We thank reviewer for insightful comments. Our responses to the comments are provided below, with the reviewer's comments italicized.

Reviewer #2

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.

Response: While examining the reviewer's analysis, we uncovered an error in the manuscript. The manuscript says that 60% of the internal OH added near the inlet was removed when in fact the amount removed was between 20% and 60% depending on the amount of C_3F_6 that was added, which was deliberately changed during the course of the study. The reviewer's comment also prodded us to answer the question "Where in the instrument is the interference coming from?" before we responded to the reviewers' comments. The results of this new laboratory work are now in the manuscript.

We reformulate the reviewer's useful analysis as follows.

The total signal detected in the OH axis can be detected as

$$OH_{wave} = OH_{ambient} + OH_{internal}$$

$$OH_{chem} = OH_{ambient} + (1-\alpha)OH_{internal}$$

where α is the fraction of internal produced OH remaining from the external addition of C_3F_6. Assuming

$$x = \frac{OH_{chem}}{OH_{wave}}$$

The relationship between OHambient (ambient OH) and OHchem can then be described as

$$f = \frac{OH_{ambient}}{OH_{chem}} = \frac{\alpha + x - 1}{\alpha x}$$

For α = 1, f = 1 and OHchem = OHambient, no matter what x is. For α = 0.8, when x=0.5, f=0.75. This analysis suggests that the ambient OH equals 75% to 100% of OHchem, depending on where the internal OH is being generated. However, recent laboratory work provides evidence that the internal OH is being generated near or in the detection axis but is not laser-generated. We added the following discussion to the paper:

"…The lamp near the inlet was shrouded so that its light shone only across the flow tube and not up into the inlet or down into the detection cell. C_3F_6 addition removed 3%-10% of the OH generated in the OH detection axis but removed 25%-60% of the OH generated just below the instrument pinhole inlet, depending on the C_3F_6 flow. Laboratory studies provide solid evidence that internal OH is being generated primarily near and in the OH detection axis and that the difference between OH without and with C_3F_6 must be multiplied by (0.80±0.08) to account for this small internal removal (see supplementary material). We retain the name "OHchem" for this corrected value."

We added to the supplemental material:

"Supplemental discussion of internal OH and its possible removal by C_3F_6 addition

OHchem represents the real OH and OHwave-OHchem represents an instrument interference only if no internal OH is removed when C_3F_6 is added. This can be seen in the following analysis.

The total detected OH by wavelength modulation is the sum of ambient, real OH and internal OH, whereas OH detected by chemical removal is the sum of the ambient OH and the fraction of internal OH that is removed. So

$$OH_{wave} = OH_{ambient} + OH_{internal}$$

$$OH_{chem} = OH_{ambient} + (1-\alpha)OH_{internal}$$

where α is the fraction of internal produced OH remaining from the external addition of C_3F_6. Assuming

$$x = \frac{OH_{chem}}{OH_{wave}}$$

The relationship between OHambient and OHwave can then be described as

$$f = \frac{OH_{ambient}}{OH_{chem}} = \frac{\alpha + x - 1}{\alpha x}$$

For $\alpha = 1$, f = 1 and $OH_{chem} = OH_{ambient}$, no matter what x is. For $\alpha = 0.8$, when x=0.5, f=0.75. This analysis suggests that the ambient OH equals .75 to 1 times OH_{chem}, depending on where the internal OH is being generated. The question then is "Where is the internal OH being generated?"

A key to determining the source of the internal OH is the removal from OH generated by Hg lamps 1, 2, and 3 by the addition of different amounts of C_3F_6 (Zhang et al., manuscript in preparation). The shapes of the three removal curves are very different, with the shape of the removal more curved for external OH, less curved for OH produced near the inlet (Hg lamp 2) and small removal for OH produced in the detection axis (Hg lamp 3). If OH were generated near the inlet, the ratio of OHchem to OHwave would go to less than 10% as more C_3F_6 was added because both external OH and internal OH generated near the inlet are effectively removed when more than 4 sccm of C_3F_6 were added. If OH were generated in the detection axis, OHchem to OHwave effectively levels off. The curve of OH produced from ozone and MBO or β-pinene matches a curve that combines curves with about 50% from external OH, 14% from internal OH generated near the inlet, and 36% from OH generated in the detection axis. . Applying the laboratory-derived internal removal, α, (0.83±0.08) to the BEARPEX09-observed average OHchem/OHwave (0.50), the equation for $OH_{ambient}/OH_{chem}$ equals 0.80±0.08. We apply this correction to OHchem but retain the name "OHchem" for this corrected value."

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 C3F6 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?

Response: C_3F_6 flow for chemical removal was 1.1 to 3.3 standard cubic centimeters per minute (sccm). Sample flow through the inlet pinhole was 7 standard liters per minute (SLPM). The estimated travel time of sampled air from GTHOS inlet to detection axis was about 20 ms, assuming plug flow. The residence time in the titration unit is approximately 20-25 ms, again assuming plug flow. The flow through the titration units consisted of 7 SLPM going into GTHOS and an additional 2 SLPM being pumped in a ring around the outside of the inlet. This external pumping made the OH loss in the titration unit immeasurably small in controlled laboratory tests in which OH was sampled from a chamber with and without the titration unit attached. This conclusion was supported by midday, cloud-free field measurements in which the titration unit was alternately removed and replaced on the inlet and no change was observed in OHwave to within the signal statistics (~<10%). The cross section of our calibration system (1 cm x 1 cm) is too small to be used with the titration unit, so the calibration for OHchem relies on the calibration of GTHOS without the titration unit and the knowledge that the titration unit did not reduce the measured OH for either the laboratory chamber or the field tests.

