Evolution of methanol (CH_3OH) above the Jungfraujoch station (46.5°N)
Variability, seasonal modulation and long-term trend.

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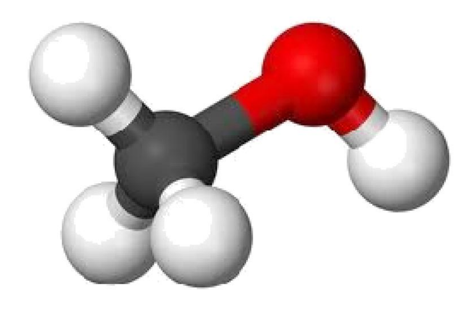

Methanol

° Methanol (CH_3OH) is, after methane, the second most abundant organic molecule in the atmosphere with concentrations close to a few ppbv, despite a lifetime of a few days (Jacob *et al.*, 2005).
° Natural sources of CH_3OH 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).

Retrieval Strategy

Windows, Fitted Species, Signal-to-noise for inversion (Figure 2 & 3)

Forward Model (SFIT-2 v 3.94)

Line parameters
HITRAN 2008
Rothman *et al.* (2009)

Atmospheric Model
~ 39 layers (from 3.95 to 85km)
~ daily p-T profiles (NCEP)
~ a priori volume mixing ratio profiles

National Center for Environmental Prediction (NCEP, Washington, USA)

Synthetic Spectra

Recorded Spectra (FTIR)
(solar zenith angle range : 60°-85°)

Minimum Residuals

NO

YES

→ VMR profiles
→ Total/partial columns (molecules/cm²)

CH_3OH
→ ACE-FTS mean profile for the 41.5-51.5 latitudinal band
→ 50%/km diagonal covariance
O_3 & $O_3(668)$
→ Satellite observations & model simulations

Figure 1

-A- *Windows* - Limits and interfering species

First retrievals of Methanol above Jungfraujoch - Mahieu *et al.*, 2012 : 2 windows

