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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.

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Reply to Referee 1 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 Abstract: - The abstract mentions nowhere that the measurements are performed in the infrared. - The abstract indicates that the time series covers the period 1992 to 2004 whereas Section 2 mentions 1992 to 2005 : this should be made consistent.

The word “infrared” has been added to the first sentence, and the dates and time span corrected to be consistent with section 2 (where the time span has been adjusted to 13 years).

- Why is so much attention paid to formaldehyde in polar regions, if the paper deals with observations at a mid-latitude station ?

The introduction section has been rewritten, particularly the section on polar HCHO which has been removed. Instead an expanded discussion on HCHO chemistry more relevant to the mid-latitudes has been added.

Moreover (Rinsland et al., 2003) is not a relevant reference as it does not deal with H2CO.

This reference was meant to show the extensive existing IR datasets that could potentially be used to quantify HCHO. It was clearly poorly worded. This section has been reworded to say that while there are extensive measurement programmes in ground based FTIR, few have been analyzed for HCHO. The reference to Rinsland has been removed.

The isoprene source that is discussed later in Section 3.2 is not mentioned at all in this introduction. Isoprene is now specifically mentioned in the introduction.

- As an advantage of the FTIR measurement technique, it is mentioned that H2CO and CO can be measured simultaneously. (1) This is not exactly true as they are measured normally in two different optical bandpasses (unless the measurement setup at Lauder is not the typical NDACC one), and (2) this feature is not exploited further in the paper. So why mention it ? More important question: Could this feature not be exploited to

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identify the origin of the high H2CO columns that are observed e.g., in 1999, 2000 and 2002 ?

The referee is quite correct in pointing out that the measurements of HCHO and CO are strictly not simultaneous. Therefore this sentence has been removed. High amounts of both HCHO and CO have been recorded at times in data from Lauder. The referees question does highlight ongoing research; this is currently the topic of another study to address specific aspects of the data, including the origin of high HCHO columns using CO, and other measures, of air parcel history.

- Line 28: I would prefer "FTIR method" instead of "gb-FTS" , because that is more specific. -

The term suggested might include a range of FTIR applications, both remote sensing and laboratory based. Our use of the term gb-FTS is meant to be quite specific to the application of an FTIR system on the ground.

From the introduction, one gets the impression that the paper includes only 3 sections, not 4.

We have added a sentence, in the introduction, that mentions the summary and conclusion as section 4.

- I believe that the introduction should include some more information about alternative ground-based measurement techniques for H2CO, as compared to FTIR solar absorption measurements. This has been added to an amended introduction.

Section 2: - Pg. 14546, Line 9: change the sentence to "The instrumentation and history of the monitoring program at Lauder are described ..." done

Pg. 14547, Line 1 mentions interferences from CH4 and N2O whereas Table 1 mentions CH4 and O3 => ?? - The table has been corrected, the text was correct.

It should be added which spectroscopic data have been used in the retrieval.

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The following sentence has been added to section 2; “The HITRAN 2004 line parameters (Rothman et al., 2005) were used in the analysis.”

A discussion of the uncertainties on the spectroscopic parameters for H2CO would be welcome, especially to justify the assumptions made in the estimation of the systematic uncertainties in Section 3.1.

The following lines have been added to the text to explain where the systematic spectroscopic error estimates were obtained from, including the specific reference where the original HCHO line parameters were computed. In doing so it was discovered that the original text had inadvertently exchanged the line strength and line width errors. This was a typographical error. The text now reflects the correct numbers (5% line strength and 10% line width). “These systematic spectroscopic errors were based on the reported uncertainties from HITRAN, (Rothman et al., 2005), who reported 2-5% uncertainties in the line strength based on reported literature values. The air broadened half widths for HCHO have remained to same since the earliest versions of HITRAN (Rothman, 1981) based on the earlier work of Tejwani and Leung (1977). In this later report, the air broadened half widths were computed for a range of lines and compared with a limited number of experimental values, and were found to agree to approximately 10%. The adopted number in HITRAN 2004 of 0.107 cm^{-1} atm^{-1} is weighted by line intensity as reported from Table 2 of Tejwani and Leung (1977). All errors in this current paper are listed in Table 2.”

- Pg. 14548 Line 7: I wonder whether the separation of the partial columns into 0-3 km and 3-12 km is a good choice, taking into account that the DOFs for the 0-3 km column is smaller than 1 (see Table 2) and that the averaging kernel does not peak at the correct altitude (see Fig. b). I believe that this partial column cannot be considered semi-independent. It might be better to consider a thicker lower partial column (e.g., from 0 to 6 km) ?

The choice of 0-3 km interval was driven in part by the information content, which the

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referee correctly points out is less than 1.0 in these layers) and our desire to compare these data with a chemical box model. As it happens, the averaging kernel for a layer from 0-6 km is very close to the total column kernel. The strong fall off in the HCHO mixing ratio with height means that we have the difficult balance between choosing layers that are too narrow, and hence loss of independence, and layers that are too wide, and become in effect a total column. In general it is very difficult to compare a mixing ratio derived from a total column to model mixing ratio. On this basis we have chosen the former option, that is, choosing a narrower column that can be compared with model calculations, and at the same time, has reasonable information content.

