Interactive comment on “OH and HO_2 Radical Chemistry during PROPHET 2008 and CABINEX 2009 – Part 1: Measurements and Model Comparison” by S. M. Griffith et al.

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We would like to thank the referees for their useful and insightful comments, which have helped to improve the clarity and quality of the manuscript. Below is a detailed response to each referee.

Referee #1:

This paper describes laser induced fluorescence measurements of OH and HO2+ isoprene-based peroxy radicals during two field campaigns in a forested environment in northern Michigan. The measurements are compared with a constrained box model based on RACM chemistry modified to include the Mainz isoprene mechanism (MIM). Other recent mechanistic changes to isoprene oxidation (i.e. formation of epoxides and hydroperoxy aldehydes) were not considered in this paper, but are to be the topic of a future paper. The model tends to overpredict both quantities, but only slightly for OH even with 1-2 ppbv of isoprene present. This is in contrast to other recent observation-model comparisons (Lelieveld et al., 2008; Kubistin et al., 2010) in which models significantly underpredicted OH and HO2. Various theories to explain these latter measure-model differences have been put forward.

The measurements of HOx radicals are described in some detail as they relate to these studies. This includes important issues of background and interference in the conversion of HO2 to OH by reaction with NO. Other supporting measurements needed for the box modeling are also described.

The paper presents data and analyses that contribute to the collection of HOx observations in forested environments and should be published. The authors may wish to consider minor comments below in the preparation of the final version.

Other comments.

Referee #1:

Line 27, page 33168 to Line 2, page 33169. The sentence is worded in a way that seems to indicate the Kubistin et al and the Lelieveld et al papers are focused on different field studies, but in fact they are both using data from GABRIEL. Suggest a slight rewording.

Reply:

We have reworded this sentence to reflect that the two references are using the same dataset but with different models.

(Introduction)

“For the GABRIEL campaign in the boundary layer over the Amazon, Lelieveld et al. (2008) reported observed-to-modeled OH ratios of 5-10, while Kubistin et al. (2010) using a simpler photochemical box model reported observed-to-modeled OH and HO_2 ratios of approximately12 and 4, respectively."

Referee #1:

Discussion of background, page 33172. Spectral interferences are discussed, but the recent reported issue of a difference between spectral background (off-line tuning) and chemical background (addition of an OH scavenger) is not discussed here (although mentioned at the bottom of page 33174, top of page 33175). I do see that it is discussed in detail on page 33183. Suggest at least a sentence or two here indicating the approach and that it will be discussed later.

Reply:

We have added a sentence indicating that the chemical modulation technique was occasionally used and will be discussed later, as suggested.

(Sec. 2.1)

"Although most of the OH measurements during PROPHET 2008 and CABINEX 2009 employed the spectral modulation technique described above, an alternative chemical modulation technique was occasionally used to test for unknown interferences and is discussed in Sec. 2.2."

Referee #1:

Bottom of page 33172 to Top of page 33173. Would be worth a sentence to indicate what happens to RO2 radicals (also discussed later – page 33175) when exposed to NO in the sampling cell.

Reply:

We added a sentence indicating that discussion of the HO_2 interference is in a later section.

(Sec. 2.1)

"Interferences from organic peroxy radicals during the HO_2 measurements are discussed in Sec. 2.3."

Referee #1:

Lines 20-25, page 33173. Detection limits are given, but how about overall uncertainties that include all of the terms associated with deriving a radical concentration (calibration, counting statistics, laser power measurement, etc.). This is important when comparing the measurements *with the box model (for which you do describe uncertainties later). I see that it is mentioned in the Figure 5 caption, but a mention in the text would be good.*

Reply:
We have added a statement about the overall calibration uncertainty, and have included references that describe in more detail the factors influencing the overall uncertainty of the instrument.

(Sec. 2.2)

"The calibration accuracies (1 σ) are ±20% for OH and HO2 using the water photolysis calibration technique. Additional information regarding the overall uncertainty of the instrument and calibration method can be found in Dusanter et al. (2008; 2009)."

Referee #1:

Discussion of peroxy radical "interference", Page 33176 and supplement. Is it possible that the degree with which the FAGE instrument is sensitive to RO2 depends on factors such as sampling cell pressure, time from NO addition to fluorescence measurement, NO concentration, or other factors? This could complicate the measure-model comparisons. Suggest at least briefly discussing the possibility. One item that would help the reader understand the importance of this issue is showing modeled HO2 in Figure S5 (I do see that it is Figure 5). One could argue that the "interference" changes with time from 0 up to including all of the ISOP peroxy radical.

Reply:
As indicated by the referee, the HO_2 interference from organic peroxy radicals in the IU-FAGE instrument is somewhat sensitive to sampling cell pressure, NO concentration, and sampling inlet, but these conditions did not change during the campaigns. We have calibrated the interference in the laboratory replicating the instrumental conditions for each campaign.