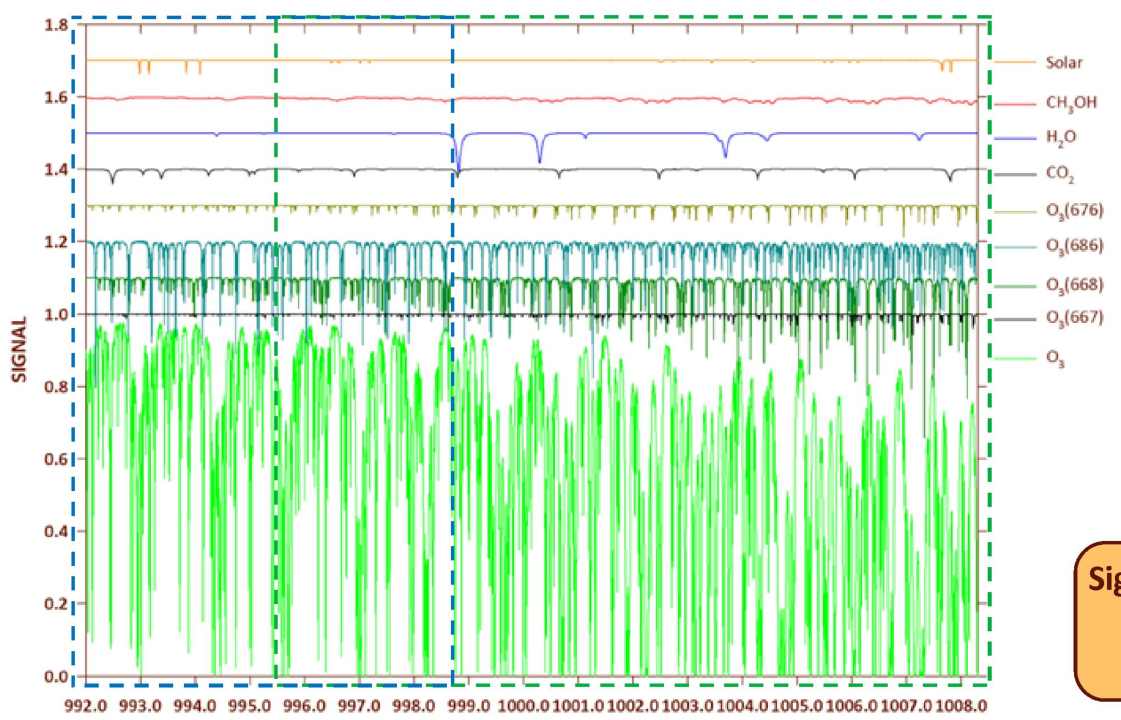

Figure 2

(1)
Rinsland *et al.*, 2009
992 - 998.7 cm-1

+

Dufour *et al.*, 2007
995.5 - 1008.3 cm^{-1}

Retrieved window
992 - 1008.3 cm^{-1}

Signal-to-noise for inversion : 180 and 40 for the (1) and (2) windows, resp.
Mahieu *et al.*, 2012

Retrieved vmr profiles
CH_3OH, O_3, $O_3(668)$
Scaled a priori
$O_3(686)$, $O_3(676)$, $O_3(667)$, CO_2, H_2O

