

## ***Interactive comment on “Global upper-tropospheric formaldehyde: seasonal cycles observed by the ACE-FTS satellite instrument” by G. Dufour et al.***

**G. Dufour et al.**

Received and published: 14 April 2009

The authors thank the referees for their interest in the article and their suggestions for improvements. The comments made are addressed below.

The major point that has been underlined by the both reviews concerns the optimism of the authors about the ability of their data set to help to improve the knowledge of HCHO budget and of HO<sub>x</sub> chemistry in the upper troposphere. The authors recognize that their enthusiasm for these new observations has likely to be toned down and that the limitation of the observations (especially concerning the sampling issue) need to be better stressed. Several changes have been made in the manuscript in order to account for the reviewers' recommendations. They are detailed along the point-by-

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point reply.

Reply to Referee #1:

Comment #1 The last sentence in the Abstract and on page 4 (discussed below) needs rewording. The Abstract statement that the HCHO observations from the ACE-FTS instrument providing a unique data set for investigating and improving our current understanding of the formaldehyde budget and upper tropospheric chemistry; is way too strong given the stated limitations on the retrieved values. The stated error bars on these measurements are 30%; 40% up to 9 km and exceed 100% above 13km, and these values become even larger for mixing ratios below 100 pptv. In addition, the stated vertical resolution is 3-4 km. As written in the Abstract and on page 4 in the paragraph before Section 2 entitled, ACE-FTS Measurements, which reads; provides a new opportunity to improve our knowledge of the HCHO upper tropospheric budget and to better quantify its role in HOx chemistry; implies that the current measurements can successfully address these issues. This reviewer believes that although the current measurements are very valuable in providing extensive seasonal and geographic HCHO coverage throughout the upper atmosphere, the accuracy, precision and vertical limitations make it very challenging to address adequately the HCHO and HOx budgets in the upper troposphere. To do so, requires high precision and high spatial resolution. Hence, these justifications should be toned down somewhat and instead the authors should emphasize the unique aspects of large temporal and geographic coverage.

Reply #1 In order to follow the recommendation of the referee, the last sentence of the Abstract has been removed. The aspect concerning the large temporal and geographic coverage is already covered in the first sentence of the Abstract.

In the Introduction, we have reworded the sentence marked by the referee as follows: "The Atmospheric Chemistry Experiment infrared Fourier transform spectrometer (ACE-FTS) onboard the SCISAT satellite (Bernath et al., 2005) provides a new

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dataset that covers a large time period (3 years are analyzed here) and large parts of the globe compared to previous measurements".

Still in the Introduction, the sentence "Measurements of formaldehyde profiles in the upper troposphere from the ACE-FTS therefore represent a unique data set for investigating this altitude region" has been replaced with "Measurements of formaldehyde profiles in the upper troposphere from the ACE-FTS therefore represent a unique data set for investigating the seasonal variation in this altitude region, with a more specific focus on the mid and high latitudes (better covered by the instrument)".

Comment #2 In the last sentence in the Introduction, reword to read "Under low NO conditions, intermediate compounds like methyl hydrogenperoxide (MHP) may possibly be removed by deposition before reaction with OH takes place";

Reply #2 The correction has been done.

Comments #3, #5, and #6 The next paragraph in the Introduction regarding HCHO production from biogenic sources like isoprene being the dominant source has not been widely accepted. Even though satellite studies suggest this, aircraft and ground-based studies indicate that methane is still the dominant source of HCHO. This should be reworded. The next paragraph on page 3 discussing that considering only methane in the upper troposphere usually does not reproduce the observed HCHO does not square with the latest measurement-model comparisons. For example, the two papers by Fried et al. in 2008 clearly show good general agreement in the upper troposphere, even during some convection events. It was only during very fresh convection, where direct HCHO sources could be important, and in the presence of enhanced NO from lightning that the HCHO observations persistently exceeded the models. Also, the suggestion by Jaegle et al. regarding heterogeneous production of HCHO from methanol is only a suggestion and one that has never really been substantiated by direct evidence other than in clouds affected by biomass burning plumes. Fried et al. [2008] examined this for more pristine clouds and found no evidence for this. Thus, I would suggest

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rewording this section. At the top of page 4, I have no problem with the statements regarding the role of convection in transporting direct HCHO and/or its precursors to the upper troposphere and that there are still some unexplained discrepancies, I do have a problem with the statement that models usually underestimate upper tropospheric HCHO. Again this is not correct (see item 5 above).

