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 RO₂ species (C₈₉O₂) was treated incompletely in the monoterpene mechanism (MTM). Since the production of this RO₂ species is small (mean: 1.5x10⁵ molec. cm⁻³ s⁻¹) compared to the production rate of HOₓ (typically of the order of 10⁷ 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 RO₂ from Equations (5) and (6). It seems to me that Equation (5) is incomplete, if isomerization of RO₂ plays an important role on the fate of RO₂ (and it should). And more importantly, isomerization of RO₂ can produce HO₂. With that taken into account, the derived RO₂ will be significantly less according to Equation (6). Therefore the whole discussion on Table 3 in Section 3.1, which seemingly involves computed RO₂, is not very convincing to me.

Equation (5) and (6) do not include isomerization reactions of RO₂. For the calculation of the HO₂ budget only the isomerization reactions (1-6-H-shift) forming HO₂ are relevant and therefore, the calculated RO₂ might be overestimating the actual RO₂ concentration during HUMPPA-COPEC 2010. Nonetheless, the significance of these additional reactions strongly depends on the speciation of RO₂, which is unknown. We will clarify in the revised manuscript that the estimate of RO₂ from the HO₂ budget following Eqn. (6) is an upper limit due to neglecting the isomerization processes.

Independent calculation of the sum of estimated RO₂ and observed HO₂ based on the photo-stationary state of NO and NO₂ leads to a similar result for the RO₂ concentration, strengthening our estimate for the RO₂ 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 HOₓ in the model could be due to some missing primary HOₓ sources (instead of recycling processes). As shown in Fig 12, when the model is constrained with observed total OH reactivity, both OH and HO₂ 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 HOₓ 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 HOₓ source could improve the model-measurement agreement. Therefore, we changed the abstract accordingly:
“Detailed analysis of the HO\textsubscript{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\textsubscript{2} with NO or O\textsubscript{3}, or unaccounted primary HO\textsubscript{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.

<table>
<thead>
<tr>
<th></th>
<th>MIM2</th>
<th>MIM3</th>
<th>MIM3* + MTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO₂ + NO → RONO₂</td>
<td>MCM v3.1 updated yields (Paulot et al., 2009)</td>
<td>updated yields (Paulot et al., 2009)</td>
<td></td>
</tr>
<tr>
<td>RO₂ + HO₂ → OH + prod.</td>
<td>MCM v3.1 updated yields and rate constants (Dillon and Crowley, 2008; Groß, 2013)</td>
<td>MCM v3.1</td>
<td></td>
</tr>
<tr>
<td>Ozonolysis reaction yields</td>
<td>MCM v3.1 updated yields (Taraborrelli et al., 2012)</td>
<td>updated yields (Taraborrelli et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>1,5-/1,6-H-shifts</td>
<td>none</td>
<td>included (Peeters et al., 2009)</td>
<td>none</td>
</tr>
<tr>
<td>HPALD photo-oxidation</td>
<td>none</td>
<td>included (Taraborrelli et al., 2012)</td>
<td>none</td>
</tr>
<tr>
<td>monoterpene chemistry</td>
<td>none</td>
<td>none</td>
<td>included</td>
</tr>
</tbody>
</table>

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. 1x10$^6$ 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., $[\text{HO}_2]_{\text{mod}}/[\text{HO}_2]_{\text{meas}}$ versus missing reactivity, or something similar? A clear relationship between these two would help solidify this conclusion.

Below the scatter plot $[\text{HO}_2]_{\text{mod}}/[\text{HO}_2]_{\text{obs}}$ 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 $[\text{HO}_2]_{\text{mod}}/[\text{HO}_2]_{\text{obs}}$ 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).](image-url)
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 $\text{H}_2\text{O}_2$, the authors should state so. Alternatively, Figure 3 could include additional lines for $\text{H}_2\text{O}_2$ calculated using 1 and 5 cm/s.

The loss of $\text{H}_2\text{O}_2$ is dominated (>90%) by deposition and photolysis (Lowe et al., 1983; Allen et al., 2013 and references therein). Thus, the decay of $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ production has a quadratic dependency on the HO$_2$ concentration, thus the concentration of $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ production, the HO$_2$ would not suffice to explain the observed $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ 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$_2$O$_2$ (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 RO₂. What values were chosen for this calculation and why?

No measurements of RO₂ during HUMPPA-COPEC 2010 are available. The lumped rate constant \( k_{RO₂:NO} = 2.7 \times 10^{-12} \times e^{(360/T)} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1} \) 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 RO₂ 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 RO₂ branch with approx. 0.90-0.95. A branching ratio \( b = 0.9 \) was used, probably leading to an underestimation of RO₂ for a monoterpane 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 HO₂ is a major source, as evidence that there is not a significant interference in observed HO₂.

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 HO₂.”

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. HO₂ originating from the 1,6-H-shift is already taken into account by using the observed HO₂. 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 HO₂ were increased to match observations.

We agree with the reviewer. The disagreement for simulated vs. observed HO₂ 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 HO₂ yield from α-pinene? Also, how does modeled RO₂ compare with that calculated from steady state (Eq. 10)?

The direct production of HO₂ 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 RO₂ to RO₂ calculated from steady state is on average 1.1 (min.: 0.01; max.: 11.5).
11. P. 28594, L. 7: \( \text{HNO}_4 \) 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 \( \text{HO}_2 \).

As the net effect is zero, we removed the fraction due to \( \text{HNO}_4 \) 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, \( \text{HO}_x \) and the total OH reactivity, is to increase our understanding of atmospheric oxidation processes in a coniferous forest. The \( \text{HO}_x \) 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 \( \text{HO}_2 \) 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 monoterpane, which is not the case. Perhaps it is meant that the MBO emission rate (per molecule?) is 1-3% of the monoterpane 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\(^{1}\)D) was consistently lower below the forest canopy. The data shown in Figure S1 suggests that J(O\(^{1}\)D) was similar when the LIF instrument was measuring on the ground and on the tower. Are the measured J(O\(^{1}\)D) 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\(^{1}\)D) values in these figures similar? If the J(O\(^{1}\)D) values shown in Figure 7 were made on the tower above the canopy, were there J(O\(^{1}\)D) 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\(^{1}\)D) 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\(^{1}\)D) 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$_2$O$_2$ with that calculated based on their measured HO$_2$ concentrations. Although it may be difficult to compare the measured H$_2$O$_2$ 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$_2$O$_2$. 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$_2$O$_2$ 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 HOx 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 HOx 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 HO2 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 HO2 detection – was it varied to investigate the effect on the HO2 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$_2$O$_2$ 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$_2$O$_2$ 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 output 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\(^{1}\text{D}\) 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\(_2\) 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 HO2?

The overlap of required data in order to calculate the steady-state concentrations of OH and HO2 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


