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Atmospheric Measurement Techniques Discussions
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Interactive comment on "A new airborne laser-induced fluorescence instrument for in situ detection of Formaldehyde throughout the troposphere and lower stratosphere" *by* M. Cazorla et al.

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Response to Anonymous Referee #2

This paper presents a summary of a new laser-induced fluorescence instrument for airborne measurements of formaldehyde. As mentioned in the paper, accurate and precise measurements of formaldehyde are needed as they can provide an important constraint to test current models of atmospheric chemistry as well as provide retrieval validation for satellite measurements. The paper provides a detailed description of

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the instrument, including details on the calibration procedure and important figures of merit. The paper is well written and suitable for publication in AMT after the authors have addressed the following comments: 1) The authors describe their procedure for calibrating the instrument in the laboratory, but do not appear to have a system to calibrate and zero the instrument in flight. As stated in the paper (page 8371) calibrations must be done over several days to ensure consistent results because "HCHO adheres to surfaces in tubing, fittings, regulators and flow meters: : :" How confident are the authors that ambient measurements of HCHO are not influenced by these effects in flight under variable HCHO mixing ratios? What is the intercept of the calibration plot shown in the inset in Figure 7? Does this intercept vary during calibrations, possibly reflecting absorption and degassing of HCHO in their system?

This issue was presented by Referee #1, also. We have added two paragraphs to Section 4.5 and a new Figure 12 to add to the discussion of time constants and contamination offsets. We are very confident that the effects of adsorption and desorption of HCHO from walls of tubing etc. are minimal in flight. Figure 12 makes this clear. The reason that the calibration is different from flight is that we use valves, fittings, regulators, etc. between our calibration tank and the instrument. Though we try to minimize surface area, the use of anything other than tubing introduces time constants. We do not use flow controllers, for example because they have horrible performance over time. Instead we use needle metering valves with miniature flow meters, but even these need time to equilibrate. The intercepts to calibrations are typically in the +/-50 pptv range.

2) The authors demonstrate that the sensitivity of the instrument depends on pressure due to absorption line broadening and quenching (Figure 7). However, there is no mention of the possibility of quenching of the signal by water. Did the authors perform calibrations as a function of water vapor concentrations to test for this?

To our knowledge H2O does not quench HCHO (like it does OH). Our in-flight diagnostics include the use of multiple gates. The ratio of the different gates is constant during flight, indicating that the fluorescence lifetime of HCHO is constant with changing H2O, CO2, O3, HNO3, SO2, Isoprene, etc.

3) The authors state that the measured fluorescence signal is normalized to the reference cell signal to account for frequency drift of their laser with temperature. This correction assumes that the sensitivity of the reference cell varies linearly with the sensitivity in the detection cell. Did the authors test this during their calibrations?

Yes, the relative sensitivity is a function of pressure. We have added several lines to elaborate on the correction in Section 3.4

4) Did the authors test for potential interferences from laser-generated HCHO in their system, perhaps from laser-generated OH (from the photolysis of ozone and subsequent reaction with water vapor) reacting to form HCHO, or perhaps from the photolysis of VOCs leading to HCHO formation in the detection cell? Although the laser power used is relatively low, potential laser-generated interferences should be taken into account given the high repetition rate and slow flow though their detection cell.

Yes, this is a concern given the fast photochemistry of OH and O1D and the photolysis of species like CH3OOH that can rapidly produce HCHO in air with NO. We have looked and we do not see anything in flight that indicates photolytic production of HCHO. This is not surprising for two reasons: (1) The photolysis and subsequent detection scales as the square of the peak laser power. Our laser has a repetition rate of 300 kHz, so the peak power is 104 times lower than that of a 3 kHz laser at equivalent power. The detection volume gets 100 times more pulses per unit time with the 300 kHz laser compared to a 3 kHz laser. The net result is that a 300 kHz laser is 100 times less likely to generate a photolytic interference than a 3 kHz laser operating at the same laser power. (2) Unlike OH, HCHO is relatively abundant compared to potential photolytic sources. OH is made from O3 and H2O that are thousands of times more abundant. Even a photolysis yield of 10-4 for O1D from 100 ppb O3 can make 104 OH, but something equivalent producing HCHO would have a neglible effect on

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HCHO. We have added O3 to the instrument in the lab to check for both photolytic and chemical effects, such as O3 + Alkenes on surfaces. We have not been able to detect any large effects. There may be small effects that we cannot detect because the ozone generator (Fisher Scientific) makes 50 - 100 ppt HCHO. We will continue looking at this possibility. We have also started looking at the possibility that ISOPOOH decomposes on hot metal surfaces to produce HCHO (Armin Wistahaler, personal communication). We do not expect an interference in ISAF because we do not have hot metal surfaces and the residence time in the inlet/instrument is small compared to what his PTRMS sees. Also, we do not see any correlation with ISOPOOH in the in situ data.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/7/C3714/2014/amtd-7-C3714-2014-supplement.pdf

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