Final Comments

We thank the referees for the very helpful comments on our paper.
Our replies to the comments are listed below.

While comparing the chemical mechanisms used for box model simulations we found that one RO_2 species (C89O2) was treated incompletely in the monoterpene mechanism (MTM). Since the production of this RO_2 species is small (mean: $1.5x10^5$ molec. cm^{-3} s^{-1}) compared to the production rate of $HO_{x,}$ (typically of the order of 10^7 molec. cm^{-3} s^{-1}) the updated mechanism has negligible impact on the results. All related figures and text passages were updated.

Anonymous Referee #1

General comments:

1. *It is important to show the difference on measured OH between the traditional LIF and LIF with the chemical modulation method. I understand that there is another paper in preparation on this. But I do think this is an important message to the community and worth mentioning briefly in the paper.*

The authors agree to the importance of the difference and its nature between the traditional LIF-FAGE and IPI-LIF-FAGE technique. In the meantime a separate article dedicated to this subject (Novelli et al., 2014) has been published.

2. *The derivation of RO_2 from Equations (5) and (6). It seems to me that Equation (5) is incomplete, if isomerization of RO_2 plays an important role on the fate of RO_2 (and it should). And more importantly, isomerization of RO_2 can produce HO_2. With that taken into account, the derived RO_2 will be significantly less according to Equation (6). Therefore the whole discussion on Table 3 in Section 3.1, which seemingly involves computed RO_2, is not very convincing to me.*

Equation (5) and (6) do not include isomerization reactions of RO_2. For the calculation of the HO_2 budget only the isomerization reactions (1-6-H-shift) forming HO_2 are relevant and therefore, the calculated RO_2 might be overestimating the actual RO_2 concentration during HUMPPA-COPEC 2010. Nonetheless, the significance of these additional reactions strongly depends on the speciation of RO_2, which is unknown. We will clarify in the revised manuscript that the estimate of RO_2 from the HO_2 budget following Eqn. (6) is an upper limit due to neglecting the isomerization processes.

Independent calculation of the sum of estimated RO_2 and observed HO_2 based on the photo-stationary state of NO and NO_2 leads to a similar result for the RO_2 concentration, strengthening our estimate for the RO_2 concentrations. The induced uncertainty of this calculation is propagated for further calculations and considered in the discussion on Table 3 in Section 3.1 of the previous manuscript.

3. *I am wondering if the misrepresentation of HO_x in the model could be due to some missing primary HO_x sources (instead of recycling processes). As shown in Fig 12, when the model is constrained with observed total OH reactivity, both OH and HO_2 are significantly underestimated. This can certainly be improved by introducing a primary source, such as ozonolysis of reactive VOCs. Given the large missing reactivity shown in the paper, I don't think the possibility of missing primary HO_x sources can be ruled out from this analysis. Therefore it seems insufficient to assume "there are additional recycling processes", as shown in the abstract.*

The authors agree that despite the suggested recycling mechanisms an unaccounted primary HO_x source could improve the model-measurement agreement. Therefore, we changed the abstract accordingly:

“Detailed analysis of the HO_x production, loss, and recycling pathways suggests that in periods of high total OH reactivity there are additional recycling processes forming OH directly, not via reaction of HO_2 with NO or O_3, or unaccounted primary HO_x sources.”

Specific comments:

1. *I think the whole mechanism needs to be better documented. The current version is not easy to follow. There is no description for each species in the mechanism. For many reaction rates, I couldn’t find the exact rate (k16HS for example).*

The names of the species and rate constants are taken directly from the MCM, according to availability. Others are defined in the revised documentation of the chemical mechanism in the supplementary material. In case of the rate constant k16HS the value by Peeters et al. (2009) for the 1-6-H-shift was used.

2. *In regards to the difference on OH measurements between ground and above canopy, if this is caused by J-values, can you compare the J-values between ground and above canopy?*

A direct comparison of the J-value time series observed above canopy and on the ground will be included in the revised manuscript (previously Figure S1 of the ACPD manuscript, now Figure 9). An indirect comparison of J-values can be found in ACPD-Figure 8.