Section 3.1 - Pg. 14548, lines 17-18: The systematic error on the monthly mean should be identical to the systematic error on each individual data point. This is not what is obtained by the approach explained here, taking the total (random + systematic) errors per individual data point.

We have separated out the random and systematic errors as suggested and reproduced figures 2, 3, and 9 with new error bars that reflect the systematic error on the monthly mean being identical on each data point.

- Pg. 14549, lines 1-3: justification for assumed uncertainties on line strength and air broadening coefficients ? (see remark about spectroscopic databases above) - This point is addressed above.

Equation 1: t should be (t - 1992.2) and normalized to 1 year to have the correct units as given in Table 3?

Correct. The equation in the text was misleading as the original calculations did use the method suggested by the referee. The equation has been modified to a simpler form, and the accompanying text also changed to correctly describe the meaning of the parameter “t”.

- Pg. 14549, lines 21-22: “The error bars in Fig. 2...”: I don’t understand what the

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significance of this information is at this point in the discussion ?

These sentences have been removed as they do not add any useful information and do seem out of place given the expanded discussion in the previous paragraph.

- Pg. 14550, line 5: can you be more quantitative than "very high values of H2CO"? Moreover, the high values that do not follow the seasonal fit seem to occur always around December: does that agree with the biomass burning season in Australia?

We have modified the text to be more quantitative. While the fire season in Australia nominally starts in late spring, some of the worst fires on record have occurred mid-summer. The material in question has been rewritten as follows: "Most of this interannual variability corresponds with local biomass burning events. Long range transport of biomass burning plumes from Australia, associated with particularly severe burning events in New South Wales (Paton-Walsh et al., 2004; Paton-Walsh et al., 2005) during austral summer months (with very high values of associated HCHO concentrations up to 20 times above background), are a possible source of HCHO over Lauder. This is discussed further in section 3.2.2."

- Pg. 14550, line 14: the reference to Notholt, 2000 is not relevant here! The correct references would be Notholt, 1997a and 1997b. This has been corrected.

Section 3.2: - Par. 5: Are the given mixing ratios from the model surface mixing ratios or mean tropospheric mixing ratios? How should one compare these values to the 0-3 km and 3-12 km mixing ratios in Fig. 3? -

The modeling section has been largely rewritten and significantly expanded. The answer to the specific question from the referee is found in section 3.2, paragraph 2, where the discussion related to NOx concludes with the following: "For comparisons with our model results we calculated monthly averages of atmospheric HCHO mixing ratios from the HCHO profiles measured by FTIR over the 13 year time period. We used the lowest layer of the FTIR measurements ranging from 0.1 to 3 km. The maxi-

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mum observed 13-year mean HCHO mixing ratio occurred in January (summer) at 870 ppt and the minimum observed 13-year mean HCHO mixing ratio occurred in August (winter) at 350 ppt HCHO (Figure 4). Based on the degrees of freedom for the signal from the FTIR measurement conditions, the retrieval algorithm very likely underestimates the HCHO mixing ratios below 1 km. Thus the 13 year mean values are likely to be underestimates of the actual HCHO values in the bottom 1 km of the atmosphere where the box model is applied. We also assume that the main source of HCHO is located at the surface. ”

Last line: it is said in the introduction that H2CO has an atmospheric lifetime of a few hours: can it then be transported from Australia directly or is it the precursors that are transported?

The short-term and longer-terms sources of HCHO paint a complicated picture. While it is true that the lifetime of HCHO is only 5 hours near the ground, this is only part of the story. Around half of the total HCHO production from fires occurs within the first day (Stavrakou, T. et al., 2008). The balance comes from other HCHO precurors that are slower reacting. There are other possible effects as well; the smoke plume itself masking out sunlight and therefore lengthening the nominal 5 hour lifetime. The following sentence has been added to the end of section 3.2.2. “While HCHO has a short lifetime of 5 hours near the surface, only 50% or so of HCHO production from fires occurs during the first day (Stavrakou et al., 2008), while the balance is produced from other HCHO precursors, for example, ethene, methanol, and acetic acid that are also produced in the fires with lifetimes of several days.”

Section 3.3 - Pg. 14552, line 26: ’with a mean slant column fitting uncertainty...’: I think that the word ’slant’ is missing. If so, what is the final uncertainty on the vertical column due to the additional uncertainty on the air mass factor?

The word slant was missing in this sentence and has therefore been added to the text. The following sentence was added to describe the final uncertainty on the vertical

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column: “For a typical scene over Lauder with a vertical column of 1x10^{16} molec cm^{-2} and an AMF of 0.91, the overall uncertainty on the vertical column is 0.7x10^{16} molec cm^{-2}.”

