TREND EVOLUTION AND SEASONAL VARIATON OF TROPOSPHERIC and STRATOSPHERIC CARBONYL SULFIDE (OCS) above JUNGFRAUJOCH

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1. INTRODUCTION

Carbonyl sulfide (OCS) is the most abundant sulfur-containing trace gas in the atmosphere and is believed to account for a substantial portion of the sulfur in the stratospheric aerosol layer which influences the Earth's radiation budget and stratospheric ozone chemistry [1].

The major identified OCS sources are oceans and anthropogenic emissions, while atmospheric loss and uptake by vegetation and soils constitute the main OCS sinks. The uptake by vegetation strongly influences the distribution and seasonality of OCS throughout most of the Northern Hemisphere [2].

There remain large uncertainties on some components strengths of the atmospheric OCS budget. A recent work showed that uptake by plants has been strongly underestimated in actual balanced budgets, suggesting that additional significant OCS sources have still to be identified [3].

In order to improve the OCS observational dataset in quality and quantity, a new approach has been developed and optimized, using the SFIT-2 algorithm, to retrieve atmospheric abundance of OCS from high-resolution ground-based infrared solar spectra [4].

Some adaptations to the retrieval strategy have been made since then to still improve the quality of our retrieved OCS products, as :

1. the use of a new combination of microwindows (2047.78-2048.22, 2049.75-2050.12, 2051.18-2051.48 and 2054.33-2054.67 cm^{-1}) in association with a narrow microwindow (2035.35-2035.45 cm^{-1}) solely devoted to fit the main isotopologue of CO_2;
2. the isotopic separation for CO_2 and H_2O;
3. the fitting of the ozone vertical profile;
4. a modified a priori covariance matrix using variability data from in situ measurements for the 3.58-8.88 km altitude range.

The tropospheric oscillation visible in the shape of the mean retrieved profile (see [4]) has now almost disappeared while information content and error budget are slightly improved. The mean DOFS value of 2.6 allows us to distinguish between tropospheric (3.58-12.71 km) and stratospheric (12.71-26.22 km) partial column contributions.

Our observations are recorded on a regular basis with Fourier Transform Infrared spectrometers (Bruker and Homemade instruments), under clear-sky conditions, at the NDACC site (Network for the Detection of Atmospheric Composition Change, *http://www.ndacc.org*) of the International Scientific Station of the Jungfraujoch (Swiss Alps, 46.5°N, 8.0°E, 3580m asl). Thanks to our current observational database including 4563 (Bruker) and 2007 (Homemade) validated spectra, we have produced an updated OCS long-term trend from 1995 to 2010, representative for both the troposphere and stratosphere at northern mid-latitudes.

