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Author Response (AR) to Referee #3

We thank Referee #3 for the time spent on reviewing the manuscript and providing constructive comments. We will work on the revised manuscript accordingly. Answers to the comments are given below.

General Referee Summary: Shutter et al. report a miniaturized instrument for monitoring grade data for formaldehyde, HCHO, based on a mid-infrared laser / Herriot cell combination. They demonstrate performance sufficient for slow time response (15-60 min) HCHO in some outdoor and (likely) many indoor environments. They compare this instrument to state of the art, research grade LIF instruments with might higher precision, showing agreement to within 10% in the slope and ±0.5 ppbv absolute difference for most conditions. They further demonstrate the utility of the instrument through a series of measurements at different locations on the Harvard campus in "personal monitoring mode".

The only significant comment is that this paper lacks a definitive statement of the instrument accuracy. Inter-comparison data are given, but there is no single statement of the accuracy of the instrument or the factors that determine it. Somewhere in the paper, perhaps after the comparison section and before the personal monitoring demonstrations, there should be paragraph that summarizes the estimates of accuracy and how it was determined. This information should also appear in the abstract.

Overall this is a short but solid paper. It will be of substantial interest to the readership of AMT. I recommend publication after attention to the comment above and the following minor comments.

Author Response: We appreciate the general and specific comments of Referee #3. We agree with the referee that an accuracy for the sensor should be quoted and also suggest the primary factor that controls the sensor's accuracy. To briefly summarize the manuscript change shown below (which has been added after the intercomparison section but before the personal monitoring demonstrations as suggested by the reviewer), we have determined an accuracy of ±(10% ± 0.3) ppbv is appropriate for the Aeris sensor (derived from ambient air sampling intercomparison) since this will be the normal operating mode of the sensor. We further believe that movements in the fringes caused etalons in the optical train (perhaps caused by temperature fluctuations) is the factor that affects the sensor's accuracy the most with other factors including particles scattering laser light and gas-phase absorbers not listed in HITRAN.

Manuscript Changes: "In determining the sensor's accuracy, there is a clear difference between how well the Aeris sensor compared to LIF instrumentation under laboratory conditions (i.e., HCHO gas standards diluted by ultra–zero air to perform stepped calibrations) (Table 2) and when sampling ambient air (Table 3). From the stepped calibrations performed in Sections 4.2.1 and 4.2.2., the mean HCHO mixing ratio at each step reported by HAPP fit was generally within ±4% of the mean value reported by LIF instrumentation. During the ambient air intercomparison with Harvard FILIF, both ART and HAPP fit showed that they were within –8% and +6%, respectively, when compared to LIF. Taking into account the 95% confidence intervals

derived from the York fits in Table 3 and a maximum offset of ~0.3 ppbv during LIF intercomparison under laboratory conditions, an accuracy of ±(10% + 0.3) ppbv should be quoted for the Aeris sensor. The factor that affects the accuracy of the Aeris sensor the most likely stems from any instabilities and movements in fringes caused by the optical train's etalons (perhaps from temperature fluctuations) since any drift can subsequently impact how well the HCHO line is fit. Other matrix effects impacting the sensor's accuracy include particles that happen to pass through the inline filter and scatter the laser light as well as minor gas-phase absorbers not listed in the HITRAN database."

Comment 1: Abstract, Line 15: "Good" agreement is not a well defined term. Abstract would be more useful if this were a number, e.g., agreement to with xx%.

Author Response: We agree with the opinion of the referee. Taking into account Comment 2, we have decided to remove this phrasing from the abstract

Manuscript Changes: "The Aeris sensor displays linear behavior ($R^2 > 0.940$) when compared with LIF instruments from Harvard and NASA Goddard."

Comment 2: Abstract, Line 17-19: Instrument precision (or LOD) is given, but accuracy is not stated. What is it?

Author Response: We completely agree with the referee. The accuracy of the sensor when sampling ambient air (as will be the case in most uses of this sensor) has been added.

Manuscript Changes: "Moreover, the accuracy of the sensor was found to be ±(10% + 0.3) ppbv when compared against LIF instrumentation sampling ambient air."

Comment 3: Page 1, Line 34: Not clear what is meant by "upwards of 15 and 40 ppbv". At least for outdoor measurement, and I suspect for indoor measurement, these appear to be high levels that would be on the upper end of a distribution, though the phrasing does not make this very clear or quantitative. Is there a better number that represents an average, especially for the indoor environment?

