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Atmospheric Measurement Techniques Discussions

Interactive comment on "Intercomparison of Hantzsch and fiber-laser-induced-fluorescence formaldehyde measurements" *by* J. Kaiser et al.

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Response to interactive comments from Referee 1

We thank the referee for the valuable feedback. The original questions and comments are shown in italics below, followed by our point-by-point responses.

General comments

The treatment of the measurement offsets (intercepts) is not as clear as the calibration (slope) comparison. I was left with the perception that there could be a significantoffset in FILIF (or even both of the measurement techniques). I assume that this was not in-

tended by the authors. Part of this offset, as the paper states, is due to changes in the calibrations (slopes) during the runs. I am curious if a different analysis or additional figure focused on the early times in the runs can clarify the magnitude of potentialoffsets in the measurements. Also, if you can clarify the zeroing of the Hantzsch instrument. In the early part of day 2 it looks as though the FILIF signal grows for the first few hours of the run with zero air while the Hantzsch stays constant at zero. Is this because the Hantzsch instrument is zeroed while the FILIF measures a few hundred ppt? There also seems to be an abrupt increase in the Hantzsch instrument on day 4 when H2O is added. Was the zeroing handled differently? If you believe these offsets are they because of sampling issues or to something inherent in the techniques?

We thank the referee for highlighting the lack of clarity in our discussion of measurement offsets. In the revised manuscript, we have included a new section that specifically addresses the offsets and zeroing methods of the instruments (section 5.5). We also refer the revised version of Table 3. Section 5.5 reads:

As seen in Table 3, a persistent negative intercept was observed in the Hantzsch/FILIF linear regressions. There are several factors to consider when addressing this offset, including instrument baselines, outgassing of either sample lines or the FILIF measurement cell, Hantzsch zeroing frequency, and curvature of the fit.

First, the methods of determining instrument baselines must be considered. The Hantzsch instrument uses scrubbed air to determine the magnitude of the PMT offset. The reported HCHO is proportional to the difference in the PMT signal of the sample air and the PMT signal of the scrubbed air. If any HCHO remains in the scrubbed air, the Hantzsch measurements will be biased by that amount. In contrast, FILIF measurements do not require an empirically defined instrument baseline. Because the spectroscopic signal verified by the reference cell is unique to HCHO, any difference between on-and-off resonance signals is the result of HCHO in the measurement cell. FILIF consistently measures $\sim$100 ppt HCHO in clean chamber air, while Hantzsch measures $\sim$0 ppt. Below, we consider if this trace amount of HCHO measured by

FILIF is an artifact of instrument outgassing, or if the clean chamber air truly contains trace amounts of HCHO not detected by the Hantzsch.

Both the instrument sampling lines and the FILIF White cell are potential sources of outgassing HCHO. Because the Hantzsch and FILIF instruments sample lines were of similar lengths and identical materials, any outgassing of the lines would affect the measurements equally and could not explain the difference between the two measurements. This leaves the possibility that HCHO from sample air deposits on the walls of the FILIF White cell and then is slowly expelled. The experiments on day 2 suggest this outgassing may be RH dependent, as humidification leads to a much larger increase in FILIF than Hantzsch measurement. However, day 4 Hantzsch measurements show humidification can cause an increase in HCHO in the chamber itself. To determine if the rise in HCHO seen during humidification is internal to the chamber or a result of FILIF White cell outgassing, an investigation of baseline measurements again becomes important.

Because of the aging of peristaltic tubes, stripping solution, and Hantzsch solution, the Hantzsch instrument's baseline is not constant in time, but interpolated or extrapolated from periodic zero measurements. On day 2, a baseline measurement is obtained before chamber humidification, and then again about 9 hours later. The readings are linearly interpolated to provide a uniformly increasing baseline. While it is assumed the change in instrument offset is constant with time, other experiments have shown the baseline does not necessarily drift at a uniform rate. This is especially relevant at high concentrations of HCHO, where the baseline can be affected by insufficient removal of HCHO by the Hopkalit catalyst. If instead we consider a situation where the baseline drift was slow, the first zero measurement would be more representative of the true instrument baseline during chamber humidification. Retaining a constant baseline increases the Hantzsch measurement by 130 ppt to 220 ppt. This is comparable to the 204 ppt observed on day 4 during humidification while the Hantzsch baseline was stable, and within 100 ppt of the FILIF measurement.