We have added clarification that HO_2 interference measurements were performed under the field conditions during PROPHET 2008 and CABINEX 2009.

(Sec. 2.3)

"Calibrations of this interference in the IU-FAGE instrument under the instrumental conditions used during PROPHET 2008 and CABINEX 2009 (inlet size, cell pressure, and NO concentration) indicates that…."

Referee #1:

Discussion of model, page 33177. The model is well described. Has it been compared with other models? If measure-model ratios are to be discussed from different studies, and with different *models (e.g. GABRIEL), then some connection between the studies is critical. The statements that RO2+RO2 chemistry may not be complete in RACM is of concern in this regard, although typically these reactions are not major loss routes for RO2.*

Reply:
Unfortunately the present model has not been compared to the results from similar models as suggested by the reviewer. Such a comparison is beyond the scope of this paper, but would be important in the future. We have expanded a statement in the discussion section clarifying that the present model has not been rigorously compared to the models used in other studies, which may have differences in their chemical mechanism and model implementation.

(Sec. 4.1)

"In contrast to these previous studies, the campaign median measurements of OH from CABINEX 2009 are in good agreement with the model predictions where median peak isoprene mixing ratios were between 1-2 ppbv (Figures 6 and 7). Many of these previous studies found that the discrepancy between the measured and modeled concentration of OH increased with increasing mixing ratios of isoprene (Ren et al., 2008; Kubistin et al., 2010). Although the models used in these studies may have differences in their chemical mechanism (Tan et al., 2001; Kanaya et al., 2007; Lu et al., 2012), or fundamental differences in the implementation of their model (Lelieveld et al., 2008; Pugh et al., 2010), and have not been compared to the present model, an analysis of the CABINEX observed to model OH ratio (Figure S7) do not reveal a significant dependence on the isoprene mixing ratio, although the precision of the correlation is poor due to the poor precision of the OH measurements.

Referee #1:

Measure-model OH and HO2 comparison, page 33180. It is not clear from the text or examination of Figure 5 that measured HO2* is overpredicted by the model. It depends on whether you are comparing to modeled HO2 or modeled HO2 + ISOP (see earlier comment).*

Reply:
We have added a statement in this section to clarify that the IU-FAGE instrument does efficiently detect isoprene-based peroxy radicals in addition to HO_2 during both campaigns, and that the measurements are best compared to the modeled sum of HO2+ISOP rather than just HO2.

(Sec. 4.2)

"As discussed above (Sec. 2.3), laboratory calibrations have shown that approximately 90% of isoprene-based peroxy radicals are detected by the IU-FAGE instrument in addition to HO_2 under the instrumental configurations during PROPHET 2008 and CABINEX 2009. Because the model predicts that isoprene-based peroxy radicals comprise approximately 80% of the total RO_2 radical pool in this environment, isoprene-based peroxy radicals are the dominant species contributing to the HO_2 interference in these measurements."

Referee #1:

Lines 7-8, page 33181. You should indicate which way you are performing the linear regression (meas vs model or model vs meas). It is also known that standard least squares should not be used when determining the best fit for scattered x values. A bivariate fit is needed to get the proper fit parameters. Suggest doing the fits this way, unless you already have, in which case you should say so.

Reply:
We agree that a "bivariate" fit should provide a more accurate correlation of the measurement vs. model data. We performed the bivariate least-squares regression using two different solvers giving slopes of 0.90 and 0.91 with y-intercepts less than 1×10^5 cm^{-3}, very similar to the linear least-squares fit shown in the ACPD manuscript.

Also, we added clarification in two places that the regression is performed as "measurement vs. model."

(Sec. 3.2)

"Figure 6 displays a correlation plot of the measured vs. modeled OH concentrations for the CABINEX 2009 campaign with a bivariate least-squares regression weighted by the measurement precision and model uncertainty (Cantrell et al., 2008)."

(Figure 6 caption)

"The blue line is a 1:1 correlation line and the solid red line shows a measurement vs. model regression of the data weighted by the precision in the measurements and the uncertainty of the model concentrations (slope = 0.90 ± 0.35), with dashed red lines representing the 95% confidence limits of the slope."

Referee #1:

Figure 3 caption, page 33208. Suggest indicating in the caption that these are diel median profiles (i.e.versus time of day). Also indicate in the caption that PROPHET is blue and CABINEX is red.

Reply:
We added clarification in the caption of Figure 3 to denote "Diel median values" and that the PROPHET 2008 values are in "blue" and CABINEX 2009 values are in "red."

