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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Insights into hydroxyl measurements and atmospheric oxidation in a California forest" *by* J. Mao et al.

Anonymous Referee #1

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This is a very interesting paper indeed showing that during BEARPEX09, a campaign in a forest in California, OH measurements by LIF made using the normal laser wavelength modulation method (called OHWave in the paper) are higher than OH measurements made using an alternative chemical method (called OHChem in the paper) which allows some subtraction of OH signal that is not due to ambient OH itself. The result is of considerable interest because there have been several publications in the recent literature which show that measured OH in such environments (forested, various locations, low NOx) are significantly higher than calculated from constrained numerical models that use our current understanding of the chemistry. Although the observation in this paper is that OHChem is $\sim$ 40-50% of OHWave, the source of the interference is not identified. A hypothesis is given that it is from the decomposition of an oxidation product of a biogenically emitted volatile organic compound (BVOC) inside

the fluorescence cell used for OH laser excitation and fluorescence collection. Evidence to support this comes from the difference in OHWave and OHChem increasing with temperature (and hence rate of biogenic emissions) and OH reactivity (again this would increase with increased presence of biogenic emissions). When OHChem is used to compare with a constrained model, better agreement is found compared with using OHWave. This paper shows good evidence that OHWave, for this instrument, is too high, and not representative of the actual OH concentration, which is better represented by OHCHem. OHChem however, may not represent the true OH concentration in this environment, due to uncertainties in the fraction of OH generated from the decomposition of another species that is removed by C_3F_6 inside the cell. An important finding is that laser-generated OH inside the cell by the probe laser is not the source of the extra OH (as was found in early versions of LIF instruments for OH measurements). There is a very good range of supporting measurements, including a wide range of oxidation products as well as hydrocarbons (quite a few more than in other studies). The OH reactivity also serves as an additional constraint. The presence of MBO as the dominant loss species for OH is different to some other forested environments. MBO oxidation products cannot undergo the Peeters type rearrangement compared with isoprene oxidation products, which is significant.

This is a very good paper with important findings, and is suitable for publication in ACPD. Just a few minor points to consider.

(1) There are two papers which have been published very recently – not in time to be cited by this paper, that could be mentioned as relevant to the current findings. In AMTD (Fuchs et al., 2012) report OH measurements made in the SAPHIR chamber in Julich, where OH is measured using both the FAGE and DOAS methods. Isoprene, and other biogenic species, for example its oxidation products, are added to the chamber, and in general there is good agreement between FAGE and DOAS, providing evidence, that for the conditions of this study, there does not appear to be a significant interference in the presence of these species. Also in ACPD 2012, MacDonald et al report

HCHO measurements using DOAS in a tropical forest, the levels of which can only be modelling using higher OH concentrations.

(2) Page 6718, there was also a forested study in Greece (Carslaw et al. 2001) which showed a similar model underprediction for OH.

(3) It is interesting that there is little variability in OH, HO2 and OH reactivity at 9, 12, or 15 m height. There are so few measurements of the height distribution of these parameters that these represent important findings. Were these results expected?

(4) On page 6722 a filter wheel is mentioned, can more details be given of this, is it a continuously variable neutral density filter?

(5) Page 6722 – photolysis rates are calculated using TUV – where any of these measured directly?

(6) Page 6723/4, it would be worth distinguishing and explaining external and internal OH.

(7) Is the sensitivity of the instrument changed through the introduction of the additional C3F6 injection point at the top of the instrument?

(8) Page 6727, Mao et al 2012 does not appear in the references.

(9) Figure 1, this is an average diurnal cycle. What does the day to day variability look like for this? Are there days when the difference in OH(chem) and the model for example, is larger or smaller?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6715, 2012.