**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "Airborne intercomparison of HO$_x$ measurements using laser-induced fluorescence and chemical ionization mass spectrometry during ARCTAS" *by* X. Ren et al.

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Reply to the Review by Referee #1

We thank Referee #1 for providing us valuable review comments that have improved the manuscript. Below we have included the review comments in italic followed by our responses. In the revision of this manuscript, we will highlight those changes accordingly.

General comments This is a well written, well presented piece of work detailing results from an intercomparison exercise between a LIF instrument, measuring OH and HO2 and two CIMS instruments measuring OH and HO2 individually. Some of the major findings from this work are particularly timely, given the recent interest in oxidation chemistry in forested regions, sparked by a number of observations of higher than expected OH in areas influenced by high biogenic emissions and low levels of NO. The OH measurements made in forested regions to date have primarily been measured using LIF and there has been recent speculation on the validity of these measurements (e.g. Mao et al., 2012). An intercomparison of OH measurements made using different techniques is key to beginning to address the cause of the model-measurement discrepancy that exists in these regions. In general the paper warrants a more in depth discussion in certain areas (detailed in the Specific comments below). There are a small number of queries/comments that also should be addressed, but I recommend publication following these amendments/additions:

Specific comments Comment (1): Pg 2537, ln 11: 'different sizes of pinholes were used in the calibration to produce different detection cell pressures'. Is the radical loss to the inlet expected to be the same for different pinholes?

Response: As discussed in Section 4.6 of Faloona et al. [2004], laboratory and in-situ flight tests (e.g., pointing the calibrator towards the inlet at different angles, different pitch angles, and varying air speed during a flight) show that there is little sensitivity dependence on angle of attack or airflow velocity, indicating that losses on the inlet external surfaces are negligible. We have added a sentence here to address this: "Laboratory and in-situ flight tests indicated that OH and HO2 loss to the pinholes is negligible (Faloona et al., 2004)."

Comment (2): Pg 2537: Please comment on the radical concentration range used during calibrations. At what H2O (v) concentrations were the calibrations conducted? How did these concentrations (radical and H2O) compare to ambient? Were any corrections applied to extrapolate if these concentrations did vary from ambient?

Response: The calibrations were conducted with OH and HO2 concentration range between 0 and ~10 pptv (or ~2.5x108 molecules cm-3) and with water mixing ratio varied from 0 to ~1% mixing ratio by volume. The OH concentrations during the calibrations covered the ambient OH levels during ARCTAS. The HO2 concentrations during the calibration covered most of ambient HO2 levels, with higher HO2 ambient levels mostly observed during the CARB phase as well as the transit flights between Cold Lake and Palmdale. The H2O levels during the calibrations covered the ambient H2O levels in most of the flights over the Artic region, but about a factor of ~2 lower than the ambient water level in the boundary layer during the CARB phase. As discussed in detail in Faloona et al. [2004], we conducted the correction for the quenching of OH fluorescence by O2, N2 and H2O. We do not feel that we should include all these details in the current manuscript and interested readers can refer to Faloona et al. [2004] for details.

Comment (3): Pg 2538, ln 2: Some longer chain alkane-derived RO2 (n-butane and upwards) are expected to interfere also, albeit to a lower extent (can be estimated from MCM chemistry). The impact of these should be considered if the model predicts significant levels of these species.

Response: The model does not predict significant levels of RO2 from C4 and higher alkanes because of relatively low levels of alkanes during ARCTAS. The sum of measured n-Butane, i-Butane, n-Pentane, n-Hexane, and n-Heptane was typically less than a few hundred ppt and many of these species were under detection limits. So we do not expect significant HO2 interference from these alkyl peroxy radicals. In fact, as we pointed out at the end of Section 2.2, the correction of RO2 influence reflects only a decrease of LIF-HO2 by 4% on average.

Comment (4): Pg 2538, section 2.3 – CIMS-OH instrument: It should be mentioned that the CIMS instrument was calibrated in flight at different altitudes. Could the presence of OH reactants in the sampled air bias the CIMS calibrations?

Response: We have added "The CIMS instrument was calibrated in flight at different altitudes." close to the end of Section 2.3. During the flight, the air speed was typically greater than 100 m s-1 and it took only ~10 milliseconds for the air passing through the photolysis zone to reach the inlet, so there is little OH loss due to its reaction with OH reactants in the sample air.

Comment (5): Pg 2539, ln 27: in HO2 mode (high NO/O2 ratio), the authors state that 15% of RO2 radicals are still detected. Have the HO2 CIMS measurements been corrected for this small RO2 contribution? Hornbrook et al., (2011) demonstrate that this conversion efficiency increases considerably for longer chain alkane and alkene derived RO2 species – could this lead to an overestimation of the HO2 concentrations determined by CIMS in this study?

