

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

Anonymous Referee #1

Received and published: 27 December 2013

This paper presented new HO_x and OH reactivity measurements in a boreal forest during HUMPPA-COPEC-2010 field campaign. The author first did an intercomparison on OH measurements between the LIF instrument with chemical modulation technique and the CIMS instrument. With good agreement on the ground, they moved the LIF instrument to the top of a tower (above canopy), to conduct measurements along with other instruments. Then the authors ran a box model with different chemical assumptions to examine HO_x and OH reactivity, and the simulations suggest that the missing OH reactivity is likely related to a missing source of HO₂. Further analysis were conducted on detailed HO_x budget.

This paper presents a tremendous amount of work both in terms of data collection and model simulation/analysis. To my knowledge, this is the very first paper on compar-

C10459

ing the LIF OH with chemical modulation technique to the CIMS measured OH. And it is important to see that they are in good agreement, for both daytime and nighttime measurements. Another interesting finding is that the significant difference on OH measurements between ground and above canopy, and this was attributed to the difference in radiation. The measurements are highly valuable. But the data analysis part can be improved. So I recommend this paper to be published after the following comments are addressed:

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.

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.

3. I am wondering if the misrepresentation of HO_x in the model could be due to some missing primary HO_x 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 HO_x sources can be ruled out from this analysis. Therefore it seems insufficient to assume “there are additional recycling processes”, as shown in the abstract.

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).

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?

3. Also it would be nice to show a detailed description on the difference between MIM3 and MIM3*.

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.

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