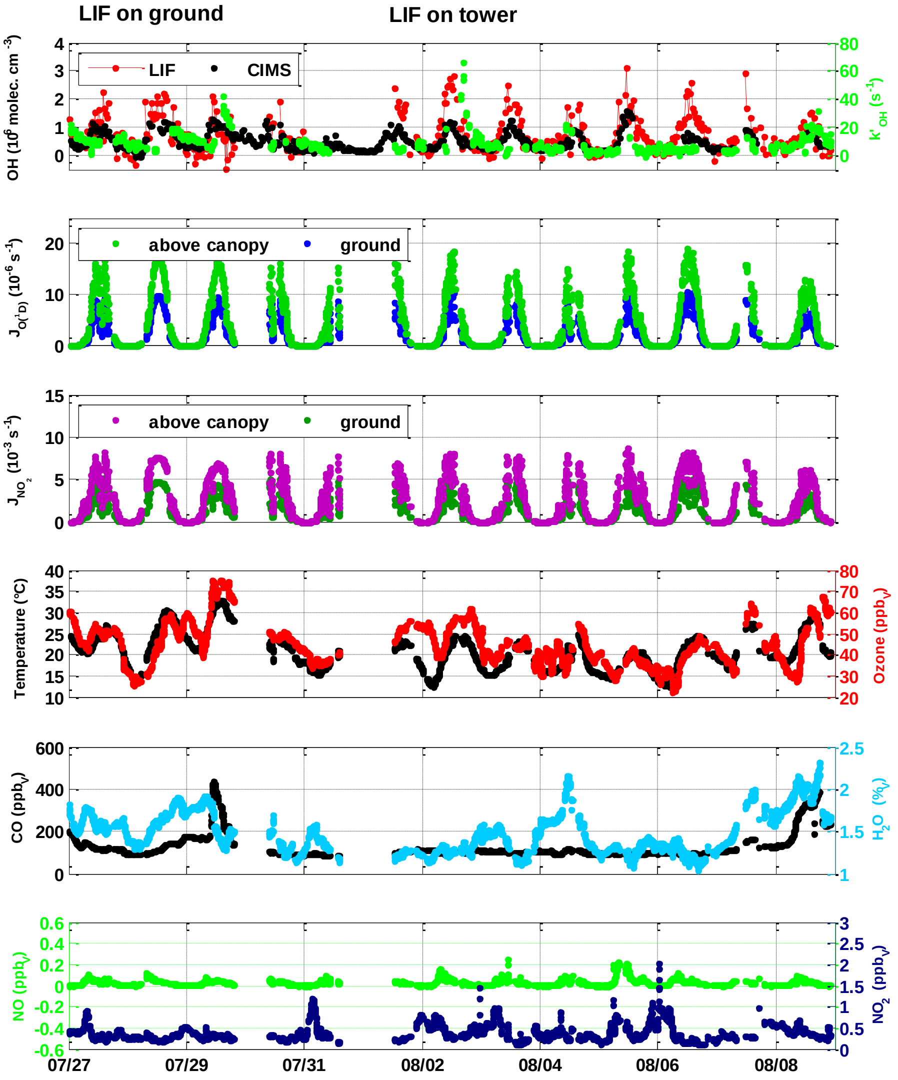
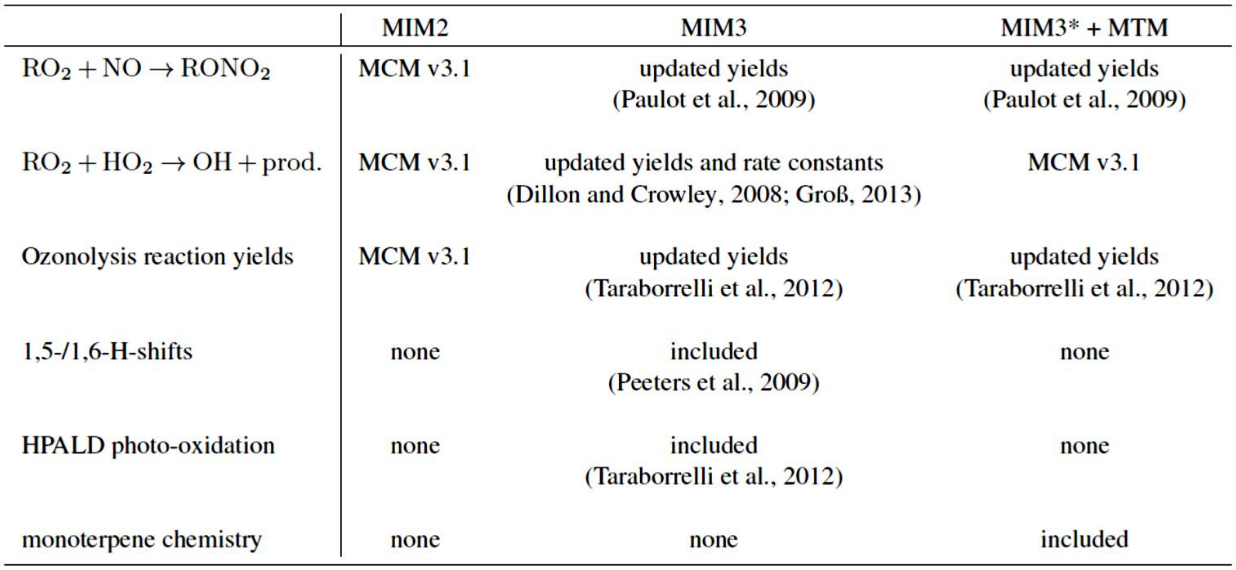


Figure C1: Time series of trace gas species and meteorological parameters during HUMPPA–COPEC 2010.

3. *Also it would be nice to show a detailed description on the difference between MIM3 and MIM3*.*

A table listing the key differences between the chemical mechanisms used for the box model simulations will be included in the revised manuscript:

Table C1: Key differences between chemical mechanisms used for the box model simulations.



	MIM2	MIM3	MIM3* + MTM
$RO_2 + NO \rightarrow RONO_2$	MCM v3.1	updated yields (Paulot et al., 2009)	updated yields (Paulot et al., 2009)
$RO_2 + HO_2 \rightarrow OH + prod.$	MCM v3.1	updated yields and rate constants (Dillon and Crowley, 2008; Groß, 2013)	MCM v3.1
Ozonolysis reaction yields	MCM v3.1	updated yields (Taraborrelli et al., 2012)	updated yields (Taraborrelli et al., 2012)
1,5-/1,6-H-shifts	none	included (Peeters et al., 2009)	none
HPALD photo-oxidation	none	included (Taraborrelli et al., 2012)	none
monoterpene chemistry	none	none	included

4. *P28587, L12, "Monoterpenes and sesquiterpenes have many more pathways to oxidise than isoprene, and the channels that allow for H-migration are therefore a smaller percentage than in isoprene." I am not sure if this is correct.*

The reviewer is right, at least some terpene species have similar or even larger OH yields compared to isoprene. We changed the sentence as follows:

"Monoterpenes and sesquiterpenes have many more pathways to oxidise than isoprene. However, not all channels lead to OH production."

Anonymous Referee #2

General comments:

Section 3.1.2 and Table 3:

The reviewer found this section and the accompanying table to be very dense and, at times, confusing. Much of the information in the table is repeated in the text, and it is difficult to discern the key points of the discussion when inundated with so many numbers.

Furthermore, this breaks the momentum that was built up in the previous section.

The following changes are recommended:

1. *Keep one of the radical cycles in the manuscript, perhaps as a figure instead of a table. The daylight, high-reactivity diagram would be fine. Move the rest to a supplement. Alternatively, perhaps combine the daylight, high and low-reactivity diagrams into a single diagram, using rate-scaled arrows, to facilitate comparison.*

2. *Most of the production rate information can be removed from the text. Try to focus on the key points, such as a subset of those bulleted in Table 3.*

Section 3.1.2 and Table 3 have been generally revised, following the suggestions of the reviewers.

