Carbonyl fluoride (COF_2) vertical information above Jungfraujoch by FTIR and multi-spectra fitting : error budget and comparisons with KASIMA 3-D CTM model calculations

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1. INTRODUCTION

The major sources of fluorine in the stratosphere are CFC-11 and CFC-12. Photolysis of these compounds leads to release of chlorine atoms, while the fluorine is, in a first step, present in the form of carbonyl compounds like COClF and COF_2. Their further photolysis liberates fluorine atoms, which are quickly converted to HF. Given its long life time, COF_2 is the second stratospheric fluorine reservoir [1].

The first COF_2 vertical distributions were derived from occultation measurements performed by the ATMOS instrument during the SPACELAB-3 Space Shuttle mission in 1985 [2]. The Canadian FTIR spectrometer ACE-FTS, onboard the SCISAT-1 satellite, is the first instrument since the last ATMOS flight in 1994, to record COF_2 vertical profiles from space. All these observations show that, at mean latitudes, COF_2 concentration is maximum between 30 and 35 km where it contributes to almost 20% to F_y [3].

Several COF_2 IR absorption lines located either in the so-called InSb (2-5.5 µm) and MCT (7-14 µm) spectral ranges can be used to determine its total column from ground-based FTIR observations. In this context, several studies concerning the evolution of COF_2 total column above various stations were published during the nineties (for example, see [3] and [4]). At this time, no study concerning the inversion of COF_2 vertical distributions from ground-based FTIR spectra has been published.

Last year, we have exposed and completely characterized an original multi-microwindows multi-spectra approach allowing to derive information on the COF_2 vertical distribution between 17 and 30 km from ground-based FTIR spectra recorded at Jungfraujoch [5]. This year, we complete the characterization by providing a full error budget affecting our COF_2 partial and total columns products. Comparisons with COF_2 model runs generated by the German KASIMA model are also presented and discussed.

2. WORK STRATEGY

Figure 1 presents the two sets of microwindows (in the InSb and MCT ranges, respectively) we have selected to retrieve COF_2 vertical distributions from high resolution FTIR spectra recorded at the International Scientific Station of the Jungfraujoch (ISSJ - 46.5°N, 8.0°E, 3580m asl). Red lines reproduce simulations (for a solar zenithal angle of 80°) of COF_2 absorptions while major interferences are indicated with black arrows. For each of these sets, such inversions have been performed using the SFIT-2 v3.91 algorithm and the HITRAN 2004 spectroscopic line parameters database. During the retrievals, all microwindows of each sets are fitted simultaneously. To increase the information content (see also relevant pannel), we also proceed to multi spectra retrievals : it consists of combining several FTIR spectra, recorded during the same day.

Between 15 and 37 km, the adopted a priori COF_2 profile is a zonal mean (for the latitudinal band [41-51]°N) of the more than 300 occultations recorded by the Canadian satellite ACE-FTS between February 2004 and September 2005. Below 15 km, a realistic decrease has been constructed to reach low COF_2 VMR values of about 1×10^{-13} at the altitude site. Above 37 km, we have kept the a priori COF_2 profile used by the ACE-FTS instrument for its own retrievals. The a priori covariance matrix S_a has been derived from the same set of ACE-FTS measurements used for the construction of the a priori COF_2 profile. We have also modelized a gaussian inter-layer correlation of 2km, deduced from the 3D VMR-altitude correlation matrix, as seen by the ACE-FTS instrument.

