JÜLICH FORSCHUNGSZENTRUM

Ground-based FTIR measurements: application to the atmospheric ethane upturn from the oil and gas boom

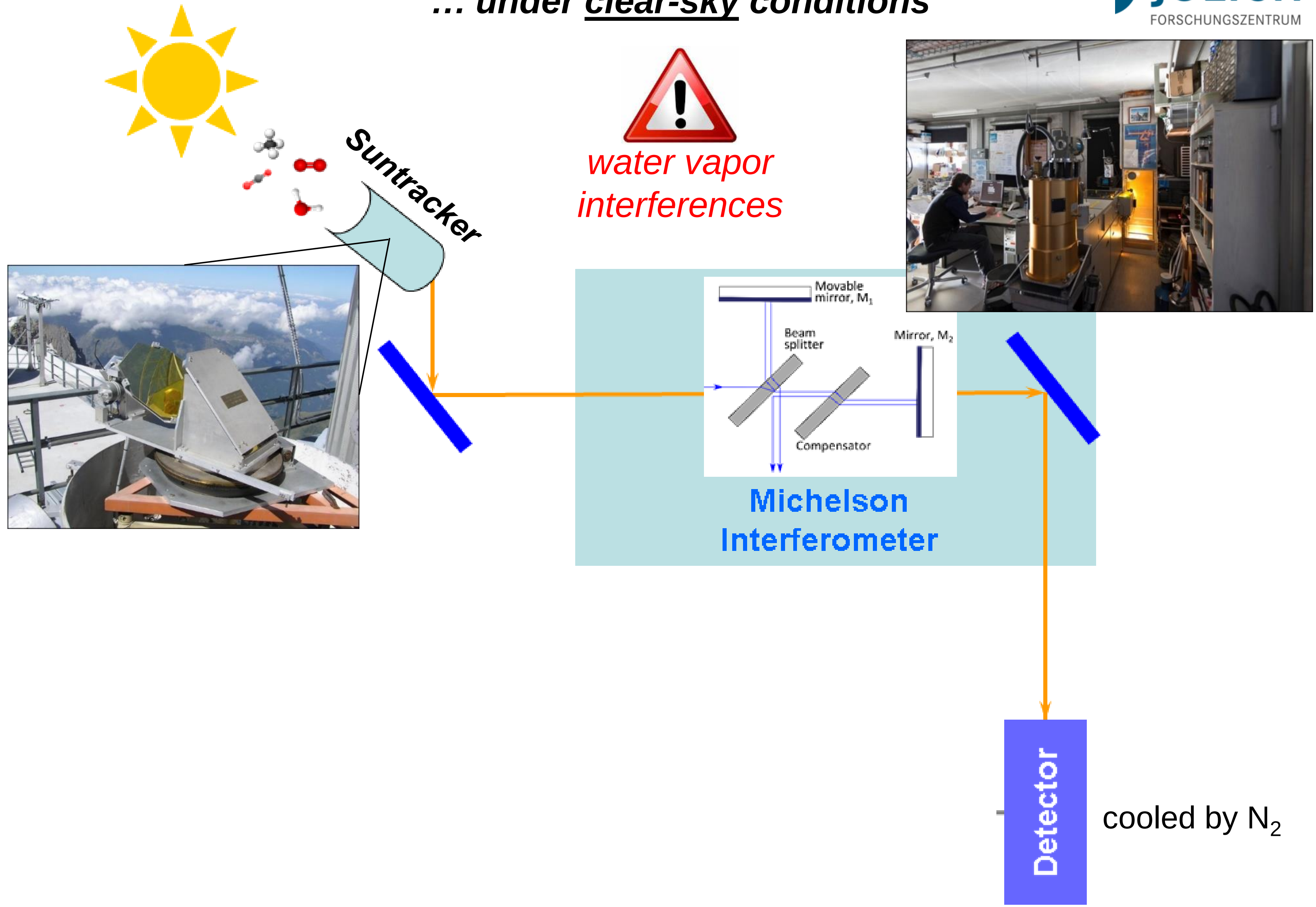
10 June 2016 | Bruno Franco

1. Ground-based FTIR observations

Jungfraujoch FTIR station
(Swiss Alps, 3580m a.s.l.)

