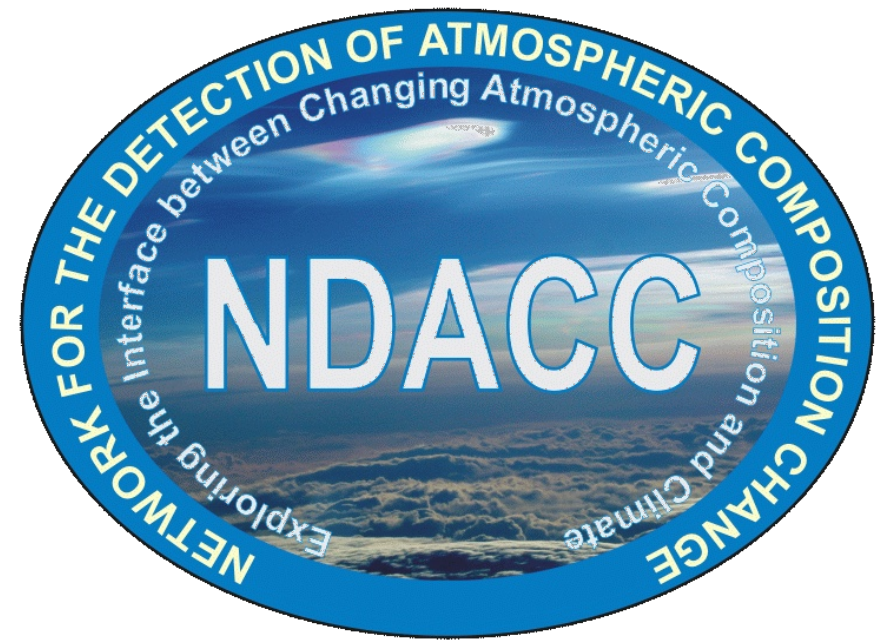


Retrieval of methanol (CH₃OH) above the high-altitude Jungfraujoch station (46.5°N): preliminary total column time series, long-term trend and seasonal modulation

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INSTRUMENTATION, SITE, OBSERVATIONAL DATABASE AND TOOLS

-- Two high-resolution Fourier Transform InfraRed (FTIR) spectrometers are operated under clear-sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (ISSJ, Swiss Alps, 46.5°N, 8.0°E, 3580m a.s.l.). Both instruments are equipped with HgCdTe and InSb cooled detectors, allowing to cover the 650 to 4500 cm⁻¹ region of the electromagnetic spectrum.

-- The ISSJ site is located on the saddle between the Jungfrau (4158m) and the Mönch (4107m) summits. FTIR monitoring activities are conducted at that site within the framework of the Network for the Detection of Atmospheric Composition Change (NDACC, see <http://www.ndacc.org>). More information on the involvement of the University of Liège at the Jungfraujoch station since the early 1950s as well as on some representative achievements can be found in Zander et al. [2008].

-- For the present investigations, we use high-resolution (0.004 and 0.006 cm⁻¹) IR solar absorption spectra spanning the 700-1400 cm⁻¹ interval. They have been recorded year-round, on a regular basis, with a Bruker IFS-120HR instrument. We focus here on a subset of our database and only include observations recorded from 1996 onwards. Signal-to-noise ratios are on average close to 800.

-- All retrievals have been performed with the SFIT-2 algorithm (v3.91) which is based on the semi-empirical implementation of the Optimal Estimation Method of Rodgers [1990]. This code allows, in most cases, to retrieve information on the vertical volume mixing ratio (VMR) profile of the species accessible to the ground-based FTIR technique.

