OPTIMIZED APPROACH to RETRIEVE INFORMATION on the TROPOSPHERIC and STRATOSPHERIC CARBONYL SULFIDE (OCS) VERTICAL DISTRIBUTIONS above JUNGFRAUJOCH from HIGH-RESOLUTION FTIR SOLAR SPECTRA

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1. INTRODUCTION

Carbonyl sulfide (OCS) is the predominant gaseous sulfur-bearing molecule in the remote troposphere, with mean concentrations inferred from surface measurements of about 500 pptv [1].

Because of its long lifetime, a significant fraction of OCS is able to reach the stratosphere where it is converted to SO_2 and ultimately to sulfate aerosols. This process is considered to be the main contributor for sustaining the stratospheric sulfate aerosol layer at background levels during quiet volcanic periods [2].

The main sources of atmospheric OCS appear to be the oxidation of DMS (dimethylsulfide) and CS_2 in the atmosphere and the gas exchange of OCS between oceans and atmosphere, while identified sinks are land plants, oxic soils and atmospheric oxidation by hydroxyl radicals. Despite recent progresses on its atmospheric budget, there remains incomplete understanding of the dominant sources and sinks of atmospheric OCS in both hemispheres [3].

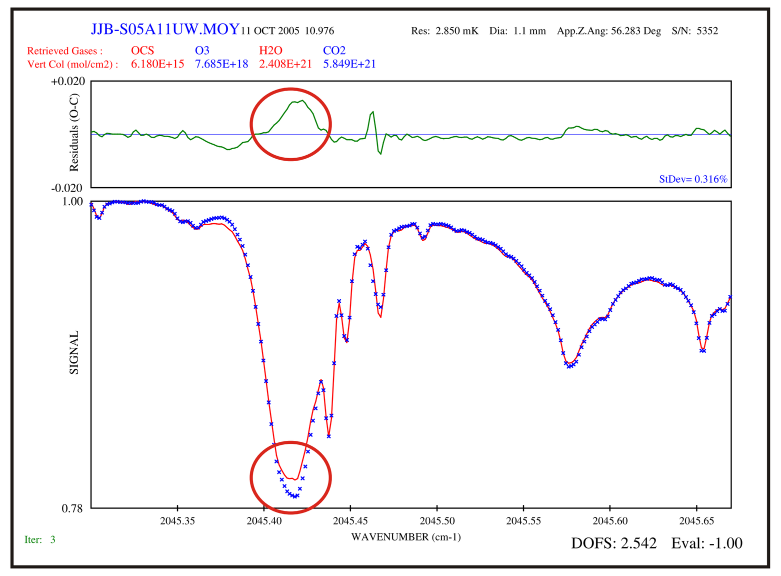


Figure 1 - Example of a significant solar line interference poorly fitted. Microwindow used comes from the old set. Orange circles highlights the poor quality of the fit. Red and blue traces reproduce measured and calculated spectra, respectively. Upper frame with green trace shows the residuals (difference between observed and calculated spectra).

