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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.

Anonymous Referee #1

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This paper addresses the issue of discrepancies between recent field observations of OH radicals, and the predictions of atmospheric chemistry models based upon current understanding of the processes occurring / conditions encountered – high profile examples of such discrepancies having been reported in "biogenic" forested environments (Borneo, the Amazon) and in the more polluted environment of the Pearl River Delta (PRD). The focus here is on instrument error, or to be precise the possibility of measurement artefacts in the LIF approach to OH measurement, under certain chemical conditions (high reactivity, low-to-moderate NOx) typical of the conditions encountered in the Pearl River Delta measurements. Measurements of OH by LIF, and by the absolute DOAS approach, in SAPHIR chamber experiments investigating the oxidation of individual parent VOCs are used to test for the presence of such interferences; while some possible indication of an issue is observed for two parent VOC systems (toluene, MVK) the extent of the possible interference is very much less than the model – measurement discrepancies previously reported for ambient field data. This agreement between the LIF OH measurements and the absolute DOAS observations gives confidence in the LIF measurements of OH performed by this instrument under these chemical conditions.

The paper thus addresses a contemporary and high-profile issue, on a topic central to the remit of AMT. It is clearly and precisely written, with appropriate detail, figures and statistical analysis. I recommend publication, subject to the minor points below – and the following point :

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 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.

Minor Points

-Introduction – clarify the O3 photolysis dominate OH in the free troposphere (cf. NO driven cycling, HONO in the urban BL etc).

-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 HOx 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.

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

-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.

-p.2083 line 15-20: Were any tests performed with C3F6 or other chemical scavenger for OH ?

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

-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.

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

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 2077, 2012.