Author Response: The reviewer is correct that HCHO mixing ratios of 15 and 40 ppbv are at the upper end of a distribution of HCHO levels found in the outdoor and indoor environments. This distribution is seen in Figure 2 of Salthammer, T. Angew. Chemie Int. Ed., 52(12), 3320–3327, 2013. We agree the phrasing could be improved and the manuscript has been modified to give the range of HCHO levels that could be observed in indoor and outdoor locations. We are hesitant to provide an average for the outdoor environment as this shows a diurnal trend and are also hesitant about providing an average for the indoor environment since it varies widely by country and building type.

Manuscript Changes: "HCHO mixing ratios are generally higher indoors (ranging from 5 – 40 ppbv) than those measured outdoors (ranging from 0.5 – 15 ppbv with rural areas being on the lower end of the range and urban areas on the higher end) (Salthammer, 2013)."

Comment 4: Page 2, Line 6: Table 1 omits the cavity enhanced spectroscopy method of Washenfelder, AMT 9(1): p. 41-52 (2016) which reports a sensitivity and accuracy within the range of the other instruments.

Author Response: We thank the referee for mentioning this omission. Broadband cavity enhanced absorption spectroscopy (BBCEAS) has a sensitivity and accuracy that indeed is within the range of other instruments and has been added to Table 1

Manuscript Changes:

Table 1. Overview of selected in situ HCHO measurement techniques

	Method	3σ Limit of Detection (pptv)	Integration Time (s)	Accuracy (%)	Reference
Chemical	Fluorimetry[a] (Enzymatic and Hantzsch)	75–120	60–120	5–8	(Kaiser et al., 2014; Wisthaler et al., 2008)
	DNPH–HPLC	60	3600	15	(Wisthaler et al., 2008)
Spectroscopy/Spectrometry	Proton Transfer Reaction–Mass Spectrometry (PTR–MS)	300	2	10	(Wisthaler et al., 2008)
	Tunable Diode Laser Absorption Spectroscopy (TDLAS)	180	1	6	(Fried et al., 1999; Weibring et al., 2007)
	Quantum Cascade Laser Spectroscopy (QCLS)	96	1	–	(McManus et al., 2010)
	Differential Optical Absorption Spectroscopy (DOAS)	600	100	6	(Wisthaler et al., 2008)
	Broadband Cavity-Enhanced Absorption Spectroscopy (BBCEAS)	450	60	6.5	(Washenfelder et al., 2016)
	Laser–Induced Fluorescence (LIF)	30	1	10	(Cazorla et al., 2015; St. Clair et al., 2017; DiGangi et al., 2011; Hottle et al., 2009)

[a]Specified values are for Hantzsch

Comment 5: Page 2, Lines 8-9: It would be useful to the reader to translate the number to a set of actual T and RH conditions – e.g., what RH would 1500 ppmv correspond to at representative temperatures of say 25, 15 and 0°C?

Author Response: We agree with the referee and have translated the mixing ratio of water to an actual set of representative temperature and relative humidity conditions. Also, the lower limit of water vapor was raised from 1500 ppmv to 2000 ppmv after more testing of the sensor showed the need to provide a more conservative estimate in the manuscript.

Manuscript Changes: "The HCHO line is reliably found when the mixing ratio of H_2O is above 2000 ppmv (corresponding to relative humidities of 6, 12, and 33% at temperatures of 25, 15, and 0°C, respectively)."

Comment 6: Page 2, Line 33: What is the sample material for the Aeris cell? Does that material show any effects toward adsorption / desorption or reaction with H_2CO?

Author Response: While the material and the coating for the Aeris Herriott cell is proprietary, any outgassing would be accounted for since this additional background would also be part of the zero reference (measured every other 15 s under default settings) and therefore subtracted out. In our experience, we have not observed any signs that the cell is reacting with HCHO.