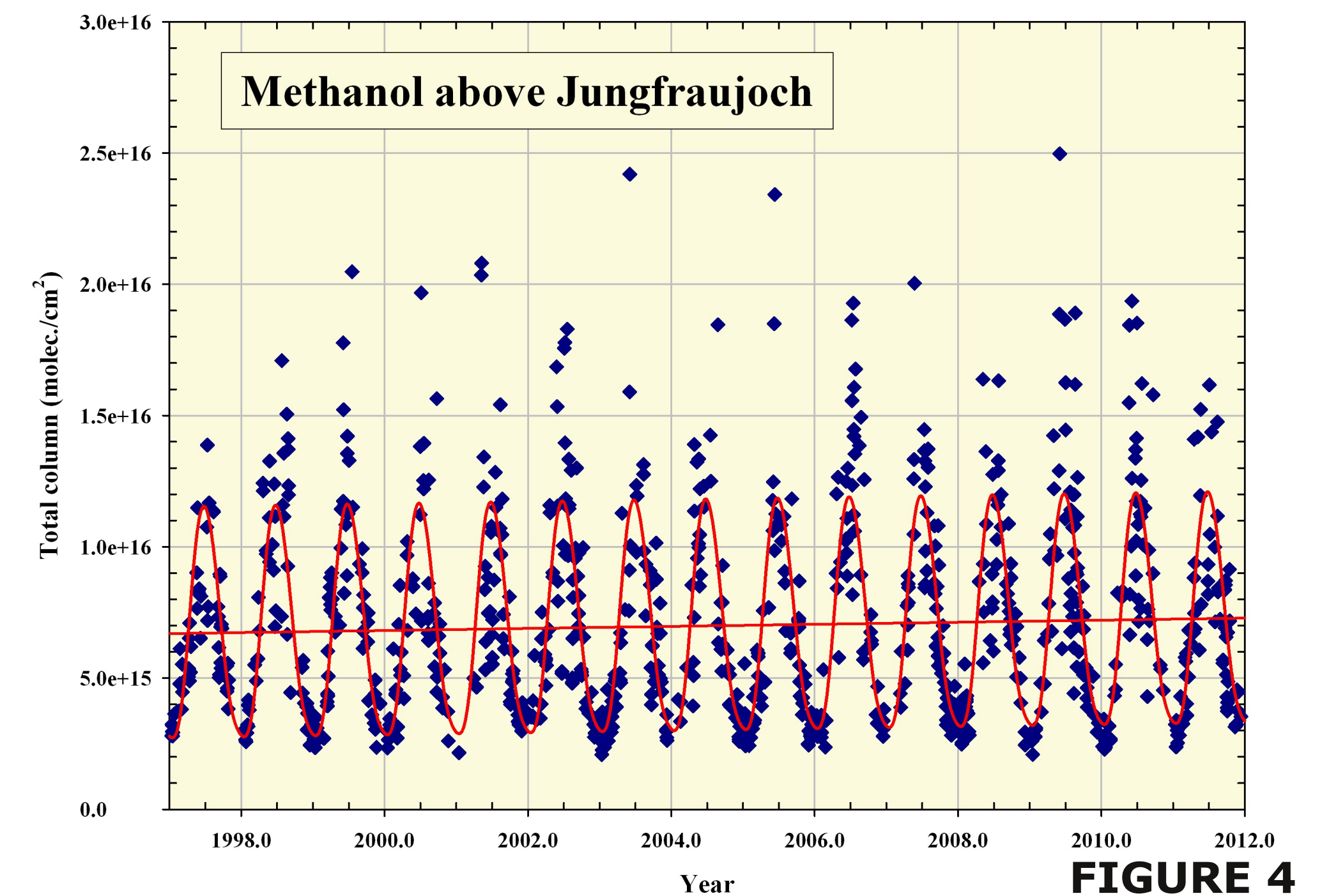


FIGURE 4

BACKGROUND INFORMATION ON METHANOL (CH₃OH)

- Methanol (CH₃OH) is a key organic compound in the Earth's atmosphere, with reported concentrations on the order of a few ppbv
- It is therefore the second most abundant atmospheric organic compound after methane (CH₄), despite an estimated lifetime of only a few days [Jacob et al., 2005]
- Natural sources of CH₃OH include plant growth, oceans, decomposition of plant matter, oxidation of methane...
- Anthropogenic sources are from vehicles, industry...; biomass burning completes the emission budget
- The main sink is oxidation by the hydroxyl radical, leading to the formation of carbon monoxide (CO) and formaldehyde (H₂CO) [e.g. Rinsland et al., 2009; Stavrou et al., 2011, and references therein]