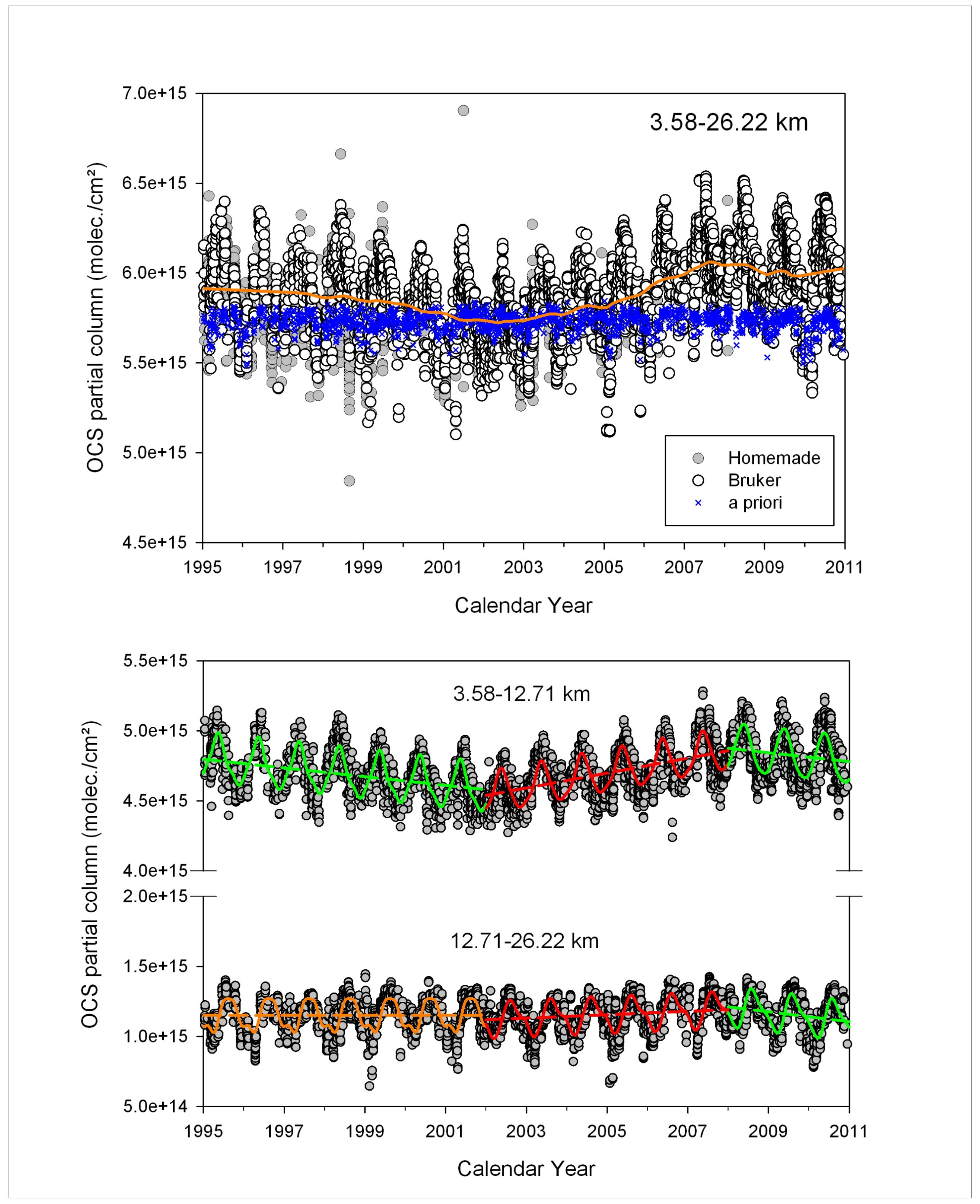

Figure 1 - Top : time series of OCS partial columns (3.58-26.22 km) above Jungfraujoch. Individual measurements are reproduced as white circles for Bruker instrument and as grey circle for Homemade FTS instrument. The blue crosses correspond to the OCS a priori partial columns (only for Bruker instrument). Orange line represents a non parametric least square fit with sampling proportion of 20 % and Gaussian weighting function calculated for individual measurements of Bruker instrument.

Bottom : time series of OCS tropospheric (3.58-12.71km) and stratospheric (12.71-26.22 km) partial column above Jungfraujoch (only for Bruker instrument). Trends have been determined using the bootstrap resampling tool developed by Gardiner et al. [5]. The mathematical function fitted to data is a combination of a Fourier series (3rd order) and of a linear function. Solid lines show linear trends and dashed lines the seasonal components. Green (or red) color is used when the trend is significantly positive (or negative). The orange color means that the trend is nonsignificant at the 2 sigma uncertainty level.

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2. OCS SEASONAL VARIATION

To highlight the OCS seasonal variation above Jungfraujoch, we use the 3.58-9.78 km partial column for which 60 % of the information is still coming from the measurements, as indicated by the corresponding Eigen vector and value.

Figure 2 shows the monthly mixing ratio anomalies for the years 2000-2010. Anomalies are calculated by substracting annual mean values for each year from the monthly means.

We observe a distinct seasonal pattern with maxima in April-June and minima in October-December consistent with terrestrial biospheric uptake during the growing season [3].

Mean seasonal amplitude for the FTIR dataset (red circles) is 36.6 +/- 4.0 pptv for the years 2000-2010 (7.90 +/- 0.81 % of the annual mean partial column).

Our results are compared with the site of Niwot Ridge (Colorado, United States, 40.0°N, 105.5°W, 3475 m) where surface flask measurements of OCS are made on a regular basis since early 2000 (blue circles) [2]. Specifications of Niwot Ridge site (continental localisation, latitude and altitude) are comparable with those of Jungfraujoch.

