Atmos. Meas. Tech. Discuss., 7, C103–C107, 2014
www.atmos-meas-tech-discuss.net/7/C103/2014/

Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #2

Received and published: 5 March 2014

Review of Atmospheric Measurement Techniques Manuscript Intercomparison of Hantzsch and Fiber-Laser-Induced-Fluorescence Formaldehyde Measurements

J. Kaiser et al.

General Comments:

This is a nice study that should be published after a number of issues are resolved. 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 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 $\sim$ 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.

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.

More minor points are as follows:

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

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"

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

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.

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 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.

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

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 $\sim$ 8:00 – 10:00 right after the initial introduction of stan-

dard into the chamber. How far apart were the collocated sampling lines from the two instruments?

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.

10. Page 242, lines 22-25: The discussion of the negative intercept relates to my point 7 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 $\sim$ 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.

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.

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 $\sim$12:00 local time remained higher. This shouldn't be caused by the same injection loss mechanism 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?

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.

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.

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