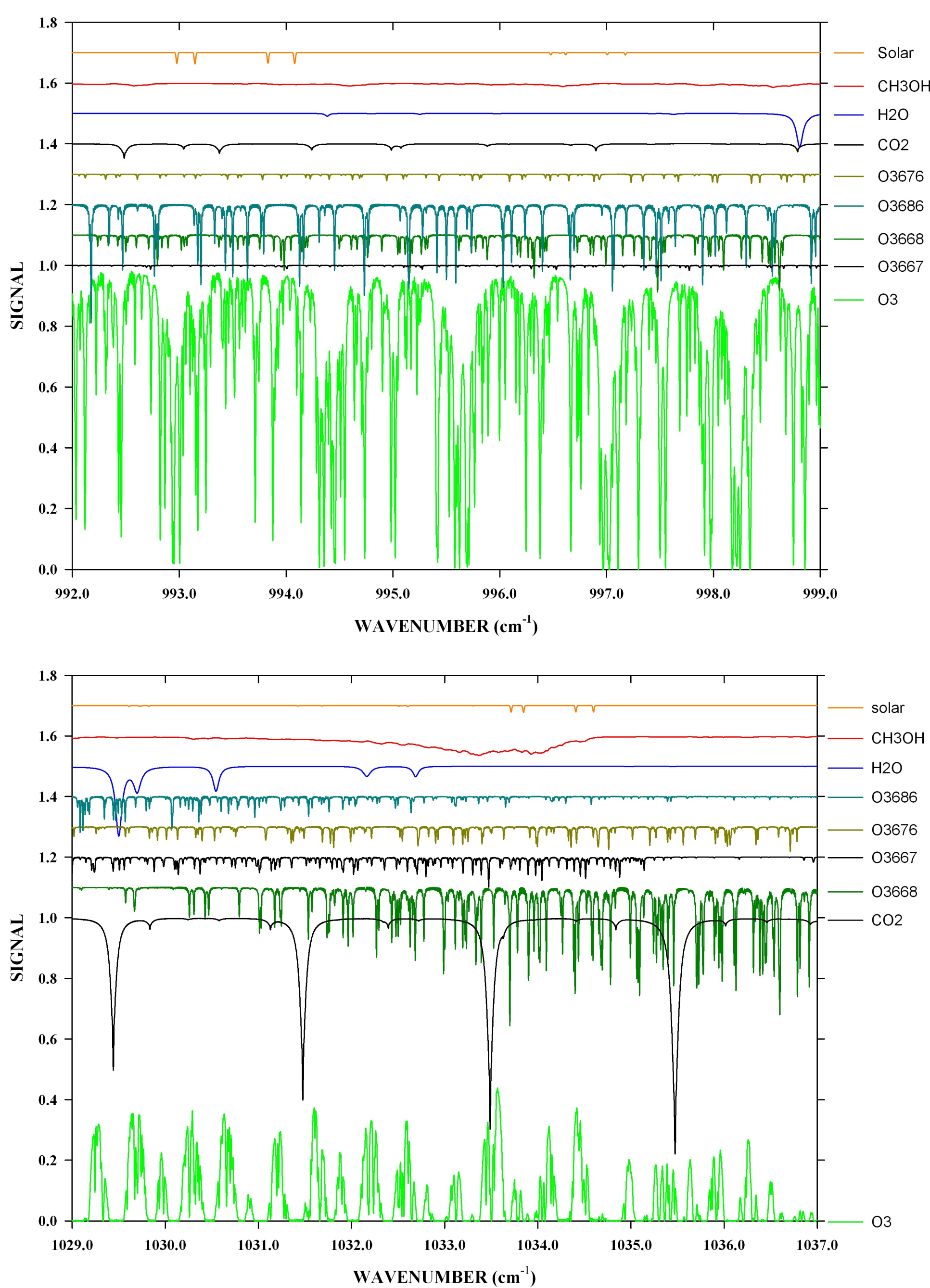


FIGURE 1

SIMULATIONS OF TWO METHANOL WINDOWS FOR THE JUNGFRAUJOCH STATION

Using HITRAN 2008 [Rothman et al., 2009] and averaged VMR profiles based on WACCM model predictions for the 1970-2020 time period [the Whole Atmosphere Community Climate Model, <http://waccm.acd.ucar.edu>], we have computed synthetic spectra (0.006 cm⁻¹, zenith angle of 80°) for the first and second order absorbers in two CH₃OH windows. They range from 992 to 999 cm⁻¹ and from 1029 to 1037 cm⁻¹ and encompass features of the strong ν₃ band of CH₃OH. These intervals were used for the retrieval of CH₃OH by Rinsland et al. [2009] and Stavrou et al. [2011], respectively. The individual gaseous absorptions are reproduced using color codes in the two frames of FIGURE 1, they have been shifted vertically for clarity. Identification of the absorbing gases is provided on the right hand side of the simulations.

Absorption by the main ozone isotopologue (¹⁶O-¹⁶O, or O₃) is prominent, particularly in the second window where it captures nearly 93% of the IR radiation, i.e. much closer to saturation than in the first window (29%). Methanol features are much weaker, with mean absorptions of 1.4 and 1.6% in the "999" and "1037" windows, respectively. Additional significant absorptions are associated to several ozone isotopologues (e.g. O3686, for ¹⁶O-¹⁸O-¹⁶O, O3668), carbon dioxide (CO₂) and water vapor (H₂O).

All relevant 2010 spectra recorded with zenith angles between 75° and 85° have been independently fitted to retrieve CH₃OH in the selected windows. We display in FIGURE 2 a scatter plot of the two total column data sets, indicating a very compact correlation. There is no significant bias between the two regions, with a mean relative difference between the two regions of -(0.6±3.0)% (1-sigma).