Response: The HO2 measurements are automatically corrected for the 15% RO2 contribution. However, in regions with high alkene mixing ratios, there may be an additional contribution to the HO2 signal from RO2, but we calculate that this contributes a small (less than a 3%) overall impact on the total HO2 for ambient air due to relatively clean conditions during ARCTAS. Accordingly, we have revised the text here to read: "...the majority of ambient RO2 radicals are measured with low efficiency, approximately 15 % (high [NO]/[O2] = 6.8 × 10−4), and the reported HO2 mixing ratios are corrected for this 15 % RO2 contribution. This new method was used during ARCTAS."

Comment (6): Pg 2540, ln 6: At a flow rate of 5 SLM, what is the time between radical generation and sampling by CIMS? Do any corrections need to be applied for radical losses caused by impurities in the synthetic air? It is not clear from the text whether the CIMS-HO2 instrument was calibrated in-flight or just on the ground?

Response: For the peroxy radical calibrator, the time between radical generation and entering the instrument inlet is ~60 ms. This time is sufficient for photolytically generated OH to react with added reagents (corresponds to 16 reaction lifetimes for CH4 and H2 at typical added amounts) while short enough to minimize wall loss of peroxy

radicals (a 1 s-1 wall loss would remove 6% of the radicals).

Since the amounts of CH4 and H2 are relatively large (∼0.2% v/v), minor components of air (up to 0.5 ppmv VOC stated by manufacturer) would have to be very reactive (k > 4000 x kCH4) to compete. While VOCs such as propene or 2-butene are very reactive with OH, it is unlikely that such large amounts are present in the air used for calibrations. NO is unlikely to be present in amounts that would react with even a small fraction of the peroxy radicals present in the reactor (1 ppbv removes about 1% of the peroxy radicals in 60 ms).

The peroxy radical channel, unlike the OH/H2SO4 channel, was not calibrated in flight. Laboratory studies (see Hornbrook et al., 2011) indicate that the calibration factor is independent of ambient pressure, and calculations indicate only a slight temperature dependence, so ground-based calibrations while not ideal should be satisfactory.

Comment (7): Section 3 – Box model description: Were any deposition lifetimes included for model intermediates? How well did the model do at replicating the measured peroxides concentrations when left unconstrained? Olson et al., (2012) comment that box model photochemistry alone is unable to explain observed H2O2.

Response: We have added a sentence here to read "A surface deposition loss of 1.0x10-5 s-1 for modeled species is included in the model for altitudes less than 1 km". As we have pointed out, we use the model results with the model constrained to observed peroxides, including hydrogen peroxide (H2O2) and methyl hydrogen peroxide (CH3OOH). As discussed in Olson et al. [2012], the box model photochemistry can not explain the observed H2O2 when left unconstrained.

Comment (8): Pg 2542, ln 6-9: 'All model results discussed in this paper were taken from the standard constrained model simulations in the ARCTAS data archive and may be different from the results presented in Olson et al. (2012) were additional constraints may be included': : :there does seem to be some significant differences in the model-measurement agreement discussed in this paper and Olson et al., (2012), particularly

for HO2. Was the box model constrained to observations of formaldehyde? What are the likely impacts of halogen chemistry? Further discussion on the cause of these discrepancies is needed.

Response: The standard model, which is used to create the model results in the ARC-TAS archive, was not constrained to the observed formaldehyde, while in Olson et al. (2012) the model was constrained to the observed formaldehyde in some cases to check the impact of this additional constraint on the model calculations. The model included halogen chemistry and we added a sentence to read: "Because halogen chemistry is expected to impact surface O3 chemistry and radical cycling near the surface and in the lower troposphere the box model is updated to include bromine photochemistry (Olson et al., 2012)."

Comment (9): Section 4.1 – Overall intercomparison, pg 2542, lns 17 and 18: Both OH and HO2 comparisons display a positive intercept – is this significant?

Response: The OH intercept should be 2.8x104 cm-3, instead of 2.8x105 cm-3 (a typo, sorry!), which is about an order less than both detection limits of the LIF-HOx instrument for OH and the CIMS-OH instrument. In the regression, the intercept has an uncertainty of ±2.79x104, further indicating this intercept is not significant. The HO2 intercept of 3.9 pptv is greater than both detection limits of the LIF-HOx instrument for HO2 and the PeRCIMS instrument. However, the PeRCIMS instrument suffered a high background issue and the uncertainty in the PeRCIMS-HO2 measurements was typically greater than 4 pptv, suggesting that this intercept may be not statistically significant.

