Atmos. Chem. Phys. Discuss., 7, S6842–S6848, 2007
www.atmos-chem-phys-discuss.net/7/S6842/2007/

Atmospheric Chemistry and Physics Discussions

ACPD
7, S6842–S6848, 2007

Interactive Comment

Interactive comment on "Growth rates of stratospheric HCFC-22" *by* D. P. Moore and J. J. Remedios

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Received and published: 13 November 2007

We thank referee number 2 for his helpful and constructive comments on the paper.

Reply to specific comments:

1) page 10516, line 17: CFCs are not only destroyed by photolysis. For some CFCs the chemical decomposition by atomic oxygen is also a loss mechanism, e.g. (Brasseur et al., "Atmospheric Chemistry and Global Change").

The sentence: "The CFCs are chemically inert in the troposphere and destroyed only in the stratosphere by photolysis." has been replaced by "The CFCs are chemically inert in the troposphere, destruction in the stratosphere can occur either by photolysis or by reaction with O(1D) (Brasseur, 1999)."

The book "Atmospheric Chemistry and Global Data" by Guy Brasseur has been added

EGU

to the list of references.

2) page 10529, line 3 - page 10521, line 7: These paragraphs provide a rather generic description of the standard optimal estimation approach as presented by Rodgers (2000). However, some more concrete information on the actual retrieval problem could be provided. E.g. it would be interesting to know how linear/non-linear the retrieval problem is (e.g. in terms of the numbers of iterations required to find a solution). I think it should be explained here or in the following section how the off-diagonal elements of the covariances were set (e.g. zero or auto-regressive model?), i.e. how correlations of errors and a priori are treated in the OPERA scheme.

We have added the statement "In our successful retrievals, the scheme converges within three to six iterations." to give the reader a little more information about the number of iterations before converegence.

The off-diagonal elements were set to zero in the measurement covariance matrix, S_y. For the a priori covariance matrix off-diagonal elements we use a simple first order auto-regressive model with a vertical correlation length of 6 km.

We have modified to the end of the paragraph on page 10520, line 23 to read,"For S_a, the off-diagonal elements were determined by a first order auto-regressive model with a vertical correlation length of 6 km. With uncorrelated a priori data (off-diagonal elements of S_a, set to zero) retrieval oscillations occurred but introducing a correlation length of 6 km efficiently reduces these oscillations with the trade-off of reducing the vertical resolution of the observations to between 3 km to 4 km. The off-diagonal elements of S_y were set to zero (implying no noise correlation between different altitudes)."

3) page 10521, line 7: In order to reproduce the results, it would be necessary to know the exact spectral ranges used for the retrieval of HCFC-22 as well as the total particle extinction. In other paragraphs the microwindow 828.95-829.15 cm^{-1} is mentioned to provide the information about HCFC-22. Which spectral range is used to provide

information about the total particle extinction or radiometric background?

The total particle extinction microwindow is 832.3-834.4 cm^{-1} based on work performed by Spang et al. 2004 (Advances Space Research). The text has been modified to include this on page 10519 at line 7: "...lowermost stratosphere and is used in this study. The microwindow used for total particle extinction retrieval is 832.3-834.4 cm^{-1}, based on the findings of Spang et al. 2004,who characterise this region as being particularly sensitive to aerosol and cloud emissions."

4) Page 10522, line 11: Please add a reference for the 2% pressure uncertainty.

We have modified the systematic pressure uncertainty to 4% in the UTLS based on the finding of Raspollini et al. 2006 paper - MIPAS-E level 2 operational analysis (figure 4a). We have changed figure 2 to include the vmr error caused by a 4% uncertainty in pressure.

5) page 10522, line 12: I was wondering why an uncertainty of 10% was assigned for interfering species instead of using the standard deviations provided by the climatology of Remedios (1999)? The standard deviation of CFC-11 (a major interfering trace gas) is up to 20% in the analysed altitude range. Hence, it seems more likely that the corresponding retrieval error is underestimated and not overestimated as stated in the text?