2. RETRIEVAL STRATEGY

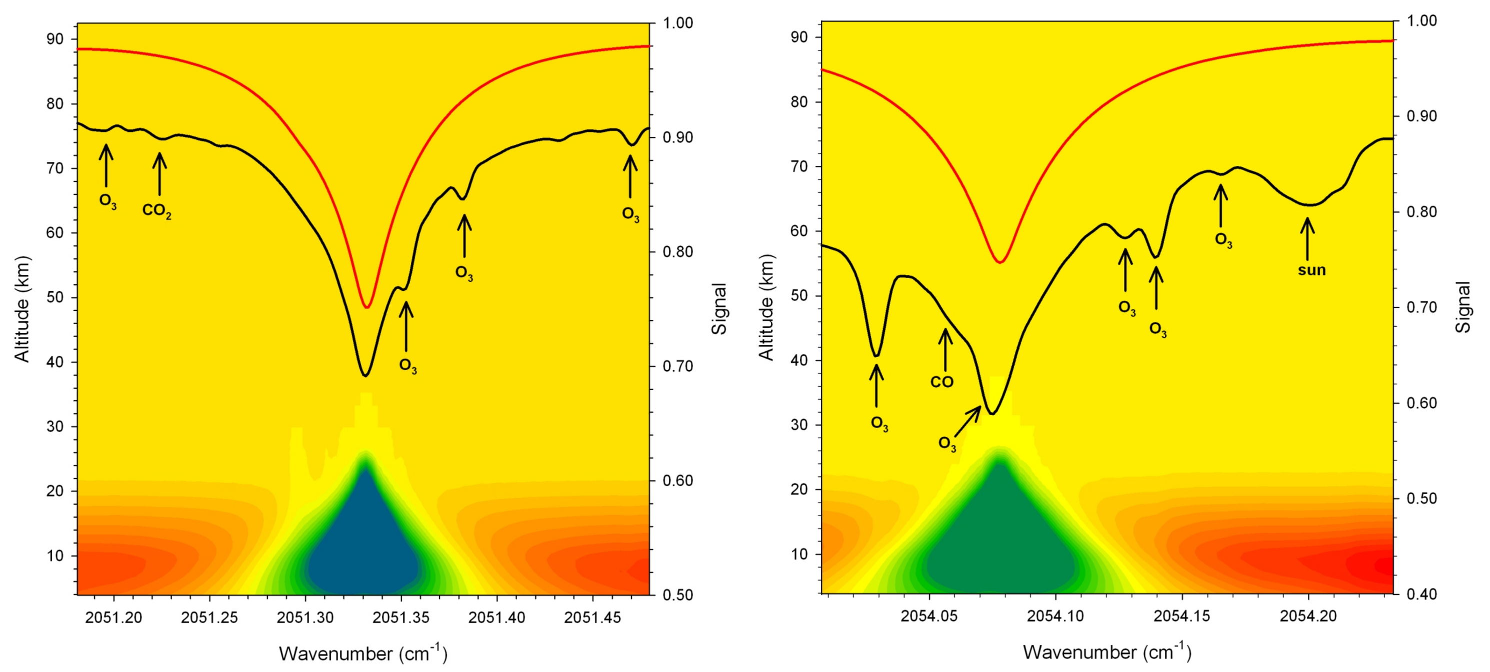
A complete and systematic re-examination of the approach used to retrieve OCS from ground-based FTIR spectra has been undertaken. The aim is to avoid significant interferences which could occur with the former set of microwindows after implementation of the new solar linelist (see Figure 1 for an example).

We use solar observations from two state-of-the-art Fourier Transform Infrared (FTIR) spectrometers operated under clear-sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (ISSJ, 46.5ºN, 8.0ºE, 3580m a.s.l.). These spectrometers are affiliated to the Network for the Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org). Among the Jungfraujoch observational database, about 5150 high-resolution (0.003 to 0.006 cm^{-1}) FTIR solar absorption spectra cover the spectral region of the strong nu3 fundamental band of carbonyl sulfide (OCS), centered on 2062 cm^{-1}. They have been regularly recorded with INSB detectors over the 1995-2010 time period. Earlier spectra covering the 1984-1994 time will be fitted in the near future.

All retrievals have been performed with the v3.91 of the SFIT-2 retrieval algorithm which implements the Optimal Estimation Method of Rodgers [4]. This tool allows to derive information on the vertical distribution of most of the FTIR target gases. In the present runs, HITRAN-2008 line parameters [5] and as the solar line compilation provided by F. Hase (v090525) have been assumed for the target and interfering absorptions. Adopted pressure temperature profiles were provided by the National Centers for Environmental Prediction (NCEP, Washington DC, USA).