(Figure 3 caption)

"**Diel** median values of several species measured from above canopy during PROPHET 2008 **(blue)** and CABINEX 2009 **(red)**. Constrained model inputs based on overlap of measurements are shown in the Supplementary Material."

Referee #2:

General comments

The authors present measurements of OH and HO2 radicals conducted above the canopy in a deciduous forest environment using a laser-induced fluorescence (LIF) technique. The measurements are compared with a chemical zero-dimensional box model in order to evaluate the current understanding of atmospheric oxidation pathways incorporating the Regional Atmospheric Chemistry Mechanism updated by the Mainz Isoprene Mechanism (RACM-MIM).

As discussed in the manuscript, previous observation-to-model intercomparisons in forested environments marked by low NOx levels and high emissions of isoprene as the predominant biogenic volatile organic compound (BVOC) have unveiled serious lacks of understanding of the underlying processes. In contrast to this, the observed OH concentrations in this study could be reproduced by the box model reasonably well.

Even though the radical observations presented in this manuscript might suffer from recently reported potential interferences in both OH and HO2 measurements by LIF (Mao, 2012 and Fuchs, 2011) which is considered by the authors in the discussion of their results, this paper is valuable to improve the current understanding of the atmospheric oxidation capacity in forested environments and suitable for publication in ACP after the authors have addressed the following comments and technical corrections.

Specific comments

Referee #2:

(P33174, L5/Supplement S2)
The authors state a "still measureable interference in the IU-FAGE instrument" by laser-produced OH equivalent to 8500 (+/-800) molecules cm^{-3}*, normalized on 1ppbv of ozone, 1% of water, and 1mW laser power, which was negligible for the above canopy measurements presented due to the low laser power available at the detection cell. At higher laser power such an interference will get significant and therefore characterization in laboratory is important as presented in supplement S2. It is not clear to me how the authors prevent from OH production by photolysis of water vapor, while producing ozone with a mercury lamp. A significant contribution of the interference signal in laboratory test could originate from externally produced OH and not being laser-induced. This would lead to an overestimation of the interference by laser-photolysis of ozone in the IU-FAGE instrument and might cover in ambient measurements (Figure S2) the effect of an additional interference.*

Reply:

During calibrations of the ozone x water x power interference, dry air was first passed through the photolytic cell to photolyze oxygen and produce ozone, then after leaving the photolytic cell, water was added before then passing through a significant length of tubing. Any OH produced from photolysis of the traces of water in the dry air cylinder would be lost on the tubing between the photolytic cell and IU-FAGE.

This has been clarified in the main text and in the supplement:

(Sec. 2.2)

"However, for the above canopy measurements of OH during the PROPHET 2008 and CABINEX 2009 field campaigns, this interference was negligible because of the low laser power (< 1 mW) reaching the sampling cell at the top of the tower through the 50 m fiber, resulting in a predicted laser-generated OH concentration of less than 2.5×10^5 cm^{-3}, which is below the detection limit of the instrument at the top of the tower. As a consequence, no correction was applied to the OH measurements presented in this study."

(Sec. S2, Supplement)

"Ozone is generated through reactions R5 and R6 with a low-pressure mercury pen-lamp (UVP 90-0012-01 (11SC-1)) set in a cell where dry zero-air is passed to avoid photolysis of water vapor. The calibration air stream is then humidified, and then sampled for ozone, water, and eventually sampled by the IU-FAGE instrument."

Referee #2:

(P33175/Supplement)
The authors do a careful job on examination of possible interferences in their LIF-FAGE measurements. From tests at the PROPHET site they have no evidence that the measurements of hydroxyl radicals suffer from an interference related to the oxidation of biogenic VOCs (Mao et al., 2012). However, the OH measurements during PROPHET 2008 (Figure 5) peak around 3 pm coincident with the maximum temperature. The OH is not following the radiation as the predominant primary source. At lower temperatures associated with less biogenic emissions during CABINEX 2009 this is not the case. Is not this indicating such an interference or how can it be explained?

Reply:

Referee #2's comments are well received. Based on tests with the chemical modulation technique below canopy at the PROPHET site in 2010, we do not think there were any substantial interferences contributing to the measurements in 2008 and 2009. However, these tests in 2010 were performed below canopy and not on top the PROPHET tower as in 2008 and 2009, so there still remains some uncertainty especially regarding the measurements during the warmer 2008 campaign. However, any unaccounted for interference during 2009 would result in a reduction of the measured OH concentration, leading to an overprediction by the model. This result would still stand in contrast to the general underprediction of measured OH concentrations in forest environments by current atmospheric chemistry models, and do not alter the main conclusions of the paper.