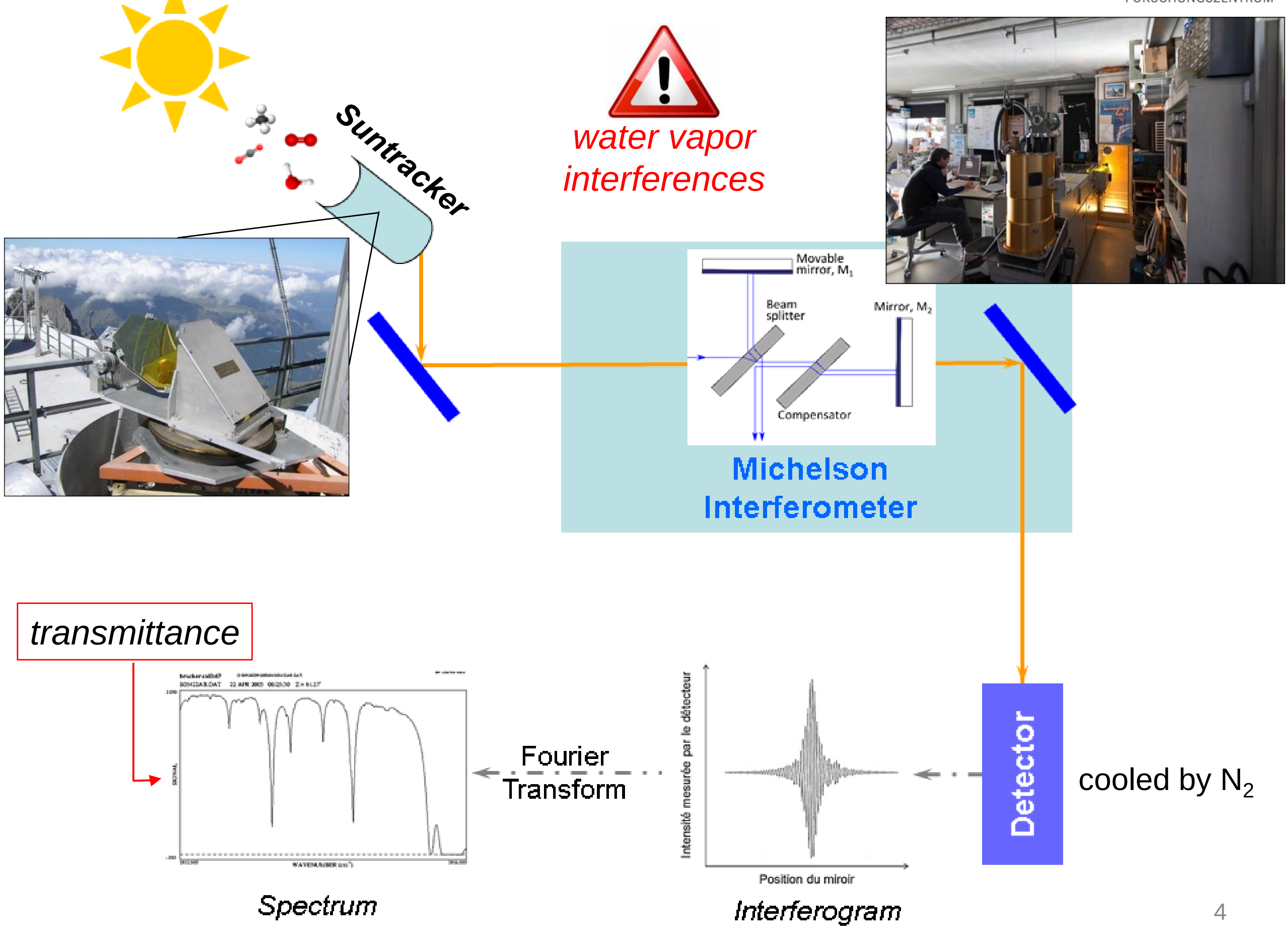
1. Ground-based FTIR observations

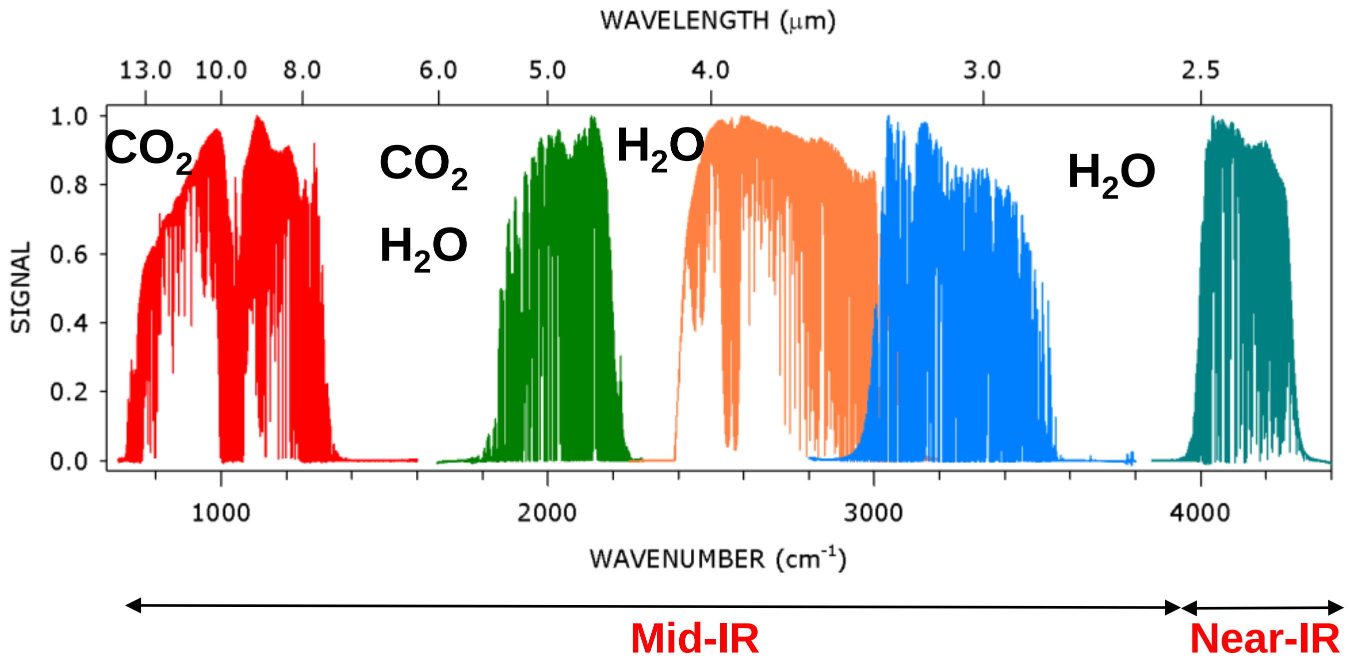
… under clear-sky conditions



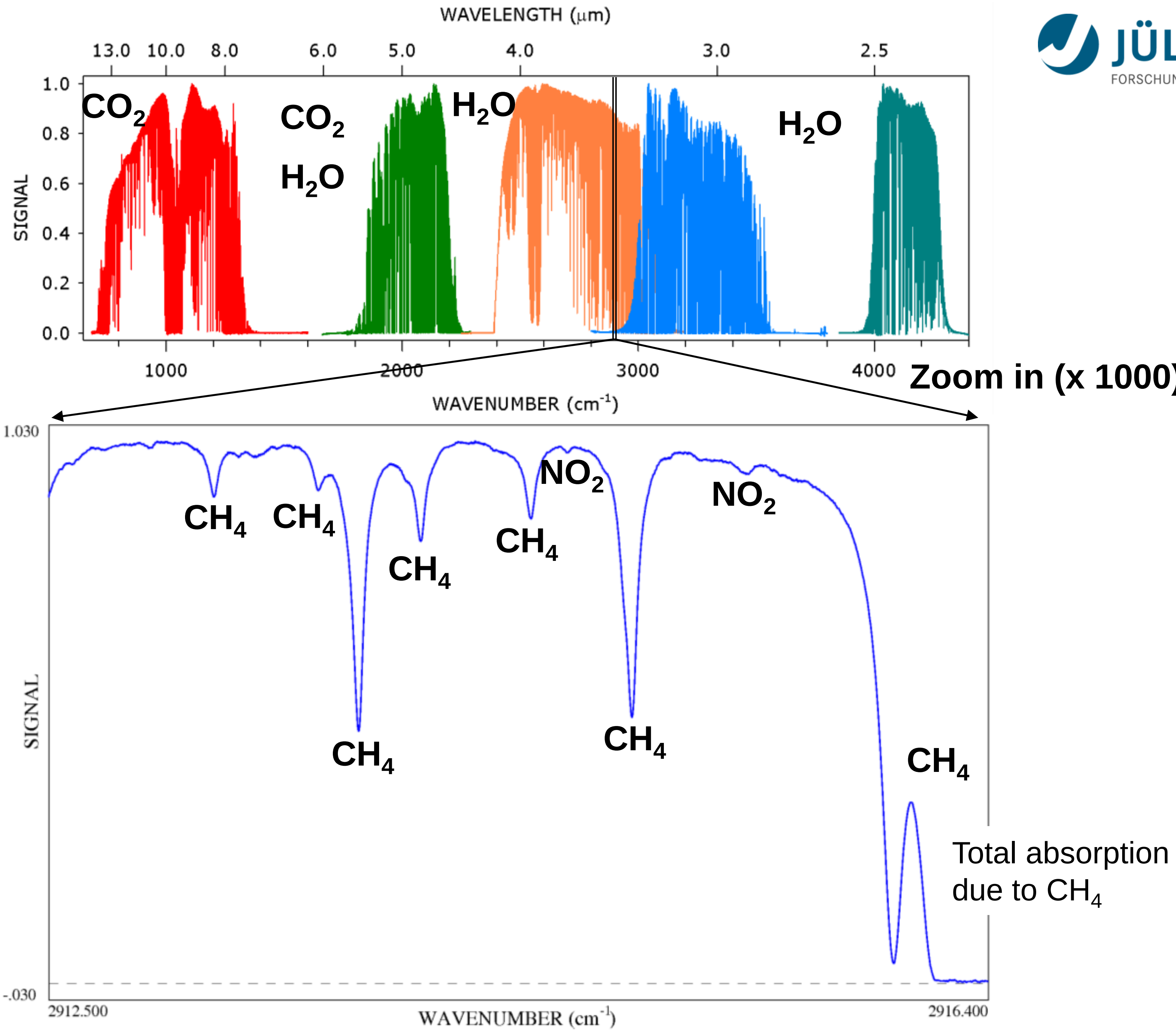
1. Ground-based FTIR observations

… under clear-sky conditions





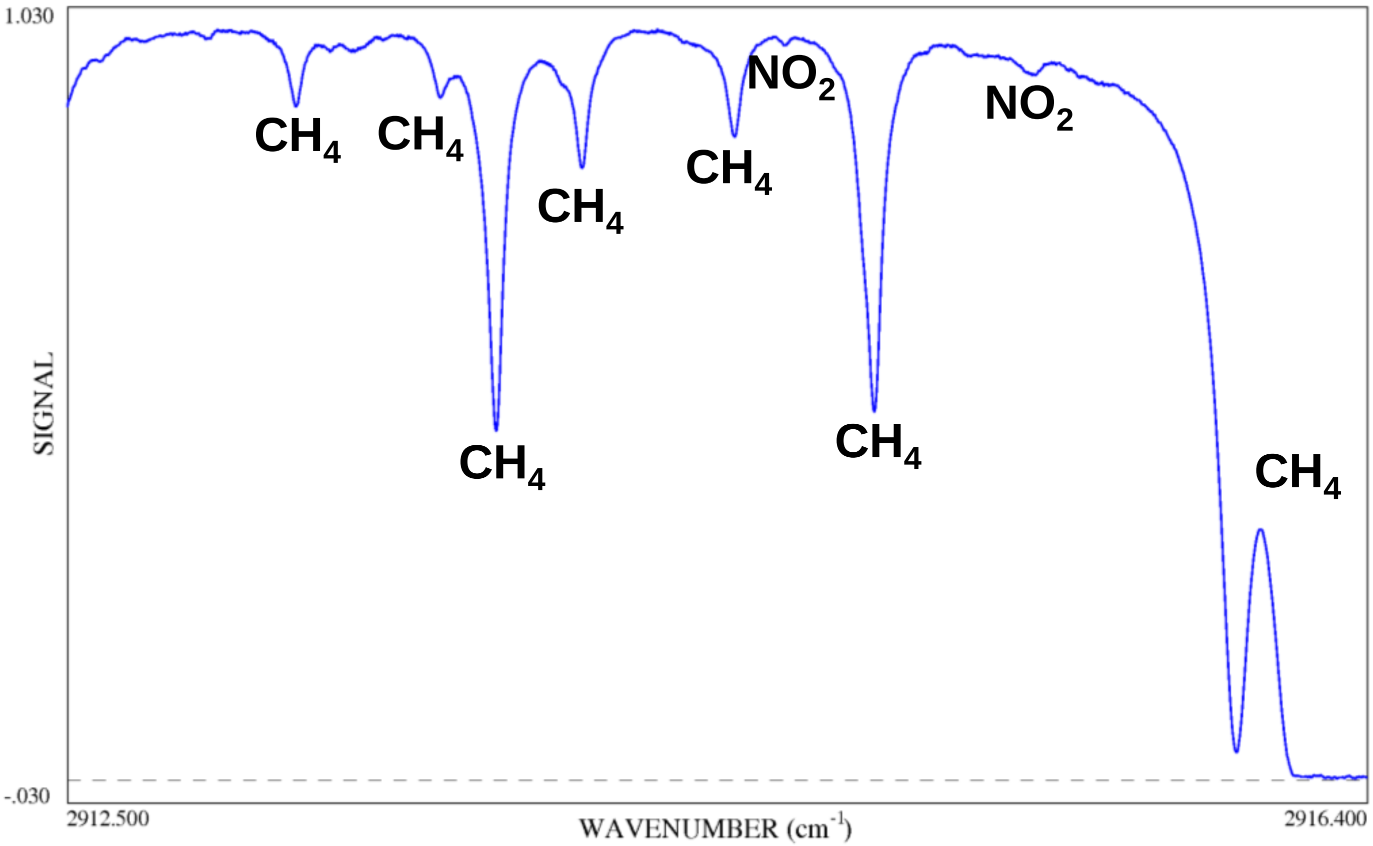
→ Optical filters to enhance the signal-to-noise ratio within specific wavelengths of the IR solar spectrum


WAVELENGTH (μm)
13.0 10.0 8.0 6.0 5.0 4.0 3.0 2.5
1.0 0.8 0.6 0.4 0.2 0.0
SIGNAL
CO2
CO2
H2O
H2O
H2O
1000 2000 3000 4000
WAVENUMBER (cm-1)
Zoom in (x 1000)
1.030
-.030
SIGNAL
CH4
CH4
CH4
CH4
CH4
CH4
CH4
NO2
NO2
Total absorption
due to CH4
2912.500
2916.400
WAVENUMBER (cm-1)

