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

We thank both of the anonymous referees for their insightful and helpful comments. We have done an extensive revision of the manuscript in response to these comments. In particular, we have revised the correction factor to better reflect the results from the laboratory tests and have used average values rather than medians in our analysis. The text has been revised throughout the manuscript to reflect these changes.

Detailed responses to the comments from the referees are summarized below. For clarity, referee comments are in *italics*, and additions to the text are in ***bold italics*.**

Referee 1:

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 if 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."*

We agree that switching between the heights at more frequent time intervals is a better approach to compare the reactivity at the different heights. Unfortunately at the time the instrument was not capable of making sequential measurements. Future measurements will involve rapid switching between each height, allowing a more direct comparison of the measured reactivity at each height.

We did attempt to address differences between each height by comparing measurements of trace gases. The similarity between measured mixing ratios of VOCs (such as isoprene and MVK+MACR) at the different heights suggests that the chemical environments were similar and can be directly compared (Figs S3-S5, Figs. 5-7 in revised manuscript). This is reflected in the sequential measurements of VOCs mentioned in Section 2.2, which show that, most of the time, VOC mixing ratios are similar among the three heights on short (on the order of 30 minute) timescales. In addition, temperatures observed at each height were in a similar range. For example, elevated temperatures observed during 27-28 July were similar to those observed on 10 July. However, the magnitude of both measured and missing OH reactivity is higher during 27-28 July. If the OH reactivity was solely driven by temperature-dependent BVOC emission, one would expect the measured and missing OH reactivity to be similar in magnitude.

However, as pointed out by the reviewer, we cannot completely rule out differences between each height for the time periods during which OH reactivity was measured. We also acknowledge that the differences in length among the three measurement periods may further complicate comparisons. As recommended, we have added the following caveats at the end of Section 4 (line 8, p. 17180):

"***Because these measurements of OH reactivity were performed during three different time periods of varying duration, measurements of OH reactivity with rapid switching between heights will be necessary to confirm these results.***"

We have also amended our conclusions with the following:

(line 5, p. 17181) "…at the 6m height. ***However, as the measurements at the three heights were performed at different time periods, the influence of other factors between these heights cannot be ruled out***. Additional 1-D modeling…as well as additional ***sequential*** measurements of OH reactivity and associated OVOCs…"

We have also added clarification in the abstract (in response to comment 1 from Referee 2) specifying that the measurements at the three heights were conducted during separate time periods:

(line 5, p. 17161): "OH reactivity measurements were made with a turbulent-flow reactor instrument at three heights from the forest floor above (21 m, 31 m) and below (6 m) the canopy ***at three different time periods during the CABINEX campaign***."

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

We used medians to obtain an aggregate picture that is unbiased by individual episodes, such as the one on 27-28 July. In comparing the diurnal averages to the diurnal medians, we have found that the differences are minor. We have revised the appropriate figures (Figs. 2, 3; Figs.

8, 9 in revised manuscript) to reflect diurnal averages. We have also moved the median plots (Figs. 2 and 3) to the Supplement, where they are now Figures S1 and S2.

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?"*

The logarithmic scale on Fig. S1 (Fig. 2 in revised manuscript) creates the appearance that the scatter within the groups of points at longer reaction times is higher than within groups of points at shorter reaction times. When the signal of OH is plotted as a function of reaction time on a linear scale, the absolute scatter within each group of points actually decreases with reaction time.

The scatter on the natural log of the OH signal adds uncertainty to the fit and consequently the derived OH reactivity. This is accounted for in the standard error on the fit.

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%."*

The tests for propane were not performed on the same day, as the tests at lower reactivity (< 15 s^{-1}) were performed over one two-day period, while the tests at higher reactivity (> 15 s^{-1}) were performed several days later. The reasons for the discrepancies are unclear. However, subsequent tests were also performed with propane and trans-2-butene several months after the tests shown in Fig. S2 (Fig. 3 in the revised manuscript). This figure has been revised to include these additional tests. The results are within the uncertainty of the fit for the previous tests and are consistent with the propane tests made at higher OH reactivity, confirming that the underestimation we observe is reproducible and that the instrument does not behave erratically.

During these tests, we have ensured that the VOC compound was well-mixed within the carrier gas by introducing it through various sampling inlet lengths. We believe that the discrepancy is due to incomplete mixing of OH with the reactants, and we are working on design improvements to promote better mixing of OH in the reactor.

