Missing Peroxy Radical Sources within a Rural Forest Canopy

Wolfe et al., 2013 (ACPD)

Responses to Referees

We thank the referees for their encouraging words and thoughtful comments. Please find below a list of responses and manuscript modifications. The reviewer's comments are given in **bold**.

REFEREE 1

The manuscript "Missing peroxy radical sources within a rural forest canopy" by Wolfe et al 2014 presents a solid and unique set of measurements within a Ponderosa Pine forest. The main focus of this paper is the observation and analysis of peroxy radicals. Therefore various gas chemical measurements were utilized to run a box model and compare the modeled diel cycle to the observations. Two features of the measured diel cycle in the peroxy radical mixing ratios were standing out and difficult to represent in the model. The authors propose two different types of missing sources: One source would photolytically produce HO2, the other source generate RO2 independently of sun-driven photochemistry. The presented findings are based on observations of peroxy radicals that only recently started to become handy for field measurements. The method is known to be impacted by interferences, which were discussed in the presented study. The data has been used to assess the oxidative chemistry within a forest canopy. By comparison to the model significant mismatch has been determined and the authors extensively discuss characteristics and possible answers. The paper generally addresses interesting scientific questions related to atmospheric chemistry and the interaction between biosphere and atmosphere and is therefore suitable for publication in ACP.

Please find below a list of more specific comments:

1) The title of the manuscript is "Missing peroxy radical sources within a rural forest canopy". After reading the manuscript I found it should be written more precisely. The peroxy radical measurements were sampling air below the forest canopy (at 1.6 m height). As the authors state, the vertical distribution of compounds below, within and above a forest canopy may vary significantly. This is what was observed via the PTR-MS measurements for the VOCs and corrected for the usage in the model. Most probably the vertical gradient of peroxy radicals also differs for the various heights. Further information could be given in the title, which is the time of the year as the results are presented for summertime observations.

> We have changed the title to "Missing peroxy radical sources within a summertime Ponderosa pine forest."

2) Abstract, page 31715, line 13: I understand that the model was used to examine sources and sinks of the peroxy radicals. However, how was the distribution analyzed?

Figure 4 shows the modeled peroxy radical distribution, which is based on the measurement-constrained VOC distribution. We discuss the features of this distribution in Section 4 (page 31727). Furthermore, we consider how missing peroxy radicals might alter this distribution (i.e. extra HO2 and acyl vs. non-acyl RO2) in Section 5.

3) Introduction, page 31716, lines 1-12: The introduction is nicely written and describes the overall role of peroxy radicals for tropospheric chemistry. Generally in this first paragraph references to the literature are missing as well as links to the presented equations. For example, (R1) could be inserted after ". . .oxidation of volatile organic compounds (VOC) (R1)" in line 4 and (R2, R3) could be referred to after ". . .photolysis of carbonyl-containing VOC (e.g. formaldehyde) (R2), alkene ozonolysis (R3) and . . . ".

We have added references to the appropriate reactions. We elect to not reference literature here as this is a review of established reactions that can be found in any atmospheric chemistry textbook.

4) Section 2.2, pages 31719-31720, lines 25-1: Technical questions: If the measurements were conducted at 1.6 m and the canopy heights was reaching up to 18.5 m, the observations seem to be rather influenced by the soil and understory than by the canopy. Could the authors comment on that?

There is negligible understory at MFO. It is possible that soil emissions of NO, or leaf litter emissions of VOC, could influence chemistry at the measurement height, and we have accounted for these effects as much as possible by using observations at the heights closest to peroxy radical observations. Multi-height measurements of VOC and NO_x suggest average vertical concentration gradients of less than 4% per meter in this region (data not shown). These caveats are discussed in Section 2.3, and we have added a reference to the above numbers.

Also, it would be good to provide more information about the inlet system: Was the inlet isolated for radiation and heated? What was the residence time of a sample within the inlet?