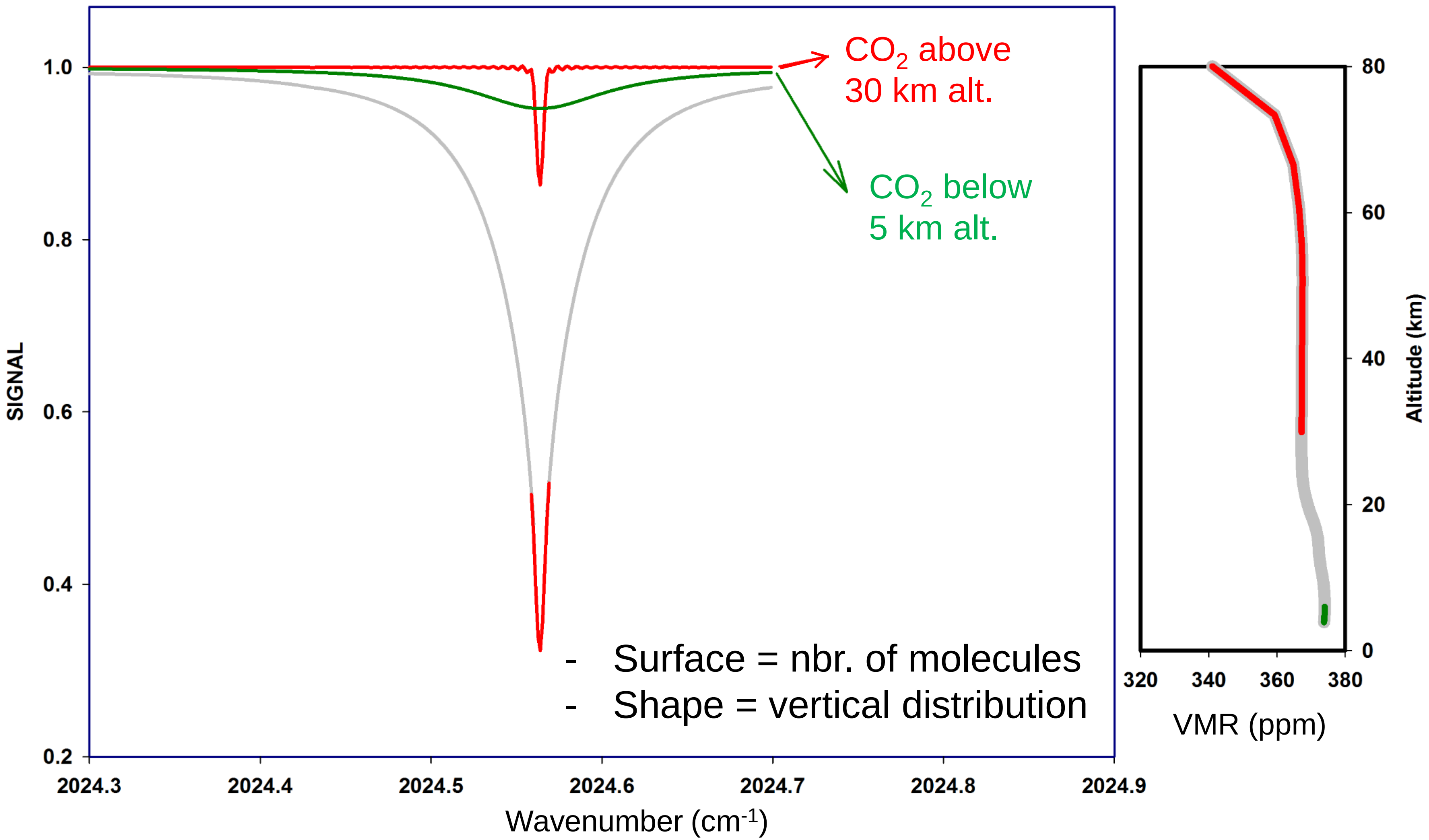
transmittance

→ determining the atmospheric composition thanks to:

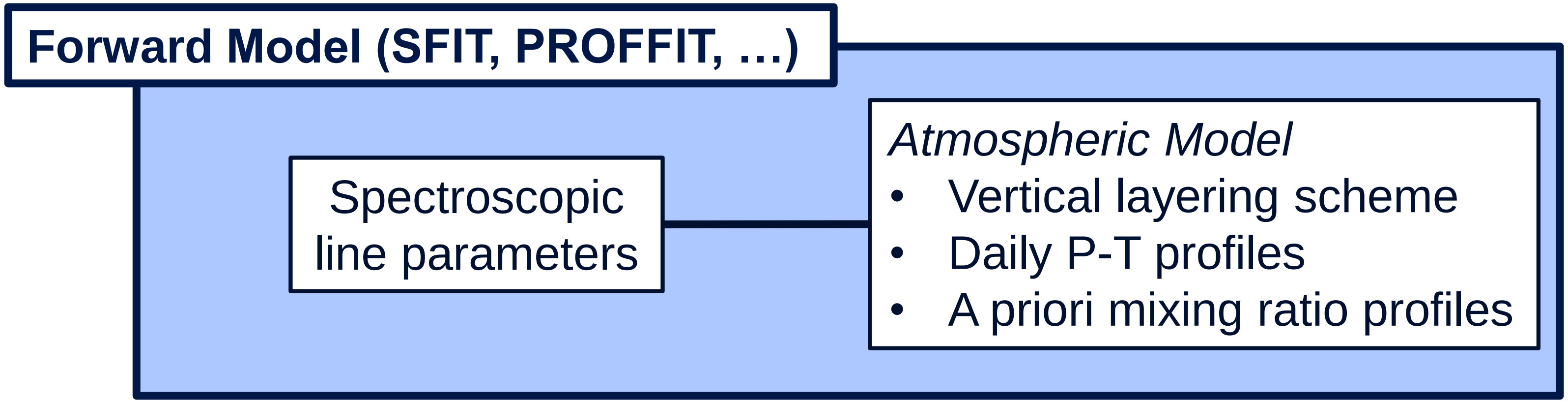
- vibrational transitions of a molecule emitting infrared radiation;
- vibrational transitions of a molecule occurring at a specific energy, frequency and wavenumber;
- the amount of energy absorbed being directly proportional to the number of molecules absorbing (P- and T-dependent).



