Long-term evolution and seasonal modulation of methanol above Jungfraujoch (46.5°N, 8.0°E)
Optimisation of the retrieval strategy, comparison with model simulations and independent observations

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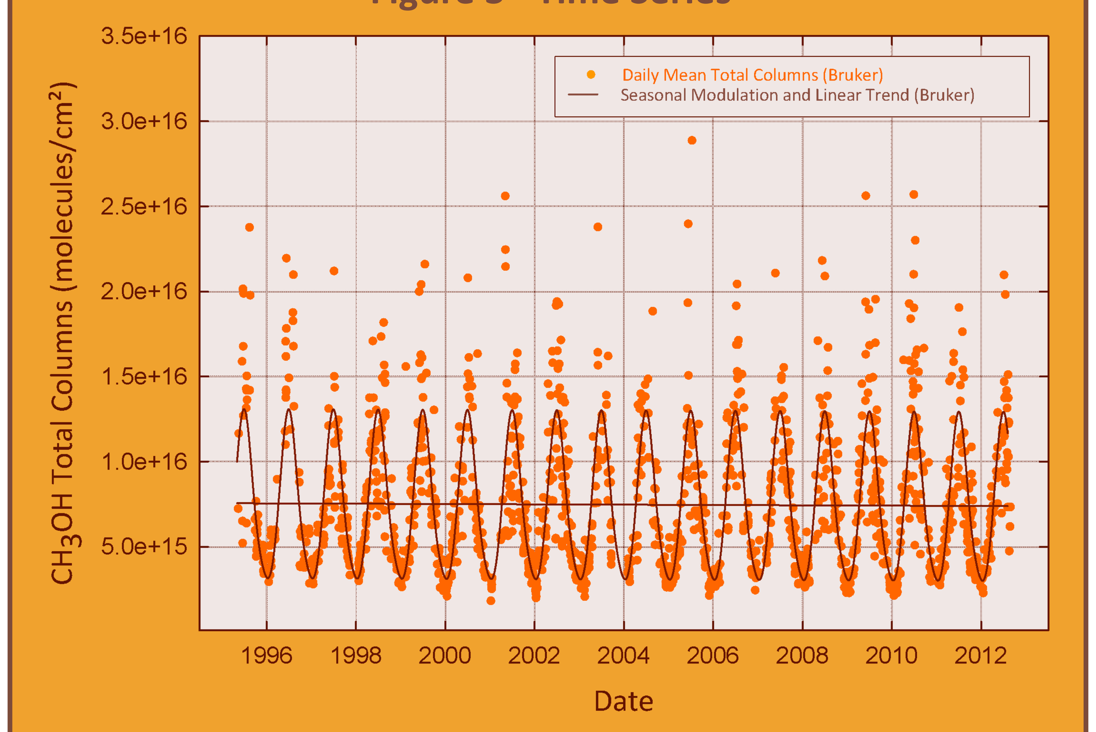
Objective : Optimization of the Retrieval Strategy

Retrieval Strategy - All retrievals have been performed with the SFIT2 algorithm (v 3.91) from a series of about 6500 spectra recorded between 1995 and 2012 with zenith angles between 60 and 85°. (i) Two spectral intervals encompassing the µ8 C-O stretch absorption band of methanol and ranging from 992 to 1008.3 cm^{-1} and from 1029 to 1037 cm^{-1} (See Figure 1). (ii) a value of 180 and 40 for the signal-to-noise for inversion is selected respectively for the "1008" and "1037" intervals. (iii) A priori profile for methanol is issued from a zonal mean (for the 41-51°N latitude band) of ACE-FTS occultations (v3.5) extrapolated to 1 ppbv to the surface and to 0.05 ppbv for upper layers (iv) while the other fitted species are based on the WACCM model climatology (Whole Atmosphere Community Climate Model). (v) The HITRAN 2008 compilation was used for the line parameters. (vi) Temperature and geopotential height data sets are provided by the National Centers for Environmental Prediction (NCEP, Washington, USA).