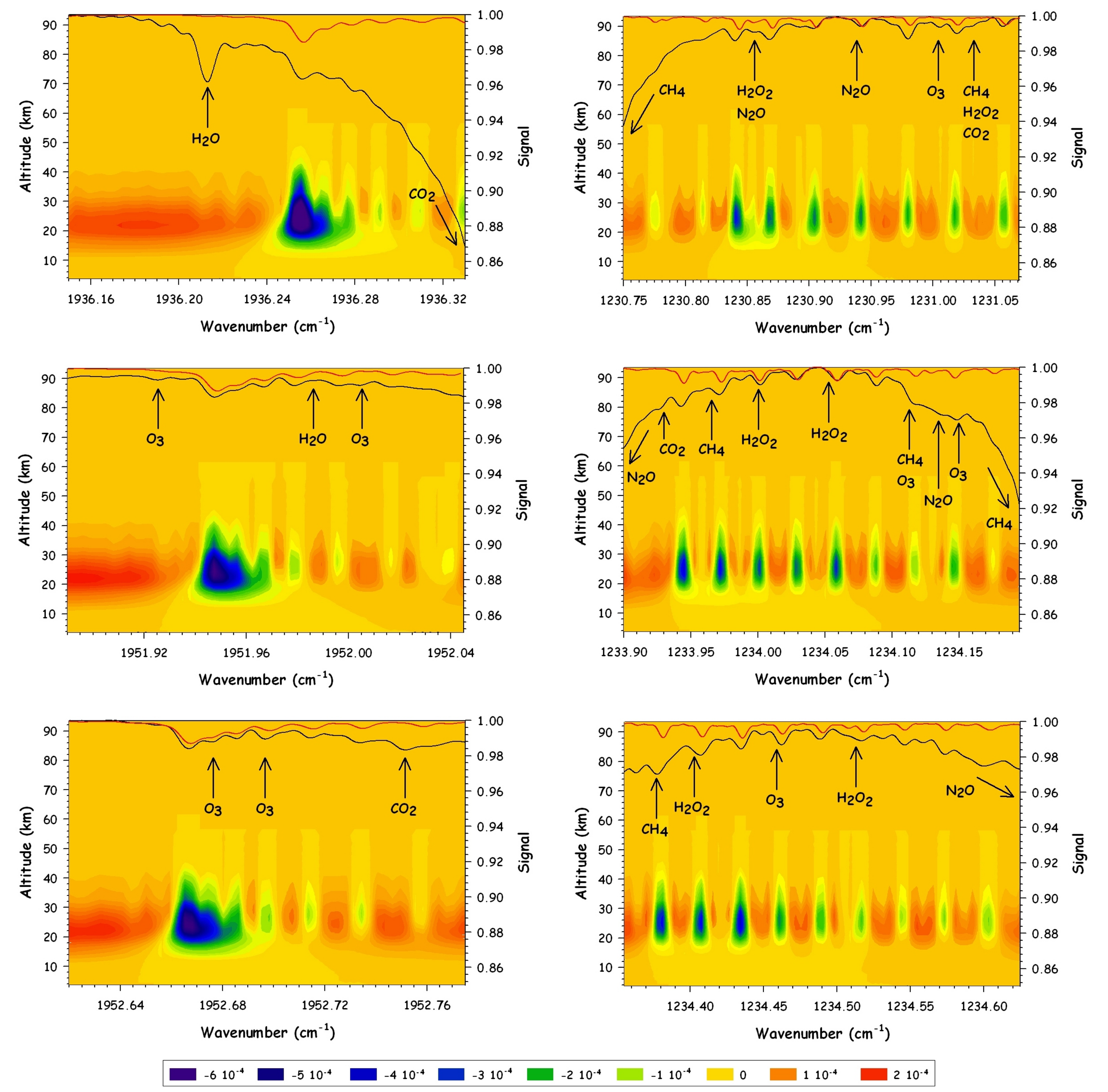

Figure 1 - Selection of microwindows in InSb (left column) and MCT (right column) ranges for COF_2 profile inversions. For each microwindow, black and red traces (slightly vertically scaled, for clarity) reproduce all gases and COF_2 absorptions, respectively (simulated spectra performed for a solar zenithal angle of 80°). Major interference gases for which VMR profiles are scaled during the retrieval procedure are indicated with black arrows. Background colored plots reproduce, for each microwindow, corresponding typical K matrix weighting functions and highlight the altitude sensitivity range of each COF_2 absorption line.

