

***Interactive comment on “Formic acid above the
Jungfrauoch during 1985–2007: observed
variability, seasonality, but no long-term
background evolution” by R. Zander et al.***

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REFEREE # 2

Specific Comments:

[RC] Pages 14779-14780. Section 4 describes the retrieval details for the formic acid analyses. However, I found that this part did not include any discussion of the sensitivity and the information content of the retrieval. I recommend this be added to the paper to give the reader a clearer understanding of the data product. Also, it would be instructive

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to include a few more details (or a reference or two) on the error analysis methods.

[AC] The information content that characterizes the retrieved HCOOH profile is quite poor when its vertical distribution is fitted. This results from the fact that the wide HCOOH Q-branch adopted here (see Fig. 1) contains hundreds of very weak overlapping lines, preventing temperature/pressure sensitivity to be exploited. Therefore, the adopted fitting process consisted in simply scaling the a priori HCOOH profile over its entire altitude span.

For clarification, the ACPD text page 14779, lines 17 and 18 will be rewritten and extended as follows:

“... , in which the distribution of the 2 most important interfering O₃ isotopomers (¹⁶O₃ and ¹⁶O¹⁶O¹⁸O) were retrieved, while the a priori VMR profile of HCOOH characterized in Sect. 2 was uniformly scaled over its entire altitude span. This simple scaling was justified, considering the poor spectroscopic pressure/temperature information content that can be retrieved from fittings to Q-branches containing hundreds of weak overlapping lines. Additional discrete absorptions...”

[[[[[[[[[[With regard to sensitivity limit, we refer to our comments made to a question raised by Referee # 1, namely:

[RC] On page 8, it is explained that a subset of results has been excluded based on objective criteria. I do not understand why a result below a certain threshold should be omitted from a timeseries (if the quality of the measured spectrum and fit etc is ok), as this bears the danger to introduce a high bias in the dataset ?

[AC] ACPD page 14780, lines 1 to 4

Any detection technique (whatever its quality) has a sensitivity limit below which measurements become questionable. In the present HCOOH case, sensitivity calculations showed that the 1×10^{14} molec./cm² was a lower limit below which the columns should be considered unreliable. This was corroborated along the retrieval process, as a large

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fraction of HCOOH columns in the 10^{13} molec./cm² range showed uncertainties exceeding the retrieved columns. Nevertheless, the reviewer's comment is sound, and we have evaluated the maximum positive bias resulting from this assumption. For the Nov-Dec-Jan period, (when most of the sub- 10^{14} molec./cm² cases occurred, namely for 125 out of a total of 2065 column measurements), a high bias was found to account for at most 0.20×10^{14} molec./cm², which translates into a high VMR bias of +2.2 pptv, thus about +5% of the mean N-D-J background level. During the rest of the year, the bias is negligible, as only a couple of total columns fell below the 10^{14} molec./cm² limit.

In response to this reviewer's comment, we shall insert the following texts on:

P. 14780, L. 2: "...with respect to the spectral S/N ratio, and all HCOOH columns falling in the 10^{13} molec./cm² range (most of which showed fitting uncertainties near or exceeding the retrieved columns). The 10^{14} molec./cm² level which was established through spectroscopic calculations as being a reasonable sensitivity limit for our HCOOH retrieval approach may, however, introduce a slight positive bias which will be estimated in the next section."

P. 14781, L. 21: following the sentence ending at the end of this line, we shall add the following text:

"The positive bias resulting from our rejection of columns below the adopted sensitivity level of 10^{14} molec./cm² (see Sec 4) was calculated to be at most 0.020×10^{15} molec./cm², thus only about 5% of the mean N-D-J background value derived here, and well within the associated standard deviation. During the rest of the year, the bias is negligible, as no columns fell below the 10^{14} molec./cm² limit."]]]]]]]]]]

With regard to our error analysis method and rejection of suspicious spectra, we believe that we have provided details in line and commensurate with other recent HCOOH-related publications. In this context, however, we shall make further reference to Remedios et al. (2007), by rewriting the end of Section 4 as follows:

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P.14780, L. 17-23:

'Overall, they are commensurate with those reported in similar researches by Rinsland et al. (2004) and by Remedios et al. (2007) which are evoked in Appendix A. One exception, however, namely the new HCOOH spectroscopic ν_6 band intensity adopted here being only affected by a systematic uncertainty of less than 7% (Vander Auwera and Perrin, 2007), as compared to 12% for the older band intensity used by Rinsland et al. (2004) and by Remedios et al. (2007), both of which are further biased by the systematic factor 2 discussed in Sect. 3.'

