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

R. Zander et al.
R.Zander@ulg.ac.be
Received and published: 10 September 2010

[RC] A figure showing the a-priori and the column sensitivity might be useful.

[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 HCOOH Q-branch adopted here 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 . . .”

[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 1x10¹⁴ molec./cm² was a lower limit below which the columns should reasonably be considered unreliable. This was confirmed along the retrieval process, as a large fraction of HCOOH columns in the x10¹³ 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- 1x10¹⁴ 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 0.20x10¹⁴ 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 1x10¹⁴ molec./cm² limit.

In response to this reviewer’s comment, we shall inserted the following texts on:
"...with respect to the spectral S/N ratio, and all HCOOH columns falling in the \(1 \times 10^{13}\) molec./cm\(^2\) range (most of which showed fitting uncertainties near or exceeding the retrieved columns). The \(1 \times 10^{14}\) molec./cm\(^2\) 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."

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 \(1 \times 10^{14}\) molec./cm\(^2\) (see Sec 4) was calculated to be at most \(0.020 \times 10^{15}\) molec./cm\(^2\), 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 \(1 \times 10^{14}\) molec./cm\(^2\) limit."

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