Information Content & Error Budget - The information content is significantly improved, with a typical Degree Of Freedom for Signal (DOFS) of 1.82, in comparison with DOFS of about 1 in previous studies. This improved DOFS allows us to compute : a tropospheric column with only 1% of a priori dependence and two partial columns with <30% of a priori dependence : a low-tropospheric, LT, from 3.58 to 7.18 km & an upper troposphere-lower stratosphere, UTLS, from 7.18 to 14.84 km. Systematic and random errors are estimated at 7 % and 5 % respectively on total columns. (See Figure 2). The dominant contribution to the systematic error is the error on methanol spectroscopic lines, while the measurement noise error is the main component of random error.

Methanol Total Columns

Figure 3 - Time Series



- Figure 3 - No significant trend for the full time series has been computed

- Figure 4 - The strong seasonal modulation of methanol is characterized by minimum values and variability in December to February and maximum columns in June-July. The mean peak-to-peak amplitude of a seasonal cycle expressed as a percentage of the corresponding CH_3OH yearly mean column amounts to 130.1±1.6 % (1-sigma). The IMAGESv2 model estimates a seasonal modulation of methanol in phase with the FTIR one but underestimates the peak-to-peak amplitude with 88.6±1.3 % and 70.4±1.2 % for "IASI" and "MEGAN" respectively.

No systematic bias is observed on the whole time series, but a seasonal bias is characterized (see Fractional differences on top panel). The IMAGES v2 model tends to overestimate methanol columns during wintertime and underestimate them on summer.