(2)
Vigouroux *et al.*, 2012
1029 - 1037 cm^{-1}

Retrieved window
1029 - 1037 cm^{-1}

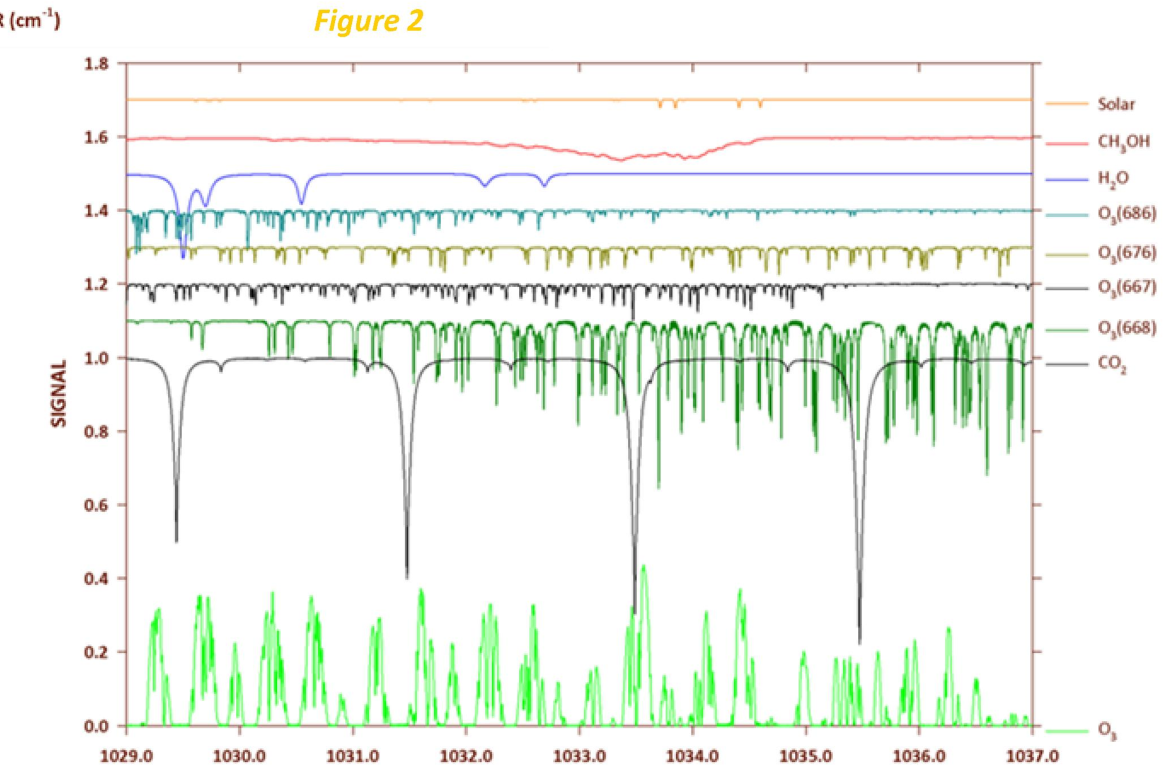

Figure 3

Instrumentation, Site and Observational Database

° Our observational database is composed of recordings from two high resolution Fourier Transorm InfraRed (FTIR) spectrometers (namely 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 mid-1980s. This site is located in the Swiss Alps on the saddle between the Jungfrau (4158 m) and the Mönch (4107 m) summits.
° Since 1991, the IR solar absorption monitoring is performed in the framework of the Network for the Detection of Atmospheric Composition Change (NDACC, visit http://www.ndacc.org). Both spectrometers are equipped with HgCdTe and InSb cooled detectors allowing us to cover the 650 to 4500 cm^{-1} region of the electromagnetic spectrum. 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}.

-B- *Optimization* - Error budget and information content

• All retrievals have been performed with the SFIT2 algorithm (v 3.91) (Rinsland *et al.*, 1998) following the retrieval strategy described in Figure 1.

• Information content and error budget have been carefully evaluated and typical results are displayed on Figure 4. The first eigen vector and corresponding eigenvalue (see left frame, in orange) show that information is mainly coming from the retrieval (99 %). Right frame gives the corresponding error budget, with identification of the main error components, together with the assumed variability (see Table I for additional errors, contributions and color codes).

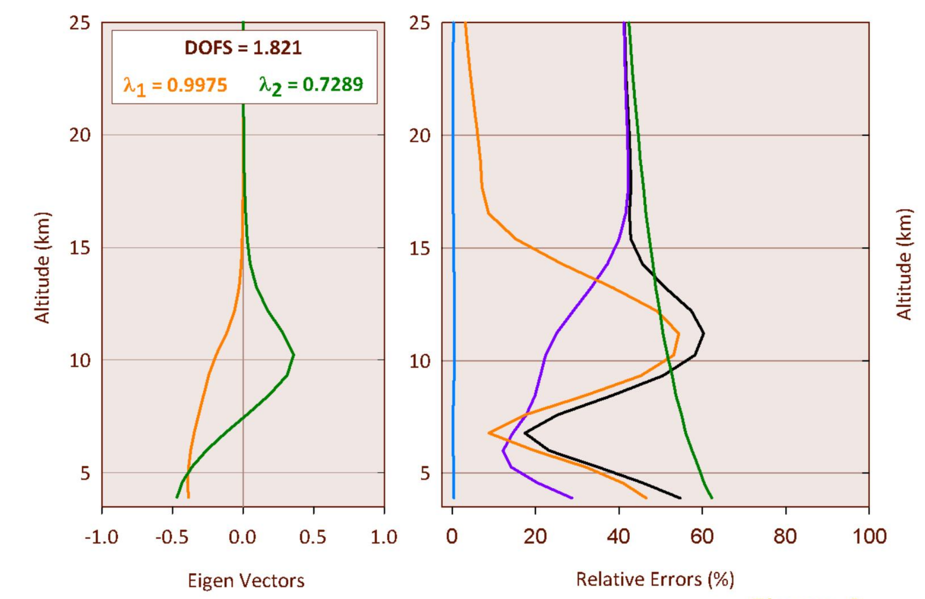

Figure 4

Error Contributions (Relative Errors - %)			
Error type	Total	LT	UTLS
Temperature	1.23 %	~ 15 %	< 10 %
Line intensities	0.33 %	~ 5 %	~ 7 %
Measurement Error	5.15 %	34.93 %	37.51 %
Smoothing Error	0.43 %	16.02 %	15.22 %
Model Parameters Error	0.22 %	0.34 %	0.53 %
Total Error	7.55 %	38.44 %	41.04 %
Variability : 39.75 %			

Table I

The increase of information content (DOFS of 1 in literature) allows us to retrieve a tropospheric column with only 1% of a priori dependence as well as two partials columns (i.e. low-tropospheric, LT, 3.58-6.39 km & upper troposphere lower stratosphere, UTLS, 7.2-14.8 km) with ~ 30% of a priori dependence.

- Table I - Error quantities associated with temperature uncertainties are provided by the NCEP while error on methanol line intensities is provided by Xu *et al.* (2004).