3. *Regarding the missing HO_2 source:*
   Can a number or range be assigned to the missing HO_2 production rate, based on model results? This would facilitate comparison with other studies, more so than just the ratio of modeled-to-measured HO_2. This number could be included in both the abstract and conclusions.

In our opinion compensating the missing HO_2 in the model by an additional source will more address uncertainties in the chemical mechanism rather than describe a missing atmospheric process. In order to account for the missing HO_2 production in the atmosphere, we calculated a budget constraint with observations and expressed this as an equivalent RO_2 source. For example in the case of high actinic flux and moderate reactivity (ACPD - Table 3, upper left panel) an additional RO_2 source of approx. 1×10^6 molec cm^{-3} s^{-1} would be required.
We added this information to the abstract.

4. *Also, a key conclusion of this paper is that missing OH reactivity in the model may explain the missing source of HO_2. Is there sufficient data to make a scatter plot of, e.g., $[HO_2]_{mod}/[HO_2]_{meas}$ versus missing reactivity, or something similar? A clear relationship between these two would help solidify this conclusion.*

Below the scatter plot $[HO_2]_{mod}/[HO_2]_{obs}$ versus missing OH reactivity is provided (Figure C2). During night time the model reproduces most of the observed reactivity, but underestimates the HO_2 concentration. During daytime the $[HO_2]_{mod}/[HO_2]_{obs}$ ratio is on average approx. 70% when the OH reactivity is reproduced by the model. Though, in case of high missing OH reactivity (more than 20 per second), the model reproduces only 20% of the observed HO_2 on average. From this difference we conclude that the conditions of high missing reactivity coincide with a not accounted HO_2 source.

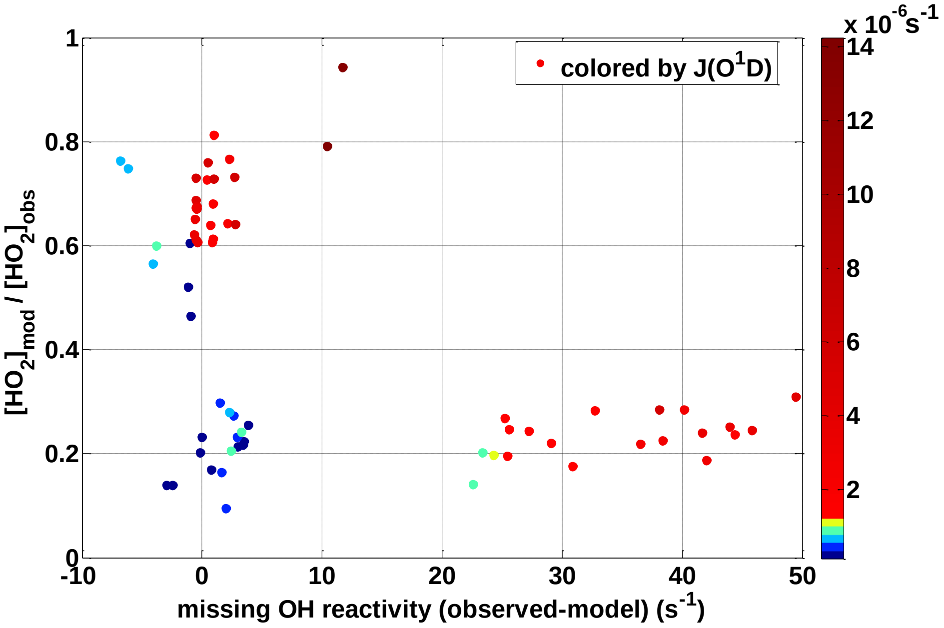


Figure C2: Ratio of simulated to observed HO_2 concentration versus missing OH reactivity (observed –model).

Specific Comments

1. *P.28565: The authors might also cite (Wolfe et al., 2013), which was published after this paper but deals with a similar topic in a different forest.*

We added the following sentence in the literature review paragraph:

"Wolfe et al. (2013) found evidence for missing peroxy radical sources within a rural forest canopy."

2. *P.28565, L.14: These observations are presented in (Edwards et al., 2013).*

We added the following sentence in the literature review paragraph:

"However, comparison of measured and calculated total OH reactivity in this environment showed that the physical loss of species that react with OH plays a significant role in the calculated OH reactivity. Furthermore, a significant sink of OH appears to be missing (Edwards, 2013)."

3. *P.28574, L.8: What is the reason for choosing 4 cm/s? If it is because it provides the best agreement with measured H_2O_2, the authors should state so. Alternatively, Figure 3 could include additional lines for H_2O_2 calculated using 1 and 5 cm/s.*

The loss of H_2O_2 is dominated (>90%) by deposition and photolysis (Lowe et al., 1983; Allen et al., 2013 and references therein). Thus, the decay of H_2O_2 in the afternoon is mainly determined by the deposition velocity. As stated in Table 2 of the manuscript (ACPD) the 4 cm/s were chosen by best fit. Sensitivity studies were performed and additional lines for calculated H_2O_2 using 1 and 5 cm/s are now included.

The point of the hydrogen peroxide budget calculation had been to investigate a possible interference in the HO_2 measurements. The H_2O_2 production has a quadratic dependency on the HO_2 concentration, thus the concentration of H_2O_2 is more sensitive to changes in the observed HO_2 than to the deposition velocity, which is only linearly related.

Assuming 50% of the observed HO_2 signal would originate from RO_2 and thus, not contribute to the H_2O_2 production, the HO_2 would not suffice to explain the observed H_2O_2 concentration (Figure C3). On the other hand, the simulation of hydrogen peroxide using twice the amount of observed HO_2 results in a significant overestimation of the observed H_2O_2 concentration. This provides confidence that the measured HO_2 is not affected by a major interference.