Error source	Error on COF_2 total column (%)		Error on COF_2 [17-30] km partial column (%)	
	InSb	MCT	InSb	MCT
Smoothing error	5.0	9.0	8.0	12.0
Measurement error	6.5	8.0	8.0	10.0
Model parameter error	0.5	0.5	0.6	0.6
NCEP T profiles	< 0.5	< 2.5	< 0.1	< 2.5
ILS	2.5	< 3.5	< 3.0	4.0
SZA	1.5	< 1.5	2.0	< 2.0
TOTAL	**< 9.0**	**< 13.0**	**< 12.0**	**< 16.5**

Table 1 - Typical individual and total errors affecting COF_2 total and [17-30] km partial columns derived from InSb and MCT spectral ranges. For both domains, these values have been obtained by using the multi-microwindows multi-spectra approach running with 3 FTIR observations recorded at solar zenithal angles close to 80°.

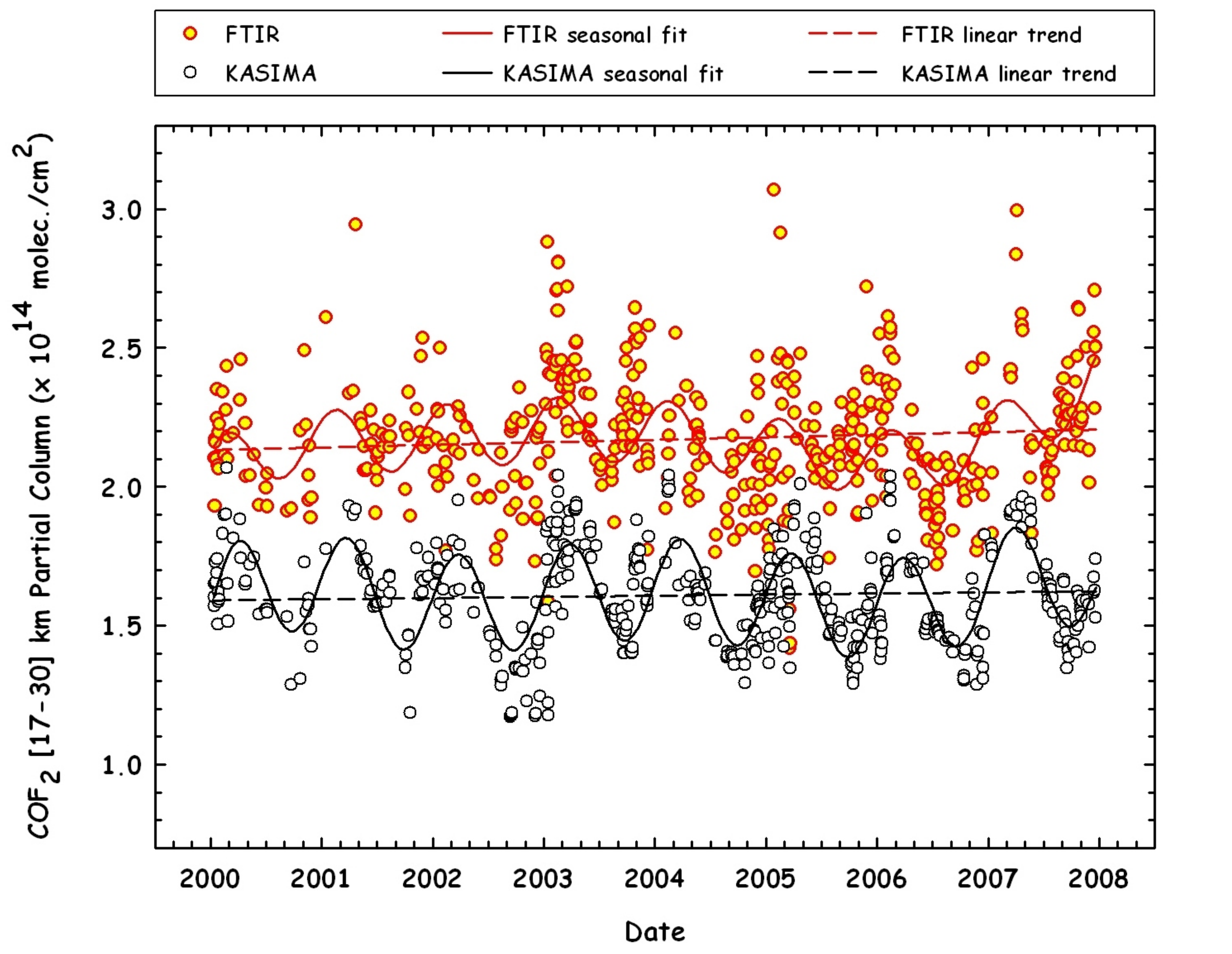

Figure 2 - COF_2 [17-30] km partial columns time series as observed by the FTIR instrument operated at the Jungfraujoch station (yellow dots) and as computed by the KASIMA 3-D CTM model (white dots). Solid lines reproduce seasonal variations adjusted to each data set while dotted lines correspond to linear adjustments to corresponding de-seasonalized time series.