We have added the following details to Section 2.2:

"The upper part of the PeRCIMS inlet is isolated from sunlight by shielding it with black felt cloth inside the inlet pylon, thereby minimizing the impact of potential artifacts from solar radiation to negligible levels. The inlet is maintained at a minimum temperature of 10 °C; for the conditions of BEACHON-ROCS, the heater rarely was active. The typical sample residence time is 0.18 s in the chemical reaction region and 0.4 s in the ion reaction region. A picture of the trailer and inlet is included in the supplementary material (Fig. S9)."

5) Section 2.2, page 31720, line 17: The detection limit of the PeRCIMS is given as 2 pptV. How was this values derived? E.g. is it 2or 3of a background signal?

As described in Section 2.4 of Hornbrook et al. (2011), Background H_2SO_4 signals are determined by redirecting the SO_2 flow to the rear of the neutral reaction region, forcing OH radicals generated via (R4) to react with the excess NO and form HONO. The detection limit is taken as the concentration at which the signal-to-noise ratio is equal to 2. We have added text to this effect in the appropriate section.

6)Section 3, page 31724, lines 11-20 (and Figure 1): The diel cycles of peroxy radicals show two very sharp rises, one from 11:30 to 14:30 and a second one at 15:30. The authors describe this as a typical feature that appeared every day throughout the measurement campaign. Later on the model is used to explore the nature of this typical sharp rises and the authors conclude that there must be additional sources, but "its exact nature remains a mystery" (p. 31737, l. 19).

Please allow me to ask, if you can rule out any local effects, that could potentially cause a diel variation in the measured signal, but does not represent the typical forest environment. Effects like this could be e.g. radiation that shines on the inlet and heats it. Due to shading and distribution of the trees or measurement containers this would cause a sharp change in the signal every day at the same time of the day. From the Supplementary Information Table S1, you can see, that the radiation (J(NO2)) was measured in 2 m height, whereas the PeRCIMS had its inlet at 1.6 m. Where these measurements co-located, e.g at the same container roof in very close distance? On page 31721, line 25 it is stated that the "J(NO2) sensor was co-located with the relatively shaded OH inlet". Does this measurement properly reflect the conditions for the PeRCIMS inlet? If the authors can rule out any kind of this local effects in inlet/set-up/aircondition/ect., then the paper would appear much more robust. Especially since the explanation of this two sharp rises of peroxy radical measurements in the afternoon is main focus of the model analysis.

As noted in our response to Question (4) above, the PeRCIMS inlet includes special provisions to ensure that artifacts from solar radiation do not influence the observations. The reviewer is correct that the OH inlet (and thus also the J(NO2) sensor) was horizontally separated from the PerCIMS inlet by ~4m. Thus, our in-canopy radiation measurements may not precisely reflect the conditions at the HO2 inlet. We have added this important detail to Section 2.3. Furthermore, we have added a picture of the setup to the supplement.

Though we think the potential for artifacts/interferences is minor, we cannot rule it out completely. Thus, we leave it to the reader's discretion.

7) Section 3, page 31724, lines 22-23: Please be careful with the usage and comparison of the entire measurements campaign data as diel averages. Although the authors state, that most data did not vary too much from day to day, it is not "fair" to compare diel cycles as averages for the entire campaign, if there are unsynchronized data gaps. Meteorology, radiation, state of the vegetation, ect. often change between the days which can be reflected by the measurements of VOCs, OH, peroxy radicals and many others. For the diel average, why don't you use only data, that are taken at times for which all relevant data are available?

We do not limit the dataset in the way that the referee suggests because, to be blunt, we would be left with very little data. For example, if we limit the data to only times when OH measurements are also available, we would exclude more than 50% of available peroxy radical observations. While averaging over the entire month of observations is not ideal, it is, in our opinion, the most "fair" that we can be with the given dataset. To clarify this point, we have added the following statement to Section 3: "Unfortunately, intermittent data gaps do not permit more refined data selection."