ACPD-Figure 3 will be replaced by Figure C3 in the revised manuscript.

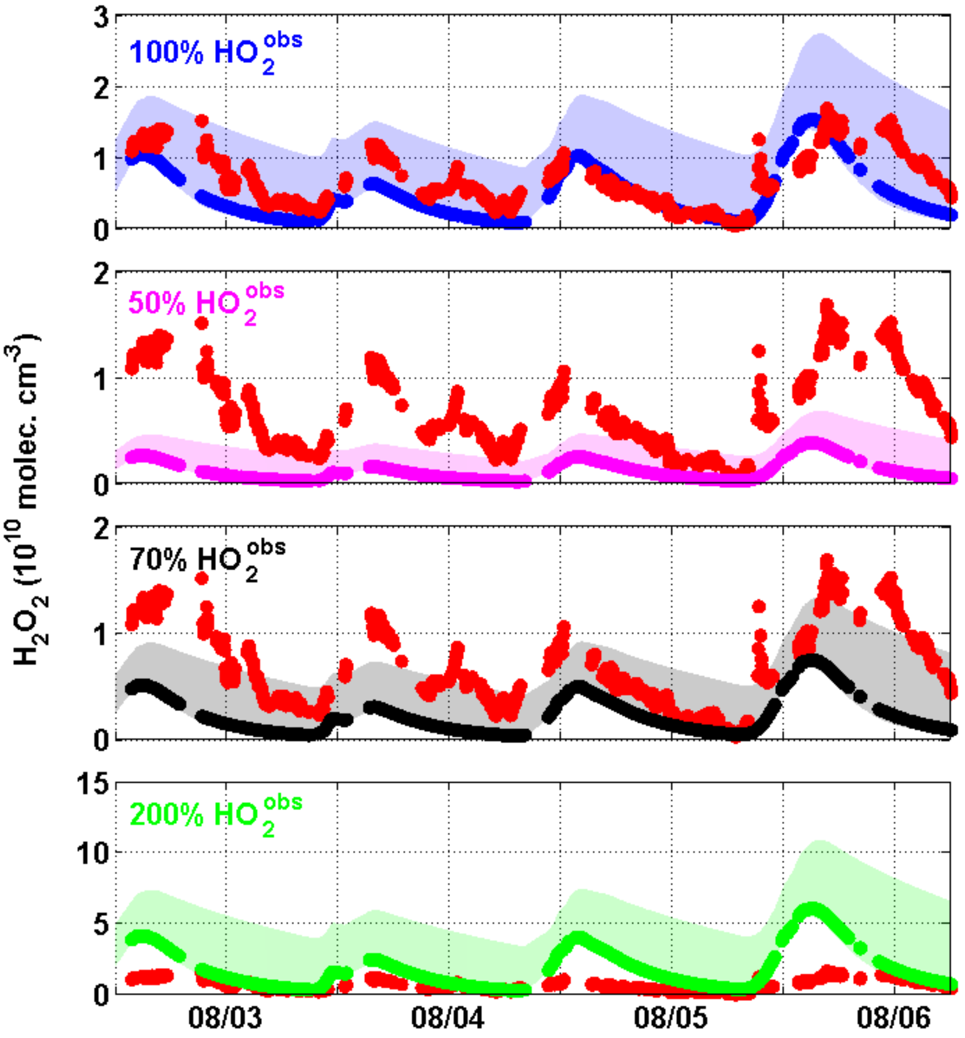


Figure C3: Comparison of measured H_2O_2 (red dots) with simulations based on assumed deviations of HO_2 measurements by LIF. Shaded areas indicate the influence of deposition velocities ranging between 1 and 5 cm/s.

4. *P. 28576, L.24: The description of what is included in the MTM is somewhat confusing. Does this include fast isoprene isomerization chemistry as in MIM3?*
   Perhaps a table summarizing key differences would help.

Please refer to our answer on Specific Comment 3 by Referee 1.

5. *P.28581, L.19: Why is a direct comparison of observed and steady-state OH concentrations not included?*

A direct comparison of observed and steady-state OH concentrations is equivalent to the comparison of known OH production rates and the observed total OH loss. Since this paper focusses on the analysis of HO_x production, loss and recycling mechanisms, the authors prefer the presentation in terms of rates, thus showing the budget instead of a comparison of concentrations.

6. *P.28583, L.8: the branching ratio and rate constant for reaction with NO is very dependent on the type of RO_2. What values were chosen for this calculation and why?*

No measurements of RO_2 during HUMPPA-COPEC 2010 are available. The lumped rate constant $k_{RO2+NO} = 2.7x10^{-12}$ x $e^{(360/T)}$ cm³ molec.$^{-1}$ $s^{-1}$from the Master Chemical Mechanism (MCM, v3.2, Jenkin et al. (2007); Saunders et al. (2003), via website: http://mcm.leeds.ac.uk/MCM,) was chosen for our calculation. Branching ratios for different RO_2 range from approx. 0.75 to 0.95 (see MCM, v3.2). Values for monoterpenes are typically approx. 0.77-0.79, while isoprene related RO_2 branch with approx. 0.90-0.95.
A branching ratio b= 0.9 was used, probably leading to an underestimation of RO_2 for a monoterpene dominated environment. The induced uncertainty was propagated and considered in further calculations.

We added the information about the branching ratio and rate constant used for calculation in the revised manuscript.

7. *P. 28584, L.9: Alternatively, one could interpret the reasonable agreement of SS and observed OH, along with the fact that HO_2 is a major source, as evidence that there is not a significant interference in observed HO_2.*

We included this in the revised manuscript:

"Furthermore, the steady-state budget being nearly closed indicates that there is not a significant interference in observed HO_2."