The uncertainties for the random model parameter error were taken from analysis of MIPAS level 2 data for pressure, temperature, water vapour and ozone. The variability for the other contaminants were taken from the climatology of Remedios et al. 2007 (note updated reference). The uncertainty of 10% refers to the systematic bias on our data, caused by systematic inaccuracies in the climatology, NOT the random error caused by natural variability in the climatology data which the climatology files encapsulate. The text in the paragraph has been re-written to make this distinction clearer.

To illustrate why we did this with particular reference to CFC-11, the tropospheric concentration of CFC-11 in Remedios 2007 is 265 pptv, compared to the reported 256 pptv in the troposphere in 2003, the year of our data, in the IPCC special report on safeguarding the ozone layer and the global climate system (2003). This difference is approximately 3%. We chose 10% as a threshold as we were more uncertain what had happened to CFC-11 in the lowermost stratosphere over the relevant time frame preceding 2003. We decided to base this on our OPERA retrieved data presented in our 2005 paper in ASR for CFC-11 (and CFC-12) from MIPAS-E which showed an indication of a high bias in the mean in the lowermost stratosphere data of up to 10% compared to the climatological mean.

6) page 10522, line 22: The authors may also want to point out that the total retrieval error is better than 30% in the best case?

Thank you for the comment. The text has been modified to include this.

7) page 10522, line 24- page 10523, line 7: This paragraph is a bit short and the authors should be more specific. They could point out that the area of the averaging kernels shown in fig. 3 is close to 100

In this paragraph we have included the statement "The area of the averaging kernels shown in Fig. 3 are close to 100%, indicating that the retrieval results are nearly free of a priori influence." Later in the same paragraph we say that "We find that the vertical resolution of the HCFC-22 observations are generally between 3 and 4 km, although at pressures below 100 mb the vertical resolution is between 5 and 6 km."

8) page 10525, line 9-12. The anomalously high HCFC-22 values in the tropics at 150 mb require more examination and explanation. As there seems to be no physical reason (dynamics/photochemistry) it may indicate a serious flaw in the retrieval scheme? The high values at 150 mbar will most probably disturb the retrieval at lower altitudes, too (e.g. leading to values too low at 200 mbar). This can be checked for by inspection of the contribution functions. Furthermore, the temperature and pressure uncertainties may be part of the problem as stated by the authors, but do not seem to fully explain

the anomaly: Fig. 2 indicates that the retrieval errors due to 2% pressure uncertainty or 1K temperature uncertainty are about 1-2% in the HCFC-22 vmr, but the observed anomaly is about 20%. Did the authors inspect the MIPAS spectra or residual spectra to identify other possible reasons of the anomaly? If the tropical data is not to be trusted at all, it seems better to not discuss them in this paper and remove statements about global values from the text and the corresponding curve in Fig. 4?

The interesting point about the tropical data was that the residuals between the measurement and our forward model were small. Of course the cost function takes into account this residual and all data we showed met our strict convergence criteria. This is why we thought that the problem may arise from either temperature or possibly pressure systematic errors in the MIPAS-E level 2 volume mixing ratio data, or a systematic error in one of the gases in our tropical climatology. Another possibility we examined is cloud contamination not detected by our CI threshold of 1.8.

In our 'radiance contribution plot' in figure 1 we have shown some of the major contaminants. Ozone is one of the major interfering species in the HCFC-22 microwindow and it has been shown (Cortesi et al. 2007, ACP) that there may be problems with the tropical MIPAS ozone data in the UTLS. We are also still carrying out work within our research group looking at the quality of MIPAS-E ozone in the UTLS. Another possible explanation is that the tropical climatology underestimates the $ClONO_2$ vmr profile between 12 and 21 km (shown below). A systematic underestimation of $ClONO_2$ in the tropics may lead to an overestimate of the HCFC-22 retrieved vmrs in the UTLS. The radiance contribution due to $ClONO_2$ is also now shown in an updated figure 1 as it is a contaminant species in the HCFC-22 microwindow. Comparison to $ClONO_2$ measurements from MIPAS-E by IMK (Hopfner et al, ACP 2007) showed that it is unlikely that our equatorial reference atmosphere profile is significantly underestimating the $ClONO_2$ profile in the UTLS.