Reply #3, #5, and #6 The authors thank the referee for these comments. The former introduction was sometimes not precise enough and also was not well constructed and this leads to misunderstanding, especially concerning the major role of methane in HCHO production. The authors are fully aware that methane is the main precursor of formaldehyde (see the sentence "Methane oxidation is known to be the main source of HCHO in this altitude range") but the construction of the introduction was confusing. The new introduction is now composed of a first part about the role of HCHO in the chemistry (this part include the former first and forth paragraphs), a second part dealing with the sources and sinks of formaldehyde (the main changes are made in this paragraph and takes into account the remarks of the referee, see below how it reads now), a third part quantitatively describing the vertical distribution of HCHO (formerly, p1053, lines 23-27, p1054, lines 1-3) and a fourth part listing the previous aircraft measurements (formerly, p1054, lines 22-26). The other paragraphs have not changed (except the changes already mentioned in the other points).

"Methane is known to be the main source of HCHO throughout the troposphere. However, close to large source regions, the oxidation of non-methane hydrocarbons can make a significant contribution to formaldehyde concentrations especially in the continental boundary layer (Pfister et al., 2008; Stavrou et al., 2008; Dufour et al., 2009). HCHO production from anthropogenic VOCs is most significant in urban areas but production from biogenic sources dominates elsewhere especially during the growing season of vegetation with the largest contribution coming from isoprene (e.g. Palmer et al., 2003; Palmer et al, 2006; Millet et al., 2008). In addition, formaldehyde is also directly emitted into the atmosphere by biomass burning (Lee et al., 1997), incomplete com-

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bustion (de Serves, 1994), industrial processes, and by vegetation (e.g. Kesselmeier and Staudt, 1999; Lathièrè et al., 2006). In the upper troposphere, the altitude range of interest in this paper, Fried et al. (2008b) have determined the contribution of different source species to the total HCHO production. More than 50% of HCHO is produced by methane oxidation. This portion decreases to about 40% in air masses with enhanced concentrations of tracer species and these fractions are in a good agreement with those derived by Stickler et al. (2006) in another region. Both studies reveal the role of convection and lightning (producing additional NO) as an additional source of formaldehyde in the upper troposphere. The non-methane part of HCHO production is mainly from biogenic primary species such as methanol or from secondary species produced from the oxidation of short-lived primary biogenic species like isoprene, and then transported to the upper troposphere. The sinks of HCHO are mainly photolysis and reaction with OH, and ultimately lead to the formation of carbon monoxide and HO<sub>2</sub>".

**Comment #4** At the end of this same paragraph on page 3 in the Introduction, reword to read "The sinks of HCHO are mainly photolysis and reaction with OH, and ultimately lead to the formation of carbon monoxide and HO<sub>2</sub>;"

**Reply #4** The correction has been done.

**Comment #7** On page 4 right before Section 3, the authors claim that the statistical component of their error reduces by the square root of the number of observations. Is the atmosphere really this stable to achieve such an improvement? The authors should provide some justification for this assumption.

**Reply #7** The term of "standard deviation" used by the authors (p 1058, lines 1-2) has likely misled the referee and is replaced by "error" in the new version of the manuscript. The statistical and systematic parts of the observation errors are not based on the calculation of the standard deviation and the rmse of a mean vmr. The errors are explicitly calculated from the retrieval process. A description of the error calculation

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and the meaning of the different terms can be found in Dufour et al., 2006. A reference to the corresponding equations in Dufour et al., 2006 is explicitly done in the new manuscript. To be clear here, we can recall that the statistical component of the error is linked with the noise in the spectra (mainly due to the detectors): the retrieval gives the projection of the noise from the spectral space (in the spectra) to the state space (vmrs). As the noise has a random behaviour (assumed gaussian), it can be reduced by the square root of the number of occultations considered in the average. There is no effective link between this error and the inhomogeneity in the HCHO distribution.

Comment #8 Page 8, 8th /9th lines from bottom change wording to read "Figure 5 shows that ACE-FTS measurements are more representative of background values than the TDLAS in situ measurements whose flight tracks were often driven by the search for plumes and convection";

Reply #8 The correction has been done.

Comment #9 Page 9, 3rd line down, either change the Perrin et al. reference year in the text (2008) to match the 2006 date in the reference list or add the proper 2008 reference in the reference list.

Reply #9 The references have been checked and updated.