8) Section 3, page 31724, line 29: The categorization between "high" and "low" NOx regimes is currently highly debated and Wennberg 2013 recommend to base the differentiation on other parameters. In the presented study it does not look like a differentiation is needed (since the campaign took place in a mixed regime anyways) and you could simply drop the statement and explain as proposed that "both NO and other peroxy radicals are expected to contribute significantly to total peroxy radical loss" (p. 31724, l. 29).

We have modified this sentence as follows: "Observed daytime NO mixing ratios of 100 – 150 pptv are typical for a rural continental site and are within a transition region where both NO and other peroxy radicals are expected to contribute significantly to total peroxy radical loss."

9) Section 5, page 31728, lines 12-16: In this paragraph uncertainties are briefly discussed. The combined uncertainties of model and measurement could lead to a difference of about a factor of 2. However, model and measurement agree as well for a great fraction of the day within these combined uncertainties. This should be mentioned at this point, too.

We have modified the first two sentences of this paragraph as follows:

"Modeled and observed peroxy radicals agree to within their respective uncertainties for much of the day (Fig. 3). Clear systematic discrepancies between average mixing ratios, however, suggest that the model is missing or misrepresenting sources and/or sinks of these species."

10)Section 5.1, page 31729, lines 21-23: How was the extra source was implemented into the model for this test?

The source is incorporated by adding a 0th-order reaction that generates HO2 at the rate given by the black line in Figure 6. We have added this explanation to the text.

11)Section 5.2, page 31733, lines 12 onwards: In this paragraph, I found the referencing to the Figures confusing and incomplete. E.g. it is written ". . .we also show the concentration-weighted average RO2* lifetime for all model species in the RO2*group." Where is this information given?

We have removed references to other figures, and some other extraneous details, to simplify this discussion. The paragraph now reads as follows:

"We can estimate the magnitude of the missing RO_2 source using an approach similar to that described for HO_2* (Eq. (1)). This method requires calculation of the missing RO_2* lifetime; however, this value depends on the assumed structure of these peroxy radicals. Figure 9(a) illustrates this point for three representative peroxy radicals. The lifetime of CH_3O_2 and MBOAO2 (the primary RO_2 from MBO oxidation) ranges from 30 to 60 seconds throughout the day, except in the morning when NO concentrations spike. In contrast, the lifetime of the acetyl peroxy radical, CH_3CO_3, is typically < 20 seconds. These differences arise mainly from NO reaction rate constants, which are 7.7, 9.0 and*

20 x 10^{-12} cm^3 $molec^{-1}$ s^{-1} at 298 K for CH_3O_2, MBOAO2 and CH_3CO_3, respectively. Figure 9(a) also shows the concentration-weighted average RO_2 lifetime for all model species in the RO_2* group. Coincidentally, this lifetime is nearly identical to that of MBOAO2 even though this radical is not included in RO_2*.*

Figure 9(b) compares the total production rate of modeled RO_2 with missing RO_2* production rates as calculated via the RO_2*-equivalent of Eq. (1). The magnitude of the missing production rate is similar to that of the "known" production rate except when RO_2* is assumed to have a lifetime comparable to CH_3CO_3. For the other three cases, missing RO_2* production follows a diurnal pattern similar to its concentration profile (Fig. 5c) except in the morning, where the steady-state assumption may be invalid due to rapidly-changing NO concentrations. Recall that the absolute magnitude of this source is dependent on our estimate of missing RO_2* and thus is highly uncertain."*

12)Section 6, page 31737, line 16: The dependence of HO2* observations and radiation is mentioned here. I agree, that in Figure 8 you can see an influence on the measured data by radiation. However, the radiation pictured here was measured in 2m and in 25m. While the 2m radiation data is not showing much variability, the HO2* data seems to drop when the radiation decreases in 25m. How can this be explained? Additionally, I found in the Supplementary Information a correlation plot (Fig. S7) which does not show strong correlation between J(NO2) and HO2*. Which J(NO2) data has been used for this graph? Was this figure mentioned in the manuscript? How can you conclude from this, that there is a "clear dependence on radiation" (p.31737, l. 17)?