The following text was added to clarify this point:

(Sec. 4.1)

"However, recent measurements by Mao et al. (2012) during BEARPEX 09 using a chemical modulation technique to detect OH radicals were significantly lower than measurements using the spectral modulation technique and were in good agreement with model predictions with isoprene mixing ratios between 1-2 ppb on average, suggesting that there may be an unknown interference associated with the LIF-FAGE technique related to the oxidation of biogenic VOCs. A similar interference could explain the high measurements of OH observed in the afternoon during the warmer PROPHET 2008 campaign coinciding with the maximum afternoon temperature and highest isoprene concentrations. However, any interference in the measurements during CABINEX 2009 presented here would result in a reduction in the measured OH concentrations, leading to an overprediction by the model. This result would still stand in contrast to the general underprediction of measured OH concentrations in forest environments by current atmospheric chemistry models."

Technical corrections

Referee #2:

(P33172, L28)

"…(~5.5-9.9hPa). using two" → please remove superfluous period.

Reply:

Removed.

Referee #2:

Please correct format of the following reference

- Poschl et al. 2000 → (should be "Pöschl" → please fix "Umlaut" typos)

Reply:

Corrected.

Referee #3:

The manuscript "OH and HO2 Radical Chemistry during PROPHET 2008 and CABINEX 2009 – Part 1: Measurements and Model Comparison" by S. M. Griffith et al. describes results of two large field campaigns from 2008 and 2009 with focus on radical chemistry in the forested environment of Northern Michigan, the same field site as has been used in previous PROPHET studies. The Indiana University FAGE instrument is used to measure OH and HO2 above the canopy height. Due to the experimental setup (long optical fibre), very low laser power was available and resulted in bad detection limits of 1.5 and 1x10ˆ6cm-3 (2-h averaging) in 2008 and 2009, respectively, compared to OH peak concentrations of some 2-4 x10ˆ6cm-3 at noon. HO2 detected by the IUFAGE is compared to modelled HO2+ISOP (isoprene-based hydroxy peroxy radicals) with fairly good agreement. Radical budgets are analysed and discussed for the two campaigns and in relation to PROPHET 1998. Main difference to PROPHET 98 is the lower OH, especially at night. For PROPHET 2008 and CABINEX, measurements and model are roughly (within the uncertainties) in line. Differences in biogenic reactive compounds at ground and above the canopy are discussed as potential explanations for the discrepancies between the PROPHET 98 and the current studies, but this issue remains unresolved.

Studies to improve our understanding of radical chemistry in forested environments are needed as discrepancies between measured and modelled values in past studies have caused questions about missing chemistry. Recently, however, artefacts of FAGE type instruments in measuring OH radicals (Mao et al., 2012) and HO2 radicals (Fuchs et al., 2011) in environments with high levels of biogenic VOC were reported. For example, Mao et al. (2012) demonstrated that their FAGE type instrument needed a modulation technique to periodically scavenge ambient OH and thus measure internally produced OH in order to correct their OH measurement for this internally produced OH. The corrected OH was inline with model predictions during day and night, whereas the uncorrected signal was higher by factors of 2-3. Thus, the question came up weather previously observed discrepancies were due to measurement artefacts. This question is also addressed in the current manuscript but not really solved for the used technique. Overall, the paper is well written and figures and tables are clear and informative. The paper is in the scope of ACP. However, the following comments should be considered:

Referee #3:

1. The authors cite and discuss recent findings on potential artefacts in LIF measurements of OH and HO2 by Fuchs et al. (2011), Mao et al. (2012) and others. They mention own results of characterisation experiments they performed with respect to OH artefacts (page 11 and supplement) which indicated potential interferences in CABINEX 2009 which were not confirmed in later experiments. However, these experiments were mostly performed under different conditions, e.g. at the ground or different locations or different times, such that it is not really clear weather artefacts have occurred during PROPHET 2008 and CABINEX 2009. With respect to HO2, the authors mention interference experiments with respect to a few organic compounds (p. 12 and supplement), but again the amount of artificially measured ROx in HO2 mode is not clear. Given the uncertainty in the scientific community concerning photochemistry in* *forested environments, the potential artefacts of the Indiana University FAGE measurements should be better presented and discussed more thoroughly.*

Reply:

OH Interferences

Unfortunately, only a limited number of interference tests were performed during the campaigns in 2008 and 2009 using CO and C_3F_6 as OH scavengers using a flow tube interfaced with the IU-FAGE instrument. These tests suggest the possibility of an interference (in addition to the laser photolysis of ozone and subsequent reaction with water vapor) on the order of 4-9 × 10^5 cm^{-3}, potentially accounting for 50-100% of the nighttime OH concentrations measured during these tests. However, it is not clear whether secondary chemistry in the flow tube could lead to the formation of a steady-state concentration of OH, such as from the ozonolysis of alkenes. As discussed in the manuscript, subsequent measurements made at the PROPHET site on ground in 2010 using a chemical modulation technique indicate that there were no significant interferences with the OH measurements except for the known ozone x water x power interference. However, as discussed in response to reviewer #2 comments, these tests in 2010 were performed below canopy and not atop the PROPHET tower as in 2008 and 2009, so there still remains some uncertainty, especially regarding the measurements during the warmer 2008 campaign. As discussed above, any unaccounted for interference during 2009 would result in a reduction of the measured OH concentration, leading to an overprediction by the model. This result would still stand in contrast to the general underprediction of measured OH concentrations in forest environments by current atmospheric chemistry models, and do not alter the main conclusions of the paper.