Regarding the use of a linear scaling factor, we have clarified our rationale for doing this in the revised manuscript:

(after line 12, p. 17170) "***Given the similar behavior for all the test compounds, whose rate constants for reaction with OH span two orders of magnitude, and the linearity of the measured OH reactivity as a function of the calculated OH reactivity, it appears that this discrepancy does not vary with OH reactivity up to 35 s^{-1}. We therefore assume a linear scaling factor to account for the discrepancy.***"

We have revised the correction for the OH reactivity to more accurately reflect the results from Fig. 3 (in revised manuscript). The text has been changed to reflect this:

(line 23, p. 17170): "Measured ambient OH reactivity values are scaled up with a factor ***derived from the fit shown in Fig. 3*** to account for the average difference observed between measured and calculated OH reactivity in these laboratory experiments."

We have included the subsequent tests in Figure 3 and mentioned them within the body of the manuscript. :

(line 21, p. 17170): "…of the reaction time. ***In addition, subsequent tests with trans-2-butene and propane showed similar behavior***."

To account for these revised corrections as well as the use of average values instead of median values in response to comment 2, we have also revised the abstract and the conclusions throughout the manuscript to reflect these changes.

5. *"Figure 4 and Figure 5 appear to give an inconsistent picture to me. In Figure 4 the graph for the 31m 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."*

The missing reactivity observed between 284 and 290 K in Figure 4 (Figure 9 in revised manuscript) occurs at the 6 m level (bottom plot), while the measured reactivity at 31 m agrees with the calculated reactivity over this temperature range (top plot). Figure 5 (Figure 10 in revised manuscript) only shows the missing OH reactivity for the 21 m and 31 m heights. We have added labels to the plots in Figures 4 and 5 (Figures 9 and 10 in revised manuscript) to clarify this.

The size of each temperature bin is 1 K, with the bin centered around the value of interest. For instance, the bin for 298 K would include datapoints with ambient temperatures ranging from 297.5 K to 298.4 K.

We have added the following to clarify this:

(line 25, p. 17174) "…Mao et al., 2012). ***The width of each bin is 1 K, with the bin centered on the temperature of interest.***"

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 31m level. This may help to understand the processes responsible for the high missing OH reactivity."*

We have expanded our discussion of possible reasons for the high missing reactivity on these days, as suggested:

(lines 14-24, p. 17177): "The reason for the high measured missing OH reactivity during the 27-28 July episode is unclear, but may be related to either a transport event or a period of high photochemical activity, as the measured mixing ratios of HCHO were elevated during this event, with a peak mixing ratio of approximately 2 ppb***v*** (Fig. ***7, panel c, red trace***) compared to ***an average*** value of 1 ppb***v*** observed during the remaining measurement period (Fig. ***4***). Mixing ratios of isoprene during this episode were also ***1–2 ppbv*** greater than the median values observed during the remaining measurement period at this height, as well as ***approximately 1 ppbv*** greater than th***e average daytime measurements during PROPHET98 (Apel et al., 2002), where conditions were similar to those during PROPHET 2000 (Di Carlo et al., 2004)*** . The higher mixing ratios of isoprene could lead to ***higher concentrations*** of oxidation products, as the higher mixing ratios of MVK + MACR and formaldehyde suggest higher photochemical activity during this episode. ***Both of these possibilities will be explored further in a forthcoming paper (Hansen et al., 2013)."***

(line 9, p. 17179): "…31 m. ***It should be noted that there was one episode of significant high missing OH reactivity at the 6 m height that occurred on 10 July (Fig. 5, panel e). As in the***

episode on 27-28 July at 31 m, the mixing ratios of isoprene and MVK+MACR were elevated on this day, with daytime mixing ratios of isoprene approximately 4 ppbv (Fig. 5, panel b), and daytime MVK+MACR mixing ratios approximately 0.75 ppbv. (Fig. 5, panel b). In addition, NO_2 mixing ratios were elevated (1-2 ppbv, Fig. 5, panel d) in the early morning. This again suggests that the elevated OH reactivity was a result of either a transport event or a period of elevated photochemical activity."