8. *P. 28587: Why do the authors only mention the 1,5 H-shift, even though the 1,6 H-shift is believed to be the dominant isomerization pathway for isoprene hydroxyperoxyl radicals? Also, several other studies should also be cited (Crounse et al., 2011; da Silva et al., 2010), as these suggest lower isomerization rates than those calculated by the Leuven group.*

In this context we focus on OH recycling mechanisms only. HO_2 originating from the 1,6-H-shift is already taken into account by using the observed HO_2. Fuchs et al. (2013) measured reduced isomerization rates for both, 1,5- and 1,6-H-shifts, showing the minor importance of the 1,6-H-shift.

Crounse et al., (2011) and da Silva et al., (2010) will be cited additionally in the revised manuscript.

9. *Section 3.2: While it is not fully clear to the reviewer what the differences are between MIM3 and MTM, the over-prediction of OH with MIM3 is consistent with isomerization chemistry being slower than the theoretical rates used in that mechanism. The disagreement would be further exacerbated if HO_2 were increased to match observations.*

We agree with the reviewer. The disagreement for simulated vs. observed HO_2 would be larger using reduced isomerization rates in the MIM3 mechanism.
For better clarification of the differences between the chemical mechanisms a table indicating the main differences will be added to the revised manuscript (see Referee 1, Specific Comment 1).

10. *P. 28589, L. 19: What is the HO_2 yield from a-pinene? Also, how does modeled RO_2 compare with that calculated from steady state (Eq. 10)?*

The direct production of HO_2 from α -pinene has a yield of 15% for the reaction with OH and 33% for the reaction with ozone (see reactions G410apint2 & G410apint148).

The ratio of modelled RO_2 to RO_2 calculated from steady state is on average 1.1 (min.: 0.01; max.: 11.5).

11. *P. 28594, L. 7: HNO_4 is not really a reservoir in this case because it is short-lived. The two equilibrium reactions in Fig. 16 should be added together to show the net effect of these reactions on HO_2.*

As the net effect is zero, we removed the fraction due to HNO_4 equilibrium reactions from Figure 16.

12. *P. 28595, Conclusions: The literature review in the first paragraph seems out of place. Recommend moving this to the introduction or discussion.*

Paragraph has been removed.

Technical Comments

1. *P.28565, L.29: concluded*

Changed accordingly.

2. *P. 28566, L.11-16: This sentence is long and fragmented. Please re-write.*

Changed to:

"The aim of the HUMPPA-COPEC 2010 campaign, by performing observations of VOCs, HO_x and the total OH reactivity, is to increase our understanding of atmospheric oxidation processes in a coniferous forest. The HO_x budget is explored using direct calculations from measured species as well as an observationally constrained chemical box model in steady state."

3. *P. 28567: Please provide a reference for HORUS and/or FAGE.*

References to Martinez et al., 2010 and Hard et al., 1984 were included in the revised manuscript.

4. *P. 28569, L.6: on the ground*

Changed accordingly.

5. *P.28570, L.5: Is "calibration air" the same as "zero air"? The latter is a more common term.*

Changed to: *"humidified zero air"*

6. *P. 28577, L.2: recommend removing footnote and defining MCM in the text. This goes for other footnotes appearing later as well.*

Changed accordingly.

7. *P. 28582, L.1: Please add a topic sentence as the discussion shifts from OH to HO_2 here.*

We revised the first sentence of this paragraph.

8. *P. 28586, L.26: Thornton et al. (2002), while perhaps an appropriate reference for this topic, was not a laboratory study.*

The sentence changed in the context of revision of section 3.1.2.

9. *P. 28587, L.24-28: This is not a sentence. Please revise.*

The sentence was removed in the revised manuscript.

10. *P. 28588, L.2: delete comma*

Changed accordingly.

11. *P. 28591, L.26: this phrase implies that MBO is a monoterpene, which is not the case. Perhaps it is meant that the MBO emission rate (per molecule?) is 1-3% of the monoterpene emission rate.*

This wrong implication is corrected. The sentence changed to:
"Previous measurements in this forest showed that MBO emission rates were only 1-3% of the total monoterpene emission rate (Tarvainen et al.,2005)."

12. *Table 1: There is no uncertainty in VOC observations?*

Values and a reference to Song et al., (2014) were added.

13. *All Figures: remove the word "in" from the axes unit labels*

Changed accordingly.

14. *Figures 9-13, 14, 16: Axes and tick labels are quite small. Please enlarge.*

Changed accordingly.

Anonymous Referee #3

General comments:

1. *The intercomparison of the LIF-FAGE instrument with the CIMS instrument is an important result, and the agreement between the two techniques gives confidence in the LIF measurements using the external scrubbing technique. It would be valuable to show the level of interference observed in this environment by showing the level of OH measured without the external scrubbing. Is the level of the interference observed in this environment similar to that observed by Mao et al. (2012)? Did the interference vary with temperature, BVOC concentrations, etc?*

Please refer to our answer to Referee 1, General comment 1. The magnitude of the interference in different environments, including the observations during HUMPPA-COPEC 2010 and technical details on the external scrubbing technique are described in Novelli et al., 2014.

2. *The LIF measurements of OH from the top of the tower above the canopy were generally greater than the measurements of OH from the CIMS instrument measured at the surface below the canopy. The authors suggest that the difference is due a greater photolysis frequency observed during the above canopy measurements (Figure 8). However, it is not clear from the information given that J(O^1D) was consistently lower below the forest canopy. The data shown in Figure S1 suggests that J(O^1D) was similar when the LIF instrument was measuring on the ground and on the tower. Are the measured J(O^1D) values shown in Figures 5 and 7 measured on the ground (Figure 5) and on the tower (Figure 7)? Are the scales for the J(O^1D) values in these figures similar? If the J(O^1D) values shown in Figure 7 were made on the tower above the canopy, were there J(O^1D) measurements made simultaneously below the canopy to help explain the lower OH observed by the CIMS on the ground? Was the level of interference in the LIF instrument measured using the external scrubbing technique similar to that observed below the canopy? This aspect of the manuscript needs additional information and clarification. Figure S1 contains important information and probably should be included in the main paper.*

The J(O^1D) values shown in Figures 5 and 7 were measured on the ground (Figure 5) and on the tower (Figure 7). The scales of the two figures are different. Figure S1 included only J(O^1D) values measured above canopy. To clarify better and avoid misunderstandings, J-values measured above canopy and on ground were included in the revised Figure S1 (see also our answer to Specific Comment 2, Referee 1).