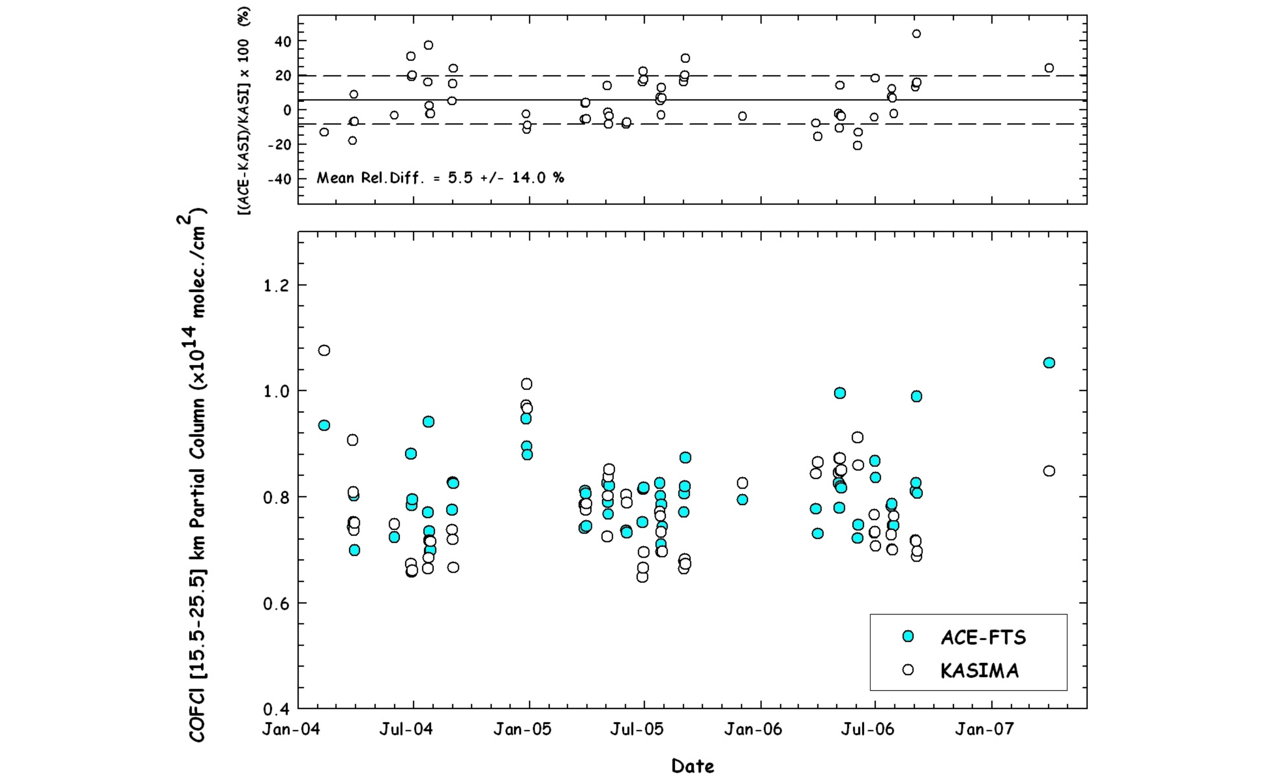

Figure 3 - COFCl [15.5-25.5] km partial columns time series as observed by the ACE-FTS space instrument (light blue dots) and as computed by the KASIMA 3-D CTM model (white dots). Top panel reproduces relative differences between each time series (solid line : mean relative difference; dotted lines : 1 standard deviation on the mean).

3. INFORMATION CONTENT AND ERROR BUDGET

We have demonstrated last year that the multi-microwindows multi-spectra fitting procedure allows to reach DOFS (degree of freedom of the signal) values greater than 1 for total column, with the largest fraction of information coming from the measurement, instead of from the a priori state. To remind the vertical sensitivity of COF_2 lines encompassed in each of our microwindow, Figure 1 plots K matrix weighting functions for COF_2 inversions. For both microwindows sets, one can see that our FTIR measurements are the most sensitive for COF_2 inversions between 17 and 30 km.

For each spectral range, Table 1 summarizes typical (i.e. obtained by using the multi-microwindows multi-spectra approach running with 3 FTIR spectra recorded at solar zenithal angles close to 80°) contributions of various errors affecting our COF_2 total and [17-30] km partial columns. Spectral resolutions used to derive this typical error budget are 4.4 mK for the InSb range and 6.1 mK for the MCT domain. The three last error sources, namely errors associated to temperature profiles used in the physical model adopted for the retrievals, to the instrument line shape (ILS) and to the solar zenithal angle (SZA), have been evaluated by using a perturbation method. While taking into account the six error sources presented in Table 1, total errors affecting our COF_2 retrieved total and partial columns are close to 10% and 15%, respectively, for both spectral ranges. Higher error values observed for the MCT domain is due to the lower information content characterizing the MCT microwindows set.

