

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 authors proved their main points that ozone and water vapor do not appear to be problems with the two techniques. However, the biggest issue for this reviewer is the persistent large negative regression intercepts, which seem to indicate systematic

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outgassing in the FILIF sampling line/sampling cell. The FILIF system was not routinely zeroed near the inlet entrance while the Hantzsch system uses zero air through their stripping coil. Although it's not clear if the Hantzsch system has similar outgassing issues, the 0 result in the clean chamber air at the bottom of page 242 seems to suggest this was not an issue. As Table 3 indicates, persistent negative intercepts from -92 ppt to -338 ppt were observed in this study. Although this will have minimal impact on typical daytime HCHO levels ~2 ppb found in forested regions such as in the BEACHON-ROCS study, it will impact lower levels below 1 ppb found at night in this study. The authors need to address this. Also, since the negative intercepts are fairly large, one cannot just compare slopes but must include the intercepts. A good way to do this is to plot either the absolute differences between the two techniques (Y axis) as a function of averaged concentration on the X axis or the fractional difference (one - other/average value) on Y axis versus the averaged value on X axis. The authors need to discuss the potential issue of FILIF sampling line outgassing and how this may (or may not) have affected their field data.

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 mea-

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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 ~ 100 ppt HCHO in clean chamber air, while Hantzsch measures ~ 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

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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

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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.

One final general comment relates to the use or lack thereof of the absolute injected HCHO mixing ratios. The authors go to great lengths to present the concept of injected standards and then seem to ignore any detailed discussions about the agreement or lack thereof between the measurements and the injected standards. This should be addressed.

In the current manuscript, section 5.1 begins to explain the lack of agreement between measurements and the injected standards. We state “calculated HCHO mixing ratios from HCHO injection are higher than both sets of measurements. This possibly could be attributed to insufficient heating of the transfer line resulting in unaccounted wall loss and an overestimate of the initial HCHO mixing ratio, as was seen in Wisthaler et al. (2008).” In section 5.2, we state “again, incomplete transfer of thermolyzed para-HCHO is suspected to cause calculated HCHO mixing ratios higher than both measurements.” While we cannot determine the accuracy of the standard injections, we have expanded our discussion in section 5.1 to highlight the similarity between our results and the Wisthaler experiment. It now reads:

While the causes of the discrepancy between injected standard and measurements at the SAPHIR chamber have not been quantified, such discrepancy is routinely observed. Wisthaler et al. (2008) showed all six HCHO measurements were at least 20% below calculated values for dry synthetic air studies, similar to the 17% observed in this study. One possible explanation for the incomplete transfer is insufficient heating of the transfer line results in unaccounted wall loss.

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Specific comments

1. Page 234, Line 20: Should mention that concentrations well below 100 ppt have been observed in the upper troposphere just to be complete

We thank the reviewer for this comment and have added this to the manuscript.

2. Page 235, line 14: After (Warneke et al., 2011), should add something like “However, these same humidity effects also decrease the sensitivity of the technique and introduce a variable sensitivity”.

We have added this to the manuscript.

3. Page 235, line 15: define “BB” in front of DOAS.

This is now included.

4. Bottom of page 235: The authors should mention for completeness that Gilpin et al. (J. Geophys. Res., 102, 21,161 – 21,188, 1997) carried out an extensive intercomparison of 6 different formaldehyde measurement techniques, including a Hantzsch approach. When normalized to formaldehyde standards employed during manifold spiking tests, matched ambient measurements between the Hantzsch and a tunable diode laser spectrometer yielded an average ratio of 1.00 over 45 hours of measurement.

We thank the reviewer for highlighting this study, which we now include in our discussion of previous HCHO intercomparisons.

5. Page 236, line 27: The authors should give the sampling pressure for the lab FILIF water sensitivity tests so the reader can assess if water should be a problem.

6. Page 236, line 29: The assumption that the water used in the DiGangi et al. 2012 humidification study contained no dissolved HCHO may not be a very good assumption. Our experience has shown that water has to be purged with clean dry air or nitrogen for many hours to remove dissolved HCHO. Although this does not invalidate

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the results of this work, since water tests were part of this study, the authors need to mention the possibility that the past results may be compromised by this problem, unless precautions were taken.

