Review of ACPD Manuscript

“Observations of Elevated Formaldehyde Over a Forest Canopy Suggest Missing Sources from Rapid Oxidation of Arboreal Hydrocarbons”

By Choi et al.

This paper thoroughly discusses HCHO production and destruction sources during the BEARPEX summer 2007 campaign in the Blodgett Forest. The authors did a very nice job of considering the various terms in the HCHO budget equation. The paper is generally well written and is very appropriate for ACPD. However, this reviewer does have concerns regarding some of the discussions related to the QCL measurements of HCHO, and these need to be clarified before final acceptance. Although these concerns are related to the measurement precision and accuracy of the HCHO results, the author’s arguments for missing HCHO sources is very compelling. The concerns raised by this reviewer do not question the conclusions of this paper, but are raised to improve the clarity and consistency of the paper.

Specific Comments

1. Page 6, Section 2.2.2: The authors should briefly expand on their description of the “independent gravimetric” tests. 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 linewidth affect these determinations? Were these measurements carried out on the “high calibration mode” standards? If so, issue 2 below calls into question the accuracy of this approach.

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 are 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? 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?

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.

4. The tests 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.

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.

6. On Page 8 where the HCHO instrument sensitivity of $2.3 \times 10^{-4}$ ppb$^{-1}$ is presented does not square with the sensitivity I calculate using Fig. 1, assuming 18.1 ppm. Here I get $6.7 \times 10^{-6}$ 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. Based upon the background differences in Fig 2 and an absorbance of $1.2 \times 10^{-4}$ for 18 ppb, I calculate a measurement precision somewhere around 2.3 ppb. I get a completely different result using the sensitivity of $2.3 \times 10^{-4}$ ppb$^{-1}$. What does the 1sigma value of $7.1 \times 10^{-5}$ in parenthesis represent? Is this the precision of replicate measurements for acquisition of standards. If so, this would imply yet another performance estimate of $\sim 0.31$ 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?

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?

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?

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.

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.

11. Page 17; please define ABL (arboreal boundary layer?)

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.