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

Anonymous Referee #2

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Review of Paper by Mao et al., ACPD 2012

The paper by Mao et al. addresses the important question, whether measurements of OH by laser-induced fluorescence (LIF) could be biased by OH interferences specifically related to oxidation products of biogenic VOCs in forest atmospheres. The investigation is motivated by an increasing number of LIF (FAGE) field studies reporting much higher observed OH concentrations than can be explained by current chemical models. The paper by Mao et al. is very interesting. It presents a new measurement approach by chemical modulation (OHchem) which is compared to the traditional LIF measurement approach (OHwave) by wavelength modulation. The comparison of both methods during BEARPEX07 demonstrates clearly that the traditional measurement

Full Screen / Esc

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of OHwave by the Pennstate LIF instrument (GTHOS) is enhanced by an unknown interference in a Ponderosa pine forest. The reported interference (roughly a factor of two) is apparently caused by internal OH formed by an unknown process inside the measurement system. The observed temperature dependence and the correlation with ambient OH reactivity suggest that the interference is related to biogenically emitted, yet unknown substances. These results are well supported by the presented experiments. However, I disagree with the conclusion "Evidence indicates that the new method measures atmospheric OH" (abstract, line 9-10). This conclusion is not supported by the presented data. In my opinion, OHchem is just an upper limit for the true ambient OH (see below), thus limiting its usefulness for testing chemical models.

The reported interference comes from a chemical reaction inside the instrument where the efficiency of production and detection of the artefact OH may strongly depend on instrumental parameters (e.g., flow speeds in the instrument, internal pressure, wall losses etc.). Further experimental studies will be needed to unravel the interference mechanism and its dependence on experimental parameters. Also, additional tests will be needed for other designs of LIF instruments to investigate their interference potential in forest environments. The paper by Mao et al. presents valuable information that helps to design such new experiments. However, the interpretation of the OH data in the present paper is not adequate. It needs major revisions before it can be published in ACP.

Measurement uncertainty of OHchem

The authors have obtained their experimental results by comparing OH data running their instrument in two operation modes. The OHwave approach uses wavelength modulation to distinguish between fluorescence signals from OH and non-resonant background signals. This mode (OHwave) is susceptible to sampled ambient OH and

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internal OH potentially formed in the instrument. The other operation mode (OHchem) is a chemical modulation approach in which ambient OH can be removed by chemical titration with C_3F_6 before the sampled air enters the instrument. Switching the reagent on and off allows to distinguish between ambient OH and internal OH which is much less affected by the reagent. The comparison between OHwave and OHchem gives roughly a factor of two difference. The authors argue that OHchem represents the true ambient OH, whereas the difference between OHwave and OHchem is a measure of the interference. A complication arises as it is not entirely clear what fraction of the internal interference OH is depleted by C_3F_6 . The authors estimate the corresponding uncertainty to be 30 % for ambient OH. In my opinion, the uncertainty is much larger.

The OH signals with and without added scavenger (C_3F_6) may be called S_1 and S_0 , respectively. With C_3F_6 turned off, S_0 contains a contribution from ambient OH (S_{ambient}) and internal OH (S_{internal}).

$$S_0 = S_{\text{ambient}} + S_{\text{internal}} \quad (1)$$

Let us assume, with C_3F_6 turned on, the signal from the ambient OH becomes completely depleted, while the signal from the internal OH is attenuated by a factor α . According to the paper (Section 3.1), α can have values between 0.4 (60 % attenuation, if the internal OH is formed just below the instrument pinhole inlet) and 1.0 (no attenuation, if the internal OH is formed in the detection cell).

$$S_1 = \alpha \times S_{\text{internal}} \quad (2)$$

The OH signal in the wavelength mode, S_{wave} , is identical with S_0 , while the OH signal in the chemical mode, S_{chem} , is the difference between S_0 and S_1 .

$$S_{\text{wave}} = S_0 = S_{\text{ambient}} + S_{\text{internal}} \quad (3)$$

$$S_{\text{chem}} = S_0 - S_1 = S_{\text{ambient}} + (1 - \alpha)S_{\text{internal}} \quad (4)$$

In general, the ratio x of S_{chem} to S_{wave} can be expressed by

$$x = \frac{S_{\text{chem}}}{S_{\text{wave}}} = \frac{S_{\text{ambient}} + (1 - \alpha)S_{\text{internal}}}{S_{\text{ambient}} + S_{\text{internal}}} \quad (5)$$

The latter equation can be rearranged to calculate the ratio f of S_{internal} to S_{ambient} .

$$f = \frac{S_{\text{internal}}}{S_{\text{ambient}}} = \frac{(1 - x)}{\alpha - (1 - x)} \quad (6)$$

Given the daytime value of $x = 0.4$ (page 6723, line 22), we may calculate the ratio f for any possible value of α (0.4–1.0).

It turns out that f becomes negative for $x = 0.4$ and $\alpha < 0.6$. Since negative values of f are not possible, it is unlikely that internal OH is predominantly formed immediately below the pinhole orifice.

If α has a value equal or greater than 0.6, then the value of f ranges between infinity ($\alpha = 0.6$) and 1.5 ($\alpha = 1.0$). A ratio f approaching infinity means that S_{ambient} is negligibly small compared to S_{chem} . In that case, S_{chem} represents mainly internal OH. A ratio $f = 1.5$ means that S_{ambient} is accurately represented by S_{chem} . Unfortunately, the accurate values of α and f are not known.