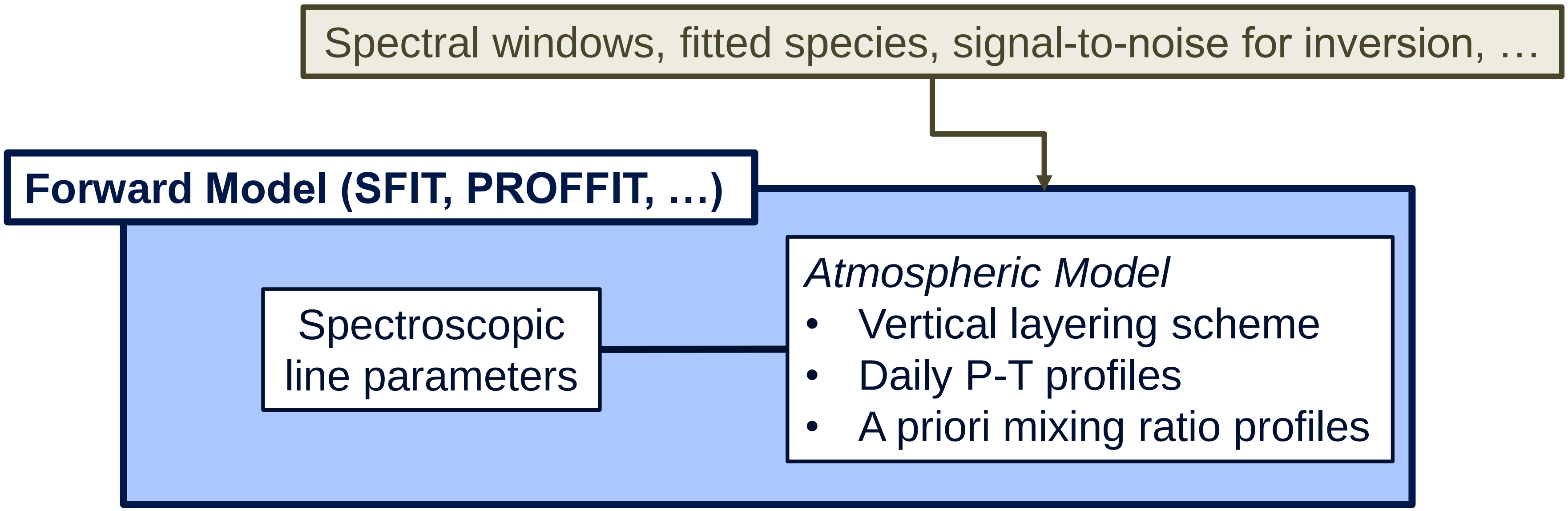
Example: CO_2 absorption feature



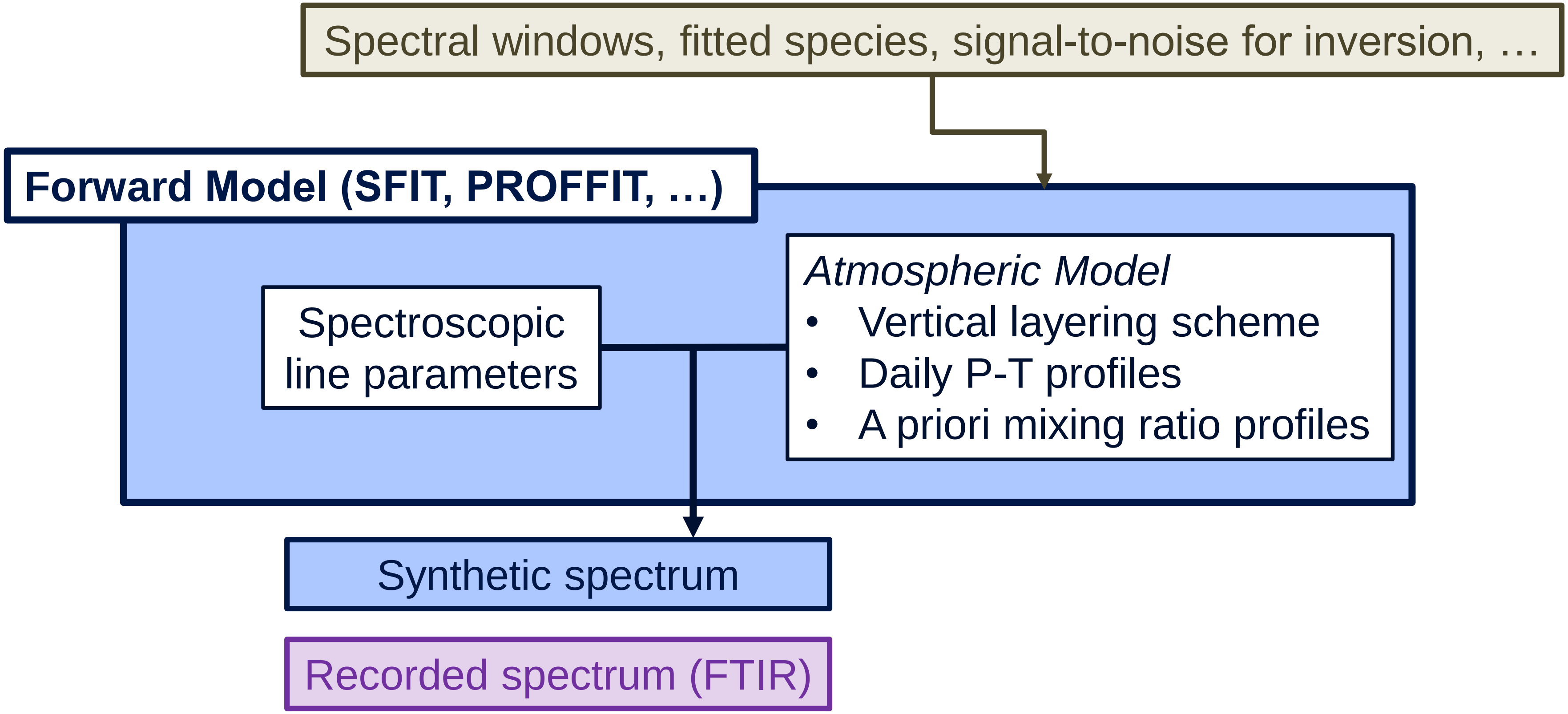
=> the retrieval is an (ill-posed) inverse non-linear problem



