

We heartily thank you for your insightful comments on the manuscript with respect to instrumentations. All comments helped us clarify and improve the manuscript.

1. Page 6, Section 2.2.2: The authors should briefly expand on their description of the “independent gravimetric” test.

Response: We initially weighed each permeation tube with a Mettler Toledo XP26 microbalnace ($\pm 1.5 \mu\text{g}$), placed them in the permeation system oven at 45°C with a constant flow rate of N₂ for 5 days (~7400 minutes), and obtained the weight loss rate. The measured loss rate was 78 ng/min ($\pm 10\text{ng/min}$). We briefly expanded the description in the revised manuscript.

Further on in this section on page 7 the authors mention agreement with absorbance calculations. As this is important to ensure the accuracy of the weight loss (i.e. no other species co-emitting from the permeation tubes contributing to the weight loss), the authors need to expound on their direct absorption measurements, by giving the estimated accuracy of the cross sections, the methods employed, the accuracy of the dispersion scale, and other aspects of these measurements. Does the laser line-width affect these determinations?

Response: We were not able to find the literature pointing out the effects of other co-emitting species in HCHO permeation tube (paraformaldehyde). Gilpin et al. (JGR, 1997) mentioned the possible effects of co-eluted species, such as H₂O, CO, H₂, CO₂, and CH₃OH, on weight loss of a permeation tube. However, previous studies, which Gilpin et al. refers to, mentioned that paraformaldehyde contains H₂O less than 5%, CO and CH₃OH result from thermal reaction of formaldehyde in the temperature range 150 ~ 300 °C and/or from heterogeneous reactions, which is not the condition of this study. Our gravimetric test was simply to double check the reported value from the manufacturer, VICI Metronics. We use “agreement” in this case to signify that the observed absorbances (not calculated) from various concentrations of HCHO standards (calculated from two permeation tubes) fell into one linear fit, which is another indicator for the accuracy of the permeation rates

reported by the manufacturer. We also revised the statement in the text to reduce the confusion.

- We mean agreement between two permeation tubes (i.e. observed absorbance of two permeation tubes falls into a linear fit line between observed absorbance and calculated concentrations). We did not perform the direct absorption measurements. So we have revised the description.

Were these measurements carried out on the “high calibration mode” standards? If so, issue 2 below calls into question the accuracy of this approach.

Response: We did compare the observed integrated absorbances vs. calculated HCHO standard concentrations from the permeation tubes as shown in the figure below to check on the linearity, where the highest concentration was from the “high calibration mode” standard. This was only used as a general check on the linearity of the system, and we thereafter did not use this excessive HCHO standard to track the instrument sensitivity.

2. On page 7, the authors discuss the generation of an 18.1 ppm HCHO standard from the permeation tube. I am not sure which permeation tube they are referring to here. Assuming the 88 ng/min tube, this would suggest a total undiluted flow of only ~4 sccm into the cell to generate such a high mixing ratio. Under these conditions the cell walls will no doubt significantly degas, thus calling into question the accuracy of the “high calibration mode” standard. Formaldehyde readily degasses from glass cell walls and this becomes more prominent as the cell flow decreases. Typically this effect becomes negligible at flow rates of a few slm. What the flow rates used here? The authors need to clarify the permeation rate issue. Do they really mean 18.1 ppm or 18.1 ppb?

Response: There was an error in presenting the concentration of “high calibration mode”. It should be 11.8 ppm not 18.1 ppm. We have corrected this mistake. This very high concentration was obtained by increasing oven temperature up to 70 °C

not by decreasing the flow rate. The concentration was calculated from the experimentally determined permeation rate as a function of temperature performed by PSI previously. The undiluted flow was fixed at a constant pressure in the oven (at 1857 mbar) at 27 sccm. This low flow rate still might cause a degassing problem as you suggest, however, we did not use the “high calibration mode” in our sensitivity analysis. This “high calibration mode” standard was just used to characterize the laser output and determine the optimal mount temperature at which the QCL emits at the HCHO peak at 1721 cm^{-1} .

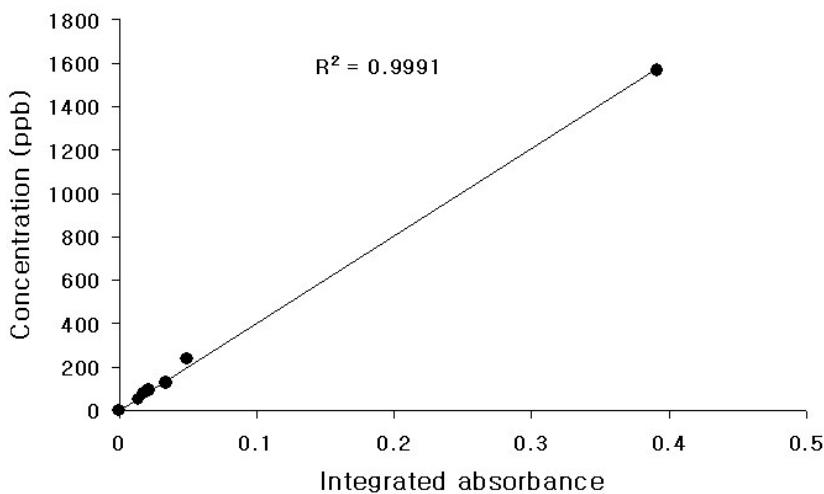
Also in fig. 1, there is enough information to calculate the real absorbance on the right hand axis. Given the cross section in this figure, I calculate an absorbance of ~ 0.12 at 1721 cm^{-1} , assuming the 18.1 ppm is correct. This in turn suggests that the 15-20 ppbv enhanced HCHO mixing ratios observed would correspond to an absorbance around $\sim 1.2 \times 10^{-4}$, which is very useful for the reader to keep in mind. Why not replace the arbitrary absorbances in fig. 1 with real ones?