We have clarified these points with the following addition to the manuscript:

(Sec. 2.2)

"A few experiments were performed during CABINEX 2009 to test for interferences with the IU-FAGE instrument located on the forest floor and using a 12-m fiber, resulting in significantly higher laser power in the sampling cell. During separate experiments, both perfluoropropylene (C_3F_6) and carbon monoxide were introduced into a long flow tube that was interfaced to the instrument inlet to scrub ambient OH radicals. This flow tube ensured that there was enough reaction time for ambient OH molecules to be scrubbed before sampling. Any interference was then quantified through measurements of the remaining OH signal when C_3F_6 or CO was added to the flow tube. Only three short tests were carried out around midnight on three different days (1 test each day). The results of these tests suggest the possibility of an interference (in addition to the laser photolysis of ozone and subsequent reaction with water vapor) on the order of 4-9×10^5 cm^{-3}, potentially accounting for 50-100% of the nighttime OH concentrations measured during these tests. However, it is not clear whether secondary chemistry in the flow tube could lead to the formation of a steady-state concentration of OH, such as from the ozonolysis of alkenes."

(Sec. 4.1)

"However, recent measurements by Mao et al. (2012) during BEARPEX 09 using a chemical modulation technique to detect OH radicals were significantly lower than measurements using the spectral modulation technique and were in good agreement with model predictions with isoprene mixing ratios between 1-2 ppb on average, suggesting that there may be an unknown interference associated with the LIF-FAGE technique related to the oxidation of biogenic VOCs. A similar interference could explain the high measurements of OH observed in the afternoon during the warmer PROPHET 2008 campaign coinciding with the maximum afternoon temperature and highest isoprene concentrations. However, any interference in the measurements during CABINEX 2009 presented here would result in a reduction in the measured OH concentrations, leading to an overprediction by the model. This result would still stand in contrast to the general underprediction of measured OH concentrations in forest environments by current atmospheric chemistry models."

HO_2 Interferences

As mentioned in the paper, we have a performed a number of tests designed to characterize the magnitude of the interference from organic peroxy radicals during the HO2 measurement. These tests were done using the same instrument configurations during the PROPHET 2008 and CABINEX campaigns. Most importantly, we find that isoprene peroxy radicals were detected with 90% efficiency during the two campaigns making it the dominant peroxy radical interference. We have clarified this point with the following addition to the main text:

(Sec. 4.2)

"As discussed above (Sec. 2.3), laboratory calibrations have shown that approximately 90% of isoprene-based peroxy radicals are detected by the IU-FAGE instrument in addition to HO2 under the instrumental configurations during PROPHET 2008 and CABINEX 2009. Because the model predicts that isoprene-based peroxy radicals comprise approximately 80% of the total RO2 radical pool in this environment, isoprene-based peroxy radicals are the dominant species contributing to the HO2 interference in these measurements."

Referee #3:

2. There exist some discrepancies in the measured atmospheric compositions between PROPHET 2008 and CABINEX 2009 which need some further discussion. NO2 differs by factor 2 between 2008 and 2009 though the NO, O3 and J(NO2) are apparently very similar. In the supplement it is mentioned that different inlet lines have been used. Has the titration of NO by ozone in the inlet line been taken into account, or what else could have caused this difference? Formaldehyde in 2008 was not measured during the campaign but only subsequently and a correlation with ozone was used to construct the levels of HCHO in 2008 (see Supplement). What is the uncertainty contribution of this assumption? Isoprene and VOC were measured by different methods in both years – how has the comparability of the results been achieved? Finally, the photolysis rates are given with 50 and 30% 1-sigma uncertainties in 2008 and 2009, re-

spectively. Also, diurnal cycles of J(O1D) on clear sky days differ by up to 20%. Given the high sensitivity of the model with respect to photolysis frequencies, NO, and VOC, the different model results in 2008 and 2009 are questionable because these may be due to errors or artefacts in ancillary parameters. This should be further discussed.