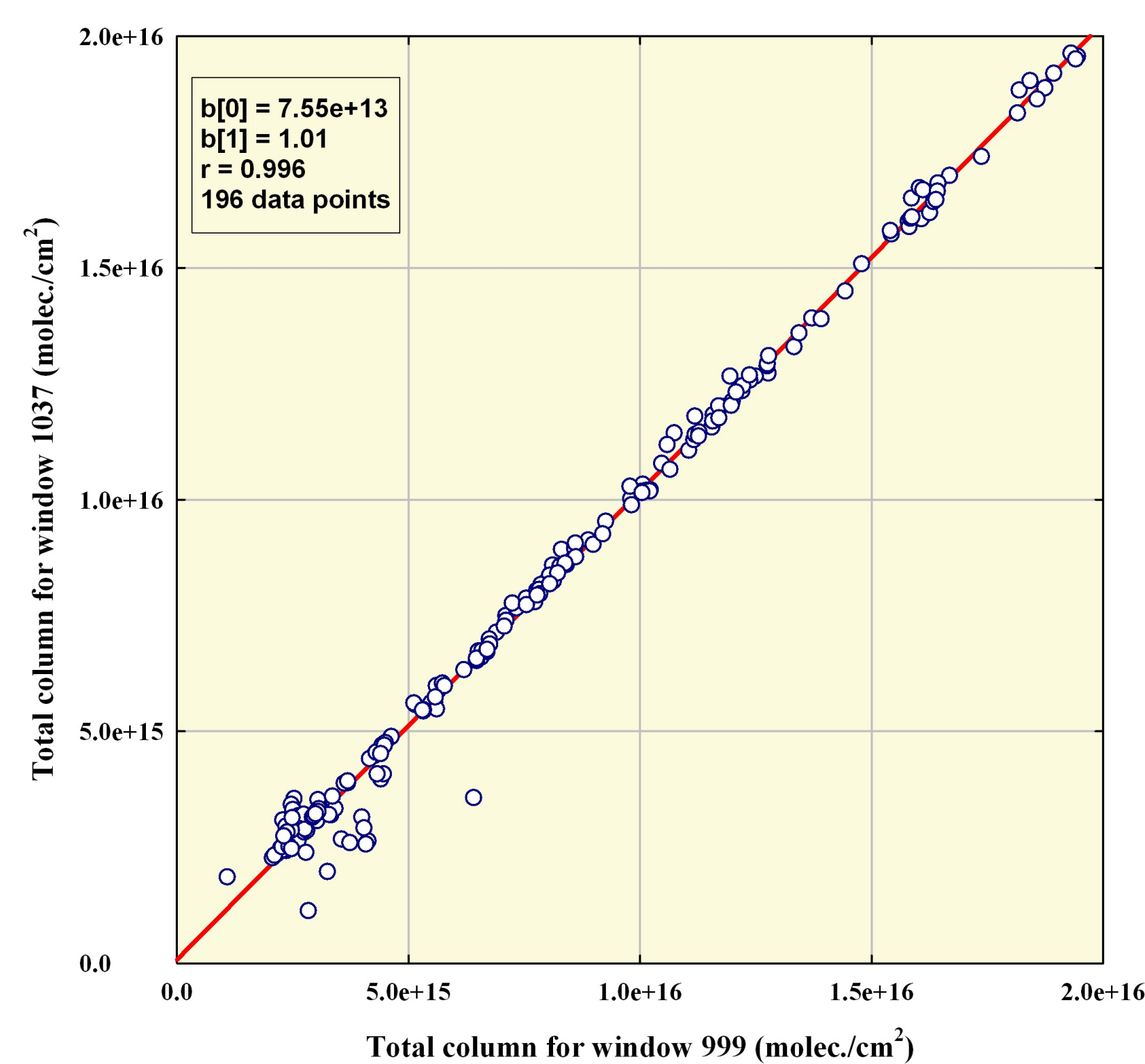


FIGURE 2

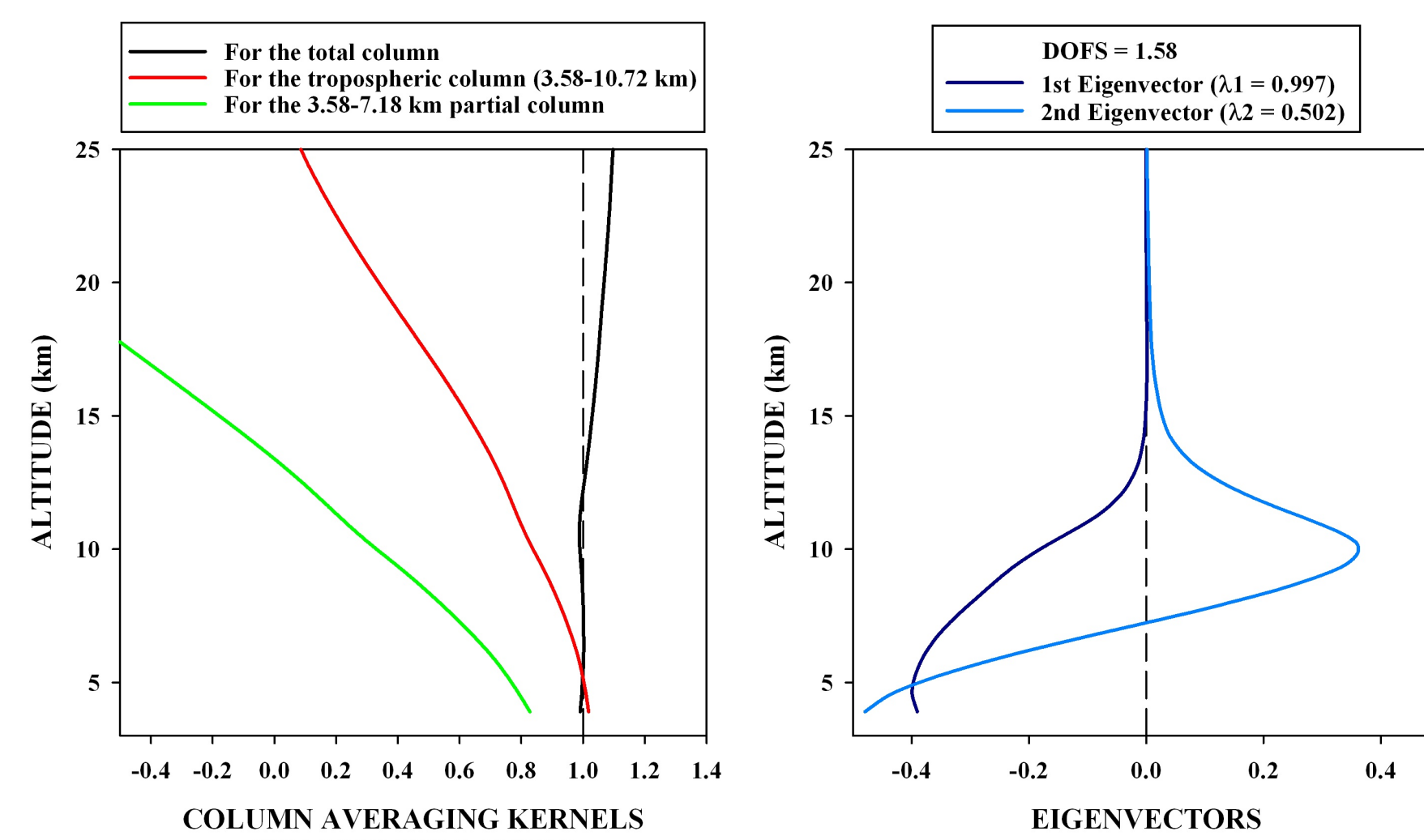


FIGURE 3

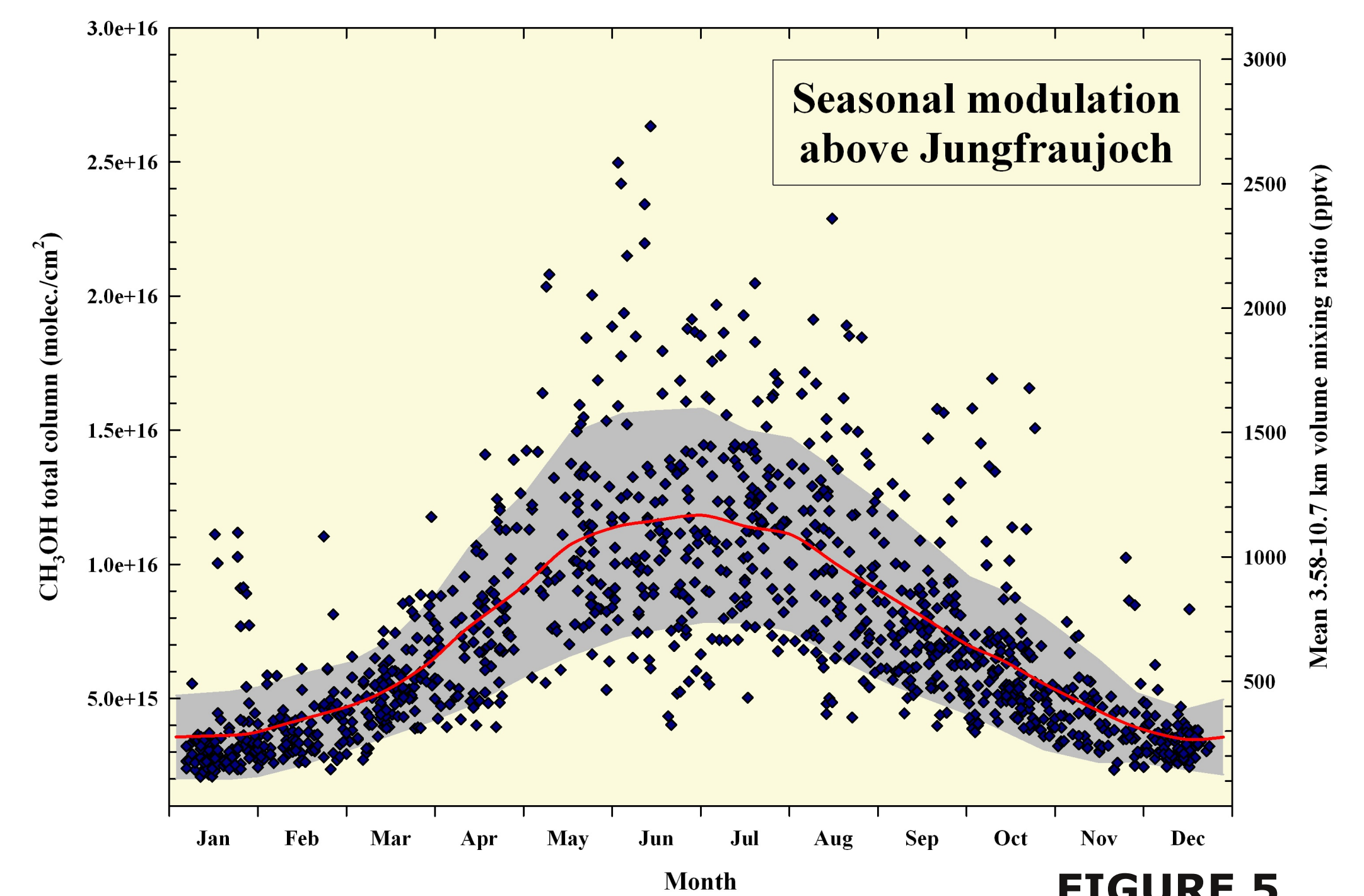


FIGURE 5

RETRIEVAL STRATEGY AND PRELIMINARY METHANOL TIME SERIES

-- Given the very good agreement found between the two selected windows, we combined them to maximize the information content. The adopted settings are: (i) two spectral intervals ranging from 992 to 998.7 and from 1029 to 1037 cm⁻¹ are simultaneously fitted, (ii) the VMR profiles of CH₃OH, O₃ and O3686 are retrieved during the iterative process while the a priori distributions of H₂O, CO₂, O3668, O3676 and O3667 are scaled, (iii) we adopted a 50%/km diagonal covariance and a Gaussian half-width for interlayer correlation of 4 km for extra diagonal elements, (iv) since the fitting quality is significantly different in both