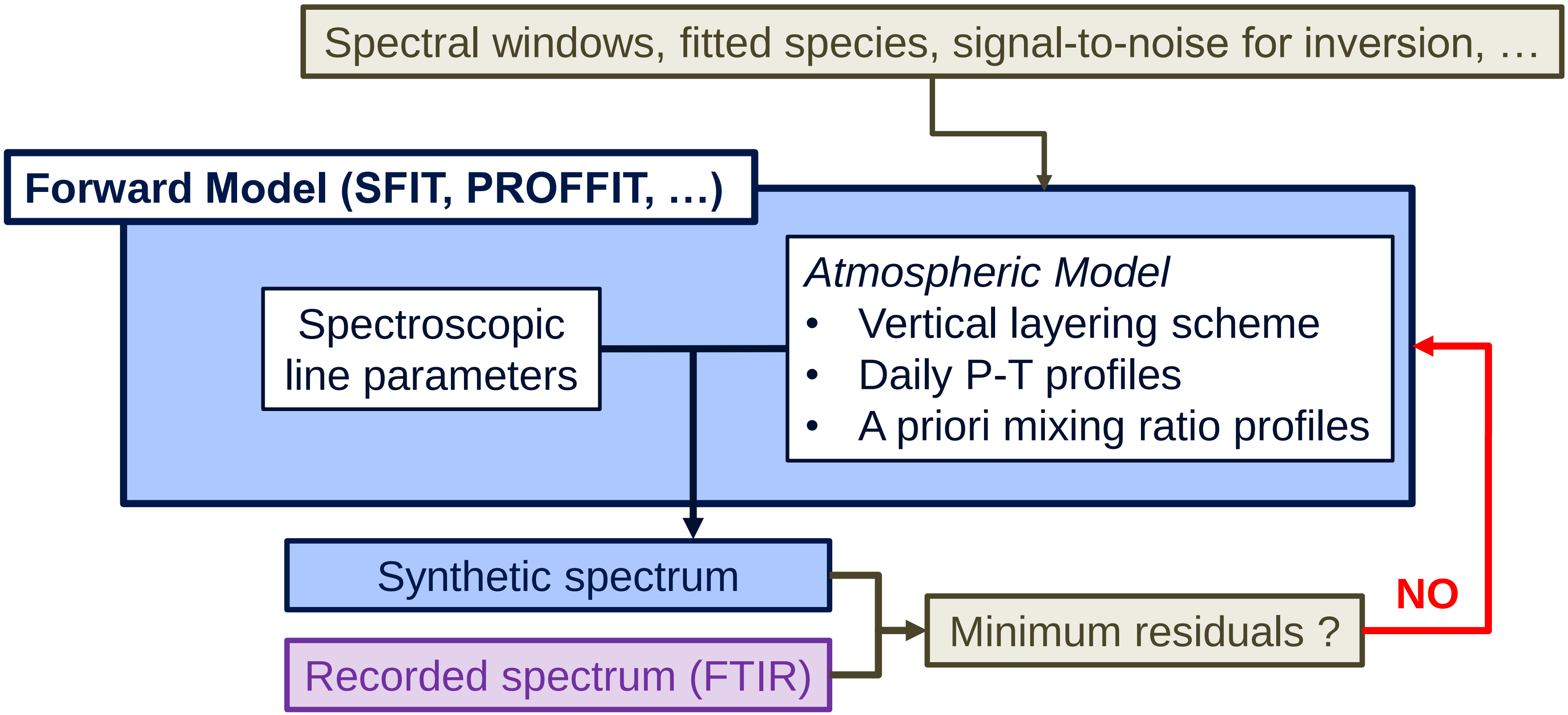
=> the retrieval is an (ill-posed) inverse non-linear problem



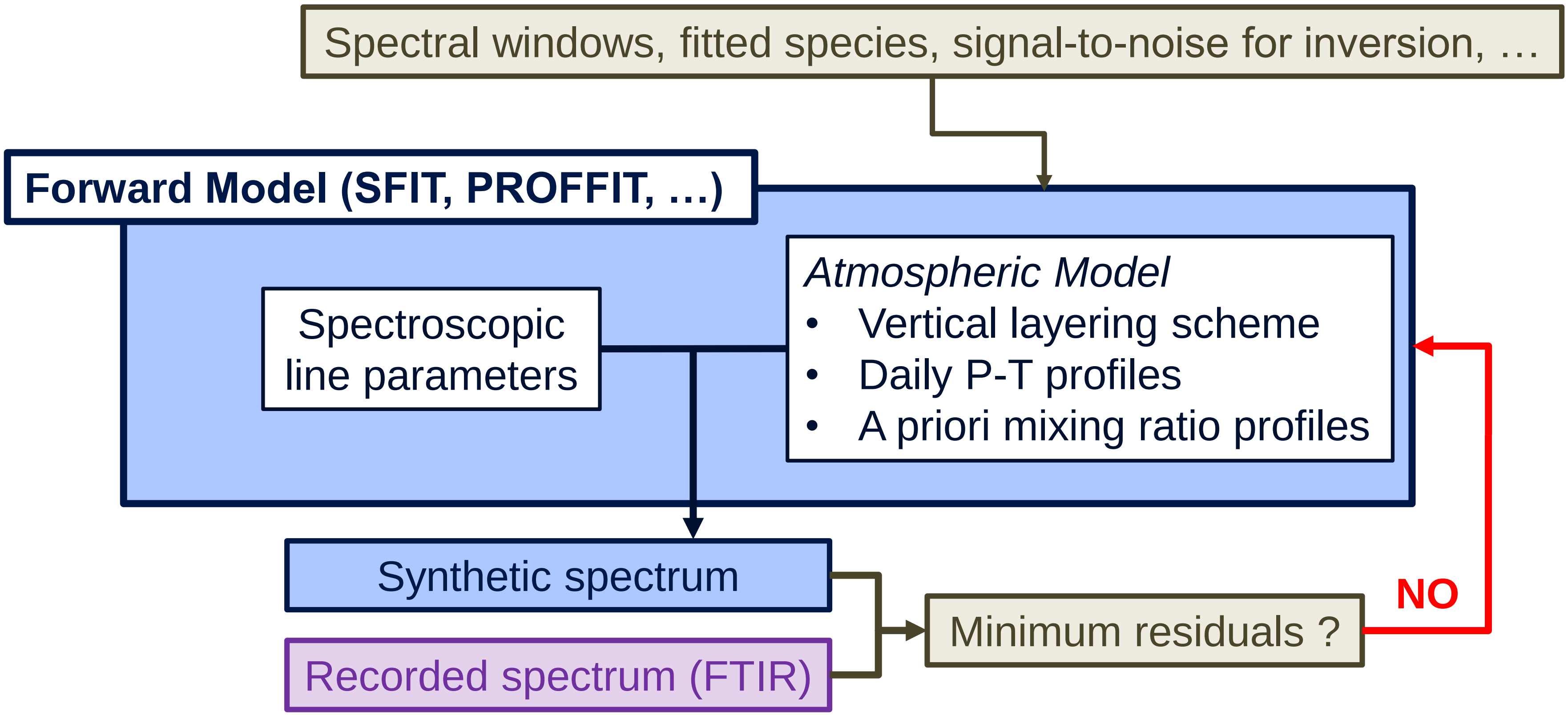
=> the retrieval is an (ill-posed) inverse non-linear problem