As the referee noted in question (6) above, and as we mention several times in the manuscript, the 2m radiation data is not representative of the "average" radiation in the canopy. This forest canopy is fairly open, thus it is possible that near-surface photochemistry is strongly influenced by direct sunlight. Our results in Figure 8 support this hypothesis. We have added the following text to Section 5.1:

"Indeed, the results in Fig. 8 suggest that direct sunlight penetrates much of the overstory throughout mid-day. This is consistent with our expectations for this relatively open canopy (LAI = 1.14, tree coverage = 38%)."

We do reference Figure S7 in the main text, in the same paragraph where we original discuss Figure 8 (p.31730, l.22). The above-canopy radiation data was used for this plot; we have added this detail to the Fig. S7 caption. Though there is much variability in the data, we contend that this plot does indeed show a clear correlation between radiation and HO_2*. The main purpose of this plot is to show that the correlation is stronger for HO_2* than for RO_2* (as indicated by respective correlation coefficients of 0.26 and 0.03, which are given in the Fig. S7 caption). We believe this point is more clearly demonstrated by the time series in Fig. 8, which is why we opted to include the latter in the main text.

Technical corrections:

1)Section 5.1, page 31729, line 12: The concentration [HO2] in the equation is explained as missing HO2* concentration. Why do you not write directly [HO2*] in the equation?

We have modified the equation.

2)Supplementary Material, Table S1, footnote a: PTRMS = proton transfer reaction mass spectrometer.

Fixed.

3)Supplementary Material, Figure S1, caption: HO2* (green line) is actually a red line.

Fixed.

4)Figure 8: J(NO2) was measured in 2 m, according to Table S1.

The correct height is 1.6m. We have modified the table.

REFEREE 2

The authors present high measured concentrations of total peroxy radicals from a Ponderosa pine forest during summer time. A box model was used to investigate sources and sinks of the peroxy radicals withing the canopy. Current chemical mechanisms are incapable of explaining the high concentration of peroxy radicals and the authors suggest that the missing sources could be underpredicted HO2 together with a radiation independent source. This topic is very interesting and timely, since peroxy radicals and HO2 are part of the atmospheric oxidation chain. The sources and sinks of OH have for some time been discussed, but it is not the only important player in that game. This paper is very good and after taking referee 1's minor comments into consideration, this paper is ready to be published.

Thank you.

REFEREE 3

General Comments:

The paper by Wolf et al. examines peroxy radical concentrations and chemistry using a detailed chemical box model constrained by a large suite of relevant chemical measurements during the 2010 BEACHON-ROCS field study. The measurements were performed in a rural forest where reactive compounds/emissions are dominated by biogenic terpenes and MBO. The observed total peroxy radical concentrations reached as high as 180 pptv with 100 pptv on an almost daily basis during the period of their observations (~ 2 weeks). The box model calculations under-predicted total peroxy radicals by as much as a factor of 3 which the authors propose are likely due to missing sources. The paper is well written and very good effort has been put in the analysis and in trying to explain possible reasons for discrepancies between the measured and modeled peroxy radicals concentrations. I enjoyed reading it. The intriguing results are certainly of relevance to ACP readers and I recommend

that the paper be published after the authors have addressed the few comments and suggestions and some minor technical points listed below, which will improve the quality of the discussion and confidence in the results.

Major Comments and Suggestions:

1) I share Reviewer 1's concerns regarding the influence of strong vertical gradients in the concentration profiles of chemical species and the resultant analysis and interpretation. To be fair, the authors have acknowledged the strong impact exerted by the chemical gradients and tried to correct for it in the measurements of several key chemical species. However, the effect may still be significant and therefore affect the conclusions of the study. In Table S1, the inlet heights for the different measurements are mentioned. I see some complication here with the inlet height for the OH reactivity measurements, which were made at 4 m and therefore differ from i) the height at which other OH reactants were measured and ii) the height at which the radical measurements were made (~1.6 m). The difference is greater than 2.4 m and sometimes as much as 15 m! Notwithstanding this difference, the authors state rather strongly in Page 31731; Lines 15-19:

"While under-represented OH reactivity could have a profound impact on peroxy radical chemistry elsewhere, we reiterate that this is not a viable explanation for missing peroxy radicals in the present study."