The OCS a priori information is essentially based on ACE-FTS occultation measurements which were performed in the 41.5-51.5ºN latitude range and in the 12.0ºO-28.0ºE longitude range from March 2004 to July 2009. We have also modelized a gaussian inter-layer correlation of 3 km, deduced from the correlation matrix based on the ACE-FTS measurements.

In this new approach, the following three microwindows have been simultaneously fitted (see Figure 2) : 2051.18-2051.48, 2054.005-2054.235 and 2054.33-2054.67 cm^{-1}. O_3, CO_2, H_2O, CO and the solar lines are the major interferences in these domains.



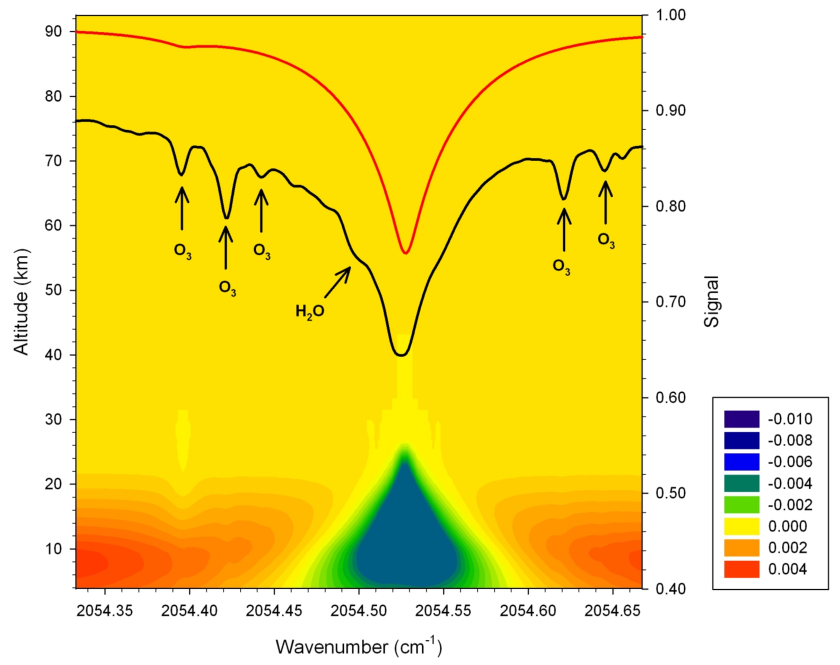


Figure 2 - Microwindows selected for OCS profile inversions. For each microwindow, black and red traces reproduce all gases and OCS absorptions, respectively (simulated spectra for a solar zenith angle of 70°). Some of the atmospheric interfering gases (for which VMR profiles are scaled during the retrieval procedure) are indicated with black arrows. Backround colored plots reproduce, for each microwindow, corresponding typical K matrix weighting functions and highlight the altitude sensitivity range (see left axis scale) of each OCS absorption line.

3. CHARACTERIZATION OF THE RETRIEVED PRODUCTS

Information content and error budget have been carefully evaluated. For a typical spectrum recorded the 11th of January 2010 above Jungfraujoch with a zenith angle of 69.8°, partial column averaging kernels confirm the altitude sensitiviy range (from 3.58 to 26 km) of Figure 2. The first three eigenvectors and corresponding eigenvalues of 0.99, 0.93 and 0.55 indicate that information on the OCS tropospheric column is coming at 99% from the retrieval. Discrimination between partial columns below and above 11 km is also mainly coming from the retrieval (93%), thus allowing to distinguish between tropospheric and stratospheric contributions. Further vertical resolution is available (third eigenvector) but with a more important contribution from the a priori (45%).

The shape of the mean retrieved profile (see Figure 3) shows a slight oscillation in the troposphere (instead of the expected constant value). Notice that the value of 500 pptv usually adopted for average tropospheric mixing ratio of OCS is generally larger than the values retrieved from our 1995-2010 database.