=> the retrieval is an (ill-posed) inverse non-linear problem



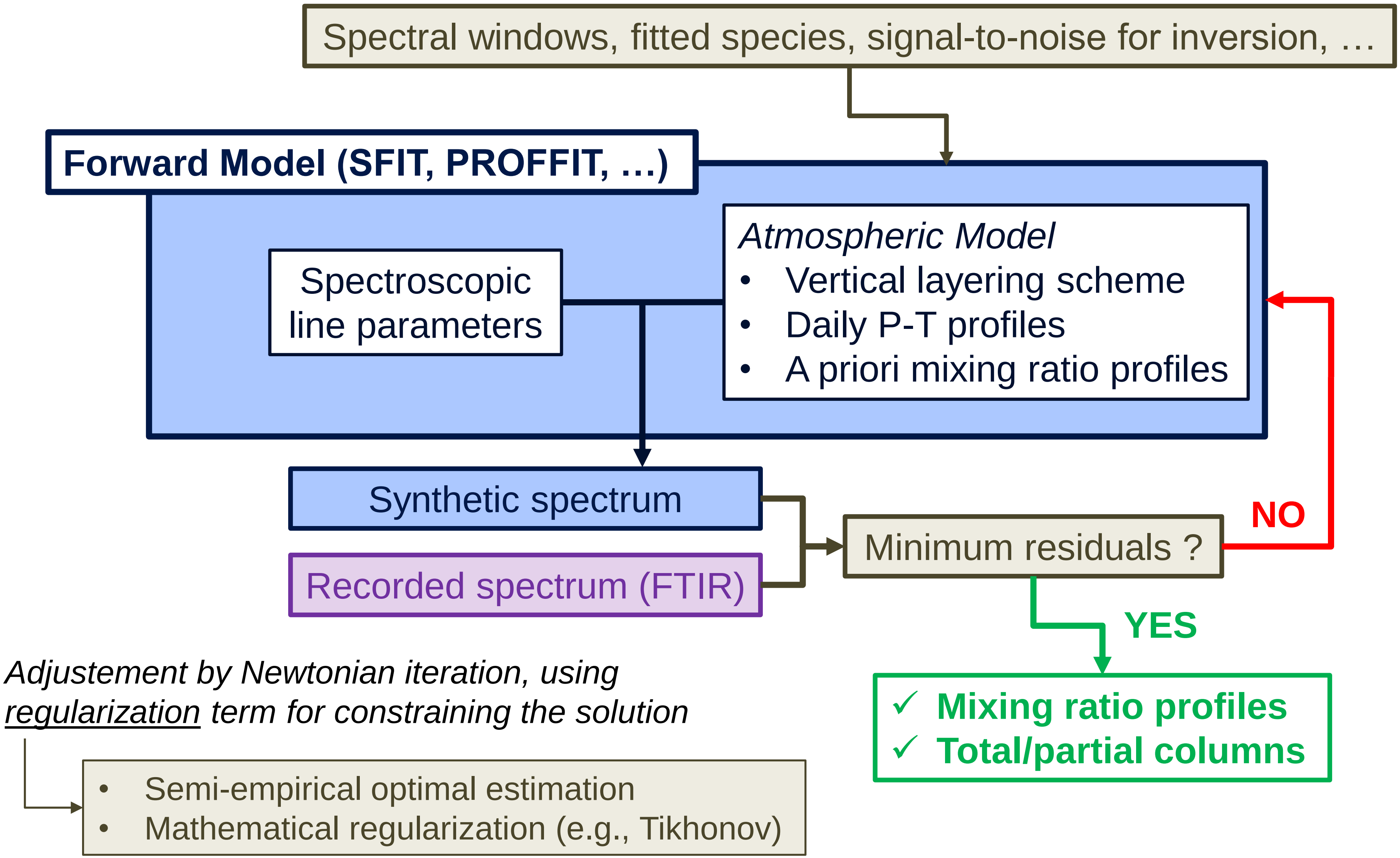
=> the retrieval is an (ill-posed) inverse non-linear problem



Adjustement by Newtonian iteration, using <u>regularization</u> term for constraining the solution

- Semi-empirical optimal estimation
- Mathematical regularization (e.g., Tikhonov)

=> the retrieval is an (ill-posed) inverse non-linear problem



Averaging kernel *(square matrix) describes:*

- how the retrieved profile is related to the *a priori* distribution and the true state of the target absorber
- the altitude range to which the measurement is actually sensitive
- the objective information content of the retrieval

