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# ***Interactive comment on “Observation and modelling of HO<sub>x</sub> radicals in a boreal forest” by K. Hens et al.***

**Anonymous Referee #4**

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## General comments

This paper which reports OH and OH reactivity measurements with steady-state and box model comparisons in a boreal forest in Finland is novel for three main reasons:

(1) On the ground a comparison is made between OH measurements made with a FAGE instrument for which a chemical modulation method is used to remove OH interferences and a CIMS instrument. There is good agreement with the interference corrected FAGE measurements and CIMS.

(2) The FAGE instrument is then moved to above the canopy, with the CIMS remaining on the ground, and two independent measurement sets are used to provide some vertical information for OH. The OH above the canopy is higher and this is ascribed to

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there being higher levels of radiation.

(3) There is also an OH reactivity instrument co-located with the LIF instrument for OH measurements enabling the OH budget to be investigated using a steady-state analysis as well as a comparison with a detailed model. The product of the OH concentration and the OH reactivity are used to calculate a loss rate and this is compared with the total production rate calculated from various source terms. In some cases the loss rate and the production rate agree, i.e. the budget is closed, but in other cases it is not, sometimes by a long-way, with additional OH needed. The authors split the behaviour into four regions according to  $J(O1D)$  levels and OH reactivity. There is also a box model used to calculate radical concentrations for comparison with measurements and also rate of production analysis.

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?

There are missing sources of OH, the magnitude of which change considerably depending on the value of  $J(O1D)$  and OH reactivity. Various mechanisms for additional OH sources are explored in the model through a variety of model extensions.

The box model calculations agree fairly well with measured OH (LIF on top of the canopy) but the model significantly underpredicts the  $HO_2$  concentration. By comparing the measured OH reactivity and that calculated it is shown there are missing OH sinks. There seems to be a link between the degree of missing OH reactivity and the degree of  $HO_2$  underprediction, suggesting that the missing OH reactivity is generating  $HO_2$  radicals which are not in the model, although a quantitative analysis of this is not presented. An important conclusion is that both OH sources and sinks are missing.

There is a considerable body of data presented in the paper, as well as some instrument characterisation (e.g.  $HO_2$  interference), and a detailed analysis and compar-

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ison with models (steady state and box), representing an impressive body of work. 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.

The paper is suitable for publication in ACP subject to consideration of the general points made above and other specific comments below.

#### Specific comments

##### 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 HO<sub>2</sub>, and some mention of this needs to be in the abstract.

##### 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.

##### 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.

##### Section 2.2.2

Line 23 – spelling is naphthalene

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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<sub>2</sub> detection – was it varied to investigate the effect on the HO<sub>2</sub> interference during the field measurements themselves?

Page 28574, line 26. Is the less than 20% stated the overall interference, or the maximum interference seen for an individual RO<sub>2</sub> species? I expect the former as the interference for a given RO<sub>2</sub> if an alkene or aromatic could be considerably higher.

Line 8 – what is the sensitivity of the H<sub>2</sub>O<sub>2</sub> analysis if the deposition velocity is changed from 4 cm s<sup>-1</sup>?

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.

Section 2.4. Page 28576, line 13, “when OH and HO<sub>2</sub> 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?

Page 28577 – line 2, which version of the MCM was used?

Line 9, photolysis frequencies of NO<sub>2</sub> and O<sub>3</sub> to form O(1D) would be better

Page 28578, line 16, insert the word “the” before “ground”

Page 28580, spelling of “occasionally”

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Page 28583. The procedure for estimating RO<sub>2</sub> is probably simplistic and will be subject to uncertainty. More complex RO<sub>2</sub>s have additional reaction channels.

Page 28584, line 24, HCHO is an oxygenated VOC?

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?

Page 28589. Line 20. This hypothesis could also be investigated further by plotting the model to measured HO<sub>2</sub> ratio versus the degree of missing reactivity.

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?

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

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 go outside the main paper?

Figure 5 and 7 – the 4 min LIF data are very faint

Figures 10 – 12. Is it possible to see an example of a time series of measured and modelled OH together, and also for HO<sub>2</sub>?

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.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 28561, 2013.

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