Comment #10 The discussion in the 3rd paragraph on page 11 regarding the reason for the maximum observed HCHO during summer in the 6-9 km range needs to be modified. The authors mention that enhanced biogenic emissions from species such as isoprene are likely partially responsible for this in combination with the increase in convection during summer months. Since isoprene has a relatively short lifetime it is unlikely that it can reach such altitudes on a sustained basis and the second cause is more likely. As discussed by Fried et al. [2008a,b], longer lived precursors of HCHO like methanol and methyl hydrogenperoxide can indeed have an influence on upper tropospheric HCHO levels during convection. The authors should consider rewording this section.

Reply #10 The authors agree that the very short lifetime of isoprene likely does not allow its transport up to the upper troposphere. However, some of the secondary products from isoprene oxidation can have a lifetime sufficiently long to be transported up to the upper troposphere and have a significant role in HCHO product. The sentence has been changed in consequence: "The maximum observed in the HCHO distribution in summer is likely related to the maximum in biogenic emissions especially of HCHO precursors like primary methanol and methyl hydrogen peroxide, and potentially the secondary products from isoprene oxidation. In combination with the increase of convection during summer, this allows the transport of HCHO precursors to the upper troposphere."

Reply to Referee #2:

The comments of the referee are not numbered. In the following, comments that can be answered in the same time are grouped together even if they appear separately in the review.

Comment #1 The authors should rephrase the whole paper in a way to clarify that the presented data set has several limitations, not only in terms of accuracy and spatial resolution but in my opinion also in terms of spatial and temporal coverage. Therefore it seems to be very difficult to draw any serious conclusion on possible problems in our understanding of HCHO chemistry in the upper troposphere on a global scale. However, since ACE-FTS provides the first HCHO data set from space for the upper troposphere it is very valuable for case studies in particular in high latitudes. A more general comment: Again I would rather prefer to focus the whole discussion on those regions where the observations have a good coverage than to speculate on universal things. E.g. that GEOS-Chem has in global average a bias of only 2% to the observations seems to be more a godsend than scientific well-founded.

Reply #1 The main concern of the review is the absence of discussion on the limitation of the observations due to the spatial and temporal coverage of the instrument. The

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authors agree that the ACE-FTS does not provide coverage as dense as nadir looking experiments for instance and are aware of the limitations of their dataset in that sense. However, the authors would not be as negative as the referee concerning the interest of the data for providing a global view of UT HCHO. The set of observations, even with coverage and precision limitations, is significantly larger than what is currently available and allows us to make some conclusions on some of the limitations of the models as shown in the paper (bias in the southern hemisphere for the LMDz-INCA, failing to reproduce the spatial variability of the observations for GEOS-Chem). The authors would like to note that the problem of inhomogeneous and low sampling especially in the south tropics and subtropics has been mentioned several times in the discussion (p1055, lines23-24; p1062, lines 11-13, line 21; p1063, lines 16-17; p1064, lines 1-3). Several changes have been done in the manuscript in order to make this limitation point clearer and more apparent in the paper and also to put the focus mainly on the mid-to-high latitudes:

In the Abstract, the sentence "with a particular focus on mid-to-high latitudes that are well sampled by the observations" has been added after "An overview of the seasonal cycle of the upper tropospheric HCHO is given for different latitudes". At lines 16-17, the sentence "fail to reproduce subtropics" has been removed.

In the Introduction, changes have been done; see the reply to referee #1 for details.

In section 2, a figure showing the numbers of occultations considered in each 20° latitude band has been added, as well as an explicit reference to Fig 1 in Bernath et al., 2006 that show the latitude coverage of the observations over one year.

In section 4, the following sentence has been added in the second paragraph: "The rather limited temporal and spatial sampling in the tropics has to be considered in the interpretation of the results. The low sampling of the tropics can lead to a lack of representativeness of the observations for this region." The sentences p1062, lines 21-25 have been replaced by "HCHO values smaller than during JJA and SON are observed

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during the other seasons (DJF and MAM) but the sampling is limited and does not allow a firm conclusion to be drawn." The last paragraph of this section reads now: "As mentioned previously the lack of sampling in the southern tropics and subtropics (Fig. 6) does not allow a firm conclusion to be made concerning the potential temporal variation of the HCHO distribution. However, the tendency given by the observations look consistent with what is expected. The mean vmr over the 2004-2006 period is larger than at other latitudes as expected. This likely reflects a larger production of HCHO from non methane hydrocarbons in the tropics due to sustained biogenic emissions of HCHO precursors during the entire year in this region (Fig. 8). The peak of HCHO during the biomass burning period is more pronounced at 6.5 km compared to 8.5 km (Fig. 7)."