Figure 4 - Seasonal Modulation

Running mean fit parameters : a 15-day step and a 2-month wide integration time

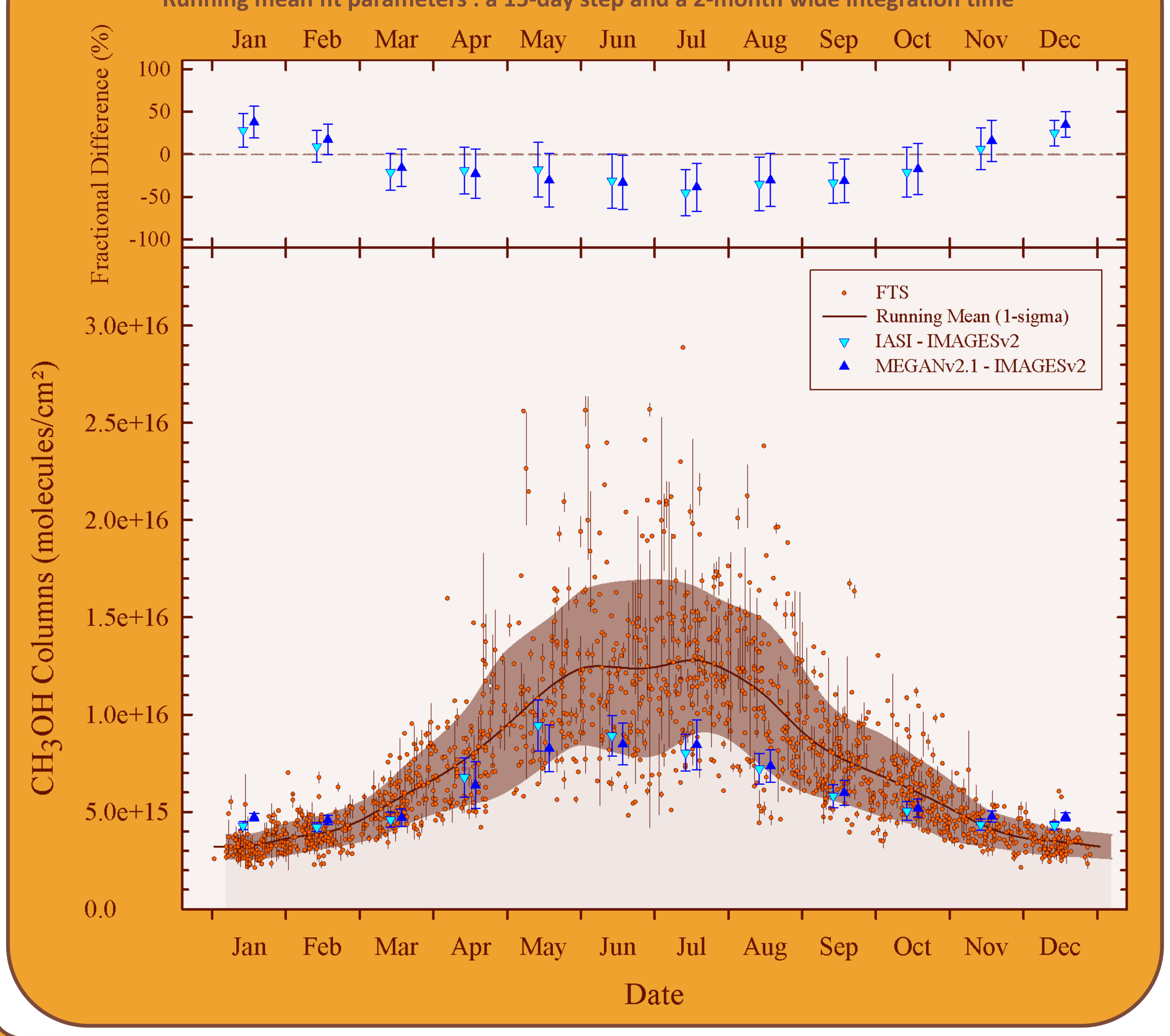
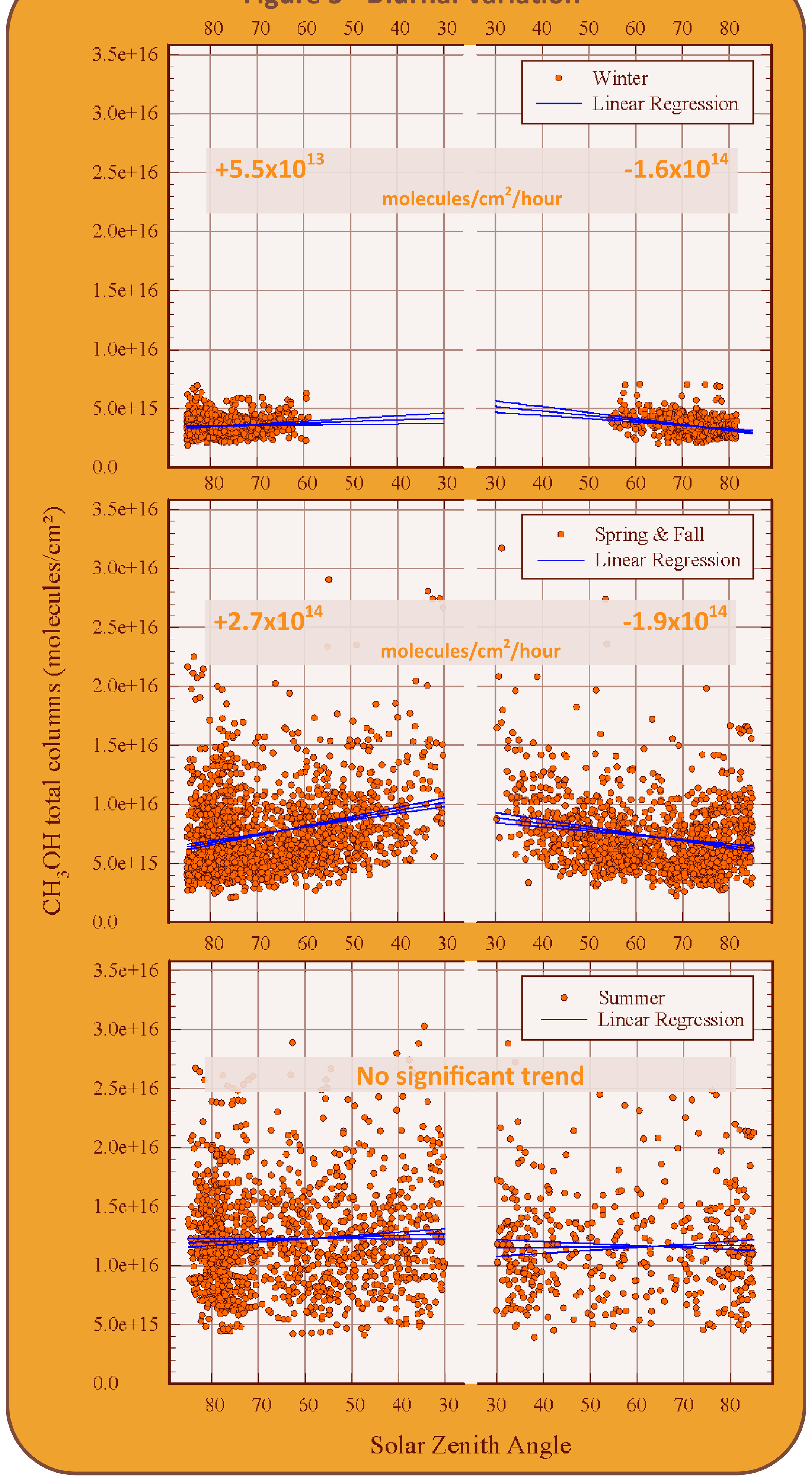