The comparison reveals a very good agreement in terms of minima/maxima timing. The amplitude seems to be lower above Jungfraujoch, while remaining within Niwot Ridge standard deviation, probably due to the fact that the influence of a typical surface process like vegetation uptake is attenuated in an air column of 6.2 km high.

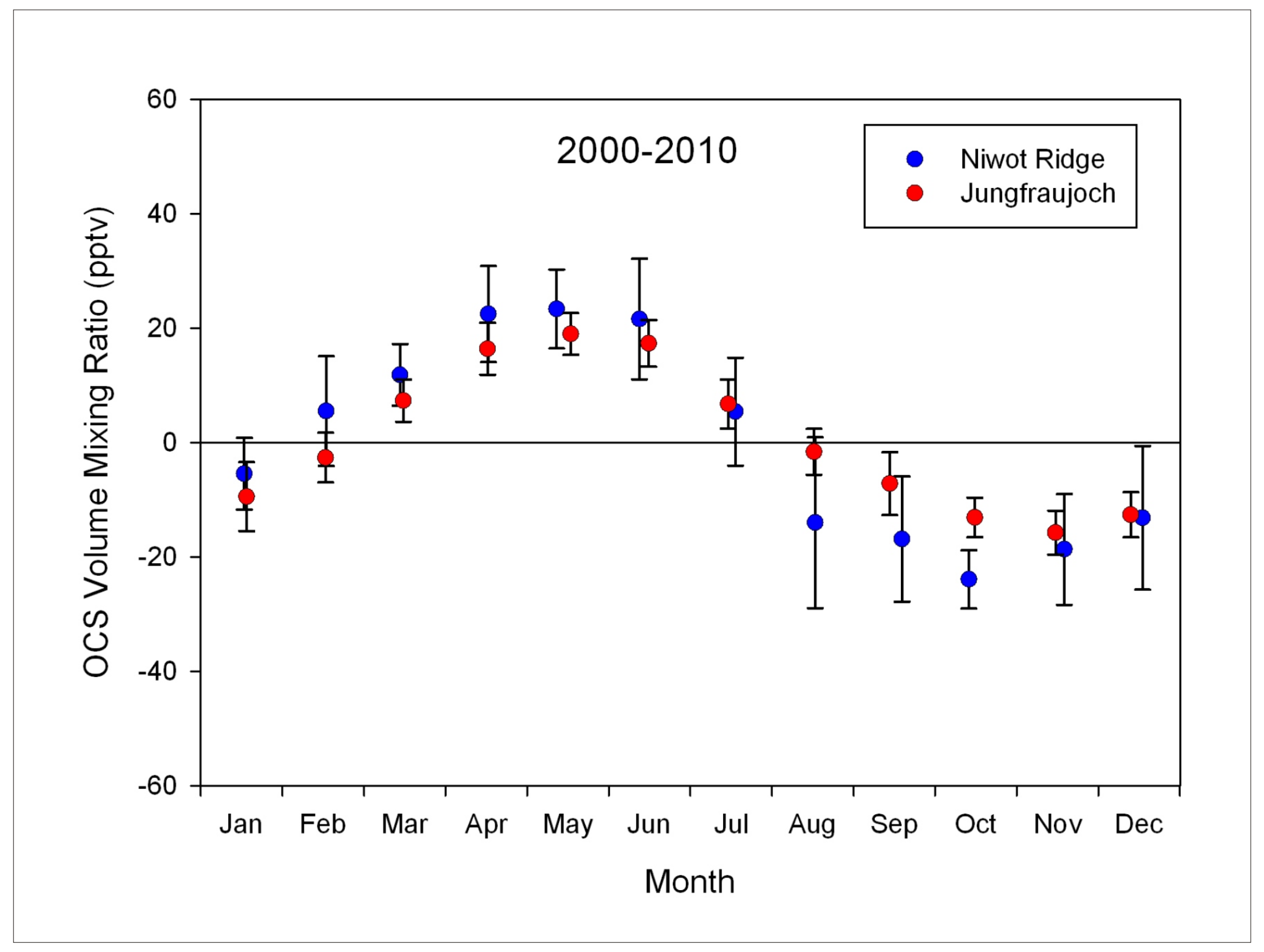

Figure 2 - Averages of the OCS mixing ratio monthly mean observed anomalies (relative to annual mean) for the years 2000-2010 at Niwot Ridge (in situ measurements - blue circles) and Jungfraujoch (mean VMR for the 3.58-9.78 km partial column - red circles). Associated error bars represent standard deviations of the monthly means.