I think the authors cannot entirely discount this effect in particular as several studies have shown occurrence of high missing OH reactivity in forested environments. A useful thing to check how important this effect is would be through additional model sensitivity runs constrained by different ratios of the total measured OH reactivity at 4 m. For example, taking 0.5 times of the measured OH reactivities at 4 m and another run with 1.5 times of the directly measured OH reactivity at 4m from 08-16 hrs local time would be very revealing to examine how the current discrepancy by a factor of 3 between modelled and measured RO2 changes in each case. Perhaps, the OH reactivity change could be done in the form of a new molecule that is as reactive as MBO with OH and with similar chemistry? The non-linearity in chemistry may bring down or increase the discrepancy depending on the run.

We contend that in-canopy gradients are too small to explain the discrepancy between observed and modeled peroxy radicals. As discussed in our response to Referee #1's comment (4), "Multi-height measurements of VOC and NO_x suggest average vertical concentration gradients of less than 4% per meter in this region (data not shown)." More specifically, MBO and monoterpenes as measured by the PTRMS exhibit a positive gradient (increasing with height) of 11% and 5%, respectively, between 1.6m and 4m. Thus, we expect OH reactivity to change by no more than ~10% between 4m and 1.6m; indeed, assuming similarity of total OH reactivity with MBO and MT, we expect the total reactivity to decrease. We have added the following statement to Section 4:

"We must also be wary of in-canopy heterogeneity. OH reactivity was measured at 4m above the ground but likely exhibits a vertical gradient within the canopy (Mogensen et al., 2011). From PTRMS observations of MBO and monoterpenes at 1m and 4m (data not shown), we expect total OH

reactivity to change by less than 10% between 4m and the peroxy radical measurement height of 1.6 m."

Furthermore, we have already performed an experiment similar to that suggested by the reviewer by implementing VRVOC reactivity in Section 5.2. In this case, model OH reactivity increases by as much as 30%, and we had added a sentence stating this point in Section 5.2.

2) Ozone production implications: Page 31724;Lines 25-30 and again in Conclusion Page 31738: The authors highlight the importance of representing radical sources and sinks accurately for getting the ozone production rates and regimes correct. Since the authors have directly measured OH, HO2 and RO2 and NO and OH reactivity at the site, even with the caveats associated (HO2 is HO2 * and inlet heights vary…), it would be very interesting to compare the "local" and potential "global" ozone production rates (see e.g. Shirley et al., ACP, 2010 and Sinha et al., ACP, 2012). This would perhaps make the reader appreciate their recommendation of using the ozone production sensor developed by Carlo and Brune , AMT, 2010 with quantitative arguments! Shirley et al. reported ozone production measurements from an urban environment, whereas the Sinha et al study was from a mixed coastal site influenced by high OH reactivity quite frequently .

We agree that calculations of ozone production (PO3) are important, so much so that we feel this topic is worthy of a separate publication. The focus of our study is on the organic chemistry underlying sources and sinks of peroxy radicals, and a discussion of PO3 would not, in our opinion, fit well into the story. Moreover, a standalone comparison of instantaneous PO3 from model and measurements may not be very informative, as we expect it to scale linearly with peroxy radical concentrations. A more useful exercise would be to compare PO3 from in situ measurements with that from a regional-scale model such as EPA's CMAQ model, and we have added this recommendation in the conclusions.

3) The radical measurements reported herein are high. As the authors discuss non photolytic sources they should also discuss the results of Andrés-Hernández et al., ACP, 2013, who found as much as 80 ppt of measured RO2 at nighttime.