Figure 5 - Diurnal Variation



- Figure 5 - We found no significant trend of methanol through the day in summer but a significant increase during winter and the rest of the year has been evaluated. The causes for the observed diurnal variation are not clear. Major methanol sources such as biogenic production by living plants and photochemical production are stronger during daytime, due to the key role played by solar radiation in photosynthesis and other biotic processes, as well as in the generation of OH radicals through photolytic processes (Logan et al., 1981). However, these sources are expected to peak during the summer, when the diurnal variation of the column is found to be negligible. Since the photochemical sink of methanol (i.e. reaction with OH) is strongest during the day, the observed diurnal variation (and absence thereof during summer) could result from the variable balance between sources and sinks. More efforts should be put in further research on processes governing the methanol diurnal variation.

Figure 1 - Simulation for Jungfraujoch (80°), 6.1 mK, HIT-08

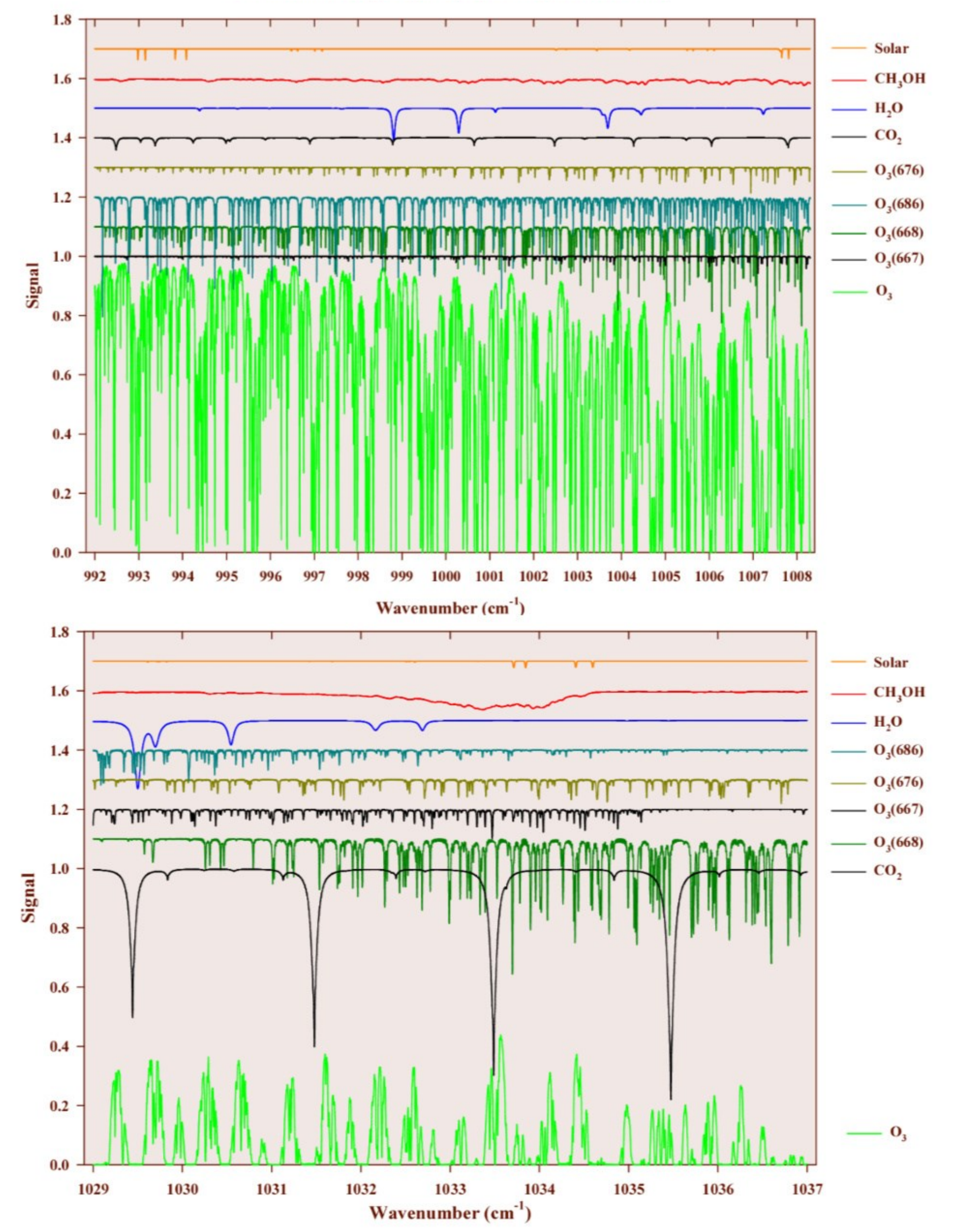
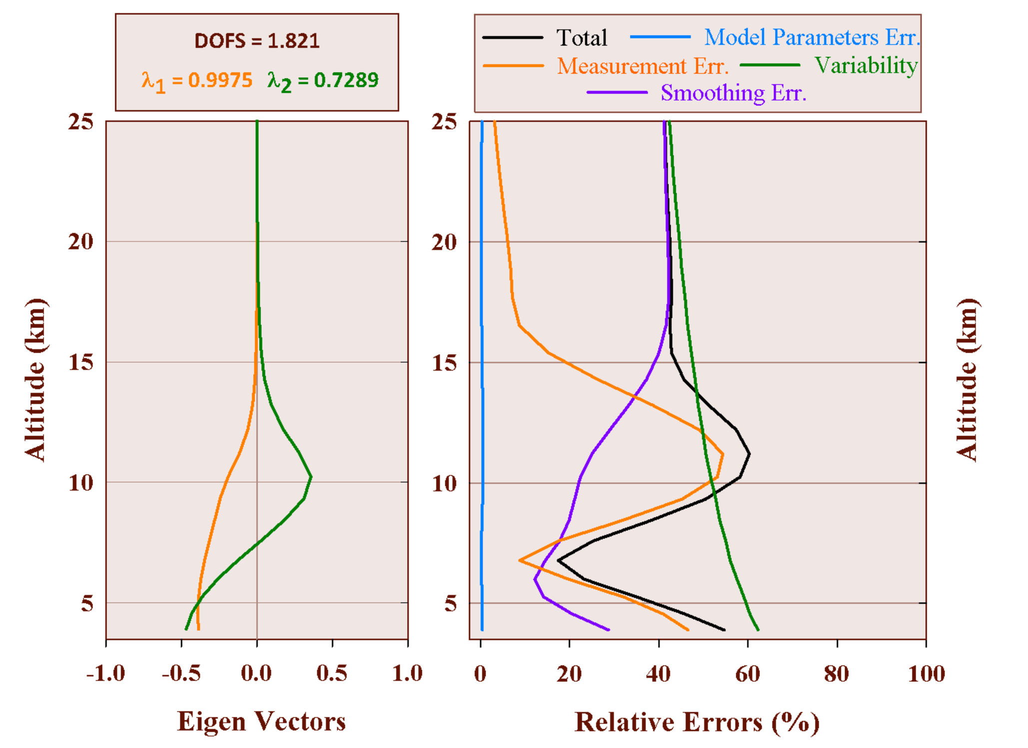