At least one instrument on each day shows that humidification can lead to increased HCHO in the SAPHIR chamber. The discrepancy on the second day is either due to a drifting Hantzsch baseline or FILIF White cell outgassing. Because outgassing has been previously observed in other FILIF measurements (DiGangi et al., 2011), and because the Hantzsch baseline was measured infrequently, we cannot determine with absolute certainty the cause of the discrepancy of zero air measurements on day 2 during chamber humidification.

Finally, we examine the possibility of curvature in the Hantzsch v. FILIF regression analysis. While the linear correlation coefficients are high for all experiments, day 3 clearly shows a second degree polynomial better represents the observed data (Fig 3). This slight curvature is the result of either one or both instruments' sensitivity changing over time. Because calibrations performed over the 4 days were in good agreement for both instruments (within 3.5% for FILIF, 2% for Hantzsch), and because all calibrations were highly linear even to high concentrations, we cannot attribute the changing sensitivity to either instrument at this time. However, we note that the leading term in the second degree polynomial is small (Table 3). For all but the first day, taking the curvature into account brings the intercept closer to zero.

The corrected intercepts considering both the curvature and instrument offsets are shown in the final column of Table 3. To provide a comparison between Hantzsch and FILIF measurements that is not affected by the HCHO measured in clean air by FILIF, we subtract the difference in clean chamber air measurements from the FILIF measurements. Because FILIF was not measuring at the start of day 4, the average clean chamber air measurement of other experiments is used. The values are much closer to zero than the intercept calculated from linear regression alone; however, a difference of as much as 110 ppt in the corrected intercepts is still observed. A secondary method for testing the purity of air used in instrument zeroing and eliminating the potential for White cell outgassing is vital, as HCHO mixing ratios in the 0-200 ppt range have been observed in the field. Similarly, the reasons for the curvature observed on some days

requires further study, for example using long-path DOAS as an independent method.

Specific comments

1. page 238 line 5: Scott/Air liquid

Corrected.

2. page 240 line 6: affect line 25: what is weighted amount? also, powder.

Corrected. The weighted amounts of powder are now listed.

3. page 243: How long is the calibration of the two instruments valid? Can you expect the FILIF to be unstable over any 24 hour period?

We thank the reviewer for the comment, as we realize the current wording may make the FILIF calibration appear unstable. We have included the following in our discussion of the FILIF instrument (section 2.1):

The FILIF calibration is valid as long as the alignment is constant (i.e., as long as the instrument stays in one location) and the laser is tuned to the same fluorescence feature. Typically, the same feature is used throughout a campaign and one calibration factor can be applied to all acquired data. For the final three days of the intercomparison, all calibrations performed agreed within 3.5%.

4. page 245: Is there any evidence for laser-generated HCHO in the FILIF white cell?

We thank the reviewer for this question, since such an effect has been seen in OH LIF instruments, where O3 photolysis can generate OH. There are two possible was HCHO could be generated in the cell: (1) similar O3 photolysis processes generating OH, and subsequent reaction of OH with any hydrocarbons present in the air, or (2) photolysis of a hydrocarbon to directly produce HCHO. Due to the low laser power (< 30 mW) and short sample residence time in the detection volume (< 35 ms), it is unlikely that either of these processes could produce detectable HCHO. We can, however, examine the possibility by looking at the HCHO signal as a function of laser power.

At a constant hydrocarbon mixing ratio, the amount of laser-generated HCHO would be proportional to laser power. While we have not performed experiments with constant hydrocarbon levels and varying laser power, we can examine the rise in HCHO observed on the third day of the intercomparison from 8:30 - 10:30 LT, during which the laser power rapidly fluctuated over a 5 mW range. In this period, the rate of change of VOCs and HCHO should be relatively smooth. Indeed, we do not see a noticeable effect of the laser power fluctuations on the HCHO signal. Due to the low probability and lack of evidence for laser-generated HCHO in the white cell, we do not believe this effect is seen in the FILIF instrument. The following sentence has been added to the discussion of the FILIF instrument (section 2.1):

As the observed fluorescence signal is a linear rather than quadratic function of laser power, we can exclude the possibility of laser-generated HCHO in the measurement cell.

5. Figures: Error bars represent 3 sigma precision

Corrected

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 233, 2014.