**Comment #2 ACE-FTS measurements:** Here the authors should give more details on the coverage of the measurements. It is not sufficient to mention that the majority of the observations are over the Arctic and Antarctic. What about a table or simple 2D-plot with number of observations for the entire period (or splitted up in years) versus latitude band in 10 or 20 degrees steps?

**Reply #2** As mentioned previously, a figure showing the numbers of occultations considered in each 20° latitude band has been added, as well as an explicit reference to Fig 1 in Bernath et al., 2006 that show the latitude coverage of the observations over one year.

**Comment #3 HCHO is the major intermediate in the degradation of VOCs in the troposphere with most of the source regions close to the equator. How many times ACE-FTS has sampled the African or the South American rain forests?**

**Reply #3** The authors have never mentioned the possibility of providing information and firm conclusions on the main source regions of the equator. They only noted that the large values observed in the UT in the tropical-subtropical band looks consistent with the large sources that can influence this region and also the possible influence of

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biomass burning in the observations taking care of mentioning the sampling issue.

Comment #4 Is there any latitudinal variation in the altitude resolution? What is the variation of this resolution with height?

Reply #4 There are two concepts to consider here. The first is the altitude sampling of the instrument, and the second is altitude resolution.

The altitude sampling does not vary specifically with latitude. Instead it varies as a function of "beta angle", the angle between the satellite's orbital plane and the look-direction to the sun from the satellite. With our orbit, in the tropics you always get a high sampling rate within an occultation (the beta angle is large). As you move away from the tropics, you get an increasingly wider variety of altitude sampling rates.

The altitude sampling rate also varies with altitude. Measurements are collected at constant time intervals. At low altitudes (below about 40 km), refraction effects cause the altitude separation between measurements to decrease. The lower you go in altitude, the smaller the altitude interval between measurements.

So, for occultations with the poorest altitude sampling (beta angle zero), the altitude separation between measurements at high altitudes is about 6 km, decreasing to about 1-2 km in the upper troposphere and lower stratosphere (due to the refraction effects). For occultations with the highest sampling, the altitude separation between measurements at high altitudes is less than 2 km, decreasing to a couple hundred meters in the upper troposphere and lower stratosphere.

Now, when you consider the notion of altitude resolution (rather than sampling), the most conservative approach is to say you can do no better than the altitude range subtended at the tangent point by the instrument's field of view, which is 3-4 km. A recent study published well after this paper was submitted (Hegglin, M. I., Boone, C. D., Manney, G. L., Shepherd, T. G., Walker, K. A., Bernath, P. F., Daffer, W. H., Hoor, P., and Schiller, C.: Validation of ACE-FTS satellite data in the upper

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troposphere/lower stratosphere (UTLS) using non-coincident measurements, Atmos. Chem. Phys., 8, 1483-1499, 2008) suggests that this might be overly conservative, and that with the ACE-FTS you can get altitude resolutions of up to 1 km.

However, rather than consider the implications of that study, we will stick with the conservative approach of saying the altitude resolution is limited by the field of view. To answer the specific comment, the altitude sampling does vary (although not monotonically with latitude), but the altitude sampling in the upper troposphere and lower stratosphere is always better than 3-4 km, so there is no effect on the altitude resolution we would report with this conservative approach.

Comment #5 The authors try to give explanations for several features in the ACE-FTS time series with some of them very hard to understand for the reader. E.g. p1062, l16: "The largest values are in the southern tropics and subtropics with maximum values during the JJA and SON periods near Africa and South America. They reflect the impact of biomass burning in the upper troposphere through either the direct injection of emitted HCHO or of precursors emitted by fires." Sorry, there are some higher values close to Africa and South America (Figure 6), but almost none of them close to biomass burning regions. I'm not going to say that there is no relationship between biomass burning and higher HCHO levels in that region but ACE-FTS observations are too sparse to support this assumption without any further evidence.

Reply #5 This paragraph has been rephrased to be clearer and to add reference to previous studies made with the ACE-FTS that show influence of biomass burning in the observations through the detection of enhanced vmrs of CO, HCN and CH<sub>3</sub>OH.

