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Interactive comment on "Missing peroxy radical sources within a rural forest canopy" *by* G. M. Wolfe et al.

Anonymous Referee #1

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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 im-

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pacted 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.

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?

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 … ".

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,

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the observations seem to be rather influenced by the soil and understory than by the canopy. Could the authors comment on that? 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?

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 2σ or 3σ of a background signal?

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.

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?

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).

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.

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

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?

12)Section 6, page 31737, line 16: The dependence of HO2* observations and ra-

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diation 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)?

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? 2)Supplementary Material, Table S1, footnote a: PTRMS = proton transfer reaction mass spectrometer. 3)Supplementary Material, Figure S1, caption: HO2* (green line) is actually a red line. 4)Figure 8: J(NO2) was measured in 2 m, according to Table S1.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 31713, 2013.

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