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 Alaghmand 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."*

There are speciated measurements from the 1998 PROPHET campaign which include C2-C6 alkenes and alkanes as well as substituted aromatics and some halogenated compounds. Calculations using the median values from the 1998 dataset yield an OH reactivity of approximately 0.2 s^{-1} for C2-C4 alkenes and all alkanes, while calculations using the maximum observed values for these compounds yield an OH reactivity of 1.5 s^{-1}. This would only explain 1 to 6% of the missing OH reactivity observed at 298K and 31 m . When the other measurements from the 1998 speciated dataset (C5-C6 alkenes, substituted aromatics, and haloalkanes) are included in the calculation, the range of OH reactivity from these compounds increases to 1.1–3.8 s^{-1}. This could account for 5 to 16% of the missing OH reactivity observed at 298 K and 31 m. However, the inclusion of these compounds cannot fully explain the missing OH reactivity during the episodes mentioned in Comment 6 above.

We will include details about the possible impact of these unmeasured compounds in the discussion of possible sources of missing OH reactivity in section 4 (after line 24, p. 17177):

"***It must be noted that many compounds are absent from the suite of measurements listed in Table 2, including C2-C4 alkenes and C2-C12 alkanes, some of which may be emitted by plants and soil (Kesselmeier and Staudt 1999). These compounds were previously measured during the PROPHET98 campaign with mixing ratios between 50 and 300 pptv. Depending on whether the median or maximum mixing ratios were used for the calculation, C2-C4 alkenes and C2-C12 alkanes could contribute 0.2 to 1.5 s^{-1} to the ambient OH reactivity. When the other compounds from the 1998 dataset (such as C5-C6 alkenes, substituted aromatics, and haloalkanes) were included, the range of OH reactivity contributed by these unmeasured***

compounds increases to 1.1 to 3.8 s^{-1}. This could account for 5 to 16% of the missing OH reactivity at 298 K and 31 m and 10 to 33% of the missing OH reactivity at 296 K and 31 m."

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 can throw some light."

Methyl peroxide is measured at m/z 49 with this instrument. Mixing ratios are derived based on the assumption that the sensitivity of the PTR-MS to methyl peroxide is similar to that of methanol. As there has been no gas-phase calibration, the uncertainty and accuracy of the methyl peroxide measurement has not been determined. Jobson and McCoskey (2010) describe previous measurements of methyl peroxide with their PTR-MS instrument. We have added a footnote to Table 2 to explain this and to refer readers to Jobson and McCoskey (2010).

The vertical profiles of methyl peroxide did not reveal any significant differences between the different heights. The R^2 values for the fit of missing reactivity to methyl peroxide are similar to those for the fits of missing OH reactivity to MVK+MACR, again suggesting that the missing reactivity may be related to unmeasured oxidation products. This has been clarified in the revised manuscript.

"…function of monoterpene mixing ratio. ***Although not shown, the linear regression of missing OH reactivity as a function of methyl peroxide mixing ratio is similar to that for the linear regression of missing OH reactivity as a function of MVK + MACR mixing ratio.***"

"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."

As suggested, we have rephrased the last full paragraph on p. 17178 (lines 13-27) to clarify this:

"Figure ***11*** shows ***linear fits of the*** measured missing reactivity at the 31 m height ***as a function of the*** measured mixing ratios of isoprene, MVK+MACR***, and total monoterpenes***. ***Although the correlation coefficients are low, the results suggest that the missing reactivity is more likely related to isoprene and its oxidation products rather than monoterpene emissions. Although not shown, the linear regression of missing OH reactivity as a function of methyl peroxide mixing ratio is similar to that for the linear regression of missing OH reactivity as a function of MVK+MACR mixing ratio. The correlation coefficient for*** the ***fit of the*** observed missing OH reactivity ***as a function of MVK+MACR mixing ratio*** is ***higher on*** 27 July ***(R^2 = 0.62)***, when the missing OH reactivity is high (Fig.***11***, top), than on a day when the missing OH reactivity is low, such as 4 August (Fig. ***11***, center) ***(R^2 = 0.08)***. These results suggest… ”

"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."