"Large values are observed in the southern tropics and subtropics especially during the JJA and SON periods near Africa and South America. They may partly reflect the impact of biomass burning in the upper troposphere through either the direct injection of emitted HCHO or of precursors emitted by fires. It is worth noting that enhanced concentrations of CO, HCN and CH<sub>3</sub>OH attributed to biomass burning emissions are

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also detected with the ACE-FTS during SON 2004 (Rinsland et al., 2005; Dufour et al. 2006). The lifetime of HCHO is short but the correlation with CO for the same period remains significant (0.65) and likely reveals the biomass burning imprint in this region."

Comment #6 Moreover, I would conclude from Table 5 and Figures 6 and 7 that highest values were found in "North America" and "Europe-Russia" in JJA.

Reply #6 The largest values observed in the tropics have been checked, of course. They are very localized and then smoothed by the mean. Moreover, the color scale chosen in Fig. 6 does not allow distinguishing these largest values.

Comment #7 In order to study temporal variations in more detail, the authors have defined four different regions. These regions should be marked for better illustration in one of the global plots (e.g. Figure 6).

Reply #7 A figure has been added.

Comment #8 For the selected areas the sampling is quite different depending on season. E.g. in JJA there are much more measurements in the southern parts of both "North America" and "Europe-Russia" regions than in MAM, when most of the observations are carried out close to the Arctic. This will introduce an additional seasonal bias and is not related to changes in emissions.

Reply #8 The authors agree that the difference in the spatial sampling within a region can introduce a bias on the absolute values. We used the LMDz-INCA model to evaluate the bias introduced by this sampling issue. The general seasonal variation is not changed. As expected the values are larger by about 20% on average with a homogeneous sampling. The possible bias introduced by the difference in the spatial sampling between the season remains within the observation errors. A sentence has been added p1063, line 17: "Note also that the uneven sampling of the data can slightly affect the seasonal cycle derived for each region. However, we ensured (by analysis of the model results) that this potential bias is lower than the observational errors." Note

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that this sampling issue does not have any impact for the comparison with the model as the model results are interpolated at the location of the measurements.

Comment #9 Similar to reviewer #1 I have problems with the simple statistical error reduction by the square root of the number of observations when considering inhomogeneous regions like "Europe-Russia" (covering 35 to 80 degrees North!). What is the typical variance of the observations?

Reply #9 See the corresponding response for referee #1

Comment #10 When the authors claim that the inter-annual variation in the HCHO is weak (I would support this), what is the reason for not averaging the data for the different years in Figure 9?

Reply #10 The phrasing may be confused for this part and has been changed as follows: "As the interannual variations seem to be relatively weak (section 4), we provide average seasonal results over the 3 years of analyzed observations and display all the data from the 3 years in a single plot for to show the horizontal distribution."

Comment #11 Why sometimes data points in the observations (Figure 9, upper panel) are missing, while the model data are shown (e.g. Indonesia hot spot in SON)?

Reply #11 The missing points in the observations are for occultations that do not go down enough in altitude. The threshold considered to discard an occultation is 9.5 km for the extra tropical latitudes and 11.5 km for the tropical latitudes. The values presented on Fig 9 are the mean vmrs between 6 and 9 km, so it can happen that an occultation is selected but the altitude range sounded stops above 9 km, but the location is considered as measured for the model without altitude range limitation. As it can be confusing, the figure has been changed and the model results are plotted only if observations are effectively going down enough into the troposphere.

Comment #12 For the negative bias between LMDz-INCA and observations in southern latitudes: why this should be related to the lower methane calculated in this model?

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What is the difference to high northern latitudes during wintertime where modelled methane concentrations are even lower compared to GEOS-Chem but the agreement to the observations much better?

Reply #12 The authors agree that the simple assumption - less methane equals less HCHO - is certainly not so straightforward because less methane also means more OH and then this can significantly change the HCHO chemistry. However, it is sure that the LMDz-INCA model underestimates methane concentrations and this should influence formaldehyde concentrations but likely in different ways (to be determined) depending on the thermodynamic conditions. To establish the actual causes of the disagreement between measurements and simulations additional investigations are needed (but it is not the purpose of the paper). This is why we have changed the phrasing to underline that it is only a hypothesis and further studies are needed to elucidate the reasons for this bias.

Comment #13 Minor points: Table 5, Units missing; Figures 4 and 5 are dispensable; Figures 6 and 9 need a much better output resolution (e.g. 300dpi)

Reply #13 Figure 4 has been removed. Figure 5 is kept for comparison with Fried et al., 2008.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1051, 2009.

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