Reply:

Uncertainties associated with the photolysis frequencies and ancillary parameters were incorporated into the Monte Carlo uncertainty analysis, and the resulting estimated uncertainty in the model for both 2008 and 2009 reflect these uncertainties in each year. Because the photolysis frequencies were not measured in 2008, the estimated uncertainties in the calculated photolysis frequencies are greater in 2008 compared to 2009, resulting in a greater impact on the uncertainty associated with the modeled OH concentration in 2008.

We have added additional statements in both the main text and the supplementary material to provide additional information about the measured atmospheric compositions between PROPHET 2008 and CABINEX 2009 as pointed out by the reviewer.

The NO_2 measurements each year were made by two different instruments, and the reason for the discrepancy is not clear. However, any uncertainty associated with the measurements of NO_2 has a minimal impact on the modeled concentrations of OH as the OH + NO_2 reaction is not a significant sink of OH during both 2008 and 2009, as this reaction contributes less than 10% to the total radical loss. This has been clarified in Sec. 3 of the revised manuscript:

(Sec. 3)

"Measurements of ozone and NO mixing ratios were similar during both campaigns, while the measured mixing ratio of NO_2 was greater during PROPHET 2008 compared to CABINEX 2009, even though the photolysis rates were similar. Two different instruments were used during the campaigns, and the reasons for this discrepancy are unclear. However, any uncertainty associated with the measurements of NO_2 has a minimal impact on the modeled concentrations of OH as the OH + NO_2 reaction is not a significant sink of OH in this environment (see Section 4.3)."

The NO_2 data was not corrected for conversion of NO into NO_2 in the sampling line, which could have resulted in 9% and 6% conversion of NO to NO_2 in 2008 and 2009, respectively. This has been clarified in the Supplementary material:

(Sec. S3)

"For measurements of NO_x, conversion of NO to NO_2 in the sampling line was not taken into account, which could have resulted in a 9% conversion of NO to NO_2 in 2008 and approximately 6% conversion in 2009."

For the Monte Carlo uncertainty analysis, formaldehyde concentrations were given an uncertainty of 100%. This has been clarified in the Supplementary Material. However, as discussed in the Supplementary Material, the uncertainty associated with the formaldehyde concentrations has a minimal impact on the modeled radical concentrations:

(Sec. S3)

"Formaldehyde was given an uncertainty of 100% for the 2008 Monte Carlo uncertainty analysis. However, a sensitivity analysis from the CABINEX modeling revealed that changing the HCHO mixing ratios by a factor of 2 had less than a 5% effect on OH and HO2+ISOP concentrations, suggesting that this difference in the 2008 estimated HCHO mixing ratios does not have a major impact on the modeling results for 2008."

Isoprene and other VOC measurements were made by two different instruments in 2008 and 2009. Unfortunately, the two instruments were not directly compared to each other. However, each instrumental technique has been previously compared to established GC methods (de Gouw and Warneke, 2007; Mielke et al., 2010). This has been clarified in Section 3 of the revised manuscript:

(Sec. 3)

"Although the different techniques used to measure isoprene and VOCs during the two campaigns were not compared, each technique has been previously compared to established GC methods (de Gouw and Warneke, 2007; Mielke et al., 2010)."

Referee #3:

3. There were substantial deviations in OH between model and measurements in the 1998 PROPHET study that were attributed to organic chemistry (Tan et al., 2001). In 2008 and 2009, such deviations are not observed. The authors do not appropriately analyse the differences between those studies and provide explanations. Especially, with respect to the known artefacts in FAGE radical measurements (see above), the authors should be able to separate experimental issues from atmospheric composition issues and model issues.

4. What can we learn from the studies at the PROPHET site? PROPHET 1998 was not in-line with models, whereas PROPHET 2008 and CABINEX 2009 agree (more or less) with model predictions. Given the current doubts in measurement technique of OH and HO2 by LIF, the large experimental uncertainties especially for OH (laser power), and the model uncertainties mainly due to ancillary data, there is a fairly unclear situation of what the comparison between measurements and model can be useful for. Accordingly, the authors should further discuss the "agreement" with the model and the disagreement in 1998 in light of uncertainties and artefacts.

Reply:

We have expanded the discussion to assist in the comparison of the 2008 and 2009 results with the 1998 measurements and modeling at the PROPHET site. As pointed out by the reviewer, the OH concentrations measured in 1998 by the Penn State FAGE instrument were significantly greater than their model results as well as the measured and modeled results reported here in 2008 and 2009. Although it is beyond the scope of this paper to fully analyze potential instrument artifacts associated with the 1998 measurements, the recently reported interferences with the Penn State FAGE instrument during the BEARPEX campaign could explain the difference between the measured and modeled concentrations in 1998, and would result in OH concentrations similar to those measured in 2008 and 2009. Although a similar interference with the IU-FAGE instrument cannot be ruled out, any interference with the measurements presented in this paper would result in a reduction in the measured OH concentrations, leading to an overprediction by the model in contrast to the general underprediction of OH measurements in forest environments by current atmospheric chemistry models.

