_2 sensitivity as one gets for the method, when CO is added.

COMMENT: 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?

RESPONSE: For MPI-LIF and FRCGC the configuration was the same for ambient

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measurements and SAPHIR experiments. Nevertheless, attaching instruments to the chamber required to disassembling part of the instruments. The calibration factor was 30% smaller during ambient air sampling for MPI-LIF. FRCGC determined a similar calibration factor for ambient air measurements and SAPHIR experiments, with the exception of the first SAPHIR experiments when the calibration factor was 10% smaller. We added on p. 21199 l. 10 and on p. 21213 l. 18 numbers for the change in calibration factors. FZJ-LIFs are two different instruments, so that calibration factors cannot be compared. The reason for a change in calibration factors is not clear. A 30% change is more likely due to changes of instrument properties e.g. caused by different alignments. The statement on p.21214 l. 16 means that although no changes in the calibration factor is expected during ambient air sampling or SAPHIR experiments (as implied by the application of constant factors), variability in the relationship of data is observed, which is larger than the difference between calibration measurements during this period. Furthermore, as stated on p.21208, the comparison of OH measurements does not exhibit the same pattern as HO_2 which would be expected, if the calibration had caused the observed differences in HO_2, because both calibrations rely on the same radical source. We added on p. 21213 l.13: ”If the difference between measurements was caused by instability of the calibration source or laser, a similar difference between OH (Schlosser et al., 2009) and HO_2 would be expected, but is only partly observed.”

COMMENT: 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?

RESPONSE: The interference was determined for a water vapor mixing ratio of 0.8% similar to the levels during the campaign. We added this number on p. 21198 l.12. The potential for this interference strongly depends on the distinct design of the detection cell and the conditions under which it is operated. There is no way to transfer measurements of this interference from one to the other instrument. The point is that all participants were aware of a potential interference due to ozone. Some of them decided that this interference is negligible for their instrument.

COMMENT: 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 HO_2.H2O cluster formation in the expansion. The observed humidity-dependence to the HO_2 data (e.g. Fig 11) is interesting and suggests that this effect, or possibly some interaction between HO_2, H_2O and NO, may be occurring in some of the systems – this would then explain the difference in humidity-dependence agreement for HO_2, not observed for OH. It may be useful to compare the humidity dependence of the HO_2 observations reported here with that observed for OH in Schlosser et al.

RESPONSE: The reviewer is correct that there are potential mechanisms that would affect the dependence of the sensitivities on water vapor for HO_2, but not for OH. However, this would have been the case during calibration measurements, too, so that one would expect, that the characterization measurements that were carried out for all instruments, would have shown the same behavior. Measurements would have been corrected in that way (p. 21211-21212). We added on p. 21212 l. 12 to make the point clearer: ”Similar characterization measurements for OH and HO_2 were used to correct data by MPI-LIF, but no dependence in the relationship between data on water vapor was observed for OH.” and on p.21211 l.16: ”. . .measurements were corrected by each group for water vapor dependencies prior to data submission based on characterization measurements. Furthermore, also OH data were corrected for a dependence of instrument sensitivities on water vapor determined from similar investigations, but no distinct dependence in the relationship of their measurements is observed (Schlosser et al., 2009).”

COMMENT: Diurnal profiles, figure 2: The morning HO_2 rise (on 9/7/05) seems to be more closely correlated with the rise in O_3 than the fall in NO, as stated in the text. May *indicate NO-driven cycling of RO2-HO_2-OH rather than simply NO acting as an HO_2 sink. Figure 8, why are there so few data points, esp. for the third panel – the ambient timeseries (e.g. Fig 6) seems to include many more data points.*

RESPONSE: We rephrased the sentence on p. 21202 l.4 to be more precise: "In the morning, HO_2 concentrations were small, when NO mixing ratios were high caused by local emissions from traffic within the Forschungszentrum and nearby roads. NO enhances the recycling of OH via reaction of HO_2 leading to the formation of ozone." Figures are generated from the same data set. The correlation plots include only data, if both instruments provided valid data within the same time interval. The number of data points, which are delivered by two instruments within the same time interval, is smaller than the entire number of data points of a single instrument. Moreover, for ambient air sampling FRCGC-LIF and FZJ-LIF did not measure during all times, so that the number of data points that can be used for the correlation plot is further reduced.

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

RESPONSE: We specified the data used for the analysis more precisely (see also response above).

COMMENT: p.21209 line 24 The O_3 levels are actually somewhat different between the time periods mentioned (10 vs. 40-50 ppb).

RESPONSE: The statement meant that the additional HO_2 signal is different for similar ozone concentrations on 19 July when ozone was varied systematically. We rephrased the sentence: "Systematic differences between the measurements by MPI-LIF and the other two instruments are also observed in the darkness during other SAPHIR experiments, but absolute deviations are not the same, when ozone mixing ratios on different days are within the range of ozone concentrations encountered on 19 July."

COMMENT: 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* HO_2*.*

RESPONSE: This is correct. We softened this statement in the response to reviewer 1 to: ”Observations for OH indicate that the ambient air was inhomogeneously mixed (Schlosser et al., 2009), which may explain at least some of the differences in the measured HO_2 concentrations.”

COMMENT: 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”.

RESPONSE: We extended the paragraph on p. 21215 l.25-29: ”Both chemicals which were identified to correlate with differences between measurements during SAPHIR experiments, were less variable for ambient air sampling. The good linear correlation between ambient air measurements does not give hints for additional species that influenced the instrument sensitivities. In contrast to SAPHIR experiments, results for nighttime data differ from daytime showing reduced HO_2 for MPI-LIF for some of the nighttime data. However, the limited number of data and the change of instrument configurations between the two nights do not allow further conclusions.”

COMMENT: 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

RESPONSE: We changed the text according to the suggestions of the reviewer.

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

RESPONSE: Numbers refer to the page on which references are cited. They are set by the typesetting process in ACPD.

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

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