Differences in the level of interference on the ground and on the tower are described in Novelli et al. (2014).

3. *It appears from the manuscript that the authors have not fully characterized the level of interference from RO_2 radicals associated with their measurements of HO_2 concentrations. They compare measured concentrations of H_2O_2 with that calculated based on their measured HO_2 concentrations. Although it may be difficult to compare the measured H_2O_2 with calculations based on measured HO_2 concentrations due to differences in lifetimes, the results suggest that the level of interference is small based on the agreement between the calculated and measured concentrations of H_2O_2. However, for these calculations the authors assume a deposition velocity of 4 cm s^{-1}, which is similar to previously reported values between 1-5 cm s^{-1}. What would the agreement look like if they assumed a deposition velocity of 1 cm s^{-1}? Would the measured HO_2 values result in calculated H_2O_2 values significantly greater than measured? Such a result would suggest that the measured HO_2 concentrations may be significantly affected by interferences from RO_2 species at this site.*

Please refer to our answer to Referee 2, Specific comment 3.

4. *The agreement of the modeled OH concentrations with the measurements when the terpene mechanism is included in the model is an interesting result, although this model does not significantly improve the agreement with the measured HO_2. Unfortunately, the day-to-day results of the model are not shown. The authors claim that the model-measurement agreement can be divided into two groups (section 3.2). Do these groups correspond to particular days or particular times of day? How well does the model reproduce the day-to-day variability of both OH and HO_2 in the measurements shown in Figure 7 and Figure S1? The paper would benefit from showing the day-to-day model results for both OH and HO_2. As mentioned above, Figure S1 contains important information and should be included in the main paper rather than in the supplement.*

The overlap of required data in order to calculate the steady-state concentrations of OH and HO_2 is very small. Thus, the dataset is highly fragmented and only small portions of individual days are available. A clear correlation for the separation of the model-measurement-agreement into two groups could not be found. The overview of complementary observations (ACPD - Figure S1) will be shifted to Section 3.1.

5. *Although the characterization of the RO_2 interference appears to be ongoing and will be published separately, can the authors estimate the maximum interference assuming a high conversion efficiency for alkene-based peroxy radicals produced in their model? Adding a comparison of the measured HO_2 concentrations with a model result that includes contributions from modeled alkene-based peroxy radicals could give additional insights into the model-measurement agreement and the potential level of interference with their HO_2 measurements. This could be added as an additional plot with the day-to-day modeling of HO_2 in Figure S1 and moved to the main paper.*

Unfortunately, the data coverage is not sufficient for day-to-day modeling. Since the model does mostly not reproduce the observed OH reactivity the simulated RO_2 concentration is not representative.

Anonymous Referee #4

General comments

1. *It is good to see that the CIMS and interference corrected LIF OH measurements agree but it is important to know how big the correction was, and whether this changed during a 24 hour period (was the correction necessary more at night than in the day for example?) or with the level of other parameters?*

The authors acknowledge the interest in the IPI-LIF-FAGE technique and the magnitude and diurnal course of the associated signals and/or corrections. Novelli et al., 2014 is dedicated to this topic. Please refer also to our answer to Referee 1, General comment 1.

2. *Owing to the amount of material, I did find the paper to be quite difficult to navigate in places, with very complex figures and lengthy discussions, and the paper may benefit from some simplification and reorganisation of the presented material, so it is easier to follow and the main messages are clearer.*

Following the ideas and suggestions of the reviewers, the authors simplified Table 3 and the associated discussion on the HO_x recycling pathways in the revised manuscript.

Specific comments

1. *Abstract.*
   Can good agreement line 8 be quantified further, as good is rather a subjective word. Could non-recycling OH sources also be missing (or perhaps some direct sources already included that are underestimated?) An important component of the paper is the discussion of the interferences for both OH and HO2, and some mention of this needs to be in the abstract.

The "good agreement" will be quantified in the abstract of the revised manuscript (Slope: 1.31 +/- 0.15; value changed slightly from ACPD version due to revised calculation of the precision of the OH measurements by CIMS). The authors agree that despite the suggested recycling mechanisms an unaccounted HO_x source could improve the model-measurement agreement. We changed the abstract accordingly (see Referee 1, General comment 3).
The OH interference is discussed in Novelli et al. (2014) and therefore not a significant part of this publication. The discussion regarding HO_2 is necessary to support the measurements but not part of the scientific result.

2. *Introduction.*
   Page 28556, line 13. The OH reactivity data in Borneo mentioned here in the context of the Pugh paper are available and are compared in detail with calculations in Edwards et al., ACP (2013)., which should be referenced.

The reference is included in the revised manuscript (see our answer to Referee 2, Specific comment 2).

3. *Section 2.1*
   Page 28568. Lines 22-23. It is stated that there is a higher uncertainty in the PTR-MS measurements owing to a cold trap connected to it. Were these data then used later for the analysis – not clear.

To clarify, we state in the revised manuscript: *"Thus, PTR-MS data was only used for estimating MBO (see Section 3.2.1)."*

4. *Section 2.2.2*
   Line 23 – spelling is naphthalene

Fixed.

