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Atmospheric Measurement Techniques Discussions

Interactive comment on "Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration" *by* H. Fuchs et al.

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Response to comments from referee 1:

We thank the reviewer for his/her comments. Here are our responses to the specific comments:

Comment: The authors may wish to refer to the paper by Mao et al. currently in open discussion in ACPD (Mao et al., Atmos. Chem. Phys. Discuss. 12, 6715, 2012). This

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paper (submitted just after the current manuscript) reports a significant interference in LIF observations of OH using the Penn State OH system (GTHOS), which is apparent when on/off line OH measurements are compared with those performed using an OH scavenger (C_3F_6 or C_3H_8); the difference between these methods alters the measured OH by a (temperature dependent) factor of up to 40-50 %, in “biogenic” environments. As the present paper, and the work by Mao et al., are at least apparently directly contradictory in their conclusions with respect to LIF OH measurements (albeit from different instruments), it would be a useful contribution if (either within the manuscript, or this discussion) Fuchs et al. could comment on this discrepancy - which may have origins in the differing instrument design / operating parameters, or the specifics of the chemical environments present in the SAPHIR chamber / BEARPEX campaign - or of course may point to one or other study being in error. Similar points would apply to the discussion of the Mao et al. paper in ACPD.

Response: The findings reported by Mao et al. need to be investigated for our LIF instrument. We will add a remark on p2091 after l12: “The study by Mao et al. 2012 reveals a significant interference of about a factor of two in the OH measurements performed by the Pennstate GTHOS LIF instrument in a California forest during BEARPEX09. Apparently, the interference is caused by OH radicals that are produced internally in the instrument. Though the production mechanism is not clear, it is likely related to reactions of biogenic VOCs or of their oxidation products in the instrument. In contrast, our study finds generally good agreement of OH measurements by LIF and DOAS in experiments involving the oxidation of various alkenes (including isoprene) and aromatics by OH. Our different result may be caused by the different design and operating conditions of the Jülich instrument compared to Pennstate instrument. For example, the distance between the tip of the inlet and fluorescence detection in the GTHOS is longer than in the Jülich LIF instrument, prolonging the reaction time for potential OH formation. Another major difference is that OH excitation is accomplished by multiple passes of the laser beam in the GTHOS, but only a single pass in the Jülich instrument. Furthermore, differences in the VOC composition during BEARPEX09 and experiments in this work could cause different interferences. Though we consider an OH interference to be an unlikely explanation for unexpected high OH observations during PRIDE-PRD2006, we will continue our studies of potential artifacts by (oxygenated) VOCs. Further tests will include a titration approach similar to that reported by Mao et al. 2012."

Comment: Introduction - clarify the O_3 photolysis dominate OH in the free troposphere (cf. NO driven cycling, HONO in the urban BL etc).

Response: We will change p2079 l6f: "The dominant primary source of OH radicals is the photolysis of ozone, nitrous acid and formaldehyde, so that OH concentrations are well correlated with solar UV radiation (e.g., Brauers et al., 2001; Rohrer and Berresheim, 2006). OH can be further enhanced by radical recycling following reactions of OH with VOCs (e.g., Lu et al., 2012a)."

Comment: p. 2079 line 10 I'm a little troubled by the word "satisfying" - a number of field campaigns have struggled to reconcile observed and measured HO_X data, in a range of "clean" environments including MBL, polar etc. (e.g. Whalley et al., ACP 2010; Chen et al., 2004) I would suggest to qualify this statement.

Response: We will change p2079 l9-11 to "Global OH concentrations were estimated indirectly from the atmospheric budget of methyl chloroform (e.g., Bousquet et al. 2005; Prinn et al. 2005). However, in order to test directly atmospheric chemical mechanisms, in-situ measurements of OH are needed for comparison. For past field measurements, model results and measurements agree mostly well within the combined uncertainties for clean and rural areas, and for urban environments with high NO_X and high VOC concentrations (e.g., review by Monks et al. 2009; Whalley et al. 2010; Lu et al. 2012a,b)."

