

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.

Anonymous Referee #1

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General Overall Comments: This is a very nice paper reflecting a very thorough assessment of a new airborne HCHO instrument. The authors did a very nice job of discussing the instrument, the data acquisition procedures, gas handling, data reduction, sensitivity, precision, detection limits, and time response. The paper is well written and should be published after the following minor points below are addressed.

However, there are two shortcomings with the ISAF instrument in its present form that should be addressed in future versions and require authors comments here: the

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present instrument does not have provisions for chemically zeroing the inlet/sampling cell to mitigate the effects of HCHO wall outgassing and the present instrument does not add HCHO standards to the inlet during flight to periodically cross check wall losses and potential instrument sensitivity changes. Providing such capabilities are common practices with many airborne instruments and future improvements to ISAF should incorporate these practices. Specific comments further discussing these issues are provided below. Because these two issues can affect measurement accuracy, this reviewer strongly urges the authors to provide comments.

Page 2, Lines 12 – 15: The statement that: direct sources of HCHO are minor compared to secondary production is a little misleading and needs to be modified. Although secondary sources of HCHO typically dominate over primary combustion sources globally, locally, primary sources (e.g., fires) can also be important. In addition, one sometimes characterizes immediate HCHO formation from combustion, such as in flares, as pseudo-primary, due to the very rapid formation. Since this is an area of debate, I would simply state here that direct and pseudo-direct sources of HCHO could also be important.

Page 2, Line 16: The 2-3 hour lifetime is around noon, and I would add this. The HCHO lifetime dramatically increases as the sun's UV radiation decreases. The statement that wet deposition is a minor sink is also misleading since uptake by liquid drops and rain out can be an important sink process locally, and this needs to be modified.

Page 3, Line 2: The authors should include the rather extensive HCHO intercomparison study by Gilpin et al. (Intercomparison of six ambient [CH₂O] measurement techniques, JGR, 102 (D17), 21,161 – 21,188, 1997).

Page 3, Line 5: The TDLAS technique is more accurately reflected by the Fried et al. (2008) study and the Weibring et al., 2007 reference refers to a similar technique called Difference Frequency Generation Absorption Spectroscopy (DFGAS). I would site both references here with their appropriate names.

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Page 4, Line 17 – 19: In theory the combination of differential on-line-off-line pumping, followed by time gated and long-wavelength wavelength selective filtering should be sufficient to ensure high selectivity. However, the UV region contains a wealth of electronic absorption features from numerous hydrocarbons and potentially high overtones and combination bands of rovibrational transitions. It is thus important to convince the reader that high selectivity is achieved by listing all the different gases and their concentrations that have been examined. After all, up until several years ago it was thought that the same high degree of selectivity ensured that LIF measurements of OH were interference-free. However, recent more thorough analysis revealed that this was not the case.

Page 6, Line 20: In the statement regarding the same absorption line width in the reference and sample cells, does the significantly different self broadening of HCHO relative to air broadening come into play here? In the IR HCHO self-broadening is about a factor of 4 times higher than air-broadening.

Page 6, Line 24: How well does the second power monitor outside the sample cell reflect the actual alignment in the sample cell? As the detected fluorescence efficiency critically depends upon the precise alignment of the laser relative to the detection zone, the authors need to give some indication of how well the monitoring beam tracks movement of the sample beam.

Page 7, Line 1: change "oxegenated to "oxygenated "

Page 7, discussion of sampling: It is important to note that the present setup has no provisions for inlet chemical zeroing. As shown by the inlet study of Wert et al., even silicosteel and PFA Teflon tubing can outgas significant amounts of HCHO after exposure to high ambient concentrations. This becomes particularly true after sampling very high HCHO levels in smoke plumes. One would expect that after sampling such large plumes one should expect erroneously high ambient HCHO measurements at high altitudes when the HCHO concentrations drop. Even the HCHO intercomparison

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study by Kaiser et al. (Atmos. Meas. Tech., 2014) between a comparable LIF system and a Hantzsch system reveals outgassing from the LIF system, which was likewise not chemically zeroed. The online-offline subtraction scheme does not account for this potential error source. Comparisons with other HCHO instruments during field campaigns, despite showing good overall agreement and correlations, do reveal issues in the upper troposphere and lower stratosphere most likely from this cause as there is significant surface area in the sampling zone from the numerous light baffles. The authors need to add some statements about this.

Page 8, Line 6-13: This is a nice discussion of the line locking procedure employed. The authors should add a very brief discussion of how specifically the small absorption changes during wavelength shifting are corrected. Also, the authors state in a previous section (Page 6, line 21) that Section 3.5 will discuss how the reference absorption cell is used to correct sample cell data. Although line 26 on page 8 in Section 3.5 mentions this, it would be helpful for the non-informed reader specifically how this is accomplished.

Page 9, Discussion on Sensitivity: The authors did a very nice and thorough job of comparing UV and IR measurements as well as their standards measurements in the lab. However, the assessment of sensitivity and its stability would be even more convincing if standard additions to the sample cell were further carried out periodically in flight, as is the common practice with many airborne instruments. In part this relates to the comment above (Page 6, line 24); in part to inlet/cell HCHO losses; and perhaps most importantly, to the potential of sensitivity changes due to varying quenching of the LIF signal by water vapor. In fact, in their discussion of precision on page 11, lines 16-18, the authors note the possibility of changing HCHO surface desorption during calibration from various surfaces due to changes in temperature. Could this be a problem in flight during ambient acquisitions? How stable is the temperature of various components in flight? How stable is the sensitivity of 75 counts s⁻¹ mW⁻¹ ppbv⁻¹? Although not stated but implied, the authors use their reference cell response factor

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and the implied stability of their HCHO glue emission source as a means of providing in-flight checks on their sensitivity. Is this correct? To first order this is reasonable. However, the authors should further provide additional evidence as to how well the reference cell calibration factors track the sample cell calibration factors. Potential differences in broadening (self broadening in the reference cell versus air broadening in the sample cell), water vapor quenching in the sample cell, and potential differences in beam alignment between the two cells (see comment page 6, line 24 above) can all result in systematic errors.

This reviewer is only suggesting that the above issues may be potential problems, and the authors need to provide additional evidence in this paper to indicate why they are not important here. Again, in the future it would be much more convincing to simply add in-flight standards directly into the sample cell periodically.

Page 12, lines 1 -12: This is a nice discussion of S/N and measurement precision for both theory and actually achieved in the laboratory and in the UT during flight in Fig. 11. Also, it would be helpful if the authors can provide any additional information, if available, on instrument stability during aircraft pitch, roll, and yaw maneuvers.

Can the authors expound on their reduction in operating laser power from 20mW to 10mW (lines 11 and 12)? Is this a fundamental problem? The pump diodes and non-linear crystal (PPLN) should have relatively long lifetimes unless the crystal does not have a MgO coating to prevent bleaching. Which component are the authors trying to protect?

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 8359, 2014.