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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 #2

We thank Referee #2 for providing us valuable review comments that have improved the manuscript. We have included the review comments in italic followed by our responses. In the revision of this manuscript, we will highlight those changes accordingly.

This paper presents results of an airborne intercomparison of several HOx instruments

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using both laser-induced fluorescence and chemical ionization mass spectrometry. This is an important area of research, as measurements of HOx radicals are often significantly greater than expected, suggesting either that there are significant gaps in our understanding of HOx radical chemistry, or that there are unknown interferences with the measurements. Intercomparions of different measurement techniques can help to identify errors in the measurement techniques and provide confidence in the measurements.

The study described in this paper is the first airborne intercomparison of HOx instruments on the same platform, and involved OH measurements using the Penn State LIF-FAGE instrument and the NCAR SI-CIMS instrument and HO2 measurements by the Penn State LIF-FAGE instrument and the NCAR PerCIMS instrument. In general, measurements of OH and HO2 by these different instruments agreed to within their combined experimental uncertainties, giving confidence in the accuracy of the HOx measurements by these techniques. The measurements were also compared to the results of a box model, and similar trends were observed with the measurements from both sets of instruments, with the observed to modeled HO2 ratio increasing with increasing NO concentrations, and the observed to modeled OH increasing with increasing isoprene concentrations. These results suggest that either there are measurement interferences with both instrumental techniques, or a problem with the model.

The paper is well written and suitable for publication in AMT after the authors have addressed the following:

1) Most of the paper focuses on a presentation of the results of the intercomparison, with little discussion. For example, the OH CIMS/LIF ratio decreases significantly below one above 5 km (page 2543-2544) but there is no discussion regarding potential reasons for the discrepancy. Similarly, there is little discussion regarding the significant difference between the CIMS and LIF HO2 measurements (page 2544). The paper would benefit from an expanded discussion of these results.

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Response: At the end of Section 4.2, we have added one paragraph and a new figure (Figure 5) to expand the discussion of possible reasons for the discrepancies: "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 HO2 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 HO2 ratio exhibits an opposite water vapor dependence compared to the OH ratio. At lower water mixing ratios (<3000 ppmv), the CIMS measured HO2 mixing ratios are greater than the LIF measured OH. When the water mixing ratio is greater than 3000 ppmv, the median CIMS-to-LIF H2O 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 H2SO4."

In the supplement, we also show temperature dependence of the observed CIMS-to-LIF OH and HO2 ratios in Figure S1 to read: "The observed CIMS-to-LIF ratios of OH and HO2 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 HO2 ratio exhibits an opposite temperature dependence compared to the OH ratio. At lower temperatures (<10 °C, in particular <-10 °C), the CIMS measured HO2 mixing ratios are greater than the LIF measured OH. When the temperature is greater than 10 °C, the median CIMS-to-LIF HO2 ratio is close to 1."

2) Similar to the LIF HO2 instrument, the PerCIMS HO2 instrument is also sensitive to the detection of RO2 radicals, with higher conversion efficiencies for the detection of alkene-based peroxy radicals (Hornbrook et al., 2011). Were the PerCIMS HO2 measurements corrected for this interference in the same way as the LIF HO2 measurements?

Response: The PeRCIMS HO2 measurements are automatically corrected for the 15%

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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. Thus in regions where alkenes are high, this may partially explain the discrepancy between the LIF and CIMS measurements. The further correction that would be required for the CIMS measurements is less than the correction that is needed for the LIF measurements because the CIMS already takes into account that there is a baseline of approximately 15% RO2 measured in the HO2 mode, and thus the correction would only be what is required on top of that.

3) Although the OH and HO2 measurements between the CIMS and LIF instruments appear to agree to within the combined uncertainty of the measurements for all flights, there is little discussion whether the agreement is independent of NO and isoprene concentration.

Response: Although we did not directly compare LIF and CIMS measurement agreement 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 shows indirectly the agreement between CIMS and LIF measurements as a function of NO and isoprene, since the same model results were used in the CIMS/model and LIF/model comparisons. As a result, the differences between the blue lines (CIMS) and the red lines (LIF) as a function of NO (now Figure 8) and isoprene (now Figure 9) is the dependence of the agreement on NO and isoprene. As we can see from Figure 8, 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 function of isoprene (Figure 9). To keep the manuscript concise, we did not include a separation discussion on this.

4) Similar to previous measurements, the authors find that the OH measurements from both the LIF and CIMS instruments are significantly greater than the modeled OH concentration at high isoprene concentrations, although there does not appear to be many measurements above 1 ppb of isoprene. The authors suggest that the high OH mea-

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surement from the LIF instrument may be due to an unknown interference based on their recent measurements using an ambient OH scrubbing technique (Mao et al., 2012). However, there is no discussion of the CIMS measurements, as it also appears to be significantly greater than the model at high isoprene concentrations. Could a similar interference affect the CIMS measurements? This should be clarified in an expanded discussion.

Response: We agree with the reviewer that there are not many data points with isoprene levels greater than 1 ppbv and that is why we think both instruments need to be further tested in the laboratory regarding potential instrument artifacts in environments influenced by biogenic emissions. At this moment the source of this OH interference in the LIF-HOx instrument has not been identified. Due to a different method to measure OH in CIMS, it seems unlikely that CIMS has the similar interference, as we have pointed out, but further investigation is needed, such as interference studies in chamber experiments.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/5/C1512/2012/amtd-5-C1512-2012-supplement.pdf

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