If we assume, for example, $\alpha = 0.7$ (i.e., 30% internal OH is depleted by added C_3F_6), we would get $f = 6$. This would mean that the unattenuated interference signal is six times larger than the ambient OH signal and S_{chem} would be 2.8-times larger than the true ambient OH signal. For $\alpha = 0.65$, S_{chem} would be 5-times larger than S_{ambient} . If $\alpha (\geq 0.6)$ approaches the value of 0.6, S_{chem} becomes increasingly dominated by internal OH and the relative contribution from ambient OH becomes negligible. Only in the ideal case when internal OH is predominantly formed in the detection cell ($\alpha \rightarrow 1$), S_{chem} approaches the true ambient OH signal S_{ambient} . From these considerations, the black curve in Fig. 1 (page 6739) must be considered an upper limit of ambient OH.

[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)
[Discussion Paper](#)


Based on the experimental data presented in the paper, the real OH could have any value between zero and the upper limit.

In conclusion, ambient OH cannot be determined with a reasonable error by the presented chemical approach, unless the actual value of α is better known. In the present case, a negative systematic error of 100% is possible.

Measurement technique

For better understanding of the new technical approach, it would be helpful to know the following instrumental parameters: volume flow through the attached titration unit; sample flow through the inlet pinhole; pressure in the detection chamber. The information is important to understand the loss of ambient OH in the titration unit (without and with C_3F_6 added). How large is the estimated residence time of sampled air in the instrument available for build-up of internal OH? How was the instrument calibrated in the chemical modulation approach?

Contrary to the statement on page 6721, the reaction of C_3F_6 with OH does propagate radicals. After addition of OH to the double bond, a peroxy radical is formed which may react with NO. The resulting oxy radical undergoes fast dissociation and the dissociation products react with oxygen and form HO_2 which may recycle OH (Mashino et al., J. Phys. Chem. A, 2000, 7255–7260). Could the secondary chemistry have an impact on the depletion of ambient OH in the titration unit or of internal OH in the instrument? Can the secondary chemistry cause an HO_2 measurement interference in the HO_2 cell where large amounts of NO are present?

How large is the laser-generated OH from 308 nm photolysis of ozone in the current instrument (page 6722, line 14)?

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Model description

To my knowledge, a description of the chemical mechanism of RACM version 2 has not been published. A few sentences explaining the main differences between the revised and original RACM would be helpful for the reader.

It is mentioned that the MBO oxidation chemistry used in the model was taken from literature. It is also stated that the possible measurement interference from MBO peroxy radicals was not considered for the correction of HO₂ measurements, because MBO RO₂ radicals were likely removed by an unknown mechanism in the atmosphere. For consistency, did you include an additional MBO RO₂ loss in your model runs? How sensitive are the modeled HO_x concentrations with respect to the level of MBO RO₂ radicals? What is the total estimated error of the model calculations?

Discussions and conclusions

In section 4 it is argued that the result of the OH intercomparison during the HO_xComp field campaign (Schlosser et al., ACP 2009) supports the conclusion of the present paper. The statement in the present paper suggests that the three LIF instruments had an OH interference in the isoprene containing atmosphere during HO_xComp, while the CIMS instrument showed no such interference. I do not agree with these assumptions. A more detailed discussion is necessary. First, it is not clear whether CIMS instruments are free from interferences in VOC containing air. In a newly published paper, Ren et al. (AMTD, 2012) find good agreement of airborne OH measurements by the Pennstate LIF and NCAR CIMS instruments below 2 km altitude at high isoprene levels. Both OH measurements are much higher than the OH

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predicted by models. As pointed out by Ren et al., either the isoprene chemistry is not well understood, or both LIF and CIMS suffer from an artefact. Second, in another recent paper, Fuchs et al. (ACPD, 2012) describe an OH intercomparison between LIF and DOAS at high VOC (e.g., isoprene) concentrations. In this study, laser longpath absorption spectroscopy (DOAS) serves as an independent calibration-free reference which is not expected to be sensitive to biogenic VOCs or their oxidation products. LIF and DOAS measurements were found to be in very good agreement. Third, Fig. 6 in the paper by Schlosser et al. (ACP 2009) demonstrates highly linear correlations between the three LIF and the CIMS instruments during HOxComp. The offsets of the regression lines show no indication of a bias caused by interferences. Rather, the slopes of the linear regressions point to calibration differences (Schlosser et al., 2009). In conclusion, reported OH intercomparisons between LIF and CIMS (Schlosser et al., 2009, Ren et al., 2012) and between LIF and DOAS (Fuchs et al., 2012) do not provide specific evidence for OH interferences in LIF measurements in forest atmospheres. Thus, the findings in the present paper by Mao et al. cannot be generalized, but point to a direction for further instrument tests.

Minor Comments

page 6721, line 19: Fig. 1 → Fig. 3 ?

page 6723, line 5: "This box model is similar to other commonly used box models". Add suitable references, or delete the sentence.

page 6724, line 29: Fig. 3 → Fig. 1 ?

page 6727, line 14: Mao et al. (2012) is missing in the references.

page 6727, line 24: Fig. 3c. → Fig. 5c ?

Fig. 3, caption: Fig. 1 → Fig. 2.

Fig. 4, caption: blue open circles → blue solid line ?

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

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Discussion Paper

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