-C- *Spectroscopy*- Remaining systematic residuals

Some systematic residuals have been identified around 1033 cm^{-1} (see Figure 5). Harrison *et al.* (2012) published new methanol cross sections which indicated problems with the existing CH_3OH spectroscopic line parameters in the HITRAN database in the same region (see Figure 6). The next step is to test those new line parameters in order to erase the remaining systematic residuals.

- Figure 5 - Mean observed (blue curve)/simulated (red curve) spectra and residuals (green curve) on 291 spectral fits (6.1 mK).

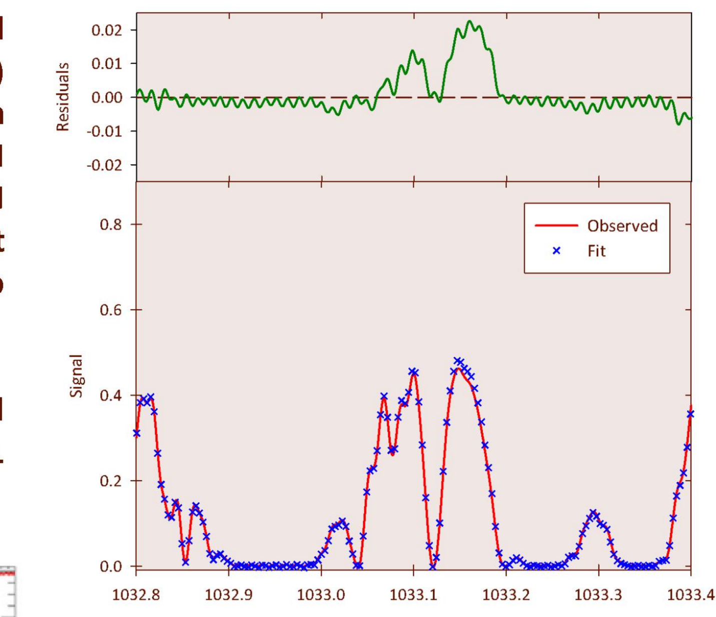

Figure 5

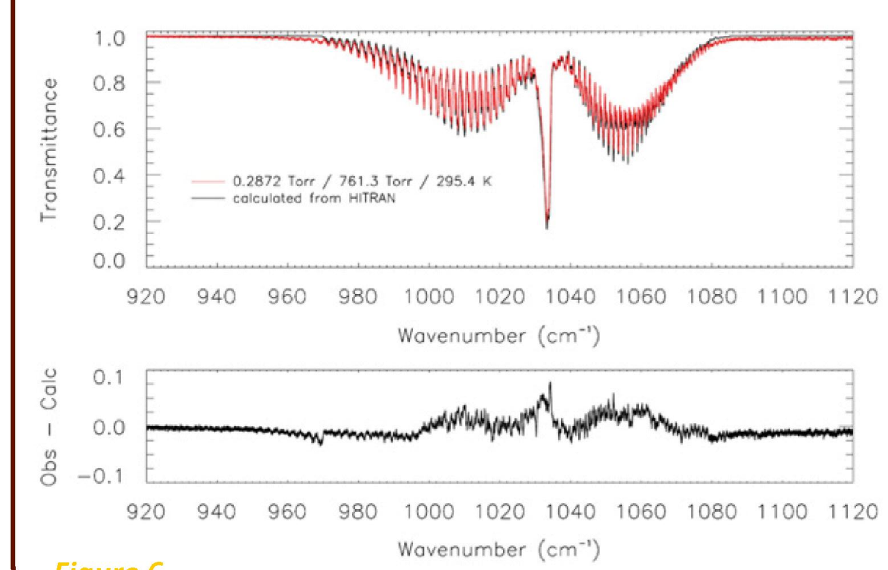

Figure 6

- Figure 6 - *"Fig. 4. Comparison between the air-broadened laboratory transmittance spectrum (10 mm) of methanol at 295.4 K (0.2872 Torr methanol, 761.3 Torr total pressure) with the corresponding synthetic spectrum calculated using the HITRAN linelist."* Harrison *et al.*, (2012).