These issues have been clarified in Section 4 of the revised manuscript:

(Sec. 4)

"The measured and modeled OH concentrations reported here during 2008 and 2009 are approximately a factor of 2 lower than the values measured at this site in 1998 using the Penn State LIF-FAGE instrument (Tan et al., 2001). However, Mao et al. (2012) recently observed that OH measurements in a ponderosa pine forest using the Penn State LIF-FAGE instrument during the BEARPEX campaign using a chemical modulation technique resulted in measured OH concentrations that were a factor of 2 lower than those obtained using a spectral modulation technique. As a result, it is possible that the measurements made during PROPHET 1998 may have also suffered from a similar interference. As discussed above, it is not clear whether the IU-FAGE instrument suffers from a similar interference even though subsequent chemical modulation tests at this site did not reveal a measurable interference. Additional measurements of HO_x concentrations are still needed to confirm that the measurements are free from unknown interferences. However, as mentioned previously, any interference in the measurements presented here would result in a reduction in the measured OH concentrations, leading to an overprediction by the model. This result would still stand in contrast to the general underprediction of OH measurements in forest environments by current atmospheric chemistry models."

Specific comments:

Referee #3:

p. 3, l.7: which other "long-lived greenhouse gases" are meant here?

Reply:

We have clarified this statement to include other greenhouse gases such as hydrochlorofluorocarbons and hydrofluorocarbons:

(Introduction)

"…the removal of methane and other greenhouse gases, such as hydrofluorocarbons and hydrochloroflurocarbons that affect the radiative balance of the atmosphere."

Referee #3:

p. 9, ll.7: please, specify the remaining laser power entering the cell and comment on the impact of all the mentioned effects (temperature and humidity) on the sensitivity of the instrument and how constant sensitivity/calibration was achieved.

Reply:

We have clarified the remaining laser power in the detection cell and how the power and humidity was monitored during the campaigns to keep track of the instrument sensitivity**:**

(Sec. 2.2)

"Measuring the laser power at the exit of the White cell using a photodiode, continuous measurements of the ambient humidity, and performing frequent calibrations allowed the sensitivity of the instrument to be closely monitored, confirming its stability throughout the campaigns."

Referee #3:

p. 10, 1st §: as also the OH fluorescence signal depends on laser power, the argument that the interference is negligible due to the low laser power is not convincing. Please specify the typical and maximum OH artefact due to this ozone interference.

Reply:

We have clarified the typical magnitude of the ozone x water x power interference for the instrument during the above canopy measurements:

(Sec. 2.2)

"However, for the above canopy measurements of OH during the PROPHET 2008 and CABINEX 2009 field campaigns, this interference was negligible because of the low laser power (< 1 mW) reaching the sampling cell at the top of the tower through the 50 m fiber, resulting in a predicted laser-generated OH concentration of less than 2.5×10^5 cm^{-3}, which was below the detection limit of the instrument at the top of the tower."

Referee #3:

p. 10, last §: In ambient measurements during HOxCOMP (Schlosser et al., 2009), two of the LIF instruments were higher by about 30% and one instrument was higher by about 60% than the CIMS instrument. At least with respect to the latter, this is not really well agreement.

Reply:

We have clarified the discussion of the measurement agreement reported during HOxCOMP:

(Sec. 2.2)

"Other potential interferences with OH measurements have been recently investigated during a formal blind intercomparison involving 3 different OH measurement techniques (Schlosser et al., 2009), including LIF-FAGE, Chemical-Ionization Mass Spectrometry (CIMS), and Differential Optical Absorption Spectroscopy (DOAS). Ambient OH measurements made by several LIF-FAGE instruments reported concentrations that were 1.3-1.7 higher than those observed using the CIMS technique, but generally within the instrument and calibration uncertainties. Chamber measurements of OH by several LIF-FAGE instruments were in good agreement with measurements using the DOAS technique. Except for one instrument consistently measuring 1.7 times higher than the CIMS instrument during the ambient measurements, these results suggest that interferences with the OH measurements in these environments were within the known measurement uncertainty (Schlosser et al., 2009).

Referee #3:

p. 11: see also general comment 1 above. Obviously, contradicting results have been achieved in the interference tests. Since these interferences are a very important issue, it is recommended to present the results of these interference tests and discuss the potential uncertainty contribution due to this interference for the presented OH results.

Reply:

Please see our response to general comment 1.

Referee #3:

p. 15, last §: Given the temperature variability of typically between 15 and 25◦C, a difference of 1-2 degrees appears rather small. Thus, it appears harsh to speak of un-typical conditions in 2009. Furthermore, isoprene emissions are mainly determined bylight and the difference in isoprene mixing ratios can not be explained by temperature differences. Please specify that analytical problems can be ruled out as explanation of the difference.

