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Interactive comment on “Measurements of total hydroxyl radical reactivity during CABINEX 2009 – Part 1: Field measurements” by R. F. Hansen et al.

Anonymous Referee #1

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General Comments:

The paper by Hansen et al. reports OH reactivity measurements below canopy (6 m) and above the canopy (21 m, 31 m) from a mixed deciduous forested field site in northern Michigan, USA in July-August 2009 dominated by aspen trees using a self built instrument based on the LIF detection technique . The measurements were performed sequentially firstly at the 6 m level from 5/7/2009 till 21/7/2009 (16 days), then at the 21 m level from 22/07/2009 till 26/07/2009 (4 days) and finally at the 31 m from 26/07/2009 till 09/08/2009 (11 days as there is a 3 day break in the dataset).

The authors compare the measured OH reactivities with the calculated OH reactivities due to the measured OH sinks at each level and conclude that the missing OH reactivity

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is not consistent with the emission of unmeasured BVOCs (Lines12-16; Page 17180). Instead they reason that unmeasured oxidation products are the likely explanation for the missing OH reactivity. While the measurements and study are interesting and very relevant, I find that the manuscript has far too many weaknesses in its current form to be accepted for publication in ACP. The basis for the authors' interpretation conclusion is not convincing as it stands. I highlight the major concerns below. The measurements in itself seem reasonable and would be valuable addition to the OH reactivity datasets in literature but the analysis and methodology is not strong enough to support the authors' conclusions in the current version of the manuscript. I encourage the authors to address the major concerns and submit a suitably revised version for publication in ACP.

Major Comments:

1) The authors' interpretation rests substantially on the assumption that the OH reactivity measurements at the different heights can be directly inter-compared. I am not convinced that this assumption is valid because the measurements at different levels were made at intervals of several days with significant variability in meteorological parameters. These changes could have created different emission regimes in the forest during the different sampling periods. Indeed the highest missing OH reactivity on 27-28 July is during a high temperature event. Moreover the statistics are also not comparable for measurements at different heights as the 6 m level was sampled for 16 days while the 21 m level was only sampled for 4 days! A better approach would have been to measure in rapid succession from the different heights at more frequent time intervals (say half hourly). The authors should acknowledge the limitation of their approach and revise their conclusions accordingly or present stronger supporting evidence for their implicit assumption.

2) Figure 2: Why do the authors use diurnal medians when they wish to quantify the reactivity contribution of the measured sinks to the total OH reactivity? Average values would make more sense in this context as the median of the isoprene concentration

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may not correspond to the median of the measured OH reactivity value. I suggest using the average profiles for the evaluating the reactivity budget.

3) Figure S1: To me it appears that the points measured after reaction time > 0.1 s have larger spread and precision error. The authors should discuss the reasons for it and explain the impact of such effects on their measured OH reactivity values. Could it be that unwanted secondary chemistry inside their reactor may be playing a role as the reaction time increases?

4) Figure S2: It does not inspire much confidence to see that the accuracy of the instrument when tested with propane, isoprene, TME and butane standard mixtures is 38% lower! The precision also appears to be poor as sometimes there is very good agreement for propane at lower reactivity range but on other occasions there is rather poor agreement. This gives the impression that the instrument performs erratically. Were all the tests with propane performed on the same day? Did some instrumental parameter (s) change? I do not find the authors' contention of systematic underestimation convincing as the precision is too poor to support that argument. If it is due to "incomplete" mixing of reactants in the reactor as stated by the authors then this is worrisome because I am not sure if a linear "scaling" correction factor can account for it accurately. The authors need to address this issue in more detail to inspire greater confidence in the results and findings. This is particularly significant as the missing OH reactivity is also of the order of 30-40 %.

5) Figure 4 and Figure 5 appear to give an inconsistent picture to me. In Figure 4 the graph for the 31 m level appears to have higher missing OH reactivity in the temperature range of 284 K till 290 K while in Figure 5, the lowest missing OH reactivity at the 31 m level is associated with this temperature range. The authors should clarify why this is so and also state the bin size employed in binning data against a particular temperature.

6) Fig S3-S5: The authors should try and explain the reason for the high missing OH reactivity periods in the time series e.g. on 10/7 at the 6 m level and 28/7 at 31 m

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level. This may help to understand the processes responsible for the high missing OH reactivity.

7) The suite of measured OH sinks in this study is not very comprehensive. For example it appears that none of the C2-C4 alkenes were measured nor were higher alkanes quantified. There is a paper in this special issue speculating on NO₂ emissions from the forest floor by Alagmand et al. I wonder if C2-C4 alkenes and/or higher alkanes which would come under primary emissions could possibly help explain the missing OH reactivity. Perhaps there are previous GC-FID or GCMS measurements from the site which could provide information on levels of such compounds. The authors should at least discuss this possibility.

MINOR COMMENTS

How well can methyl peroxide be measured using the PTR-MS technique? At what m/z is methyl peroxide detected? Perhaps the vertical profile and correlations of missing OH reactivity with methyl peroxide could throw some light.

Figure 6: With r² values of 0.3 and large spread in most cases, I find any suggestions of correlation rather farfetched and potentially misleading. The authors may wish to re-phrase the text appropriately.

Mogensen et al. 2011 (Modelling atmospheric OH-reactivity in a boreal forest ecosystem) analyzed the contribution of oxidation products and assessed the gradient of OH reactivity in a boreal forest where measured average OH reactivity values appear to be similar in level to levels measured in the present work. The authors could discuss the work of Mogensen in their study as it is quite relevant.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17159, 2013.

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