Response: Unfortunately, we did not perform a full sensitivity analysis for “the high calibration mode” standard. The values on the right axis are arbitrary line absorbance intensities (not integrated) that do not consider the background correction. These values (and their units) are different from the integrated absorbance we derive and report from the ambient spectra and the sensitivity checks. The label presented in this figure may confuse readers and so we changed it to “Arbitrary absorbance intensity”. This experiment was performed solely to find the optimal wavenumber for HCHO absorption and was not intended as a check on the absolute sensitivity.

3. On page 7, the authors indicate standard errors for the permeation scans but no information on how the “high calibration mode” agrees with lower level standards.

Response: The multipoint calibration showed good linearity between observed integrated absorbance and concentrations of HCHO as mentioned in the manuscript.

Although degassing to the cell wall may be a problem in some circumstances, the multipoint comparison shows a good linearity even including the “high calibration mode” indicating that it was not apparent in this particular test (which allowed for approximately 2 hours for the system to equilibrate before the sensitivity reported in the below figures was derived.) Nevertheless, we reiterate that the “high calibration mode” was not used in routine sensitivity analyses, and was only used in searching for HCHO lines because of its easy and rapid detection.



4. The test to look for zero air HCHO contamination is very worthwhile, as compressed gas cylinders can in some cases add as much as several hundred pptv of HCHO. However, are these tests where the cell pressure is changed complicated by the fact that the background optical structure may also change with differences in pressure? The authors should explain.

Response: We concluded there was no change in background optical structure because first, the tests mentioned at ~60 mbar and at 1.8 mbar were conducted within 15 minutes of one another, and secondly the spectra so obtained were very nearly identical. We do not expect that a putative difference in spectral intensities between the two cell pressures would be compensated by changes in the optical structure throughout the entire spectral range. Furthermore, through experience in the lab we never observed a strong sensitivity of the background spectrum to cell operating pressure.

5. On Page 7 in the second paragraph discussing the 8 hour time duration between zero air acquisitions and the assumption of a gradual background change and the validity of using a 9th order polynomial to fit background changes is highly questionable. It is well known from many papers on IR spectrometers using a variety of laser sources that changes in background structure typically occur on minute time-scales not hours. Such changes, furthermore, can be very abrupt depending upon the cause. The net effect of such changes will depend upon the instrument sensitivity and the equivalent background absorbance noise.

Response: We agree that the 8 hour time duration between zero air acquisitions is not optimal, but we believe that the background changes were more or less gradual throughout the experiment because:

- 1) The 9th order polynomial curve fits matched the background spectra for at least 10 minutes during the background scans, throughout the entire measurement period,
- 2) the background spectral structure outside of the HCHO absorption feature, observed at the 8 hr calibration times and during the ambient scans intervening, quite regularly agreed with each other, and
- 3) no abrupt jump or dip in ambient HCHO concentrations was observed within any 8 hour time duration, which is expected if there were an abrupt change in the background spectra.

6. On Page 8, where the HCHO instrument sensitivity of 2.3×10^{-4} ppb⁻¹ is presented does not square with the sensitivity I calculate using Fig. 1, assuming 18.1 ppm. Here I get 6.7×10^{-6} ppb⁻¹, again assuming no errors from cell degassing from the low flows used to generate the 18.1 ppm standards. The authors need to indicate whether or not these “high calibration mode” standards were even used in any of their quantitative determinations. These inconsistencies need to be cleared up.

Response: The absorbance (corrected to “arbitrary absorbance intensity”) presented in Fig. 1 is different to “integrated absorbance” used in our sensitivity analysis and

ambient measurements. The “Integrated absorbance” was obtained from the integration of the differences between ambient and background spectra, that is $\int_{\kappa_2}^{\kappa_1} A dk$, where κ_1 and κ_2 are wavenumbers when HCHO absorption starts and ends, respectively. For example, in Fig. 2, integrated absorbance is obtained by the integration of differences between ambient and background from scan point 40 to 180 (which is equivalent to an interval of 0.1cm^{-1}). Therefore, the direct comparison of sensitivity calculated in Fig. 1 does not correspond to those in sensitivity analysis and ambient determination. In addition, the “high calibration mode” standards were not used in any of quantitative determinations.

