

Interactive comment on “Observation and modelling of HO_x radicals in a boreal forest” by K. Hens et al.

Anonymous Referee #3

Received and published: 31 December 2013

This paper presents measurements of OH and HO₂ radicals in a pine dominated forest during the HUMPPA-COPEC-2010 field campaign. OH and HO₂ measurements were done using a Laser-Induced Fluorescence–Fluorescence Assay by Gas Expansion (LIF-FAGE) instrument, while OH measurements were also measured by a Chemical Ionization Mass Spectrometry (CIMS) instrument. An intercomparison of the OH measurements by the two techniques was done with both instruments located below the canopy on the ground. The results of these measurements were in good agreement with each other, suggesting that interferences associated with the LIF technique have been accounted for in these measurements.

Subsequent OH and HO₂ measurements by the LIF instrument were made from the top of the tower above the forest canopy and were compared to the results of several photochemical box models.

The models were able to reproduce the observed OH mixing ratios reasonably well, although the base Mainz Isoprene Mechanism (MIM) overpredicted the observed OH by approximately 40%. Including terpene oxidation improves the agreement with the observed OH concentrations. However, the models significantly underpredicted the observed mixing ratios of HO₂. The measured OH reactivity was also underpredicted by the model, suggesting that a source of HO₂ radicals may be missing from the model.

The paper provides some new information regarding the chemistry of HO_x radicals in low NO_x high biogenic VOC environments, as many previous measurements have been significantly greater than predicted. The paper is suitable for publication in ACP after the authors have addressed the following 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?

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(O¹D) was consistently lower below the forest canopy. The data shown in Figure S1 suggests that J(O¹D) was similar when the LIF instrument was measuring on the ground and on the tower. Are the measured J(O¹D) 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(O¹D) values in these figures similar? If the J(O¹D) values shown in Figure 7 were made on the tower above the

canopy, were there J(O¹D) 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.

3) It appears from the manuscript that the authors have not fully characterized the level of interference from RO₂ radicals associated with their measurements of HO₂ concentrations. They compare measured concentrations of H₂O₂ with that calculated based on their measured HO₂ concentrations. Although it may be difficult to compare the measured H₂O₂ with calculations based on measured HO₂ 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 H₂O₂. 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 HO₂ values result in calculated H₂O₂ values significantly greater than measured? Such a result would suggest that the measured HO₂ concentrations may be significantly affected by interferences from RO₂ species at this site.

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 HO₂. 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 HO₂ 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 HO₂. As mentioned above, Figure S1 contains important

C10563

information and should be included in the main paper rather than in the supplement.

5) Although the characterization of the RO₂ 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 HO₂ 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 HO₂ measurements. This could be added as an additional plot with the day-to-day modeling of HO₂ in Figure S1 and moved to the main paper.

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

C10564