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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term tropospheric formaldehyde concentrations deduced fromground-based fourier transform solar infrared measurements" *by* N. B. Jones et al.

N. B. Jones et al.

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Reply to Referee 2 for the manuscript by Jones et al, "Long-term tropospheric formaldehyde concentrations deduced from ground-based fourier transform solar infrared measurements"

We thank the referee for their very helpful and thoughtful comments on our manuscript. The manuscript has been extensively modified, particularly the modeling section, in response to the comments made by both referees. In the following reply, we have outlined the referee comment that needs a response in italics, while our answers are in normal text.

Specific comments: The introduction on the HCHO chemistry focusses polar regions

above snow surfaces, which might not be so important for Lauder. It would be helpful for the discussion of the HCHO sources to also indicate the photo-chemistry of (biogenic) VOCs as the main precursors for HCHO. Moreover, in section 3.2, the biogenic precursor isoprene is discussed, but not snow and ice surfaces.

The introduction has been rewritten and expanded, and reference to polar chemistry has been removed.

Why was the function for HCHO(t) taken in the form of Equation 1 with 7 fitted parameters? Later it is stated that the semi-annual and square parameters are not significant.

The function used to fit the data has been simplified to an offset, linear trend and annual cycle. This is now described in the text, table 3 modified to reflect these new coefficients, and figures 2, 3, and 9 (and the computations to produce them) redone.

Therefore, I suggest to use a simpler function. Gautrois et al. (2003) discussed the form of the function for seasonal cycle and trend; they applied Bootstrap re-sampling to independently determine the estimated standard deviations of the seasonal and trend part of their fitting function. Table 3 (Total column vs. FTS) already adverts that re-sampling would increase the errors of the parameters.

As suggested by the referee, a boot strapping algorithm was applied to our data. In all cases, except for the phase, the bootstrapping results were very close to the original non-linear fit (to within 1%). The phase determination, the one parameter most sensitive to noise, changes from typically 17 to 22 days, still within the estimated errors of both techniques (4-12 days). We added the following text to explain this test.

"To test the accuracy of the retrieved coefficients and estimated error terms, a bootstrapping test was used (Gautrois et al., 2003). The non-linear fitting procedure was repeatedly called (n=200) with the HCHO data resampled with replacement. The coefficients and their errors estimated from this pool of results were within 1% of the non-linear fitting results. The exception was the estimation of the phase, which differed

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by 4-5 days, but still within the estimated error limits."

Figure 9 shows the correlation of HCHO by FTS versus GOME. The figure would improve if the statistical errors were included as error bars. How was the line fitted to the data, what are slope and intercept of the regression line? Were the errors in both coordinates considered? Please refer to Press et al. (1992) for a discussion of linear regression with errors and the question if the data are consistent with a linear model.

Error bars have been included in figure 9, with the slope and intercept of the regression line reported on the figure as well. The regression line was fitted using IDL routines (gradient expansion method) based on the technique outlined in Press et al (1992) taking into account errors in both directions.

The section on model calculations is not very helpful and does not justify the conclusion that "... high HCHO values cannot be explained by oxidation of CH4 alone." I suggest that the authors run their simple box model with included isoprene chemistry for one year (with spin-up) and perform a sensitivity study with respect to the level of NOX (10ppt, 100ppt, 1ppb, ...), isoprene (off, summer 1 ppb, winter off, ...) and other significant parameters. Pöschl et al. (2000) and Karl et al. (2006) developed a condensed mechanism for the isoprene oxidation with HCHO as one of the products. The HCHO output of the different runs could then be compared to the measurements in an additional figure. Alternatively to own box model calculation on the basis of estimated input parameters, the authors could consider to compare their measurements to existing global model (see e.g. Abbot et al. 2003). In addition these models could be compared to the profile information from the presented measurements.

We have completely rewritten the modeling section to take account of the referee's comments, and no longer claim that "... high HCHO values cannot be explained by oxidation of CH4 alone." . Unfortunately, it is not possible to run the model continuously in time, so we have continued to focus on summer and winter extremes. However, we have included a sensitivity study with respect to the level of NOx, and have estimated

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plausible ranges of NOx mixing ratio using likely ranges of the modeled HO2/OH ratio. We thank the referee for his/her more general suggestions, but at present we do not have the resources to carry out these suggestions.

Minor comments: 1. Figure 2 and 3 could merge into one figure sharing the time-axis.

We considered this suggestion, but it is our view that figure 3 is already quite busy, with 4 plots on the one graph. We felt it better to leave these as two figures.

2. Please use HCHO or CH2O in the entire manuscript.

Corrections made; we have uniformly used HCHO.

3. "Long-term" should be specified when used in the abstract.

The length of the data set in time is stated in the first sentence of the abstract. Since the original manuscript the data has been extended an extra year, so the full length of the data is 13 years, which is clearly stated.

4. Table 3: How can the units of a1 and a2 be molecules cm^{-2}? Was the fit done with error weights?

The units of a1 and a2 are in molecules cm^{-2} yr^{-1}. This has been corrected in the table. The fits for the data in table 3 were done using a non-linear gradient expansion method without weights.

5. Figure 8: red line is nearly invisible.

This figure has been adjusted to make the red line more visible.

6. Figure 9: x-axis and y-axis could cover the same range, or introduce a 1:1-line.

Figure 9 has been redrawn with the axes covering the same range and the 1:1 line added for reference.

References

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Gautrois, M. et al., 2003. Seasonal variability and trends of volatile organic compounds in the lower polar troposphere, J. Geophys. Res., pp. 4393.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14543, 2007.

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Interactive Comment