4. COMPARISONS WITH MODEL DATA

In order to validate our results, we have compared daily means FTIR COF_2 [17-30] km partial column (where FTIR retrievals are the most sensitive) to daily values specifically computed for the Jungfraujoch conditions by the German KASIMA (Karlsruhe Simulation model of the Middle Atmosphere) model. This 3-D CTM (Chemical Transport Model) has been specifically developed to simulate the behavior of physical and chemical processes in the middle atmosphere [6]. Between January 2000 and December 2007, there are 475 days available for comparisons with daily KASIMA simulations. It's also important to notice that InSb and MCT data sets have been merged to obtain a more homogeneous FTIR time series and to increase the number of coincident points with the KASIMA dataset. Indeed, no significant relative difference (0.3±7.3 %) has been observed between InSb and MCT retrieved COF_2 partial columns.

Figures 2 plots the so-merged FTIR time series with coincident KASIMA data. Seasonal variations of each data set have been fitted by using a function combining a polynomial as well as a cosine component (see red and black solid lines on Figure 2) and are well captured in both cases : maximum COF_2 abundances occur in winter, when photodissociation processes are running low, while minimum concentrations are reached in late summer. Some specials events, linked for example to polar vortex overpasses (e.g. high COF_2 values observed in January and February 2003) are also well catched by both data sets. To estimate linear trends (see red and black dotted lines on Figure 2), seasonal variations of each series have been removed. Linear trends so deduced for the time period [2000-2007] are 3.5±0.2 % and 2.1±0.2 % for FTIR and KASIMA time series, respectively. This corresponds to linear COF_2 increases of 0.4 %/year and 0.3%/year, for FTIR and KASIMA data sets, respectively.