[RC] Page 14781, Lines 14-15. Were specific criteria used for eliminating outliers? If so, this should be described. With the density of points in Figure 2, it was difficult to see these example points to figure out the criteria used.

[AC] This page deals primarily with the determination of a mean daytime background loading of HCOOH above the Jungfraujoch during N-D-J, and reasons for rejecting some data points.

Lines 14-15 will be rewritten as follows:

'... as well as a few abnormally high outliers (i.e., 21 January 1996, 16 November 2006 and 14 January 2007, which exceeded by over a factor 4 all other daily mean columns measured during these specific months), a linear adjustment to...'

[RC] Page 14783, Lines 16-21. It would be helpful if the authors could provide an uncertainty estimate for their values obtained from the fits of the AM and PM data for each month range for this part of the discussion.

[AC] Due to time limitation, it has only been possible to deal with this matter for a subset of the data considered in this section. The outcome of this limited evaluation will be inserted at the end of Page 14783, Line 25, as follows:

... in Table 3. 'An estimate of the statistical significance of the mean AM increases and PM decreases, was established by application of the bootstrap resampling method de-

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scribed by Gardiner et al. (2008) to the 3 pairs of lines featured in Fig. 4, namely for N-D-J, May, and J-J-A. During the morning, the column increases (expressed in $\times 10^{13}$ molec./cm² per degree of zenith angle change) and their 2-sigma uncertainties were found equal to $(+0.81 \pm 0.25)$, $(+0.79 \pm 0.34)$ and $(+1.24 \pm 0.49)$, respectively for N-D-J, May, and J-J-A. The corresponding PM decreases were equal to (-0.26 ± 1.2) , (-0.66 ± 0.43) and (-1.34 ± 0.52) . With the exception of the PM decrease for N-D-J (which is severely biased due to missing low sunset observations above 80° zenith angle), all other examples show that the diurnal modulation of the free tropospheric HCOOH loading can be quantified statistically, despite the high short-term variability characterizing the present database.

[RC] Page 14784, Lines 23-26. It was a bit unclear which of the previous references this

information was taken from. It should be rephrased to make it clearer.

[AC] The sentence will be rephrased and expanded as follows:

‘Overall, the observed seasonal modulation of the HCOOH loading is also in phase with the solar insolation cycle measured at the Jungfraujoch by the Swiss Federal Office of Meteorology and Climatology (<http://www.meteoswisse.admin.ch>), and with the water vapor content above the Alpine Plateau which we monitor as part of our involvement in the NDACC; however, it is off-phase with our observed seasonal modulation of CO₂ above the site (Zander et al., 2008) whose minimum is an indicator of photosynthesis activity during springtime (a feature already evoked by Talbot et al. (1997b; see Appendix A) .

[RC] Page 14796, Lines 27-29. The Hartmann et al. (1989) results seem not to be included in Table 4. Is there a specific reason to omit this work from the tabulation?

[AC] Our manuscript was not intended to be an exhaustive review of all past HCOOH investigations. For Table 4 to fit on one page (with reasonable fonts), we decided to

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list relevant activities published after 1990, although earlier ones such as Goldman et al., (1984), Hartmann et al., (1989), were referred to in the text, but not in Table 4 (they have already been tabulated in earlier reviews, e.g., by Khare et al., 1998; Kesselmeier and Staudt, 1999).

Consequently, we have rewritten the header of Table 4 as follows:

Table 4. ‘Time-coincident comparison of recent relevant free tropospheric concentrations of HCOOH at Northern mid-latitudes with mean values above the Jungfraujoch (all in pptv).

[RC] Page 14810, Table 4. Here it was nice to see all of the formic acid results presented together. However, it was unclear what uncertainties were presented in the table. The authors should be clear in specifying if these are 1-sigma standard deviations, fitting errors etc. It would be helpful if the location of the MIPAS-B2 flight was listed here and in the text. It was not clear to me what "partim." refers to in the PEM-west and SCISAT row entries. Also, should the Jungfraujoch comparisons with the PEM flights be listed with the 2-7 or 7-12 km results?