Our intent is not to present this previous work as evidence for a lack of RH artifact, but to motivate the need for further studies. We agree that the assumption of no dissolved HCHO in the humidification study may not be valid. In fact, while the calibration slopes in the previous study agreed over a range of water vapor pressures (0-73% RH), an enhanced background was observed with increased humidity studies. This enhanced background was assumed to be caused by HCHO contamination from the water. We have reworded this section to explicitly state the conclusions and shortcomings of the previous experiments, and provide a more direct reference to a detailed discussion of those experiments. Unfortunately in these lab studies, only relative humidity was measured, and without pressure measurements, absolute water vapor pressure data is unavailable. The section now reads:

Previously, lab-based RH-dependent calibrations have been performed to test for water interference for FILIF (DiGangi, 2012). HCHO fluorescence was monitored at RH ranging from 0% to 73% and a constant temperature (19°C). An enhanced background signal was observed with increasing RH, and this was assumed to be indicative of dissolved HCHO in the water used to humidify the sample. Provided the background signal was subtracted, there was no significant deviation in HCHO concentrations at different humidities, indicating no significant water interference for HCHO LIF.

7. Page 238, lines 9 & 10: The negligible inlet effect found by Wert et al. 2002 was only for HCHO loss and not gains from sample line outgassing. The outgassing will of course depend on the particulars of the surface and surface area of the sampling system as well as the recent exposure history. It is encouraging that no differences in instrument zeros were observed during testing, however, this does not eliminate the possibility that sample outgassing could not be a problem during the actual intercomparisons. How frequently were the FILIF and Hantzsch systems zeroed? The authors

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need to discuss this since may be the cause of the rather large intercepts retrieved (to be discussed) from the linear regression fits.

Wert et al. 2002 examines HCHO adsorption and desorption from both PFA inlets. The authors state the only minimal adsorption and desorption (<5%) occurred even at low temperatures (-25°C to -42°C) for PFA tubing. However, absorption/desorption from the cell Herriot Cell's stainless walls was observed. As discussed above, we now include a discussion of possible outgassing from the inlets and the cell walls.

8. Page 242, lines 10-12: The authors should also include the possibility of heterogeneous chamber mixing. This is further suggested by the temporal differences in the FILIF and Hantzsch from 8:00 – 10:00 right after the initial introduction of standards into the chamber. How far apart were the collocated sampling lines from the two instruments?

Measurements of other injected species, especially methane, suggest the chamber is well mixed, and the HCHO inlets were very close to one another. We have included the following in the updated manuscript:

While heterogeneous chamber mixing would be a plausible explanation for the temporal differences in the Hantzsch and FILIF measurements, the instruments' inlets were located within 6 inches of one another. A strong concentration gradient is not expected to exist for an extended period of time on this spatial scale.

9. Page 242, line 18: Was the initial time period included or excluded in the entire day's fit? My feeling is that unless non-uniform chamber mixing can be discounted, this early time period should not be included. This would explain the low slope. Even though a bivariate least squares fit is used, high concentrations tend to govern the fit due to large absolute residuals.

In the fits for both days 1 and 2, the quick initial rise was not included in the regression analysis, as deviation from the 1-1 line during this time is more indicative of instrument

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time response and synchronization than measurement accuracy. We have now stated this in the manuscript. However, as we discount non-uniform chamber mixing, all other time periods are included in the analysis.

10. Page 242, lines 22-25: The discussion of the negative intercept relates to my point above and should not be dismissed. The authors note that the Hantzsch uses zero air to determine and remove instrument backgrounds while the FILIF does not. Again, HCHO sample line/system outgassing cannot be ignored and may be the cause of the significant negative intercepts. The authors note this in the -100 pptv offset measured in zero chamber air before HCHO addition on line 26 but this does not appear to be further considered in the comparison of the two techniques.

11. Page 243, line 1: Same comment as 8 above.

The new section 5.5 addresses these concerns.

12. Page 243, line 9: The authors should also include the possibility that the added water may have enhanced HCHO wall outgassing from the FILIF sampling line. Even though this reviewer agrees with the author's assertion that the added water cannot be ascribed to a water quenching interference in the FILIF, the overall agreement with the Hantzsch after this initial period is a better argument of this.

This is now discussed further in section 5.5. We have altered section 5.2 to clarify our argument. It now reads:

The Hantzsch-FILIF relationship seems to differ slightly from the earlier measurements after reconnection to the chamber, possibly due to Hantzsch baseline drift...