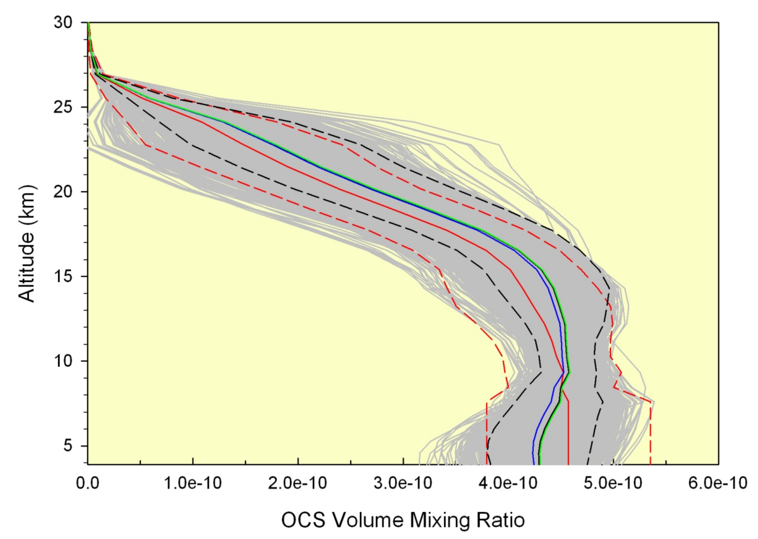


Figure 3 - Retrieved profiles of OCS. Grey curves represent each individual measurement. The solid black and red curves show respectively the mean retrieved profile and the a priori profile. Dashed curves correspond to 2-sigma values. The blue profile is the mean retrieved profile for the FTS1 instrument (850 spectra). The green one corresponds to the Bruker instrument (4305 spectra).

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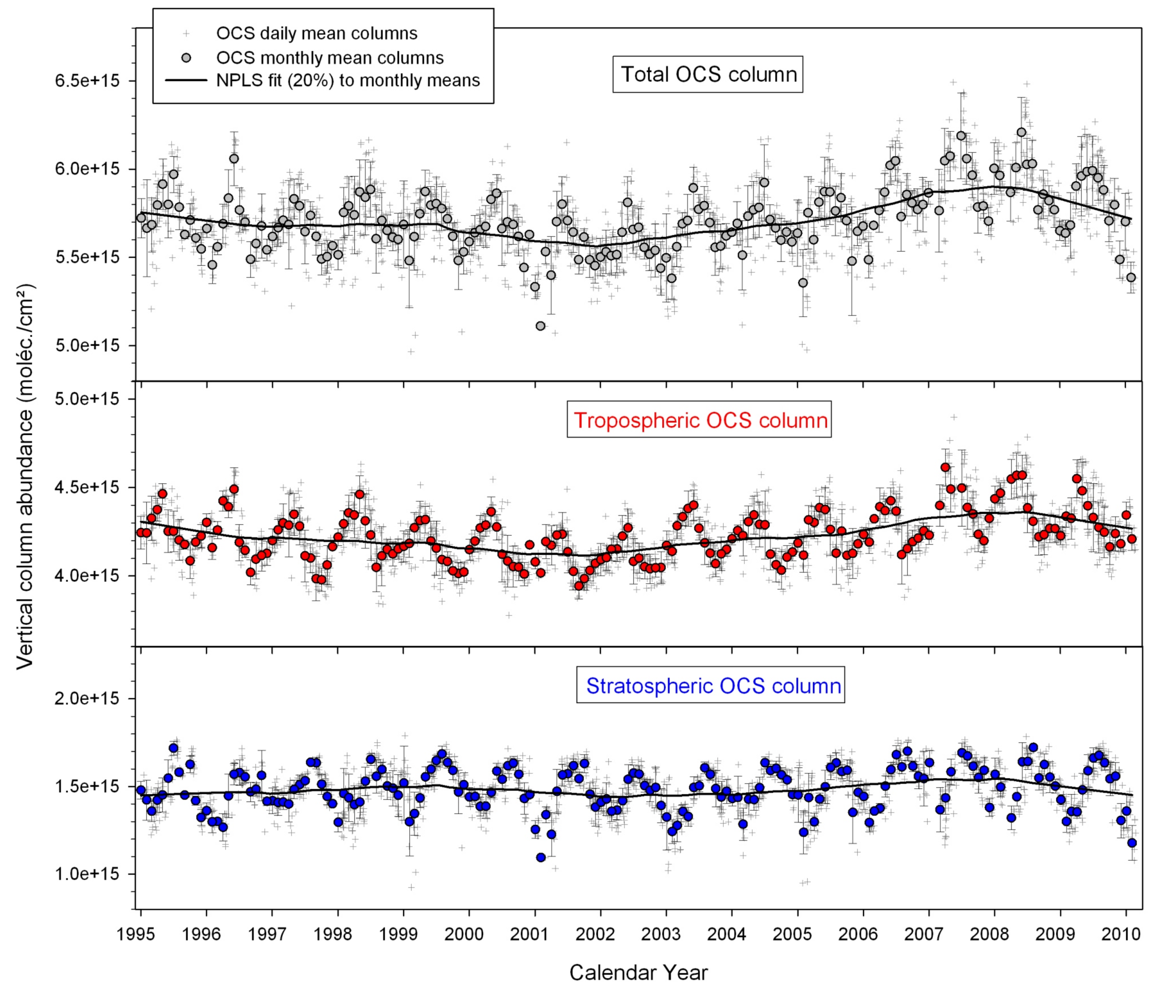