We agree that the Mogensen et al. paper is relevant to this work, as this paper focuses on forested environments as well as the vertical gradients within a forest canopy. A more detailed discussion of their results will be included in the subsequent paper. We have included references to this paper within this manuscript:

(After line 21, p. 17164): "…above and below a forest canopy. ***One-dimensional modeling by Mogensen et al. (2011) shows that ambient OH reactivity can vary with height in a forest environment.*** The likelihood…"

(line 20, p. 17179): "…the one used in Bryan et al. (2012) ***and Mogensen et al. (2011)*** would also be useful…"

(line 27, p. 171): "…below the canopy. ***A modeling study of a boreal forest performed by Mogensen et al. (2011) suggests that summertime OH reactivity is higher below the canopy during the night but decreases during the day due to efficient mixing, in contrast to measurements at this site (Sinha et al., 2010).***"

Referee 2

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."*

The abstract has been revised to clarify this point:

(line 5, p. 17161): "OH reactivity measurements were made with a turbulent-flow reactor instrument at three heights from the forest floor above (21 m, 31 m) and below (6 m) the canopy ***at three different time periods during the CABINEX campaign***."

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

This sentence has been revised: "Due to its high reactivity, there are numerous sinks of OH in the atmosphere. ***Among the most important are nitrogen oxides and Volatile Organic Compounds (VOCs).***"

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."*

This sentence has been revised: "The Community Atmosphere-Biosphere INteraction EXperiment (CABINEX) campaign during the summer of 2009 provided an opportunity to measure OH reactivity at multiple heights within a forest canopy where previous measurements from this site highlighted missing OH reactivity above the canopy ***at a height of 29 m*** (Di Carlo et al., 2004).

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."*

We agree that mentioning some of the preliminary results of the model would strengthen the conclusions of this paper. However, we are still analyzing the results and are not prepared at this time to draw any major conclusions.

5. *"Page 17165, line 22, "other intake arm" is ambiguous, for Figure [1 states] this is clear where the injector goes, but there are also other intake arms shown."*

We have clarified the description of the instrument as suggested. "To determine the loss rate of OH … is introduced through ***an*** intake arm ***perpendicular to the main axis of the reactor (Figure 1)***. The OH radical source injector is inserted ***along the main axis of the reactor (Figure 1)***."

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."*

The sentence on line 10 of p. 17166 was revised as follows: "The OH radical source injector…stainless steel tube. ***The top of the mercury penlamp is positioned approximately 1 cm upstream of the exit of the injector***."

It is unclear how much impact the Hg lamp had on the temperature of the air sample. However, as we explain in our response to comment 7 below, the temperature of ambient air flowing in the flow tube is measured. Thus, even if the penlamp affects the temperature of the gas in the flow tube, this is taken into account in the analysis.

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))."*

We have revised the instrument description for clarification:

(lines 15-18, p. 17166): "A turbulizer … is attached to the injector 10 cm upstream of the cap ***to help promote mixing and to help establish turbulent flow conditions (Seeley et al., 1993).***"

A thermocouple is used to measure the temperature within the flow tube, which was often different from the ambient temperature, especially at night. It is important to note that the temperature measured by this thermocouple, not the ambient temperature, was used in the calculation of OH reactivity values.

Before the first full paragraph of p. 17166 (line 9), we have inserted the following: ***"To measure the temperature of the air inside the flow tube, a thermocouple was placed inside the flow tube within a port closest to the exit, approximately 12 cm from the exit of the flow tube."***

To address the use of the flow tube temperature for OH reactivity calculations, the following sentence was added after the second sentence of the first paragraph of Section 3 (p. 17172, lines 22-23): "***The temperature measured within the flow tube was used to calculate temperature-dependent rate constants.***"

8. *"N2 was used in the injector, so OH + H is formed. It is stated that the H atoms will react once they 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 quantities, what other impact might H atoms have on the OH sinks? (reaction of VOCs with H atoms will be fast)."*