- How exactly are summer/ winter seasons defined?

Assuming that the referee is referring to section in the text (3.3 paragraph 2) that computes the averaging kernels (Figure 7), the scattering weights that are required are calculated from a radiative transfer model. We found that the scattering weights (function of surface pressure, surface albedo, and aerosol optical depth) were similar throughout the year. We therefore used scattering weights from the months of January, and July of 1999, and computed a mean averaging kernel for two broadly defined seasons.

- Pg. 14554, lines 5 to 7: why taking a monthly mean for the gb FTIR data and a running 21 day mean for the GOME data? Why 21 days? -

The 21-day running mean represents the best temporal resolution we could provide from the GOME data - originally we wanted to show the data at a higher than monthly resolution. We did not want to provide discrete time means because we would miss intramonthly structure associated with fires. The following sentence was added to the paper to clarify this point. “Figure 8 shows monthly mean smooth gb-FTS total columns along with GOME total columns over the time period 1996-2001. The GOME data has been smoothed with a 21-day filter to reduce noise on a sub-monthly timescale, and regridded spatially to match all gb-FTS monthly mean data points, resulting in 51 data points over the five year period studied.”

The Gratien et al., 2007 compare IR and UV cross sections for H2CO? but the IR X sections are not taken in the same wavelength region as the one used here. Therefore the question arises whether the conclusion from Gratien et al can be adopted as such ?

The paper by Gratien et al points out that a 20% over estimation of the HCHO column

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occurs for studies that use the UV-cross section data of Cantrall et al 1990 (Cantrell, C.A., J.A. Davidson, A.H. McDaniel, R.E. Shetter, and J.G. Calvert, Temperature-dependent formaldehyde cross sections in the near-ultraviolet spectral region, J. Phys. Chem. 94, 3902-3908, 1990.). The Gratien paper concludes that the most reliable cross section data is that of Meller and Moortgat (2000) (Meller, R., and G. K. Moortgat (2000), Temperature dependence of the absorption cross-sections of formaldehyde between 223 and 323 K in the wavelength range 225- 375 nm, J. Geophys. Res., 105, 7089-7101.). This latter paper cites a number of studies using infrared spectra that cover the bands used in our study, which are consistent with the Meller and Moortgat 2000 UV cross sections. Since the GOME data used in our study was based on the Cantrall et al cross sections, it is therefore appropriate to use the 20% scaling factor. A sentence to this effect has been added to the manuscript.

Pg 14555, line 25: "A simple box model reproduces the seasonal cycle": this has not really been demonstrated in the paper.

We agree that this statement is misleading. We say instead that the box model estimates summer and winter extreme values.

Acknowledgements: Add the affiliation (BIRA-IASB) behind I. de Smedt. Done.

Table 1:- Is the first window of Step 1 again included in Step 2? - why are the SNR ratios in step 1 about a factor 10 to 20 smaller than in step 2?

The main purpose of step 1 is to pre-fit the main interfering molecules, but not in the sense that they are an accurate representation, but to give a better first guess. Because this is just a crude initial scaling of these interfering species, the window for HDO was included in both.

Fig. 8: last line: what is meant with: "The vertical error bars are mean GOME errors derived from the original smoothed GOME data". What smoothing is referred to here ?

This sentence does appear confusing. The errors bars were recalculated using the re-

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gridded GOME data by a simple perturbation method. The sentence has been rewritten as follows: “The vertical error bars are the GOME errors derived from the regridded GOME data by interpolation”.

Technical corrections: - Abstract line 16: “compare” instead of “compares” Corrected.

- Table 3: Erroneous footnotes with phi1 and phi2 corrected.

- Pg. 14554 line 6: “have” instead of “has” Corrected.

- Pg. 14554 line 18 indicates red dotted line in Fig. 2 which in reality in the figure is a black solid line. Corrected in the manuscript (well spotted by the referee).

- Pg. 14555, line 1: four instead of three outliers are marked with green stars.

Corrected.

References

Paton-Walsh, C. et al., 2004. Trace gas emissions from biomass burning inferred from aerosol optical depth, Geophys. Res. Lett., pp. L05116. Paton-Walsh, C. et al., 2005. Measurements of trace gas emissions from Australian forest fires and correlations with coincident measurements of aerosol optical depth, J. Geophys. Res. Rothman, L.S., 1981. AFGL Atmospheric Absorption Line Parameters Compilation: 1980 version. Applied Optics, 20: 791. Rothman, L.S. et al., 2005. The HITRAN 2004 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer, 96(2): 139-204. Stavrakou, T. et al., 2008. Evaluating the performance of pyrogenic and biogenic emission inventories against one decade of space-based formaldehyde columns. Atmos. Chem. Phys. Discuss., 8(5): 16981-17036. Tejwani, G.D.T. and Yeung, E.S., 1977. Pressure broadened linewidths of formaldehyde. J. Chem. Phys., 66(11): 4915.

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