[AC] All reported uncertainties correspond to 1-sigma standard deviations, except ⁽²⁾ for Reiner et al. (1999), Singh et al. (2000) and González Abad et al. (2009), whose uncertainties were estimated from Figures, and ⁽³⁾ those for Remedios et al. (2007), which correspond to systematic errors. These informations will be provided at the bottom of Table 4.

‘partim’ will be replaced by ‘subset’

We have listed the Jungfraujoch comparisons next to the 2-7 km PEM results, as the largest fraction of the measured HCOOH loadings above the site is located between 3.6 and 7 km altitude.

Technical Corrections:

[RC] Page 14772, Line 6; Page 14780, Line 5; Page 14786, Line 15. The paper uses

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two numbers for the total number of days included in the dataset. It appears that at first there were 1537 days and this was reduced to 1501 days after filtering based on the quality of the spectral fitting. I think that a consistent number should be used to describe the dataset used in the analyses while providing the details of how many spectra were not of suitable quality.

[AC] P. 14772, L. 6: In the Abstract, ... 'over 1537 days'..., will be replaced by 'over 1500 days'.

P. 14780, L. 5: we shall maintain ... 'encompassing 1501 days'.

P. 14786, L.15: we shall replace ... 'during 1537 clear-sky days'..., by 'during over 1500

clear-sky days'...

[RC] Page 14776, Line 26. The word stratospheric is repeated twice in this sentence.

[AC] ... 'and stratospheric'..., will be deleted (this was an editorial typographic error).

[RC] Page 14776, Line 22; Page 14797, Line 10; Page 14810, last line of table. A consistent acronym should be used for SCISAT.

[AC] In all 3 places, 'SCISAT' consistency will be ensured (as also requested by Referee 1).

[RC] Page 14777, Lines 14-15 and 22. Dashes should be removed when commas are used.

[AC] Dashes will be removed in all 3 lines identified by the Referee

[RC] Page 14778, Line 13. An "and" is missing between final two citations.

[AC] An 'and' will be inserted as requested, i.e., ... '2006 and 2007')...

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[RC] Page 14779, Lines 17 and 27. Two and six should be used instead of 2 and 6.

[AC] 2 and 6 will be spelled out.

[RC] Page 14780, Line 26. Suggest "...in Fig. 2a, while Fig. 2b...".

[AC] We agree with the Referee's suggestion and shall implement it.

[RC] Page 14782, Line 4; Page 14784, Line 22; Page 14787, Line 26. The quarterly averages are defined explicitly always for J-J-A and sometimes for N-D-J but never for S-O-N. This should be done consistently through the paper.

[AC] On P. 14781, L. 9-10, we mentioned our abbreviation approach for successive month groupings. As was done for N-D-J and for J-J-A at their first use, we shall do the same for S-O-N,

namely P. 14784, L. 22 as follows: ... 'The September-October-November (S-O-N) decrease...';

[RC] Page 14783, Line 17. Suggest "shown" instead of "featured".

[AC] OK, 'featured' will be replaced by 'shown'.

[RC] Page 14785, Line 6. Suggest "obtained" instead of "performed".

[AC] The suggested replacement of 'performed' by 'obtained' will be made.

[RC] Page 14772, Line 9; Page 14785, Line 17; Page 14785, Line 17; Page 14810, Table 4. Use "time-coincident" rather than "timely".

[AC] After consulting an OXFORD Dictionary, some nuances will be added to the recommended 'timely' replacements, namely:

P. 14772, L. 9: by 'time-evolving'...

P. 14785, L. 17: by 'most appropriate time-coincident Jungfrauoch findings...'

P. 14810, Header of Table 4: by 'Most appropriate time-coincident comparison of ...'

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[RC] Page 14786, Lines 16-18. Suggest rephrasing for clarity. "... has allowed various aspects of the free tropospheric loading of formic acid (HCOOH) to be characterized above the...".

[AC] The rephrasing will be implemented as suggested by the Referee.

[RC] Page 14786, Line 23. "two-step" rather than "two-steps".