5. *It is good to see a significant section on interferences. Although further details will appear in Novelli et al. 2013, it is important to give some indication here in this paper where ambient data are presented of how big the interference is for OH compared with the ambient OH signal – and how this varies with time of day and other parameters. What flow of NO was used in the field measurements for HO_2 detection – was it varied to investigate the effect on the HO_2 interference during the field measurements themselves?*

Regarding the OH interference, please refer to our answer to General Comment 1 by Referee 1. Regarding HO_2, a flow of approximately 5 sccm of pure NO was used for conversion in field measurements during HUMPPA-COPEC 2010. As stated in the manuscript, this corresponds to "… NO mixing ratios of about 400 ppm_V occurred inside the detection system of HORUS by injection of pure NO into sample air, yielding a conversion efficiency from HO_2 to OH of more than 95% at the operating conditions of the instrument." (P28573, L4)

The flow was varied manually from time to time during calibrations in order to determine the conversion efficiency, but unfortunately not on a regular basis during ambient measurements in this field campaign. Being aware of the possible interference due to RO_2 radicals reported by Fuchs et al. (2011), we estimated a possible contribution by H_2O_2 budgeting, literature values (Lu et al., 2012; Fuchs et al., 2011; Mao et al., 2012; Whalley et al., 2013; Griffith et al., 2013) and titration experiments during subsequent field campaigns in forest environments using lower NO mixing ratios for conversion of HO_2 to OH.

We state in the paper:
"NO titration experiments during calibration and ambient air measurements in two forest environments in Germany have been conducted after HUMPPA-COPEC 2010, quantifying the maximum observed interference by RO_2 in the HORUS instrument in these environments to be less than 20% (Tatum Ernest et al., 2012)"

6. *Page 28574, line 26. Is the less than 20% stated the overall interference, or the maximum interference seen for an individual RO_2 species? I expect the former as the interference for a given RO_2 if an alkene or aromatic could be considerably higher.*

The "less than 20%" is the overall observed interference caused by RO_2 species on the HO_2 signal during ambient air measurements in two German boreal forests.
We will rephrase this in the revised manuscript for better clarification.

7. *Line 8 – what is the sensitivity of the H_2O_2 analysis if the deposition velocity is changed from 4 cm s^{-1}?*

Please refer to our answer to Specific comment 3, Referee 2.

8. *Section 2.3. The budget of OH is examined through comparing the loss rate of OH from [OH] x OH reactivity with the rate of production from adding up the sources, by applying the steady-state. Another way to show if the budget is closed is to use the OH reactivity and the measured OH sources to calculate the OH concentration, and to compare this with the measured OH concentration, both as an average 24 hour behaviour and as a time series of this comparison.*

With respect to the budget vs. comparing steady-state concentrations of OH, please refer to our answer to Specific Comment 5, Referee 2.
Unfortunately, the data coverage of the species for calculation of source and sink terms is not sufficient to provide a conclusive time series.

9. *Section 2.4. Page 28576, line 13, "when OH and HO_2 reached steady-state, typically after about 48 hours?" Some further words are needed, does this mean that the box model ouput did not change after a spin-up period of 48 hours?*

Yes, for better clarification we changed this in the revised manuscript accordingly:
"The simulations were conducted in steady-state mode, i.e., until the relative change in number concentration of OH and HO_2 was less than 10^{-6} within a second, when steady-state for both species was reached. This corresponds to a spin-up period of typically around 48 hours. "

Page 28577 – line 2, which version of the MCM was used?
As stated in the associated footnote, MCM version 3.2 was used. On request of referee 2 "MCM" including the version is defined in text in the revised manuscript.

10. *Line 9, photolysis frequencies of NO_2 and O_3 to form $O(^1D)$ would be better*

Changed accordingly.

11. *Page 28578, line 16, insert the word "the" before "ground"*

Changed accordingly.

12. *Page 28580, spelling of "occasionally"*

Changed accordingly.

13. *Page 28583. The procedure for estimating RO_2 is probably simplistic and will be subject to uncertainty. More complex RO_2 have additional reaction channels.*

The authors agree that the attempt to estimate RO_2 from the HO_2 steady-state budget is probably incomplete in terms of detailed inclusion of RO_2 reaction channels. Nonetheless, the significance of these additional reactions strongly depends on the speciation of RO_2, which is unknown.

Please refer also to our answer to General Comment 2 by Referee 1.

14. *Page 28584, line 24, HCHO is an oxygenated VOC?*

The idea of this calculation is to quantify the source strength for RO_2 production by reaction of OH with VOCs and OVOCs, while the reaction of HCHO with OH yields HO_2. We will rephrase in the revised manuscript for better clarification.

15. *There is quite a long section of text (page 28585 and 28586) which repeats quite a bit of what is in Table 3. Are both needed in this level of detail?*

The associated section will be generally revised.

16. *Page 28589. Line 20. This hypothesis could also be investigated further by plotting the model to measured HO_2 ratio versus the degree of missing reactivity.*

Please refer to our answer to Referee 2, General comment 4.

17. *Page 28591. Line 15. HCHO calculated by the model when free-running are up to 4 times higher than the observed levels. An alternative explanation could be that the HCHO measurements are too low? It would need a substantial additional HCHO source to bring the two into agreement?*

There is no evidence that the measurements of HCHO are too low by a factor of up to four. Box model studies indicated that in addition to chemical mechanisms, atmospheric physical processes (e.g., transport, dilution, wet deposition) have to be well considered for a box model predicting HCHO (e.g. Li et al., 2013). As we are running our model only for steady-state HO_x conditions, neglecting transport processes an overestimation of HCHO by a free running model could be possible.

18. *Table 1. It is titled above canopy observations but the CIMS for OH was on the ground?*

Title changed to *"Instrumentation applied during HUMPPA-COPEC 2010"*.

19. Table 3 – this is very complex. Could one of these be made into a figure – the detail below the cycle diagram is repeated in the text and so is this needed here as well? Perhaps some of the panels could to outside the main paper?

Please refer to our answer on General Comment 1 & 2 by Referee 2.

20. Figure 5 and 7 – the 4 min LIF data are very feint

Changed accordingly.

21. Figures 10 – 12. Is it possible to see an example of a time series of measured and modelled OH together, and also for HO_2?