Figure 2 - Information Content and Error Budget



The Jungfraujoch Station

° Our observational database is composed of recordings from two high resolution Fourier Transorm InfraRed (FTIR) spectrometers (a homemade and a Bruker IFS-120HR) operated under clear sky conditions at the International Scientific Station of the Jungfraujoch (46.5°N, 8°E, 3580 m a.s.l.) since the early 1990s. This site is located in the Swiss Alps on the saddle between the Jungfrau (4158 m) and the Mönch (4107 m) summits.

° The IR solar absorption monitoring is into regular operation since 1984. Since 1991, the FTIR instrument is affiliated to the framework of the Network for the Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org). All high resolution (0.004 and 0.006 cm^{-1}) spectra investigated here have been recorded with a Bruker IFS-120HR instrument and range from 700 to 1400 cm^{-1}.

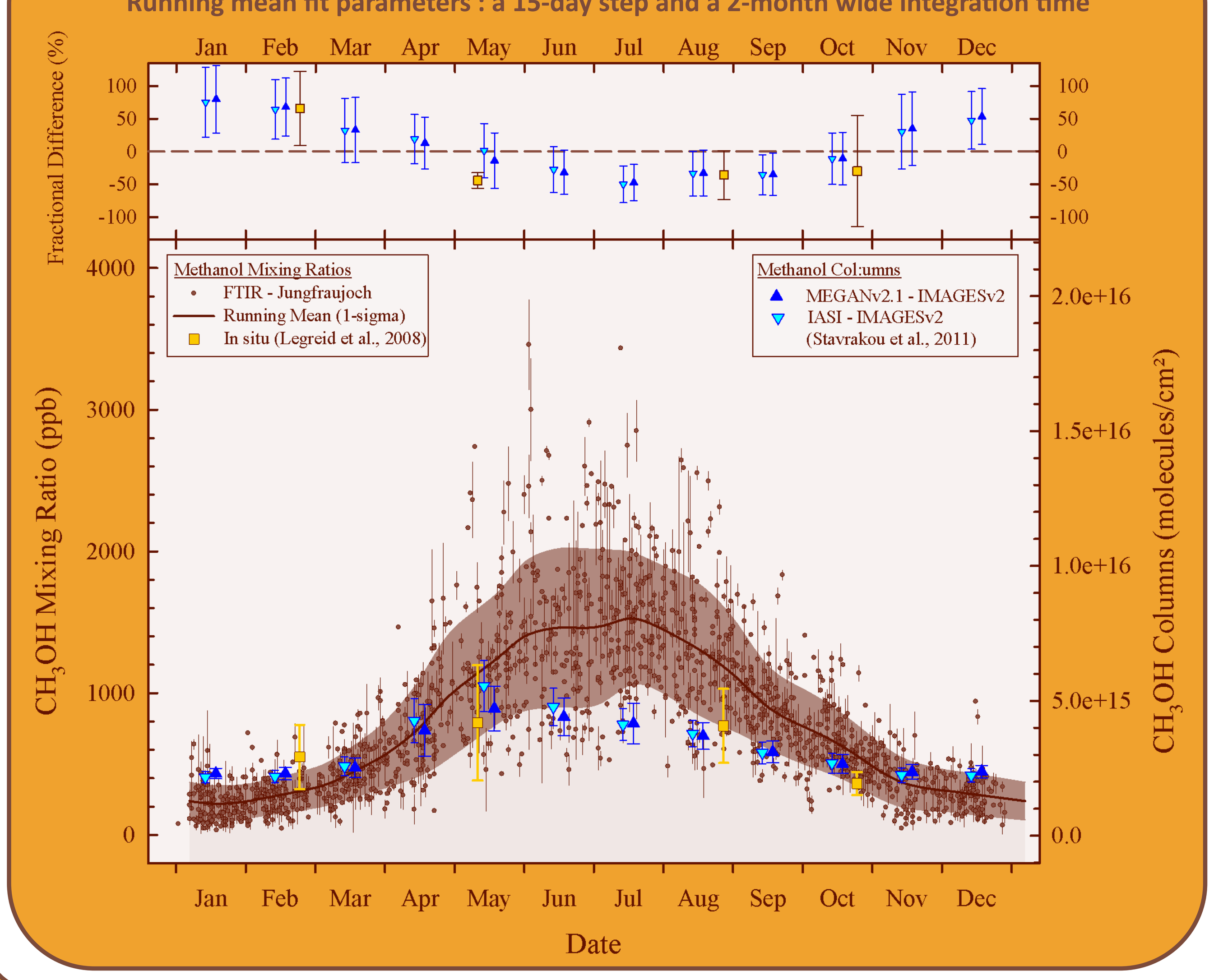
Methanol background information

Methanol (CH_3OH) is an organic compound of the atmosphere with concentrations close to a few ppbv. Despite a lifetime of a few days (Jacob et al., 2005) CH_3OH is the second most abundant organic molecule in the atmosphere (after methane). Natural sources of CH3OH include plant growth, oceans, decomposition of plant matter, oxidation of methane and other VOCs,... Anthropogenic sources are from vehicles, industry,... biomass burning completes the emission budget. The main sink is the oxidation by hydroxyl radical, leading to the formation of carbon monoxide (CO) and formaldehyde (H_2CO).

Lower tropospheric and upper-tropospheric lower-stratospheric partial columns

Figure 6 - LT Seasonal Modulation (3.58-7.18 km)

Running mean fit parameters : a 15-day step and a 2-month wide integration time



- Figure 6 - Methanol lower tropospheric columns shows a wider peak-to-peak amplitude of 168±3% than the total column seasonal modulation. Both of IMAGESv2 series underestimate the peak-to-peak amplitude with 78±2 % and 101±2 % for MEGAN and IASI, respectively. For both series, methanol is overestimated in winter (DJF) and shows a good agreement in spring (MAM) as well as in October and November. During summertime, results during July are significantly underestimated but the difference for the remaining 3 months (June, Augustus and September) is close to non-significant.