[AC] 'two-steps' will be replaced by 'two-step'

[RC] Page 14788, Line 8-10. I am not sure what is really meant in this statement by "reactualized". It should be made clearer.

[AC] In response to this remark, we have rewritten the sentence as follows:

'However, numerous recent Northern mid-latitude HCOOH-related findings listed in Table 4 show that the infrared remote sensing approach has again been successfully implemented in applications based on either the solar occultation- or the thermal limb emission mode, using primarily fast FTIR spectrometers.' In particular,...

[RC] Page 14788, Line 17. should be "...to achieve optimal complementarity...".

[AC] Suggestion adopted.

[RC] Page 14790, Line 6. Here "trough" should be "through".

[AC] Correction adopted.

[RC] Page 14791, Line 1 and 23. Minimum and maximum should not be abbreviated here

to be consistent with the rest of the paper.

[AC] Throughout the manuscript, 'max.' and 'min.' will be replaced by 'maximum' and 'minimum'.

[RC] Page 14791, Lines 11-15. The measurement method should be mentioned to

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ensure that the reader is clear on the technique being discussed.

[AC] The measurement methods as well as an additional reference will be mentioned as follows:

'Earlier HCOOH investigations (e.g., Talbot et al. (1989), from in situ air samplings in Virginia, USA; Arlander et al. (1990) from in situ air samplings along a sea cruise in the Pacific- and Indian Oceans; Moody et al. (1991), by the chemical analysis of precipitations at Amsterdam Island; Baboukas et al. (2000) from in situ air samplings during a N-S Atlantic sea cruise) suggested some evidence for a seasonal variation, with maxima during local summer and minima in winter, but their significance was statistically weak, because of time limited campaigns.'

[RC] Page 14791, Line 19. Should this be "chaotic" rather than "cahotic"?

[AC] The OXFORD dictionary indicates that 'chaotic' is in line with the French 'cahotic' meaning. Replacement will be done.

[RC] Page 14792, Line 29. Acronym PEM should be defined at first usage.

[AC] Will be defined at this first usage as 'Pacific Exploratory Mission'.

[RC] Page 14793, Line 6. "cruise" rather than "cruse".

[AC] 'cruse' will be replaced by 'cruise'.

[RC] Page 14794, Lines 8-11; Page 14797, Lines 3-5. These statements should include a reference to the Jungfraujoch location to be clearer to the reader.

[AC] will be done in both cases as;

P. 14794, L. 8-9: 'The mean tropospheric VMR concentration above the Jungfraujoch read off the thick curve of Fig. 3 for...'

P. 14797, L.2-3: 'The mean HCOOH concentrations above the Jungfraujoch read off the thick curve of Fig. 3 for the periods...'

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[RC] Page 14794, Lines 15-19. The location of the MIPAS-B2 measurements should be

included in the discussion here.

[AC] The location, as reported by Remedios et al. (2007), namely ‘...in the upper troposphere over the Western Mediterranean region’ will be included in Line 15-16.

[RC] Page 14795, Line 5. Acronym SONEX should be defined when it is used first.

[AC] Will be defined at this first usage as ‘Subsonic Assessment Ozone and Nitrogen Oxide Experiment’.

[RC] Page 14795, Line 20. There should not be a space between the _ and 17.

[AC] To be corrected as ‘... 39±17 pptv. ...’

[RC] Page 14796, Line 8. "February" rather than "Februar".

[AC] Yes, ‘Februar’ to be replaced by ‘February’.

[RC] Page 14813, Last line of caption for Fig. 3. Should this only refer to Sec. 5?

[AC] The submitted manuscript showed: ... ‘Section 5, § 2 and 3’. The revised text will read: ‘For details, see Sect. 5, Paragraphs 2 and 3.’

[RC] Page 14815, Table 1. “a priori” should not have any italicized letters.

[AC] Table 1 is found on Page 14807. The italic ‘*a*’ in the second ‘HCOOH *a priori* profile’ will be replaced by a normal ‘a’.

In this same Table 1 (and since the early manuscript distribution and submission, the ‘O’ in the Remarks column associated to the line “Other interferences” should obviously be replaced by ‘O₃’, and this will be done.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 14771, 2010.

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