3. RECENT OCS TREND EVOLUTION

Figure 1 confirms, for the OCS partial column corresponding to the 3.58-26.22 km altitude range, our previous results with a significative negative trend over the 1995-2001 period (-0.52 +/- 0.06 %/yr) followed by a significant positive trend over the 2002-2007 period (+1.15 +/- 0.06 %/yr). Since 2008 the evolution of the trend has to be considered carefully because of the shortness of the period and the apparent contradiction between the estimated but significant negative trend (-1.10 +/- 0.19 %/yr) and the shape of a non parametric least square (NPLS) fit suggesting that no significant trend can yet be determined.

The distinction between tropospheric (3.58-12.71 km) and stratospheric partial column (12.71-26.22 km) shows that the recent OCS trend evolution is mainly driven by tropospheric processes. The almost insignificant trend for stratospheric partial column (+ 0.09 +/- 0.05 %/yr for the years 1995-2010) is in contradiction with increases observed in stratospheric sulfate aerosol, contributing to the questioning of the real contribution of OCS to sulfate aerosol [6].

We have checked (see figure 3) if these trends could be related to a specific period of the season. Comparison of years 2001 (end of the decline trend period) and 2009 (end of the growth trend period) OCS partial column (3.58-9.78 km) suggests that each season period follow the same evolution (with an increase of OCS abundance of about 5 %).