We have added a reference to this paper in Section 3, though we caution that the chemical environments of BEACHON and DOMINO are very different. Specifically, the latter study was strongly influenced by anthropogenic alkenes, NOx and other emissions. Furthermore, as noted in Section 3, peroxy radical measurements are high but not inconsistent with previous observations (Cantrell et al., 1992;Qi et al., 2005).

4) At Page 31726; Lines 1-15 they state: "To our knowledge, there are no published data comparing within and above-canopy peroxy radical levels; however, detailed 1-D canopy modelling results predict relatively minor gradients in HO2 and total RO2 at other forests (Bryan et al., 2012; Makar et al., 1999; Wolfe and Thornton, 2011; Wolfe et al., 2011a)." This may be true for radical levels but there is at least another modelling study by Mogensen et al., 2010 that examined vertical gradients in OH reactivity from a pine forest in Finland (monoterpene rich air) using a model. The authors may find the study relevant.

We thank the referee for the reference. We do not feel that it is appropriate to reference this paper in regards to the above-mentioned discussion, as Mogensen et al. do not present peroxy radical observations or model results. We have, however, cited this paper in our discussion of OH reactivity gradients (following Referee 3's comment (1) above) and in reference to missing VOC discussed in Section 5.2.

MINOR\TECHNICAL COMMENTS:

1) Introduction: In R1: O2 is missing , from VOC+OH RO2.

Fixed.

2) Section 2.1: The site is above 2000 m asl. How important are mountain winds here? How would the diel dynamics of mixing affect chemistry and chemical concentrations? A wind rose could be added to the supplement for data periods relevant to this study.

As we state in Section 2.1, "The closest major urban areas are Colorado Springs (33 km SE) and Denver (70 km N). The site is occasionally impacted by anthropogenic air masses, but prevailing winds bring relatively clean air from the south and southwest." These wind patterns are discussed in more detail in the recent BEACHON overview paper by Ortega et al. (2014). Chemically, variations in wind direction/advection determine the level of anthropogenic influence (e.g. more NOx and AVOC). We have not screened the data for anthropogenic influence, but visual inspection of the data suggests no obvious dependence of peroxy radical mixing ratios on wind direction.

We have added a statement to this effect in Section 2.1, along with a reference to the BEACHON summary paper.

3) Lines; 1-5; Page 31720: …. the inlet protruding 0.5m from the trailer wall at a height of 1.6m and oriented to the southeast. If available, a picture of the inlets would be helpful and could be added to the supplement.

We agree and have added this (Fig. S9).

4) Section 2.3: First paragraph: It would be good to give full names of PAN and PPN at the beginning of the Section.

Fixed.

In the discussion where the authors mention non speciated monoterpenes and then the speciated monoterpenes in the form of alpha pinene, beta pinene etc.. It was not very clear which ones the authors used …..

We use all available observations. As stated in Section 2.3, "Additional observations used in this analysis include OH, NO, NO_2, O_3, CO, PAN (peroxyacetyl nitrate), PPN (peroxyrpopionyl nitrate), formaldehyde, glyoxal, a suite of VOC (MBO, isoprene, α-pinene, β-pinene, limonene, camphene, a group of non-speciated monoterpenes, acetone, methanol, benzene, toluene, methyl vinyl ketone, methacrolein, acetaldehyde, propanal, n-butanal, 1,3-butadiene), total OH reactivity, temperature, pressure, relative humidity and NO_2 photolysis frequencies." We have added the words "a group of" to try to clarify our methods. These monoterpenes are all derived from the TOGA measurements.

Furthermore, in Section 2.4, we state: "The MCM mechanism subset includes all reactions from oxidation of MBO, isoprene, α-pinene, β-pinene, limonene, benzene, toluene, butadiene, acetaldehyde, propanal, n-butanal and methane. The simple MT mechanism of Wolfe and Thornton (2011) is used for camphene and a group of unspeciated monoterpenes (the latter are assumed to have the same chemistry as β-pinene)." The last part of this sentence has been modified to again clarify how we incorporate the measurements into the model.

References:

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