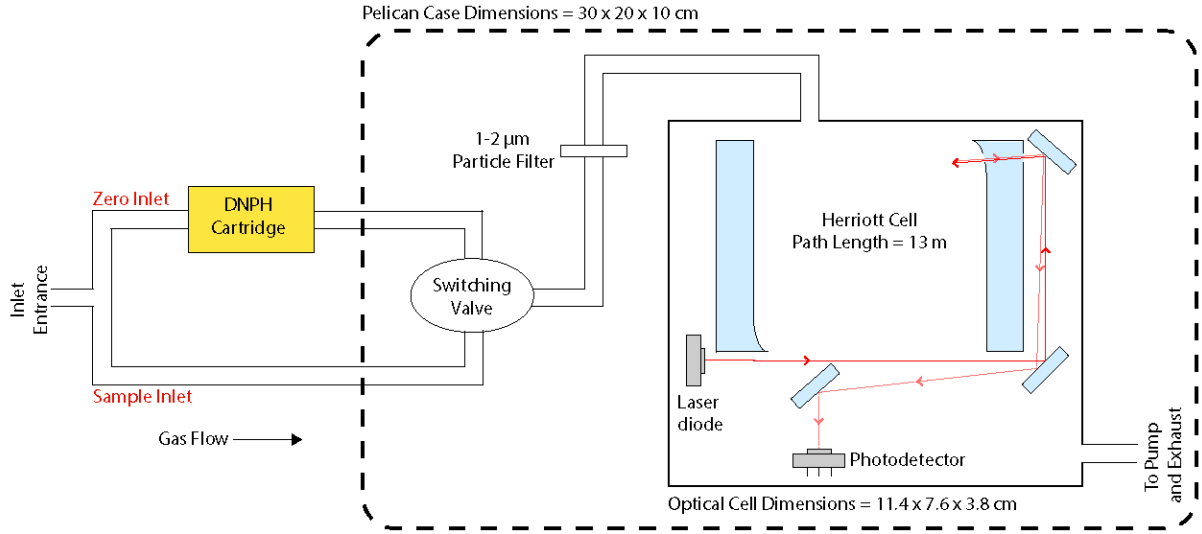
Manuscript Changes: "Since a zero is effectively calculated every other 15 s with default settings, the inlet and valve setup employed by the sensor helps to minimize the effects of thermal drift and other background effects (such as outgassing) on the reported HCHO mixing ratio."

Comment 7: Page 3, Lines 10-11: Is the inlet system in figure 3 external to the package in Fig 1? This seems likely, and should be noted.

Author Response: The sample and zero inlets are indeed external to the package in Fig 1 and this is now duly noted in the manuscript and in the instrument schematic (Fig S1)

Manuscript Changes: "Using default settings, the three–way valve cycles between the two external inlets every 30 s"

Figure S1 shows how the inlets are external to the portable Pelican case housing the sensor.



Comment 8: Page 3, Lines 12-13: The zero switch time is 15 s on / off, and the acquisition rate is 1 Hz. How much time is required to achieve stable operation after a switch? Some of the data must not be valid, limiting the actual time of measurement or duty cycle.

Author Response: The referee is correct that not all data collected during a 15 s period of sampling either the zero or sample inlet are valid. In fact, the first 7 s of data for each sampling period is ignored to prevent any hysteresis effects from the inlet previously being sampled. The manuscript has been modified to make this clearer, and the reference to the 50% duty cycle has been removed.

Manuscript Changes: "For the purpose of eliminating any hysteresis effects from the inlet previously being sampled, the first seven seconds of data are ignored for each 15 s inlet sampling period."

Comment 9: Page 3, Line 14: Is there a quantitative measure of the scrubbing efficiency of the DNPH cartridge for H_2CO? Even a limit (e.g., > xx.x%) would be useful to quote here if specified by the manufacturer or measured.

Author Response: In response to this comment, an additional experiment was performed on the Aeris sensor where a known amount of HCHO (~22 ppbv) was flowed into the sensor, but inline DNPH cartridges were on both the sample and zero inlets. From this experiment, >99.3% of the HCHO was removed by the DNPH cartridge. This scrubbing efficiency was determined with a flow rate of 750 sccm and 30% RH at 24°C.

Manuscript Changes: "containing an inline DNPH cartridge (LpDNPH S10L Cartridge, Sigma–Aldrich) that filters out all aldehydes, including more than 99% HCHO, from the air flow"

Comment 10: Page 3, Line 29: Out of curiosity, is H_2CO ever observed outgassing from new Teflon tubing, filters, or their packaging?

Author Response: Our general practice has been to use PFA tubing wherever possible since other types of tubing can outgas HCHO upon opening. That being said, sometimes the rigidity of the PFA prevents its use in some applications (like the inside of the Aeris sensor), so small lengths of flexible Tygon tubing are sometimes utilized.