Comment (10): Section 4.2 – Comparison as a function of altitude: Are there any differences in H2O(v)/temperature/other parameters that could shed light on the differing altitude trends observed for CIMS and LIF? Could there be a problem with the sensitivity as a function of pressure for either instruments? Mao et al., (2010) mention high altitude transport of peroxides, whilst Olson et al., (2012) note that Obs/calc HO2 ratio

correlates with temperature. This is an area were the discussion should be expanded (even if no definitive conclusions to the discrepancies can be drawn).

Response: We have included a paragraph to expand the discussion of possible reasons for the discrepancies at the end of Section 4.2 by adding one paragraph and a new figure (Figure 5) as: "The reasons for the altitude dependence are unclear. However, as shown in Figure 5, there is a clear water vapor dependence of the CIMS-to-LIF OH and HO_2 ratios. At lower water mixing ratios (<5000 ppmv), the CIMS measured OH mixing ratios are smaller than the LIF measured OH on average. When the water mixing ratio is greater than 6000 ppmv, the median CIMS-to-LIF OH ratio is close to 1. The observed CIMS-to-LIF HO_2 ratio exhibits an opposite water vapor dependence compared to the OH ratio. At lower water mixing ratios (<3000 ppmv), the CIMS measured HO_2 mixing ratios are greater than the LIF measured OH. When the water mixing ratio is greater than 3000 ppmv, the median CIMS-to-LIF HO_2 ratio is close to 1. This water vapor dependence may be related to the need of water in the CIMS technique to convert OH to H_2SO_4."

In the supplement, we also show the temperature dependence of the observed CIMS-to-LIF OH and HO_2 ratios in Figure S1 and added the sentences: "The observed CIMS-to-LIF ratios of OH and HO_2 show similar dependence on temperature as on water mixing ratio (Figure S1). At lower temperature (<5 °C), the CIMS measured OH mixing ratios are smaller than the LIF measured OH on average. When the temperature is greater than 5 °C, the median CIMS-to-LIF OH ratio is close to 1. The observed CIMS-to-LIF HO_2 ratio exhibits an opposite temperature dependence compared to the OH ratio. At lower temperatures (<10 °C, in particular <-10 °C), the CIMS measured HO_2 mixing ratios are greater than the LIF measured OH. When the temperature is greater than 10 °C, the median CIMS-to-LIF HO_2 ratio is close to 1."

Comment (11): Section 4.3 – Comparison with box model, pg 2546, ln 2-4: If the significant differences between LIF HO_2 and modelled HO_2 during ARCTAS A is caused by missing aerosol uptake in the model how is this likely to impact the agreement observed

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between the model and CIMS-HO2 measurements during this mission? In contrast to Mao et al., 2010, Olson et al., 2012 find, through box model calculations that the loss of HO2 to aerosols cannot fully reconcile the model with LIF observations. A comment on this should be included in section 4.3.

Response: We have revised the sentences here as: "In fact, an HO2 uptake by aerosols has been proposed to explain this model overestimate of LIF HO2 during ARCTAS-A (Mao et al., 2010). However, a recent study by Olson et al. (2012) shows that the parameterization suggested by Mao et al. (2010) is insufficient to reconcile the discrepancy between model and LIF observations. We attribute this in part to the large uncertainties associated with the measurements of HOx precursors (Olson et al. 2012) and aerosol surface area (particularly hygroscopicity), and in part to an under-estimate of HO2 uptake coefficient (J. Mao, S. Fan and D. J. Jacob, Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, submitted). This HO2 uptake was expected to have less impact on HO2 concentrations during ARCTAS-CARB and ARTCAS-B because of the relatively fast gas-phase photochemistry during these two phases.

Comment (12): Section 4.4- Comparison as a function of NO: As this paper is primarily concerned with an instrument intercomparison, the CIMS/LIF ratio for OH and HO2 against NOx should be shown in a figure and discussed as ratios in the text (as well as the individual obs/mod ratios). Can you be sure that the higher observed OH at high isoprene are not skewing the obs/mod NOx plot at low NO?

Response: Although we did not directly compare LIF and CIMS as a function of NO or isoprene, the dependence of the model comparisons on NO and isoprene in Section 4.4 and Section 4.5 indirectly shows the agreement between CIMS and LIF measure-ments as a function of NO and isoprene, since the same model results were used in the CIMS/model and LIF/model comparisons. The differences between the blue lines (CIMS) and the red lines (LIF) as a function of NO (Figure 7) and isoprene (Figure 8) is the dependence of the agreement on NO and isoprene. As we can see there are

some CIMS/LIF differences as a function of NO, which has been discussed in Section 4.4, but there is little difference between CIMS and LIF measurements as a functions of isoprene (Figure 8). To keep the manuscript concise, we did not include a separation discussion on this.