-D- *Methanol Above Jungfraujoch* - Variability, seasonal modulation and long-term trend

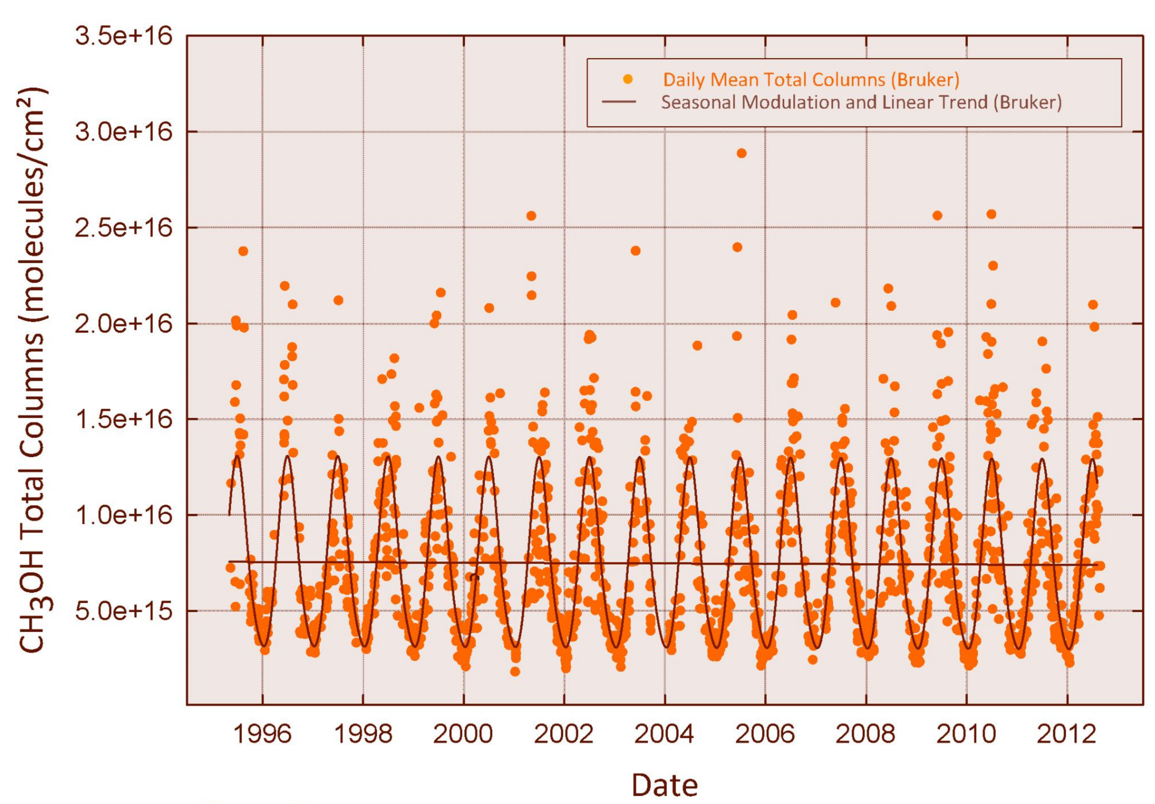

Figure 7

Figure 7 reproduces the daily mean total column time series of CH_3OH above Jungfraujoch. We evaluated the trend of methanol over 1995-2012 with the boostrap resampling statistical tool (Gardiner *et al.*, 2008) and found a yearly negative trend of (-0.95±2.61)x10^{13} molecules/cm² (2-sigma), i.e. a non significant trend at this level of confidence which is consistent with those computed by Rinsland *et al.* (2009).

The strong seasonal modulation 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, computed by Gardiner's tool and expressed as a percentage of the corresponding CH_3OH yearly mean column amounts to 133.2±8.1 % (1-sigma).

Figure 8 shows the daily mean total columns over a 1 year time base. The brown curve corresponds to a running mean fit to all data points, with a 15-day step and a 2-month wide integration time. The area corresponds to the 1-sigma standard deviation associated to the running mean curve.