Reply:

We have clarified that the unseasonably cold temperatures were in reference to a historical average temperature at the site, and may be responsible for the difference in the measured mixing ratios, although errors associated with the different instrumental techniques cannot be ruled out.

(Sec. 3)

"Temperatures during July 2009 were unseasonably cold, resulting in temperatures approximately 1-2 degrees Celsius lower than in 2008 and 3-4 degrees Celsius cooler than the historical average (Bryan et al., 2012), while the average photolysis rate constants were similar (Figure 3). The low temperatures observed during CABINEX 2009 may be a factor in the difference between the observed isoprene mixing ratios for the two campaigns (Figure 3), as temperature has been shown to have both instantaneous and cumulative effects as a driving factor along with UV/visible light in biogenic VOC (BVOC) emissions (Monson et al., 1994; Petron et al., 2001; Sharkey et al., 2001; Blanch et al., 2011), although unknown errors associated with the different VOC measurement techniques cannot be ruled out."

Referee #3:

p. 17, ll. 6-12: Please specify the percentage of data which are different from zero beyond their 2-sigma uncertainty.

Reply:

During the daytime, between 30%-50% of the 2 hr OH measurements are different from zero beyond their 2σ uncertainty value. This has been clarified in Section 3.2 of the revised manuscript.

Referee #3:

p. 19 and Fig. 9: the main message of Figure 9 is that data are of insufficient quality to check for the corresponding dependencies. This should be mentioned in the text and the figure could be discarded.

Reply:

We have added a statement to describe the lack of dependence of the observed/modeled OH concentrations on isoprene and on the quality of the data to section 4.1 of the revised manuscript. We have also moved Figure 9 and the corresponding discussion to the supplementary material. Figure 9 has been renamed Figure S7. References to Figures 10-13 have been corrected in the main text.

(Sec. 4.1)

"…an analysis of the CABINEX observed to model OH ratio (Figure S7) does not reveal a significant dependence on the isoprene mixing ratio, although the precision of the correlation is poor due to the poor precision of the OH measurements."

Referee #3:

p. 20, 1st §: There is a huge discrepancy with the results obtained in 1998, and the authors should discuss this further. Have any modifications to the instrument been made which might have affected the results? It is hard to follow the argument here, that in other studies interferences existed (Mao et al., 2012) but this remains vague for the Indiana university instruments. It is strongly recommended to include results of corresponding tests in this paper such that the interference problem can be quantified.

Reply:

As discussed in response to general comments 3 and 4, it is beyond the scope of this paper to address uncertainties associated with the 1998 measurements made using the Penn State FAGE instrument, which likely operated under different instrumental conditions of pressure and flow rate compared to the IU-FAGE instrument. However as discussed above, we have added an expanded discussion of the 1998 results in light of the recently reported interferences with the Penn State FAGE instrument during the BEARPEX campaign that could explain the difference between the measured and modeled concentrations in 1998 (see response to general comments 3 and 4). Although a similar interference with the IU-FAGE instrument cannot be ruled out at this time, any interference with the measurements presented in this paper would result in a reduction in the measured OH concentrations, leading to an overprediction by the model in contrast to the general underprediction of OH measurements in forest environments by current atmospheric chemistry models (see response to general comments 3 and 4 above).

Referee #3:

p. 24, section 4.3: Please, specify in the text how the budget is closed. Apparently, Figures 12 and 13 show balanced production and loss, however, the HO2 and the RO2 are not individually measured and the constrained model is partly not consistent with observations (Figures 5, 7 and 8).

Reply:

We have clarified that the radical budget discussion refers to the model results rather than the measurements.

(Sec. 4.3)

"Given that the model reasonably reproduces the measured OH concentrations, these model derived radical budgets can provide insights into the importance of individual radical sources and sink in this environment, even though, the modeled HO2+ISOP overpredicts the measured HO_2* in both years."

Referee #3:

p. 26, middle §: NO2 was about a factor 2 higher in 2008 with similar NO and ozone as well as J(NO2). Thus one would expect higher NO in 2008. The model, however, uses lower NO in 2008 with effects discussed in this §. It is recommended to discuss the uncertainty of the used constraints and assumptions and their effect on the model results

Reply:

As discussed in response to general comment 2, the difference between the measured mixing ratio of NO_2 in 2008 and 2009 is unclear. However, the impact of this difference on the modeled radical concentrations is small, as the OH + NO_2 reaction is not a significant sink of OH during both 2008 and 2009. The model uncertainty resulting from the uncertainty associated with the measured concentration of NO and other measured constraints is taken into account in the Monte Carlo analysis (Sec. 2.4).