Another possible explanation that we favour is residual cloud contamination in the UTLS, not detected by our cloud flagging of 1.8. Greenhough et al. explored the use of cloud index in their Advances in Space research paper in 2005 and suggested that the CI threshold of 1.8 may need to altered in different latitude regions by considering setting a different CI threshold for each altitude to get the same effective extinction value. By that idea, it may be that in the tropics a CI of >1.8 is too low to filter optically thick cloud and hence the residual cloud is affecting the retrieved HCFC-22 vmrs.

The tropics show clouds at very high altitudes close to a cold tropopause which cause particular difficulties for current MIPAS retrievals in the tropical UTLS. Therefore we have a higher confidence in retrievals away from the tropics.

We have modified the text in the article to highlight residual problems of clouds in our tropical data. We have modified the paragraph page 10525, line 6, to read "Finally the tropical data, although expected to be mostly tropospheric and therefore show no decrease in HCFC–22 over the measured levels, does show some unexpectedly high HCFC–22 vmrs at approximately 150 mb of over 195 pptv. The exact cause of this anomalously high HCFC–22 is most likely due to residual cloud contamination in the tropical UTLS spectra, not detected by our cloud detection ratio of 1.8. Greenhough et al. (2005) explored the use of the cloud index (CI) for cloud-flagging MIPAS-E data and calculated that the CI threshold of 1.8 corresponds to effective extinctions of 5x10^{-4} to 2x10^{-3} km^{-1} at altitudes of 12 and 18 km respectively in the tropics. Although we use a low CI threshold of 1.8, these results show that it may be necessary to increase the CI threshold in the tropics, possibly up to a value of 4, to flag all cloud-contaminated spectra in the tropical upper troposphere."

9a) page 10526, line 9 and caption of Fig.3: I think the terms 'vertical resolution' (as represented by the peaks of the averaging kernels or the degrees of freedom for signal) and measurement information (as represented by the area of the averaging kernels) get mixed up. Concerning the text. How do the authors use degrees of freedom for signal to filter individual tangent heights as this quantity describes the whole profile?

We agree that it is not clear in the text that we filter individual heights. Of course the degrees of freedom is simply defined as the trace of the averaging kernel matrix (i.e. sum of the diagonals) and therefore no direct information on each individual measurement level is given in the degrees of freedom value. The key is in the diagonal elements themselves. As we state in the paper, we use "only data at heights with significant measurement information" determined by a test to see whether more information comes from the a priori estimate or the measurement.

The Fisher Information matrix is equal to the inverse covariance matrix. From Rodgers (2000), the terms in the Fisher matrix equation can be treated as information matrices, indicating that the posterior information matrix is the sum of that of the prior and that of the measurement. We follow the approach as discussed by Moore et al. (2005) [The potential for radiometric retrievals of halocarbon concentrations from the MIPAS-E instrument, Advances in Space Research, 37, issue 12, 2238-2246] we look at the mean percentage 'improvement' to decide whether more information arises from the measurements or the a priori information. We have modified the sentence beginning "Only data at heights with..." to read "We restrict our analysis to data at heights where there is more information in the retrieval arising from the measurements than the a priori information by analysis of the Fisher information matrix described by Rodgers (2000). Note that we also correct for the remaining small a priori bias, using a technique described in Sect. 2.4."

9b) Concerning the caption of figure 3, the peak values of the averaging kernels do not measure the amount of measurement information (this is approximately measured by their area. The peak values measure the vertical resolution of the observations.

We agree with this and have removed this statement from the figure 3 caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10515, 2007.