It turns out that the higher observed OH levels at high isoprene are not the points in the obs/mod HOx plot (new Figure 8/old Figure 7) at low NO. For the data points with isoprene greater than 500 pptv, the mean NO mixing ratio is 58 pptv and the mean NO2 mixing ratio is 420 pptv. There were sufficient NOx levels in these regions with high isoprene levels. In Figure 8 (was Figure 7), the median observed-to-modeled OH ratio is close to 1 when NO is around 50-60 pptv.

Comment (13): Section 4.5 – Comparison as a function of isoprene, pg 2547, ln 17 – 24: The authors mention a new method used to determine the LIF OH signal by addition of C3F6 to chemically remove ambient OH to determine a background signal. This method of ambient OH removal is also employed to determine OH signals in the SI-CIMS (in the CIMS case, through the addition of propane (Mauldin et al., 1998)). Would the propane addition in CIMS remove an artefact OH signal in the same manner as C3F6 addition does for LIF or would any internally generated OH also be removed by propane? This is a key question in determining whether the model measurement discrepancy shown at high isoprene, low NOx is caused by instrumental problems or missing chemical mechanisms within the box model.

Response: The CIMS instrument uses the propane for similar, but different purposes. The CIMS measurement of OH involves the conversion of OH into H2SO4 via the addition of SO2, and then the subsequent measurement of the H2SO4. The propane is added in the CIMS background OH measurement to account for processes other than reaction with OH that can oxidize SO2. These processes have recently been attributed to the reaction of stabilized Criegee intermediates, sCI, with SO2 [Mauldin et al, 2012]. As these bi-radical species can be formed from the ozonolysis of isoprene, it would make sense that there would be a correlation between the artifact observed by

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Discussion Paper

the LIF and the background observed with the CIMS. The reviewer is correct however that any internally generated OH would be removed by the addition of propane – either from the front injector during the background measurement, or by the propane added continuously through the rear set of injectors (meant to scavenge any OH generated from NO+HO2) and to the sheath flow (meant to scavenge any OH generated in the ion source).

Comment (14): The authors mention that CIMS typically measures less OH than LIF in forests – I have looked through the reference given and find little support for this statement. Are the authors referring to the ambient measurements made during HOxComp? If so, the concluding remarks from the study were that measurement inhomogenities likely cause the discrepancies. Further details on this statement should be given.

Response: We have revised this sentence to read: "... while the OH measured by CIMS was found to be less than the OH measured by LIF during HOxComp, although sampling inhomogeneities and calibration problems might contribute to the discrepancies (Schlosser et al., 2009)."

Comment (15): One point raised by Mao et al., (2012) is that the level of interference suffered is likely dependent upon individual LIF instruments and also on the particular region studied. Although the identity of the interfering species has yet to be determined, it is speculated that it may be a product of ozonolysis. What were the levels of O3 during the high isoprene flights?

Response: During ARCTAS when isoprene levels were greater than 500 pptv, the O3 levels varied from $\sim$30 to 90 ppbv with a mean value of 48 ppbv, which is possible for ozonolysis of isoprene in those regions.

Comment (16): It would be useful to reference the recent Fuchs paper (Fuchs et al., 2012) which compare LIF and DOAS OH measurements made in the SAPHIR chamber under conditions similar to those experienced during the PRIDE-PRD campaign in section 4.5 when possible LIF interferences are discussed.

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Discussion Paper

Response: Fuchs et al. [2012] was published in AMTD shortly after we submitted our manuscript, so we were not able to cite this reference. In Section 4.5 where we discuss possible LIF interferences, we have cited this reference as: "In a more recent LIF-DOAS OH intercomparison study in chamber experiments with high VOC but low NOx levels, the scatter plot of LIF and DOAS had a slope of 1.02 and an intercept of 1.0x105 cm-3, indicating general agreement between the two techniques. However, LIF measurements were about 30–40% larger than those by DOAS after methylvinyl ketone (MVK) and toluene had been added (Fuchs et al., 2012), indicating a possible interference that the authors said they would investigate in the laboratory."

Comment (17): Table 1 – it is not clear how the ratios stated in the table were determined

Response: The mean and median ratios were calculated when both CIMS and LIF measurements were available. We added a note at the bottom of Table 1 as: "**: The mean and median ratios were calculated when both CIMS and LIF measurements were available."

Technical corrections (1) Pg 2532, ln 19: An appropriate reference for the UK FAGE instrument should be given.

Response: Besides Heal et al. [1995] which is already cited, we also added a more recent reference, Commane et al. [2010], which describes the latest UK FAGE in details.

(2) Pg 2546, ln17: Change 'this' to 'these'

Response: Corrected.

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Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/5/C1499/2012/amtd-5-C1499-2012-
supplement.pdf

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 2529, 2012.