We added the following to the manuscript:

"In order to inject C_3F_6 into the upstream of inlet flow, a 4 cm-long aluminum cylinder (OD 5.1cm and ID 2.5 cm) was installed on top of the GTHOS inlet. A 5-cm long PFA tube with ID of 1.9 cm was installed inside this cylinder to reduce the residence time of ambient air inside the cylinder to ~100 ms. The flow through cylinder consisted of 7000 standard cubic centimeters per minute (sccm) that was sampled by the inlet and another 2000 sccm that was pulled by a vacuum pump through a ring-shaped gap between the tube and the inlet. This "ring" flow minimized the sampling of air that had been near the cylinder walls. Gaseous C_3F_6 was injected simultaneously through four 0.25 mm needles pointed toward the center, which were located about 1 cm above the inlet (Figure 1). C_3F_6 was added for two minutes every four minutes; four different flow rates were used (1.1, 1.7, 2.2, and 3.3 sccm). An N_2 flow of 100 sccm was continuously added through the needles so that the periodic C_3F_6 addition did not perturb the flow. This injection system, without C_3F_6 addition, caused negligible OH loss according to several laboratory and field tests in which the injection system was removed for an hour and the OHwave signal did not change."

Contrary to the statement on page 6721, the reaction of C3F6 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 HO2 cell where large amounts of NO are present?

Response: We agree with reviewer that the reaction of C_3F_6 with OH does propagate radicals, which then can generate HO_2 from the peroxy radical reacting with NO (Mashino et al., 2000). This amount of HO_2 is small compared to ambient HO_2. The recycling has no effect on the OH removal because even if NO = 50 ppbv and ambient HO_2 is 100 times ambient OH, the OH removal still exceeds 95%. Ambient NO was always less than 1 ppbv at BEARPEX, so the impact of recycling is even smaller. The HO_2 measurement was reduced about 7% during C_3F_6 addition, likely due to removal of the OH generated by the reaction between HO_2 and reactant NO. However, the reported HO_2 comes only from the HO_2 measurement when no C_3F_6 was being added, so the C_3F_6 addition has no effect on the reported OH and HO_2 measurements. We now remove the statement of radical propagation for C_3F_6.

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

Response: The equation for laser-generated OH in GTHOS is

OH(pptv) = 0.0028*ozone(ppb)*water mixing ratio (fraction)*OH UV power(mw)

The laser-generated OH is rather small and was less than 6×10^4 cm^{-3} during BEARPEX. Since this dependence is quantified and understood, this small interference signal is subtracted from the OH values discussed here.

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.

Response: We now state : "Compared to the original RACM mechanism (Stockwell et al., 1997), RACM2 now includes 117 total species (77 in RACM) and incorporates large number of updates from Master Chemical Mechanism (MCM), JPL kinetics and IUPAC updates."

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 HOx concentrations with respect to the level of MBO RO2 radicals? What is the total estimated error of the model calculations?

Response: We did not include additional MBO RO$_2$ loss in the model, but any additional removal of MBO RO$_2$ will lead to less OH and HO$_2$. However, given the constraints from OH reactivity, we expect that modeled HO$_x$ concentrations are relatively insensitive to the level of MBO RO$_2$. While we have not run a sensitivity analysis specifically for this study, our analysis of uncertainty for RACM in Houston was $\pm(25\text{-}40)\%$ (1σ confidence) (Chen and Brune, 2012). This careful analysis provides a good estimate for the uncertainties in the models used here and is in line with other uncertainty analyses for other models.

In section 4 it is argued that the result of the OH intercomparison during the HOxComp 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 HOxComp, 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 Penn state LIF and NCAR CIMS instruments below 2 km altitude at high isoprene levels. Both OH measurements are much higher than the OH 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.

<u>Response</u>: We agree with the reviewer in his analysis for CIMS and LIF. While the CIMS does not see nighttime OH, neither do several of the LIF instruments. However, there is no published evidence, to our knowledge, that an interference for CIMS has been ruled out. Thus, we remove the statement in section 4 that says that CIMS have shown no interference. While it seems that other LIF instruments do not have the interference that we claim for GTHOS, the reviewer should look much more closely at the two reference papers she/he cites because the slopes don't tell the whole story. For example, in the Fuchs et al. paper, the reviewer should look at the LIF/DOAS comparisons as a function of VOCs, which show evidence of a problem. None-the-less, we can only talk about GTHOS, which is why the reviewed version of the paper has the statement: "It is not clear whether these findings also apply to other forest atmospheres or to the OH measurements with other FAGE-type instruments in other forests."

For Fuchs et al. (2012), we now state : "A recent intercomparison study in SAPHIR chamber between LIF and DOAS instrument, also show positive bias by 30-40% from LIF instrument for several VOC species (MVK and aromatics), but not others (isoprene and MACR) (Fuchs et al., 2012). Further tests for terpenes and other BVOCs are required to quantify a possible interference."

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