windows, we selected two different values for the signal-to-noise for inversion, i.e. 170 and 40 for the 999 and 1037 domains, respectively. Line parameters from the HITRAN 2008 compilation were used while we assumed pressure and temperature profiles provided by the National Centers for Environmental Predictions (NCEP, see <http://www.ncep.noaa.gov>). Resulting typical information content is illustrated in FIGURE 3, the mean Degree Of Freedom for Signal (DOFS) amounts to 1.6 (instead of ~1.2 for the single window approaches). The retrieval is essentially sensitive to the troposphere, with limited vertical resolution (second Eigenvalue close to 0.5). Typical uncertainty on the total columns -including the smoothing error component- is on the order of 7%.

-- FIGURE 4 reproduces the daily mean total column time series of CH₃OH above Jungfraujoch, normalised to 654 hPa. We evaluated the trend of methanol over 1997-2011 with the bootstrap resampling statistical tool described in Gardiner et al. [2008], we found a yearly positive increase of (3.94±3.62) 10¹³ molec./cm² (2-sigma), i.e. at the limit of being statistically significant at that confidence level.

-- FIGURE 5 shows the daily mean total columns over a 1-year time base. The red curve corresponds to a running mean fit to all data points, with a 15-day step and a 2-month wide integration time. The grey area corresponds to the 1-sigma standard deviation associated to the running mean curve. The strong seasonal modulation is characterized by minimum values (and variability) in December to February and maximum columns in June-July. The ratio between these observed seasonal extremes is equal to about a factor of 4.

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ACKNOWLEDGMENTS

The University of Liège contribution to the present work has primarily been supported by the SSD and PRODEX programs (AGACC-1 and ASC projects, respectively) funded by the Belgian Federal Science Policy Office (BELSPO), Brussels, and by MeteoSwiss within the GAW-CH program. Laboratory developments and mission expenses were funded by F.R.S. - FNRS and the Fédération Wallonie-Bruxelles, respectively. We thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFJG, Bern) for supporting the facilities needed to perform the observations. E. Mahieu is Research Associate with the F.R.S. - FNRS. We further acknowledge the vital contribution from all the Belgian colleagues in performing the Jungfraujoch observations used here.

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