Manuscript Changes: No changes were made to the manuscript.

Comment 11: Page 4, Line 24: very minor comment, but "nearly 16±9%" does not make sense, in that the number and its uncertainty is given precisely, so the word "nearly" should be omitted.

Author Response: We agree with this comment, and the manuscript has been changed.

Manuscript Changes: "HAPP fit outperforms ART fit by 16 ± 9% at all integration times"

Comment 12: Page 5, Line 20: Are the differences between fit methods a statement of the instrument accuracy? Can this be the number quoted in the abstract?

Author Response: We do not feel that the difference in fit methods presented in Equation 2 represents a statement of the instrument's accuracy since there are subsequent measurements later on that show the bounds on the accuracy should be greater than what is indicated by Equation 2.

Manuscript Changes: No changes made to manuscript.

Comment 13: Page 6, Line 13: Is there any evidence for passivation of the Aeris sensor inlet or internal surfaces, or can the entire response time be attributed to the H2CO delivery system. See question above regarding Aeris sample cell material.

Author Response: The entire time can be attributed to the HCHO delivery system since both Harvard FILIF and the Aeris sensor observe the same general equilibration time for the HCHO mixing ratio to stabilize. This can be visually observed by looking at Fig. 5a and noting how both instruments show that few ppbv rise in HCHO in the first non-zero step (starting around 10 h).

Manuscript Changes: No changes made to the manuscript.

Comment 14: Page 6, Line 21: Another very minor comment, but suggest remove "good" since the numbers given above speak quantitatively about the instrument accuracy.

Author Response: We agree with the reviewer, and the manuscript has been changed accordingly.

Manuscript Changes: "These results obtained with a different calibration tank and different LIF instrument are in excellent agreement with the ones obtained during the intercomparison at NASA Goddard, demonstrating the Aeris sensor's accuracy and linearity even at low mixing ratios."

Comment 15: Page 6, Lines 34-39: Do the authors know of any reason why the different fit methods should differ by 14%? This difference is larger than given above. Identifying the cause may help to address it. Is this number the one that should be used for instrument accuracy?

Author Response: There's a few aspects of the ambient air dataset that differ from the more controlled laboratory stepped calibrations performed with NASA and Harvard LIF instrumentation (in Sections 4.2.1 and 4.2.2). The laboratory calibrations were performed where the absolute water content was kept relatively constant and the air temperature the same, and the absolute water content and air temperature did indeed change throughout the ambient air sampling period that very likely affected the fits. Also, particles scattering laser light and gas-phase absorbers not listed in the HITRAN database could have affected measurements during the ambient air intercomparison. Moreover, as noted in Table S1 for HAPP fit, a superior fit was obtained when fitting all lines listed in the table when sampling ambient air as opposed to only the lines listed in blue when sampling HCHO diluted by ultra-zero air.

Indeed, understanding how the Aeris sensor would perform when sampling outside a controlled laboratory environment was one of the primary reasons for performing the ambient air intercomparison in Section 4.2.3. Without this test, there would be uncertainty as to how well the sensor would perform when sampling ambient air.

Manuscript Changes:

- This was added at the start of Section 4.2.3 to show how the results are different from Section 4.2.1. and Section 4.2.2: "In order to ascertain the performance of the Aeris sensor when sampling ambient air".
- Additionally, section headers were changed for Section 4.2 to better clarify for the reader the difference between the stepped calibrations (Section 4.2.1 and 4.2.2) and ambient air intercomparison (Section 4.2.3)
- The following sentence was also included at the start of Section 4.2: "Sections 4.2.1 and 4.2.2 show how the Aeris sensor compares with LIF instrumentation in the laboratory (i.e., using HCHO gas standards diluted with ultra–zero air to perform stepped calibrations); whereas, Section 4.2.3 shows how the Aeris sensor compares against LIF instrumentation from Harvard when sampling ambient outdoor air over a period of several days."

Comment 16: Page 7, Lines 24-26: While the statement is clearly correct, it is also somewhat of a throwaway. The sensor is not close to achieving the time resolution or precision for this application, but the "in its current state" implies this to be a future goal. Suggest omitting. At authors discretion.

Author Response: We agree with the reviewer since this the only time in the paper where eddy-covariance flux measurements are brought up.

Manuscript Changes: Sentence was removed from the manuscript.