Comment: p.2080 line 8 indirect methods include OH clock / VOC ratio approaches

Response: We will add on p2080 l9: "Furthermore, OH can be determined indirectly in reaction chambers from the decay rate of VOCs that are oxidized by OH (e.g., Poppe et al. 2007; Barmet et al. 2012).”

Comment: p.2081 line 23, please give more details of the origin of the DOAS accuracy - a short paragraph considering the cross section accuracy, any lineshape/resolution effects etc would be useful.

Response: We will extend the last paragraph on p2082 starting at l27 with a more detailed description of the accuracy of DOAS measurements:

“The accuracy of tropospheric OH measurements by long-path absorption spectroscopy is ultimately limited by the uncertainty of the effective OH absorption cross sections. The latter were determined from calculated spectra for the $A^2\Sigma^+, \nu^{'} = 0 \leftarrow X^2\Pi, \nu^{''} = 0$ band at 308nm. The line shape calculations took into account the published Einstein coefficients for spontaneous emission, Doppler broadening, the collision line broadening by air molecules, and the broadening caused by the width and shape of the instrumental response function of the spectrograph. The absolute values of the absorption lines were scaled to the fluorescence lifetime of OH, for which three measurements were published, which agree within 3 % (Dorn et al., 1995).

The accuracy and long-term stability of the line shape calculation was frequently controlled by comparison of measured OH with the calculated OH spectra according to Hausmann et al. 1997. For this purpose OH radicals were formed in the SAPHIR chamber in front of the end mirrors of the multiple reflection cell by photolysis of water vapor at 185 nm using a mercury pen-ray lamp. The mean total uncertainty of the DOAS OH measurement is 6 % and covers the OH lifetime measurements (3 %), the line shape calculation (2 %), and optical path length plus spectral filtering effects (1 %) (Hausmann et al. 1997).”

Comment: p.2083 line 15-20: Were any tests performed with C_3F_6 or other chemical scavenger for OH?

Response: So far we did not perform tests using the chemical titration method, but this will be done in the future.

Comment: p.2086+ did spectral scans across the OH line(s) reveal any unexpected signatures?

Response: Each LIF data point is obtained from measurements at four different wavelength positions across the OH absorption line, and two wavelengths positions which are off-resonant. No unexpected behavior was observed in the shape of the on-resonance signal or in the magnitude of the off-resonant signal.

Comment: p.2089/2090. Was there any variation in the (ratio of) the LIF and DOAS OH signals with the amount of parent VOC present or reacted (rather than just the amount added)? While the amount injected is a suitable proxy for the sum of all potential interferant daughter products, the time variation of the two observations may contain some more information. For example Fig 3 panel for 2 Aug seems to show such a trend, esp. for the 9.00-11.00 window.

Response: Our sentence on p2089, l23 is probably misleading. In fact, values on the x-axis in Fig. 6 show the amount of the parent VOC present and not the added (initial) concentration. We will change the text to "...depending on the actual concentrations of the parent VOCs during the experiment runs." For some species the number of data points is too small to divide the data set into subsets depending on the VOC reacted away to investigate trends in a statistical way as we did e.g. for isoprene. The referee is correct that for data on 2 August one can get the impression that there is a change in the relationship between LIF and DOAS data with time. However, such a change is not observed on 7 July for a similar experiment, so that it is more likely that the disagreement on 2 August is caused by a change in the performance of either one of the instruments independent on the chemical conditions. Further analysis of a possible trend would require a much larger number of experiments, in order to derive significant results.

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Comment: Was there any variation in the LIF-DOAS comparison with temperature (if any significant T range was encountered)?

Response: We will add at p2091 in addition to the statement given in the answer to the first comment of the referee: “Here, experiments were performed at temperatures between 293 K and 303 K without a notable dependence of the relationship between LIF and DOAS measurements on temperature. In contrast, Mao et al. (2012) observed a strong temperature-dependent increase of the OH interference in their GTHOS instrument over the same range of temperatures.”. We will also add the temperature range during the experiment in Table 2.

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