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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 #2

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In this paper total OH reactivity measurements are made within/below and above a forest canopy during the CABINEX field study. The results are novel in that there is some vertical information regarding OH reactivity – which in principle should enable some separation between missing reactivity that is due to directly emitted species, and missing reactivity that is due to subsequent oxidation of directly emitted species (whose role will increase with reaction time away from source). Vertically resolved measurements of OH reactivity are an important addition to the measurement set in this type of environment.

The main result of this paper, which is Part 1 field measurements (with a Part 2 modelling paper to come), is that above the canopy (21m, 31m data) the % of OH reactivity that is missing (determined by comparing with OH reactivity calculated from co-

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measured OH sinks) was significantly higher than the % missing reactivity within/below the canopy itself (6 m data). The results suggest that the OH reactivity below the canopy (which is closer to the calculated values) is mainly from directly emitted species that tend to be measured, whereas above the canopy there is additional reactivity due to oxidised products more of which tend not to be measured. There is indeed evidence from the observations that the missing reactivity is not due to unmeasured directly emitted BVOCs (as agreement is good below/within the canopy), but rather due to unmeasured oxidation products, but a complication is that the measurements at the different heights were not made at the same time, and so other things could have changed (temperature, meteorology), and also that not all of the emitted species were measured. Part 2 (in preparation) which is referenced will look at this more closely via modelling to calculate the oxidised products which are formed from the measured directly emitted species and assess the additional reactivity from that. Previous work has shown that modelled OH reactivity (which includes unmeasured OH sinks which are oxidation products of measured primary VOCs) can be closer the measured value compared with the OH reactivity calculated just from measured sinks. However, until this work is completed (part 2), it is difficult to be sure of the conclusions drawn from this paper. This paper describes the instrument in some detail as this is the first paper that reports measurements from it, and hence I can see the rationale between splitting the instrument description / field measurements, with some empirical analysis, as presented in this paper, from the modelling work (presumably using a detailed mechanism) which will appear later, in order to avoid an overly long paper. However this approach means there is less evidence to support the conclusions given in this paper.

The dataset is important and fairly unique, and represents the first measurements from this OH reactivity instrument in an interesting environment, and is an important addition to the literature. There are several assumptions in reaching the conclusions of the paper, which based on the evidence are not as strong as they could be, and need some further discussion in the paper. Part 2 may provide further evidence for the hypothesis. Are some of the additional findings of that study available yet to support

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the conclusions here?

After considering the general points above, and specific ones given below, the paper should be suitable for publication in ACP following modifications.

(1) The abstract is a little misleading in that the OH reactivity was not determined as a real vertical gradient (i.e. determined at the 3 heights at the same or very similar times) – this ought to be clarified.

(2) Page 17162, line 2. VOCs are usually the most important sinks for OH, but this is not necessarily always the case. In some polluted urban environments reaction with NO2 can be the major loss for OH.

(3) Page 17164 – line 26, give the height above the ground for completeness in the Di Carlo study, particularly as comparison is given with these measurements in this paper.

(4) Page 17165, line 4. At the end of the introduction it would seem sensible to mention the paper in preparation which is about modelling the OH reactivity for this campaign. This paper may help to strengthen the conclusions of this part 1 paper –and the authors might want to consider stating the major result from part 2, if it is available, to support their findings here.

(5) Page 17165, line 22, "other intake arm" is ambiguous, for Figure this it is clear where the injector goes, but there are also other intake arms shown.

(6) Page 17166, state how far from the end of the injector the Hg lamp was positioned. Did it heat up the gas in the flowtube in any way, for example.

(7) A turbulizer was used. Did this lead to better mixing? Was the velocity profile altered significantly in the presence of it? Also, is there a thermocouple in the flowtube to measure the temperature (in case different to ambient, important for using the correct rate constant in equation (2)).

(8) N2 was used in the injector, so OH + H is formed. It is stated that the H atoms

will react once thay come into contact with O2. However, the time from production to mixing with O2 in the sampled air will be quite long, and it is therefore more likely that H atoms will react in other ways first, and impurities of O2 in the N2 injector flow may in fact lead to the production of the HO2? This should be clarified. Otherwise, if H atoms were to emerge from the injector in significant quantitites, what other impact might H atoms have on the OH sinks? (reaction of VOCs with H atoms will be fast).

(9) Page 17167 – line 1, is this range of OH concentrations the initial OH concentration after mixing, or at some point downstream?

(10) page 17167 line 15, 5-10 Torr seems quite a wide range. Is it normally at a given value within this range?

(11) add the word “pulse” before “repetition” on line 17 page 17167.

(12) I think there is a case for some/most of the supplementary material being included with the main paper. The additional text in the supplementary is quite short, and would be useful additional details in the paper. Figures S1 and S2 are important to be included with the first paper from this instrument. The time series of the measured and calculated reactivity should be in the main paper – as this is the major experimental result from the work – in addition to the averages which are already presented in the main paper. The time series of the rest of the parameters (JNO2 etc, O3) could stay in the supplementary, but actually it is helpful to see the changes in those with time and whether the OH measured and calculated reactivity correlate on a day to day basis with them, and so consider having them in the main paper also.

(13) Page 17169. For the wall loss experiment (dry?) N2 was used. Would the wall loss perhaps be different under field conditions when there will be variable amounts of water vapour? The presence of O2 should make no difference to the wall loss. Is the uncertainty in the wall loss rate at higher flows (not measured) reflected in the overall uncertainty of the measurements?

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(14) Page 17170. The analysis of the decays begins after 60 ms – what distance away from the injector does this correspond to in the flowtube?

(15) Page 17170. The 38% difference for the calibration with the standard mixtures is unfortunate, but the fact it is the same for all the standard mixtures does provide some confidence that it is a flow/mixing/velocity issue that ought to provide a robust scaling of the field data. It would be good to understand the reason for the differnece. This will add some uncertainty though to the reported OH reactivity as the 1.38 scale up will have an error bar associated with it. Is there a standard deviation on the average of 38% which could then be used to estimate any increased uncertainty in the OH reactivity?

(16) Page 17171. I think given this is the first paper describing the instrument that consideration should be given to showing figures S1 and S2 in the main paper.

(17) Table 1 does contain a significant number of OH sinks, but some notable absences are small alkenes and alkanes. Are these expected to provide a significant OH reactivity in this environment? Perhaps during previous PROPHET campaigns there is some information about these species which could be used?

(18) Page 17178, line 24. In this section on future work the Part 2 paper is referenced. Is it possible to provide some headline results, if they are available, which could help to provide evidence that the oxidised products are a significant fraction of the missing reactivity above the canopy?

(19) Figures. I think an OH decay would be useful in the main paper, and also a time series of the measured and calculated OH reactivity for the 3 heights, before the diurnal means are shown.

(20) Figure 4. There are different colours in each bar which are not referred to in the caption. I assume that the colour scheme for the various components making up the bar is the same as for figure 3, if so, this should be made explicit in the caption.

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Supplementary Page 3, line 6 – this should be fig S1 and not fig S2? I wasn't sure how this figure shows the successive on- and off-resonant measurements? Or is the variation in the signal for a given reaction time the change in signal as it goes from on to off resonant (I don't think so as off-resonant would give a signal that is independent with reaction time?). This needs clarifying. In the caption make it clear that forward and reverse refers to the injector movement.

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