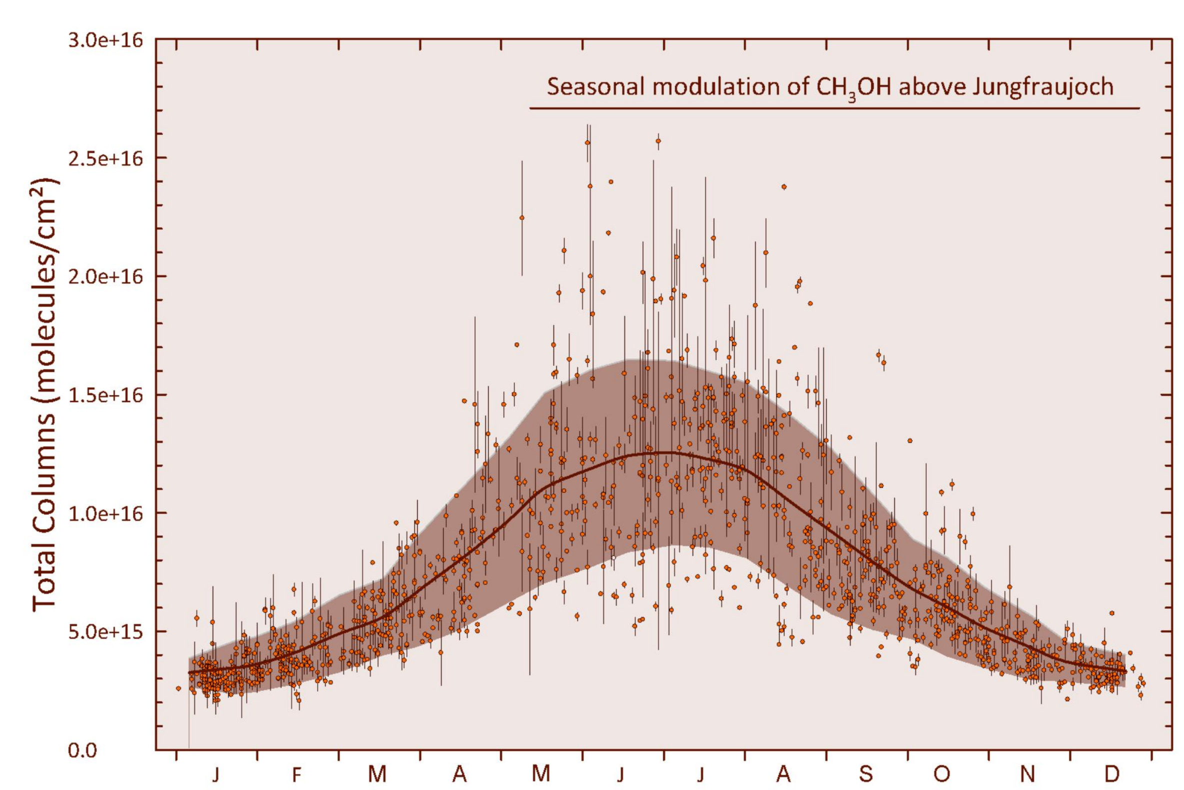

Figure 8

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~ Dufour, G. *et al.* (2007), Atmos.Chem. Phys., 7, 6119. ~ Gardiner, T. *et al.* (2008), *Atmos. Chem. Phys.*, 8, 6719. ~ Harrison, J. J. *et al.* (2012), J.Q.S.R.T., 113, 2189. ~ Jacob, D.J. *et al.* (2005), *J. Geophys. Res.*, 110, D08 303. ~ Mahieu, E. *et al.* (2012), *Poster presented at the General Assembly of the EGU in Vienna.* ~ Rinsland, C. P. *et al.* (1998), *J. Geophys. Res.*, 103, 28 197. ~ Rinsland, C.P. *et al.* (2009), *J. Geophys. Res.*, 114, D04 309. ~ Rothman, L.S. *et al.* (2009), J.Q.S.R.T., 110. ~ Vigouroux, C. *et al.* (2012), Atmos. Chem. Phys., 12, 10 367. ~ Xu, L.H. *et al.* (2004), J. Mol. Spectrosc., 228, 453.

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