Figure 4 - From top to bottom : OCS monthly mean total, tropospheric and stratospheric partial column time series. Error bars correspond to standard deviations around the monthly means. Non parametric least square (NPLS) fits with sampling proportion of 20% and Gaussian weighting are reproduced by thick black curves. Grey crosses represent daily mean values.

4. OCS COLUMN TIMES SERIES

The retrieval approach described here has been applied to all available Jungfraujoch spectra from 1995 to February 2010. Resulting time series of monthly mean columns (total, partial tropospheric and partial stratospheric) are displayed in Figure 4.

We notice that an increase of OCS total column has started in 2002 after a long decreasing period observed since the late 1980s [6]. OCS total columns have culminated in 2007-2008. Since then, a significant decrease is ongoing. Causes for these successive and significant changes in the OCS abundance have still to be identified.

Our results show also that our column abundance values are biased by about -15% with respect to other values published in the litterature. This results from an increase in the OCS line intensities adopted in the 2004 version of the HITRAN spectroscopic parameters database.

Annual changes of OCS total column above Jungfraujoch		
Period	*10E+13 molec./cm²*	*%*
1995 - 2010	+ 1.51 +/- 0.12	+ 0.25 +/- 0.02
1995 - 2001	- 2.01 +/- 0.34	- 0.35 +/- 0.06
2002 - 2007	+ 6.40 +/- 0.37	+ 1.16 +/- 0.07
2008 - 2010	-14.80 +/- 2.07	- 2.46 +/- 0.34
Annual changes of OCS troposphere column above Jungfraujoch		
1995 - 2010	+ 1.29 +/- 0.09	+ 0.31 +/- 0.02
Annual changes of OCS stratospheric column above Jungfraujoch		
1995 - 2010	+ 0.22 +/- 0.06	+ 0.15 +/- 0.04

Table 1 - OCS annual changes above Jungfraujoch. All the uncertainties correspond to the 95% confidence interval.