There was approximately 600 ppbv of O_2 in the N_2 used for the injector during CABINEX according to the Certificates of Analysis provided by the supplier. Thus, it is likely that the O_2 present in the N_2 is sufficient to convert the H atoms to HO_2. Any unreacted H atoms leaving the injector would react with O_2 in the ambient air rather than with VOCs given the high concentration of O_2 in ambient air. For the laboratory tests, however, the mixing ratios of O_2 are in the ppbv-ppmv range. Comparing the mixing ratios of VOCs to the mixing ratios of O_2 in the nitrogen cylinders (500–600 ppbv), the mixing ratio of O_2 is still 1–2 orders of magnitude greater than that of VOCs. With a rate constant for H + O_2 + M of 1.04×10^{-12} $cm^3 molecule^{-1} s^{-1}$ (Atkinson et al., 2004) and rate constants for H + VOC in the 10^{-12}–10^{-14} $cm^3 molecule^{-1} s^{-1}$ range (e.g. Šlemr and Warneck, 1977; Vinckier and Van Hoff, 1994; Clarke et al., 2000), the reaction rate for H + O_2 should still be greater than that for H + VOC by at least a factor of 50. This value assumes a bimolecular rate constant for H + VOC of 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and a VOC mixing ratio of 10 ppbv. Thus, the impact from the reaction of H atoms with VOCs should be small.

We have clarified this point in the revised manuscript:

(Line 24, p. 17166): "The H atoms ***produced from reaction R1*** can then react rapidly with molecular oxygen ***present as an impurity in the nitrogen carrier gas*** to produce HO_2 radicals***. Any unreacted H atoms leaving the injector would react with ambient O_2 to form HO_2 radicals due to the large excess of oxygen in air compared to trace gases.***"

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

This represents the initial OH concentrations after mixing. We have revised the sentence starting on p. 17166, line 28 as follows: “Under field measurement conditions…that the ***initial concentration*** of OH radicals in the reactor ***after mixing*** was on the order of 1 to 5 x 10^9 cm^{-3},…”

10. *“Page 16167 line 5, 5-10 Torr seems quite a wide range. Is it normally at a given value within this range?”*

This is the range of pressures used on this instrument, which is dependent on the orifice used with the FAGE inlet. For CABINEX, the pressure in the cell was approximately 10 Torr throughout the campaign. The following sentence was added to clarify this: “***This range of pressures is dependent on the orifice used with the FAGE inlet. With the orifice and pumping setup used during CABINEX, the pressure in the FAGE cell was 10.8 ±0.5 Torr.”***

11. “[A]dd the word “pulse” before “repetition” on line 17 page 17167.”

The sentence has been revised as follows: “A tunable dye laser…operating at a ***pulse*** repetition rate of 5 kHz…”

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.”*

We have moved Figures S1 and S2, as well as the entirety of sections S1 and S2, to the main body of the paper as suggested. Section S1.1 was merged into the second full paragraph of p. 17169 (starting at line 11). Section S1.2 was incorporated into the second full paragraph of p. 17168 (lines 20-23). Section S1.3 was included in the first full paragraph on p. 17168, while

Section S2 was incorporated into the first full paragraph on p. 17169. Figures S1 and S2 are now Figures 2 and 3 in the revised manuscript. Furthermore, all figures have been renumbered, both in the captions and in references within the body of the paper.

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?"*

Dry N_2 was used for the background OH reactivity/wall loss experiments for tests in both the laboratory and field. There is an excess of water vapor from the output of the injector whenever humidified N_2 is flowing through the injector. However, after accounting for dilution within the reactor, this would result in a mixing ratio of water in the reactor of approximately 0.1%, assuming that the mixing ratio of the humidified N_2 is 2%. This is approximately 10 to 20 times lower than the range of ambient water vapor mixing ratios (1–2%) measured during CABINEX. During CABINEX, there were variations in ambient water vapor mixing ratio on the order of 0.5–1%. Given the magnitude of the difference in water vapor mixing ratios between the laboratory tests and field conditions, we cannot rule out the possibility that water vapor could have an impact on the wall loss. The impact of water vapor on wall loss within the reactor would more likely arise from surface processes facilitated by the adsorption of water vapor onto the reactor walls than from reactions of water vapor with gas-phase species in the reactor.

The uncertainty in the wall loss has not been reflected in the overall uncertainty on the OH reactivity measurements. We can estimate this uncertainty from the standard error on the mean (1σ) of the wall loss measurements under field conditions, which is 0.5 s^{-1} at the highest measured flow (200 L min^{-1}),. This uncertainty has been incorporated into the error bars on Figs. 8-10 and Figs. S1-S2 in the revised manuscript. This has been clarified in the revised manuscript.