The slopes of each time period as well as the entire data set falls within the stated uncertainty of FILIF, indicating no water artifact for the FILIF instrument

13. Figure 2: After the initial decay, the input HCHO came into agreement with both measurements after exposing the chamber to sunlight and then about 12:00 local time remained higher. This shouldn't be caused by the same injection loss mechanism

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unless the water was taken up HCHO. However, one should also expect the same behavior in Fig. 4, but this was not the case. Although the authors may not be able to explain this behavior, they should at least mention this. Again, was the entire period of Fig. 2 included in the fit, including the short duration large spike in the FILIF?

While the reviewer states that the agreement between the model and measurement between 11:00 and 12:00 LT is in need of further explanation, we believe the large size of the markers may be leading to confusion here. As shown below and in figure 2c, the model is consistently higher than measurements during this time period (See HCHO calculated=4-8 ppb). We have adjusted the figure to be more legible. However, we recognize that due to the quick decay, the comparison in this time frame is highly sensitive to model time steps and synchronization of the dilution tracer measurement. The figure below shows the original model result and the result when the CH₄ is shifted so that the model better represents both observations. We used this revised model in result in the update manuscript. As no liquid water was formed in this experiment, it is unlikely there is uptake of HCHO into water.

14. Figure 3: The authors should try and explain the growing discrepancy with the Hantzsch with time. It appears that the malfunctioning zero air valve may be responsible for this? Was this the case? Also, the behavior of the temporal modeled HCHO input is significantly different here than the 1st two figures. Can this be due better-conditioned injection lines or the more gradual increase in input concentration and the possibility of more uniform chamber mixing? This should be mentioned.

The malfunctioning zero valve is not responsible for the discrepancy over time. While we have no explanation for the growing discrepancy, we have now highlighted this for the readers in section 5.3.

The temporal behavior of modeled HCHO in this figure is significantly different from the first two figures as HCHO was not directly injected, but form from the ozonolysis of 1-butene within the chamber. As shown in figure 3b, this ozonolysis occurs over time

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to deplete the 1-butene, which leads to a gradual increase in HCHO. We have now reworded the introductory sentences in section 3 to include anticipated timescales:

Introduction of HCHO into the chamber was performed either quickly by thermolysis of para-HCHO powder or more gradually through ozonolysis of 1-butene (C₄H₈).

15. Page 244, lines 1-3: *What happens at < 400 ppt and > 20 ppb? It appears that the latter is affected by the malfunctioning Hantzsch valve. Is this the case? One cannot see the comparisons < 400 ppt clearly from Fig. 3. The discrepancies here should be explained. Most likely the large negative intercept is the cause.*

In light of the above comment and the additional section 5.5, we have reworded this to read:

With the exception of low concentrations where instrument offsets become more important (see section 5.5), and at the later times (HCHO > 20 ppb), Hantzsch and FILIF measurements fall within 15% of each other. At this time, we have no explanation for the growing discrepancy between Hantzsch and FILIF with time.

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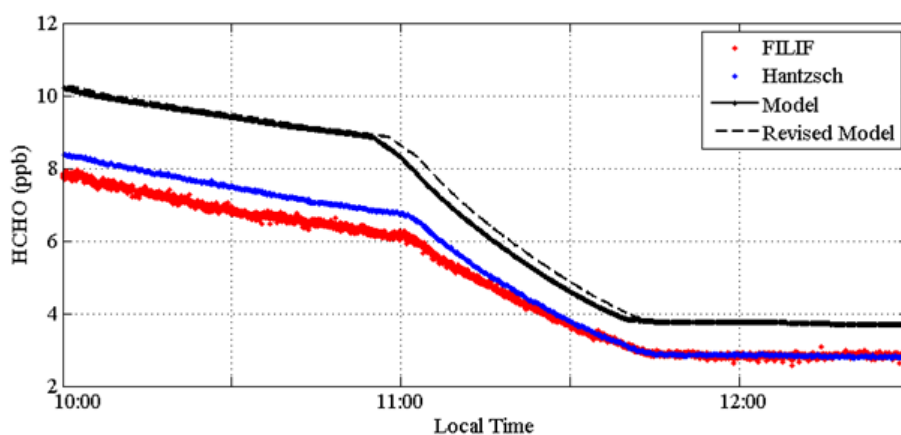


Fig. 1. Revised day 2 model, corrected for lag in dilution tracer measurements

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