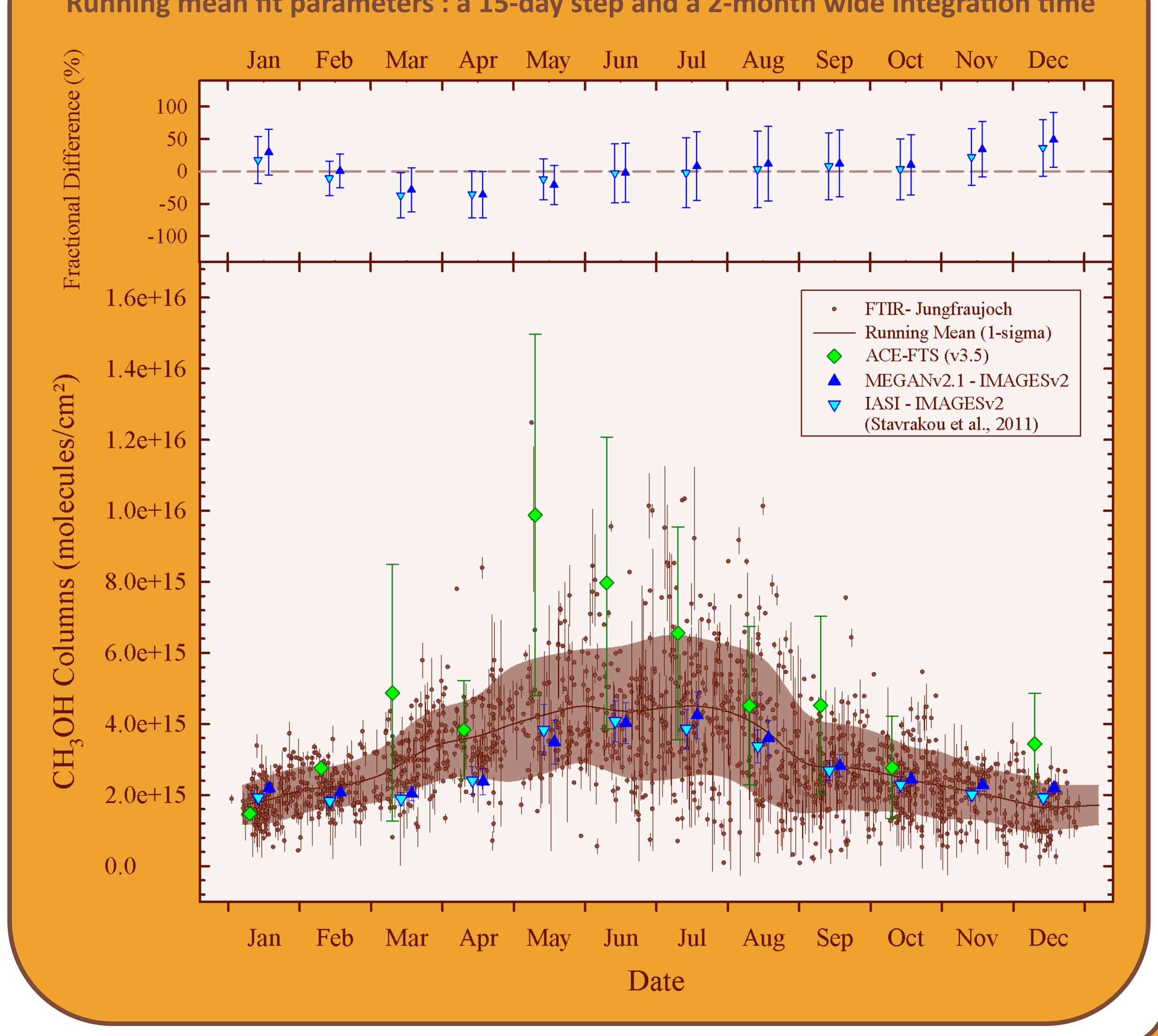
The seasonal amplitude of the in situ measurements is significantly lower than in the FTIR data, although a good agreement is found on the data dispersion (see error bars) except for the fall season with more compact values.

- Figure 7- The comparison between the UTLS FTIR columns, both IMAGES datasets and monthly mean results from ACE-FTS occultations shows an overall good agreement. The peak-to-peak amplitudes of the three series, i.e. 93±2 % for FTIR, 82±2 for MEGAN and 92±2% for IASI are in very good agreement as well as the timing of the maximum (June-July).

A close to statistical agreement is observed between Jungfraujoch results and the UTLS columns derived from ACE-FTS data with a mean fractional difference of 33±30% despite substantially higher ACE methanol columns in March and May. The differences for these two months may be attributed to the fact that monthly mean results from ACE-FTS encompass a 10° latitudinal band and therefore occultations may be capturing local events such as plumes from biomass burning out of range for the Jungfraujoch station.

Figure 7 - UTLS Seasonal Modulation (7.18-14.84 km)

Running mean fit parameters : a 15-day step and a 2-month wide integration time



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