Atmos. Meas. Tech. Discuss., 5, C730–C735, 2012
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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.

Anonymous Referee #1

Received and published: 18 April 2012

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

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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

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?

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?

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.

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?

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

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– could this lead to an overestimation of the HO2 concentrations determined by CIMS in this study?

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?

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.

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.

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

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).

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Section 4.3 – Comparison with box model , pg 2546, ln 2-4: If the significant differences between LIF HO2 and modelled HO2 during ARCTAS A is caused by missing aerosol uptake in the model how is this likely to impact the agreement observed 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.

Section 4.4- Comparison as a function of NO: As this paper is primarily concerned with an instrument intercomparison, the CIM/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?

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.

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.

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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?

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.

Table 1 – it is not clear how the ratios stated in the table were determined

Technical corrections

Pg 2532, ln 19: An appropriate reference for the UK FAGE instrument should be given.

Pg 2546, ln17: Change 'this' to 'these'

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