Based upon the background differences in Fig. 2 and an absorbance of 1.2×10^{-4} for 18 ppb, I calculate a measurement precision somewhere around 2.3 ppb. I get a completely different result using the sensitivity of $2.3 \times 10^{-4} \text{ ppb}^{-1}$. What does the 1sigma vale of 7.1×10^{-5} in parenthesis represent? Is this the precision of replicate measurements for acquisition of standards? If so, this would imply yet another performance estimate of ~ 0.31 ppb. The optical fringe noise in Fig. 2 gives yet another precision estimate. The authors need to be clear on their minimal replicate precision performance in ppb units. As it stands now this reviewer is totally confused as to what minimum HCHO mixing ratios their instrument can really see during ambient measurements. The discussion in this section only deals with sensitivity change and not imprecision caused by significant background changes. Can the authors provide any replicate precision estimates?

Response: Because the absorbance was obtained from the integration of the spectral difference between ambient measurements and the interpolated background in the ranges of scan points 40~180 ($1720.96\text{--}1721.04\text{ cm}^{-1}$), your calculation based on the line strength at 1721 cm^{-1} is not exactly compatible with our sensitivity evaluation. The reported 1σ value of 7.1×10^{-5} is a standard deviation of the instrument sensitivities obtained during the experiment. We revised that part of the text to make a more clear statement about replicate precision estimates. We

estimated ~14 % of standard error from the sensitivity changes around 25 ppb, which is our best replicate precision estimate, ± 3.5 ppb at 25 ppb. The detection limit was calculated from the optical fringe noise with the signal to noise ratio of 2 (S/N=2). The mean noise level was obtained from the background spectra, and then the Gaussian fit with the same width as ambient HCHO spectra and the height of S/N=2 was obtained to estimate the detection limit to be 2.1 ppb, which is quite large but sufficient to detect the high concentrations of HCHO encountered at Blodgett Forest.

7. Again, returning to the practice of zeroing every 8 hours and the fact that background changes perhaps as large as several ppb in HCHO could result, the authors are adding instrumental noise to their ambient measurements when averaging over 30 minutes. Although the diurnal averages in Fig. 5 look reasonable and there is a clear increase of extra HCHO production in the High Phase, this reviewer still wonders how much of the scatter is instrumental and how much is from the atmosphere?

Response: Even assuming that an abrupt change in background did occur at some point in between background scans, we don't expect these to exceed 3~4 ppb at the very most. However, considering the answer in the previous "comment 5", the actual precision degradation caused by these hypothetical background changes is expected to be much less than those values. Therefore we expect an additional ~15% possible error from the background changes. We added the above descriptions in the revised manuscript.

8. On Page 10 regarding the different temporal profiles of HCHO and O₃ the authors should comment on the finite amount of time it takes to produce O₃ after HCHO is emitted. Also what does "fumigation of the residual layer" mean?

Response: We do not expect much contribution to the HCHO budget from direct emissions at Blodgett, so it is unclear exactly to what time scales the reviewer is referring. The relative growth rates in the midday for both O₃ and HCHO are about

5-10% per hour, and the photochemistry of both is occurring simultaneously. So within a typical 2-3 hour midday lifetime of HCHO, substantial ozone may be produced (~8 ppb.) If the reviewer is simply pointing out a time lag of the peaks between HCHO and O₃, we have added it.

- Fumigation is a term commonly used in the air pollution literature meaning the process of mixing air from the residual layer aloft into a newly developing boundary layer. We restate this in the revised manuscript for added clarity.

9. Bottom of Page 11: Given that there is still some controversy regarding the nocturnal OH and the possibility of unknown spectral interferences in the LIF OH measurements, it would be worth commenting on this here.

Response: We cannot find any signs of said controversy regarding the unknown spectral interferences in OH measurements in the published literature. There is also preliminary data from the HO_x coauthors that additional diagnostic testing during BEARPEX 2009 provided further evidence for the validity of the nocturnal measurements (Elevated nocturnal OH is still the subject of ongoing verification and testing). Without any paper trail of the controversy we feel uncomfortable bringing this issue up in this particular work.

10. Does the HCHO calculation of Eq. 4 include the growth in boundary layer height other than the loss term due to dry deposition? Please explain.

Response: The growth in boundary layer height was not included in Eq. 4. However, the calculation was started from 10:00 am PST with the initial [HCHO] from 09:30 am. According to sonde measurements conducted in BEARPEX 2007 and 2009 (Choi et al., in preparation), the boundary layer is already well developed by that time, and thus the growth in boundary layer height is not expected to significantly affect the HCHO levels directly for the interval under consideration.

11. Page 17: Please define ABL

Response: Added the definition of ABL (atmospheric boundary layer) in the revised version

12. Page 19: perhaps the authors should also list the maximum in the missing production term for the hours only between 10 and 15. From Fig. 12 this missing term looks to much larger than 0.8 to 1.3 ppb hr⁻¹.

Response: Corrected in the revised manuscript. The results came from the average diurnal profiles. Thus, we think it better to present averaged levels of missing sources rather than the certain value at a specific time. We revised the averaged values for 10:00~15:00 instead of the current 10:00~18:00 interval.