The overlap of required data in order to calculate the steady-state concentrations of OH and HO_2 is very small. Thus, the dataset is highly fragmented and only small portions of individual days are available.

22. Figure 11, 12. The captions are more like an explanation of the behaviour (better in the text) rather than saying what is shown on the plots.

Captions were changed.

References

Allen, N.D.C., Abad, G.G., Bernath, P.F., Boone, C.D.: Satellite observations of the global distribution of hydrogen peroxide (H2O2) from ACE, Journal of Quantitative Spectroscopy and Radiative Transfer, Volume 115, 66-77, ISSN 0022-4073, http://dx.doi.org/10.1016/j.jqsrt.2012.09.008, 2013.

Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, Phys. Chem. Chem. Phys., 13, 13 607–13 613, doi:10.1039/C1CP21330J, http://dx.doi.org/10.1039/C1CP21330J, 2011.

da Silva, G., Graham, C., and Wang, Z. F.: Unimolecular beta-Hydroxyperoxy Radical Decomposition with OH Recycling in the Photochemical Oxidation of Isoprene, Environmental Science & Technology, 44, 250-256, 2010.

Edwards, P. M., Evans, M. J., Furneaux, K. L., Hopkins, J., Ingham, T., Jones, C., Lee, J. D., Lewis, A. C., Moller, S. J., Stone, D., Whalley, L. K., and Heard, D. E.: OH reactivity in a South East Asian tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project, Atmospheric Chemistry and Physics, 13, 9497-9514, 10.5194/acp-13-9497-2013, 2013.

Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., andWahner, A.: Detection of HO2 by laserinduced fluorescence: calibration and interferences from RO2 radicals, Atmos. Meas. Tech., 4, 1209–1225, doi: 10.5194/amt-4-1209-2011, 2011.

Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H.-P., Haseler, R., Holland, F., Kaminski, M., Li, X., Lu, K., Nehr, S., Tillmann, R., Wegener, R., and Wahner, A.: Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, Nature Geosci, advance online publication, –, http://dx.doi.org/10.1038/ngeo1964, 2013.

Griffith, S. M., Hansen, R. F., Dusanter, S., Stevens, P. S., Alaghmand, M., Bertman, S. B., Carroll, M. A., Erickson, M., Galloway, M., Grossberg, N., Hottle, J., Hou, J., Jobson, B. T., Kammrath, A., Keutsch, F. N., Lefer, B. L., Mielke, L. H., O'Brien, A., Shepson, P. B., Thurlow, M., Wallace, W., Zhang, N., and Zhou, X. L.: OH and HO2 radical chemistry during PROPHET 2008 and CABINEX 2009 – Part 1: Measurements and model comparison, Atmos. Chem. Phys., 13, 5403–5423, doi: 10.5194/acp-13-5403-2013, 2013.

Hard, T. M., O'Brien, R. J., Chan, C. Y., and Mehrabzadeh, A. A.: Tropospheric free radical determination by fluorescence assay with gas expansion, Environ. Sci. Technol., 18, 768–777, 1984.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31(1), 81–104, 1997.

Lowe, D. C. and Schmidt, U.: Formaldehyde (HCHO) measurements in the nonurban atmosphere, J. Geophys. Res.-Oceans, 88, 10844–10858, doi: 10.1029/JC088iC15p10844, 1983.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Häseler, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO2 concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, Atmos. Chem. Phys., 12, 1541–1569, doi: 10.5194/acp-12-1541-2012, 2012.

Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J.-H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Saunders, S. M., Jenkin, M. E., Derwent, R. G. and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degra- dation of nonaromatic volatile organic compounds, Atmos. Chem. Phys., 3,161–180, 2003.

Thornton, J. A., and Brune, W. H.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, Atmos. Chem. Phys., 12, 8009–8020, doi: 10.5194/acp-12-8009-2012, 2012.

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., Fischer, H., Klüpfel, T., Gurk, C., Königstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Williams, J., and Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements, Atmospheric Chemistry and Physics, 10, 3759–3773, doi:10.5194/acp-10-3759-2010, http://www.atmos-chem-phys.net/10/3759/2010/, 2010.

Novelli, A., Hens, K., Tatum Ernest, C., Kubistin, D., Regelin, E., Elste, T., Plass-Dülmer, C., Martinez, M., Lelieveld, J., and Harder, H.: Characterisation of an inlet pre-injector laser induced fluorescence instrument for the measurement of ambient hydroxyl radicals, Atmos. Meas. Tech. Discuss., 7, 819-858, doi:10.5194/amtd-7-819-2014, 2014.

Song, W., Staudt, M., Bourgeois, I., and Williams, J.: Laboratory and field measurements of enantiomeric monoterpene emissions as a function of chemotype, light and temperature, Biogeosciences, 11, 1435-1447, doi:10.5194/bg-11-1435-2014, 2014.

Whalley, L. K., Blitz, M. A., Desservettaz, M., Seakins, P. W., and Heard, D. E.: Reporting the sensitivity of Laser Induced Fluorescence instruments used for HO2 detection to an interference from RO2 radicals and introducing a novel approach that enables HO2 and certain RO2 types to be selectively measured, Atmos. Meas. Tech. Discuss., 6, 6249–6292, doi: 10.5194/amtd-6-6249-2013, 2013.

Wolfe, G. M., Cantrell, C., Kim, S., Mauldin III, R. L., Karl, T., Harley, P., Turnipseed, A., Zheng, W., Flocke, F., Apel, E. C., Hornbrook, R. S., Hall, S. R., Ullmann, K., Henrey, S. B., DiGangi, J. P., Boyle, E. S., Kaser, L., Schnitzhofer, R., Hansel, A., Graus, M., Nakashima, Y., Kajii, Y., Guenther, A., and Keutsch, F. N.: Missing Peroxy Radical Sources within a Rural Forest Canopy, Atmospheric Chemistry and Physics Discussions, 13, 31713-31759, 2013.