Caption to Fig. 9: "…uncertainties on … flow velocity, injector distance, $\boldsymbol{k_b}$, and the correction factor…"

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

At a flow velocity of 200 cm s^{-1} (typical for CABINEX), the reaction time of 60 ms corresponds to an injector distance of 12 cm upstream of the FAGE axis. The sentence starting on line 10 of p. 17170 was edited to reflect this: "For this reason, analysis of the OH decays was started at a reaction time of 60 ms***, when the injector was approximately 12 cm upstream of the FAGE inlet.***"

15. *"Page 17170. The 38% difference for the calibration with the standard mixtures is unfortunate, but the fact that 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 [difference]. 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?"*

The relative standard error on the slope itself, which was determined from all the combined measurements, is 2.9%. However, the relative standard deviation among the slopes for the fit of each of the four species is 12%. Using the latter value in the error propagation would increase the uncertainty on the OH reactivity measurement from 12% to 17%. We have changed the error bars in the relevant figures (Figs. 8-10, S1-S2) to reflect the increased uncertainty.

We believe that the discrepancy observed between measured and calculated values of OH reactivity during calibration experiments is due to incomplete mixing of OH with reactants in the air sample. As stated in the response to comment 4 from Referee 1, we are working on design improvements to address this issue.

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."*

As stated in the response to comment 12 above, Figures S1 and S2 have been moved to the main body of the paper, and are now Figures 2 and 3 in the revised manuscript.

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?"*

This was also addressed by Referee 1 (comment 7); we provide a full response in that comment. Briefly, these species were measured during the 1998 PROPHET campaign. Also, as mentioned in our response, small alkenes and alkanes can contribute as much as 1.5 s^{-1} to the OH reactivity, based on calculations from canister measurements made during the 1998 PROPHET campaign. A discussion of the potential impact of small alkanes and alkanes as well as larger alkenes, haloalkanes, and substituted aromatics was added to Section 4. (See the response to comment 7 from Referee 1).

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?"*

Please see our response to comment 4.

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."*

As stated above, Figure S1 has been moved to the main body of the paper, and is now Figure 2 in the revised manuscript. Figures S3-S5 have also been moved to the main body of the paper, and are now Figures 5-7 in the revised manuscript.

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."

The following sentence was inserted into the caption for Figure 4 (Figure 9 in the revised manuscript) after the first sentence: "***The color scheme for the bars is the same as that for Fig 8.***"

(21.) *"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."*

The sentence does refer to Fig. S1 (Fig. 2 in the revised manuscript), which only shows the net OH signal for the on-resonant points for the OH decay; the gaps represent time periods of off-resonant measurements.

Lines 5-6 of p. 3 of the Supplement have been revised as follows: "***Groups of on-resonant measurements*** can be seen in the OH decay displayed in Fig. ***2***."

Furthermore, we have revised the first sentence of the caption to Figure S1 (Figure 2 in the revised manuscript) as follows: "Two subsequent OH decays from CABINEX, one measured ***with the injector traveling*** in the forward ***direction*** (crosses) and one measured ***with the injector traveling*** in the reverse ***direction*** (circles) on 10 July 2009."

REFERENCES

Clarke, J. S., Donahue, N. M., Kroll, J. H., Rypkema, H. A., and Anderson, J. G.: An Experimental Method for Testing Reactivity Models: A High-Pressure Discharge-Flow Study of H + Alkene and Haloalkene Reactions, J. Phys. Chem. A, 104, 5254-5264, 2000.

Mogensen, D., Smolander, S., Sogachev, A., Zhou, L., Sinha, V., Guenther, A., Williams, J., Nieminen, T., Kajos, M. K., Rinne, J., Kulmala, M., and Boy, M.: Modelling atmospheric OH-reactivity in a boreal forest ecosystem, Atmos. Chem. Phys., 11, 9709-9719, 2011.

Seeley, J. V., Jayne, J. T., and Molina, M. J.: High-Pressure Fast-Flow Technique for Gas Kinetics Studies, Int. J. Chem. Kinet., 25, 571-594, 1993.

Šlemr, F., and Warneck, P.: Kinetics of the Reaction of Atomic Hydrogen with Methyl Hydroperoxide, Int. J. Chem. Kinet., 9, 267-282, 1977.

Vinckier, C., and Van Hoof, N.: Rate Constant of the α-Pinene + Atomic Hydrogen Reaction at 295 K, Int. J. Chem. Kinet., 26, 527-534, 1994.