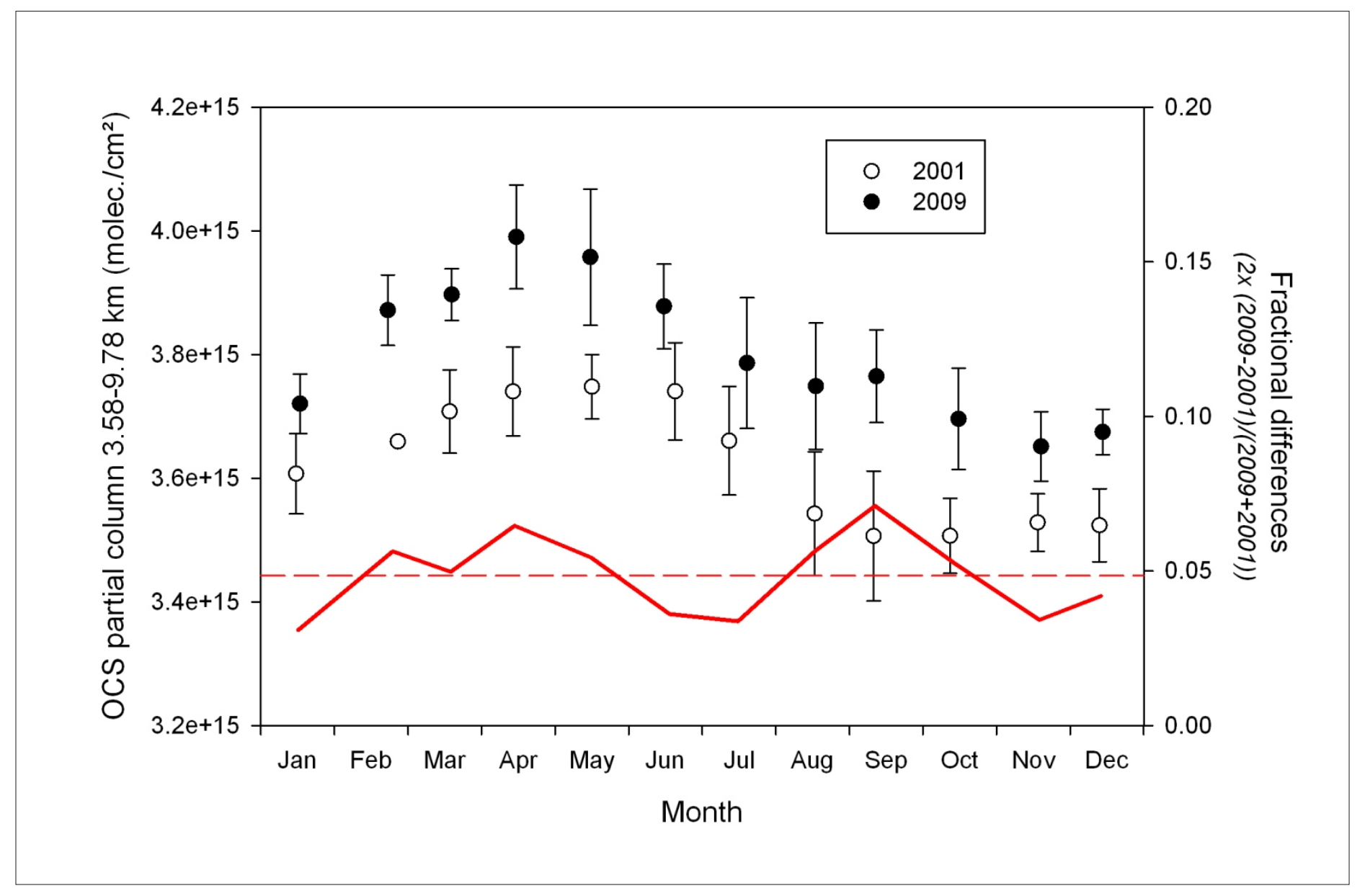

Figure 3 - OCS partial columns (3.58-9.78 km) monthly means measured at Jungfraujoch in 2001 (white circles) and 2009 (black circles). Associated error bars represent standard deviations of the daily means. The red solid line shows the fractional difference between 2009 and 2001 for each month (mean value of fractional differences is represented by the red dashed ligne). Please note the two different Y axes.

4. DISCUSSION OF THE RESULTS

The slight decline of the tropospheric OCS trend at least since the begining of the 1990s has already been observed at several sites (see [7] for references). On the other hand, to our knowledge, no one has reported about the growth period which started in 2002. Niwot Ridge data seem to present the same trend (see fig. 4) but our interpretation is currently based on a simple fit and should be further investigated.

Anthropogenic emissions represent about 25 % of the OCS total emissions. The main associated processes are the conversion of anthropogenic CS_2 (0.20 +/- 0.10 Tg/yr), aluminium production (0.080 +/- 0.060 Tg/yr) and coal combustion (0.036 +/- 0.011 Tg/yr) [8].

The production of regenerated cellulose (in the form of rayon fibers, cellophane, sponges and casing) is the dominant industrial application of carbon disulfide, accounting for 70% of total demand. Viscose-rayon production was essentially constant between at least 1970 and 1990, but then dropped by 24 % by 1999 [6]. Coupled with the geographical shift of the production from Europe to Asia, it seems reasonable to assume that the decline of viscose production in the northern latitudes has contributed to the tropospheric OCS negative trend measured until 2002.

Aluminium production using the Hall-Héroult process requires high amount of anode carbon which are made from coals with sulfur mass contents of above 2 % [9]. OCS is found as a major sulfur compound in anodic gases of commercial aluminium electrolysis. During the 1990s, the impact of aluminium production was within the range of the natural variability of OCS. But the actual constant growth of aluminium production (driven by the economic explosion in China - see fig. 5) can lead OCS emissions from aluminium smelters to reach a level of the same order of magnitude as naturel sources of OCS. We can reasonably assume that there is a link with the increase of tropospheric OCS found in our results since 2002.

The level of OCS emissions coming from coal combustion is less important, but again we have to be careful with the evolution in China where coal is the first energy source.

To conclude we would like to remind that emission factors for anthropogenic sources of OCS and CS_2 are few and based on extremely limited measurements [10]. This adds greatly to the uncertainty still surrounding all budget estimates. This discussion and figure 5 should be considered keeping this aspect in mind.