It's obvious from Figure 2 that it still subsists a large bias (mean relative difference between both time series is 36.7±15.0 %) between FTIR and KASIMA data. There are two main hypothesis that could explain this KASIMA underestimation : the first one suggests that KASIMA model uses incorrect COF_2 VMR values at its lowest level (7 km). This could introduce biased COF_2 abundances in the lower stratosphere. The second hypothesis lies in the fact that the KASIMA partitioning between fluorine species (HF, COF_2 and COFCl) in the CFC's break up reactions could be erroneous. As FTIR retrievals have no sensibility to COF_2 inversions below 17 km, it was not possible for us to compare FTIR and KASIMA COF_2 partial column between 7 and 17 km to check the validity of the first hypothesis. However, as previous comparisons have shown the good agreement between FTIR and KASIMA abundances for HF [7], we have thus compared COFCl partial columns computed by KASIMA with ACE-FTS space satellite data (low panel of Figure 3) to check the validity of the second hypothesis. Satellite data are well suited for this exercise as ground-based FTIR technique is not appropriate to retrieve COFCl abundances. Only ACE-FTS occultations located in the [40-50]°N latitudinal band have been used for comparisons with KASIMA data, which represents a set of 64 coincident points. Partial column limits ([15-25] km) adopted here are representative of the altitude range where the ACE instrument is able to record COFCl vertical profiles. Top panel of Figure 3 plots relative differences computed between both time series. The mean relative difference value (5.5±14.0 %) indicates that there is no significant bias between both data sets and thus suggests that the second hypothesis evoked here above could be therefore rejected. We also have to mention that similar COF_2 comparisons (not presented here) made between FTIR data and the SLIMACT 3-D CTM model [8] have been performed and don't show such bias between both time series. A manuscript dealing with all results evoked here is in preparation.

References

[1] Kaye, J. A., A. R. Douglas, C. H. Jackman, R. S. Stolarski, R. Zander and G. Roland, Two-dimensional model calculation of fluorine-containing reservoirs species, J. Geophys. Res. 96, 12865-12881, 1991.
[2] Rinsland, C. P., R. Zander, L. R. Brown, C. B. Farmer, J. H. Park, R. H. Norton, J. M. Russell III and O. F. Raper, Detection of carbonyl fluoride in the stratosphere, Geophys. Res. Lett. 13, 769-772, 1986.
[3] Zander, R., C. P. Rinsland, E. Mahieu, M. R. Gunson, C. B. Farmer, M. C. Abrams and M. K. W. Ko, Increase of carbonyl fluoride (COF_2) in the stratosphere and its contribution to the 1992 budget of inorganic fluorine in the upper stratosphere, J. Geophys. Res. 99, 16737-16743, 1994.
[4] Mélen, F., E. Mahieu, R. Zander, C. P. Rinsland, P. Demoulin, G. Roland, L. Delbouille and C. Servais, Vetical column abundances of COF_2 above the Jungfraujoch Station, derived from ground-based infrared solar observations, J. Atmos. Chem. 29, 119-134, 1998.
[5] Duchatelet, P., E. Mahieu, P. Demoulin, P. Bernath, C. Boone, K. Walker, S. Wood and D. Smale, Determination of COF_2 vertical distributions above Jungfraujoch by FTIR and multi-spectra fitting, Geophysical Research Abstracts 9, 06906, 2007.
[6] Kouker, W., I. Langbein, T. Reddmann and R. Ruhnke, The Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA), Version 2, FZK Report 6278, Forschungszentrum Karlsruhe, Germany, 1999.
[7] Ruhnke R., T. Blumenstock, P. Duchatelet, K. Hamann, F. Hase, W. Kouker, I. Kramer, E. Mahieu, S. Mikuteit, J. Notholt, T. Reddmann, M. Schneider, B.-M. Sinnhuber, R. Sussmann, V. Velazco, T. Warneke and M. Wiehle, Measured and modelled trends of stratospheric Cl_y and F_y column amounts in the northern hemisphere, Geophysical Research Abstracts 9, 07597, 2007.
[8] Chipperfield, M.P., New version of the TOMCAT/SLIMCAT Off-Line Chemical Transport Model: intercomparisons of stratospheric tracer experiments, Q.J.R. Meteorol. Soc. 132, 1179-1203, 2006.

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