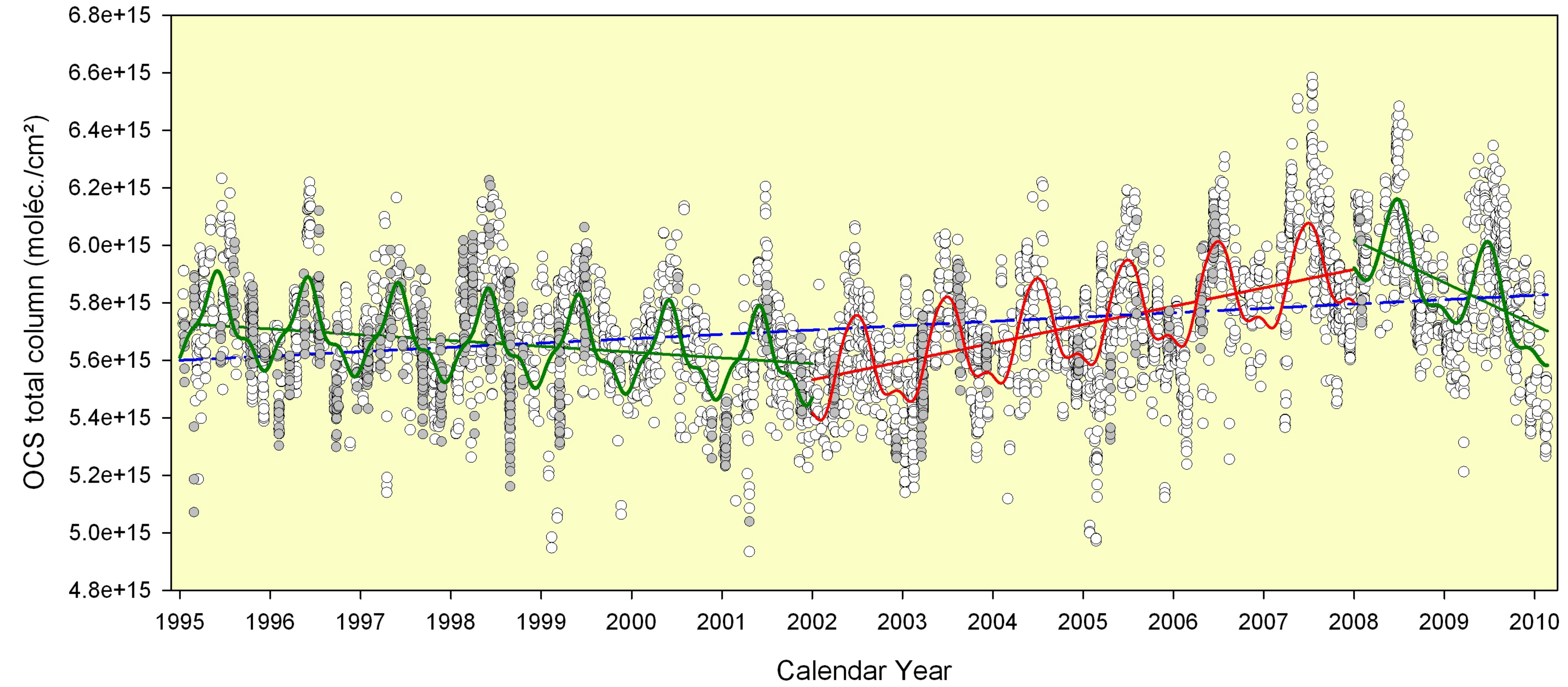

Figure 5 - Time series of OCS total column above Jungfraujoch. Individual measurements are reproduced as white circles for Bruker instrument and as grey circles for FTS1 instrument. Trends have been determined using the bootstrap resampling tool developed by Gardiner et al. [7]. The mathematical function fitted to the data is a combination of a Fourier series (3rd order here) and of a linear function. See Table 1 for trend values derived from this analysis. Blue dashed line corresponds to the 1995-2010 linear trend. Solid green lines and curves show linear and seasonal trends of the 1995-2001 and 2008-2010 decreasing periods. Solid red line and curve show linear and seasonal trends for the 2002-2007 increasing period.

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