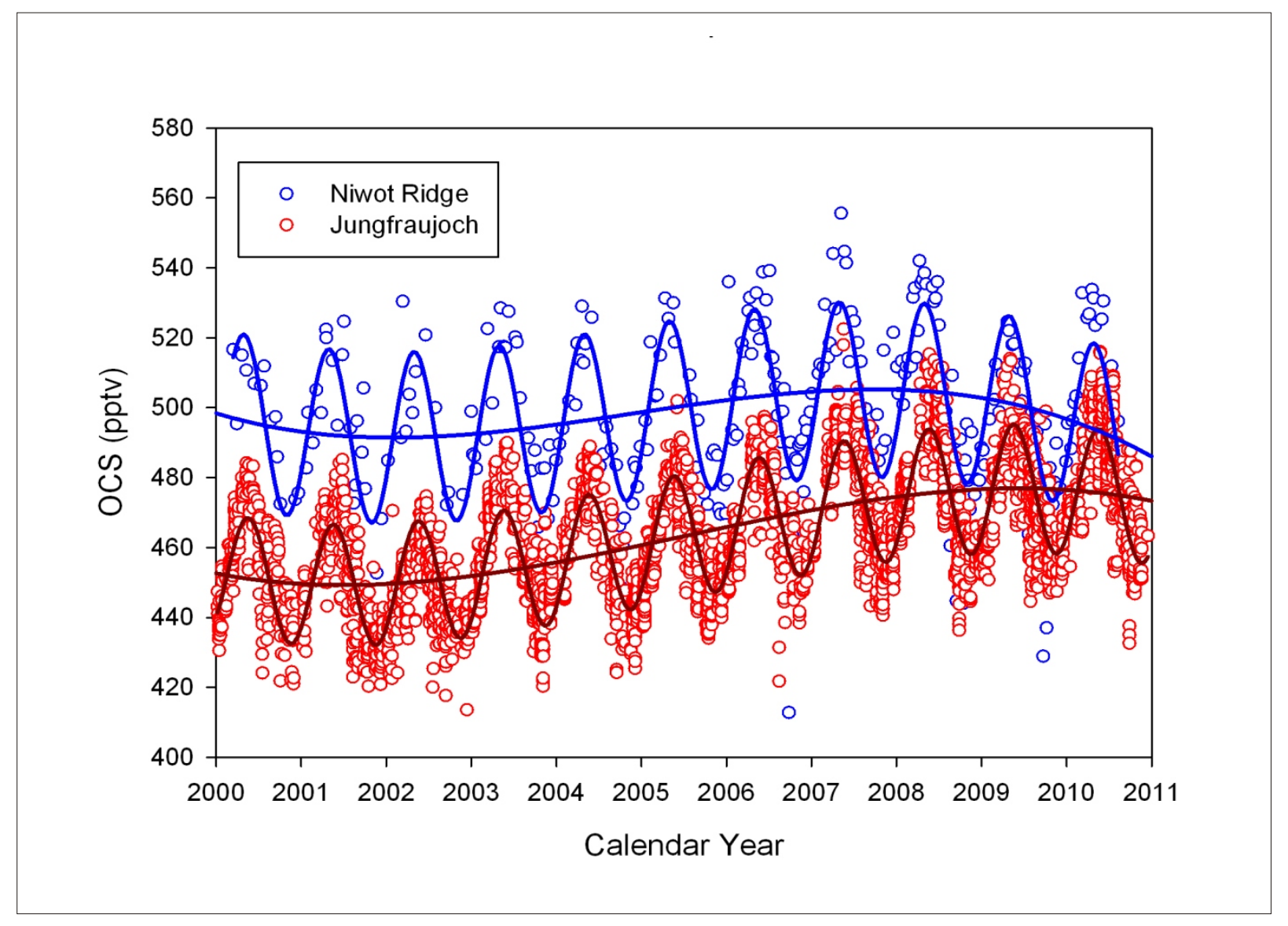

Figure 4 - Time series of OCS mean volume mixing ratio (3.58-9.78 km) above Jungfraujoch (red circles) and in situ OCS volume mixing ratio at Niwot Ridge (blue circles). Data sets have been fitted using a function combining a sinusoidal and a third order polynamial compononent. Resulting curves are displayed in red for Jungfraujoch and in blue for Niwot Ridge.

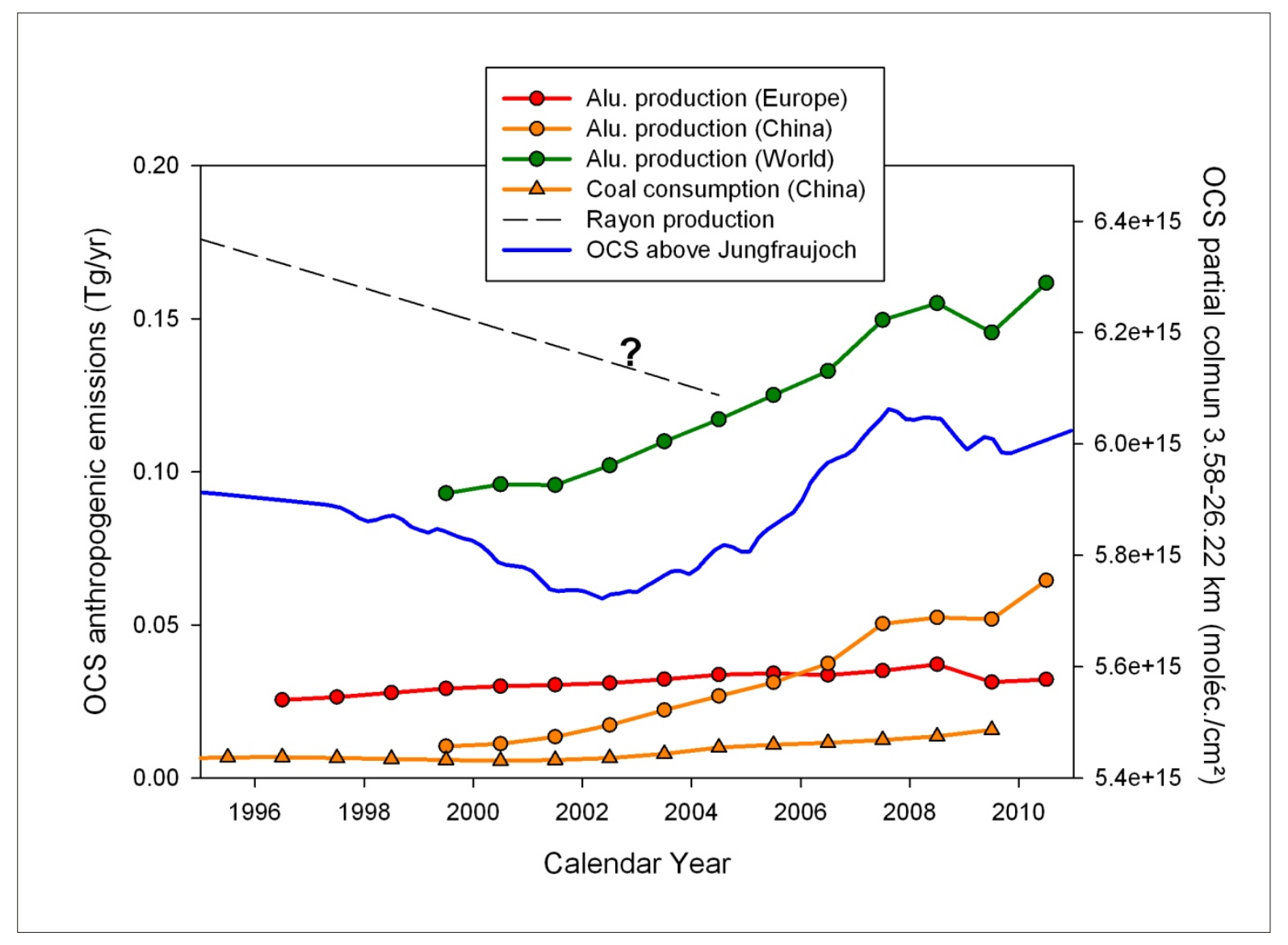

Figure 5 - Evolution of OCS anthropogenic emissions. We use the following conversion factors : 4 kg OCS/t(Al) [9] and 0.005 g OCS/kg coal burned [10]. We assumed that industrial CS_2 originates entirely from the viscose-rayon industry [6,11]. Data are coming from International Aluminium Institute for annual aluminium production, from U.S. Energy Information Administration for annual coal consumption and from [6] for the decline of rayon production. Please note the two different Y axes (right one is for OCS partial column above Jungfraujoch). The question mark reminds the large uncertainty concerning the emission factor in viscose-rayon production and the fact that we have still to collect more recent production data.

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