Degree of freedom for signal

O_3 at Jungfraujoch

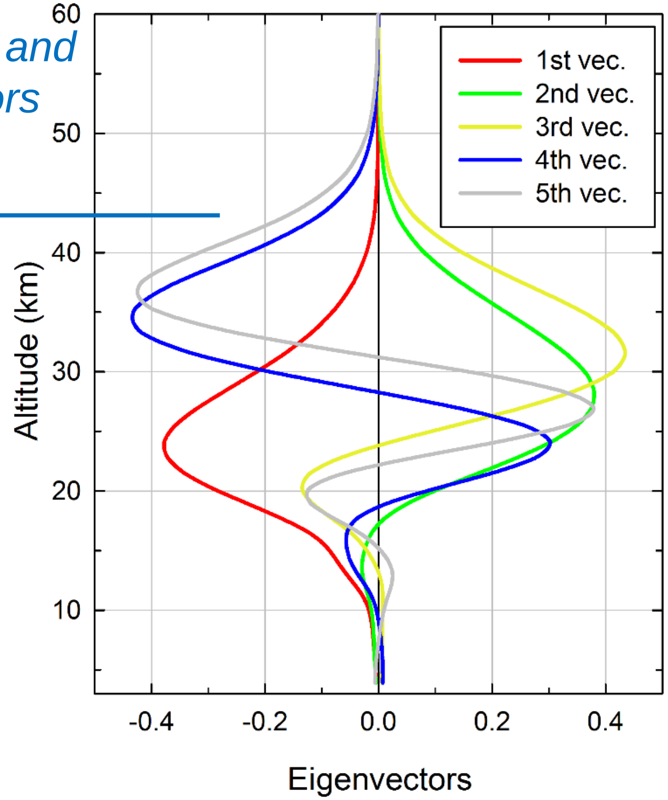
DOFS = 4.57

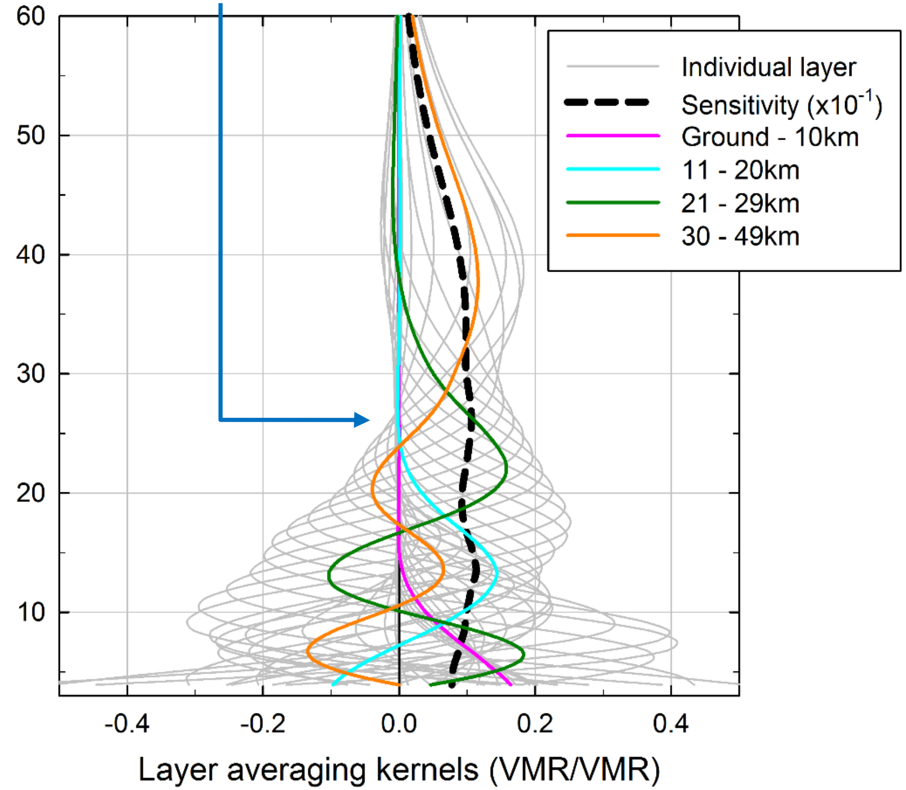
λ_1 = 0.99 - λ_2 = 0.99 - λ_3 = 0.99

λ_4 = 0.89 - λ_5 = 0.55 - λ_6 = 0.13

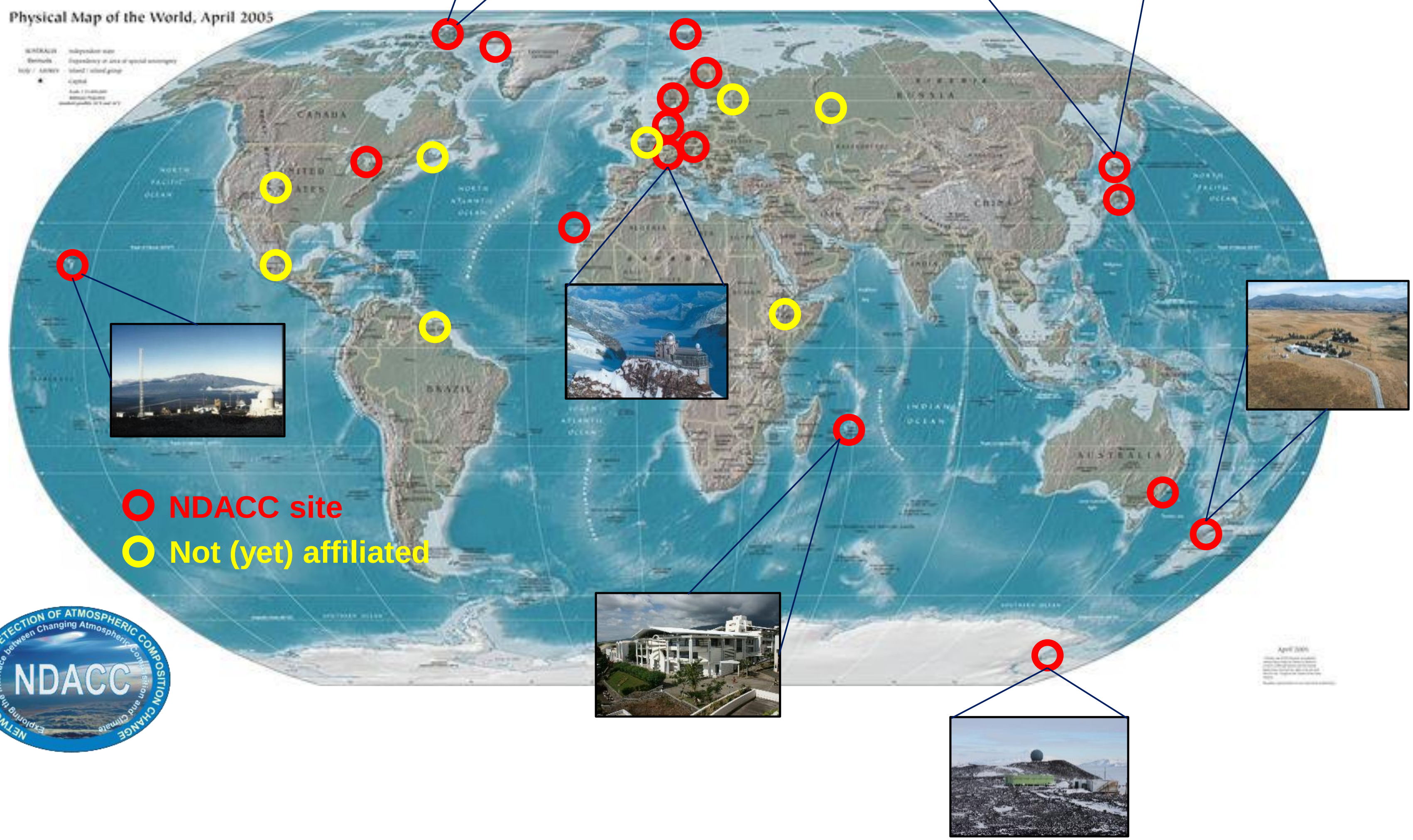
Layer averaging kernels and sensitivity

Eigenvalues and eigenvectors





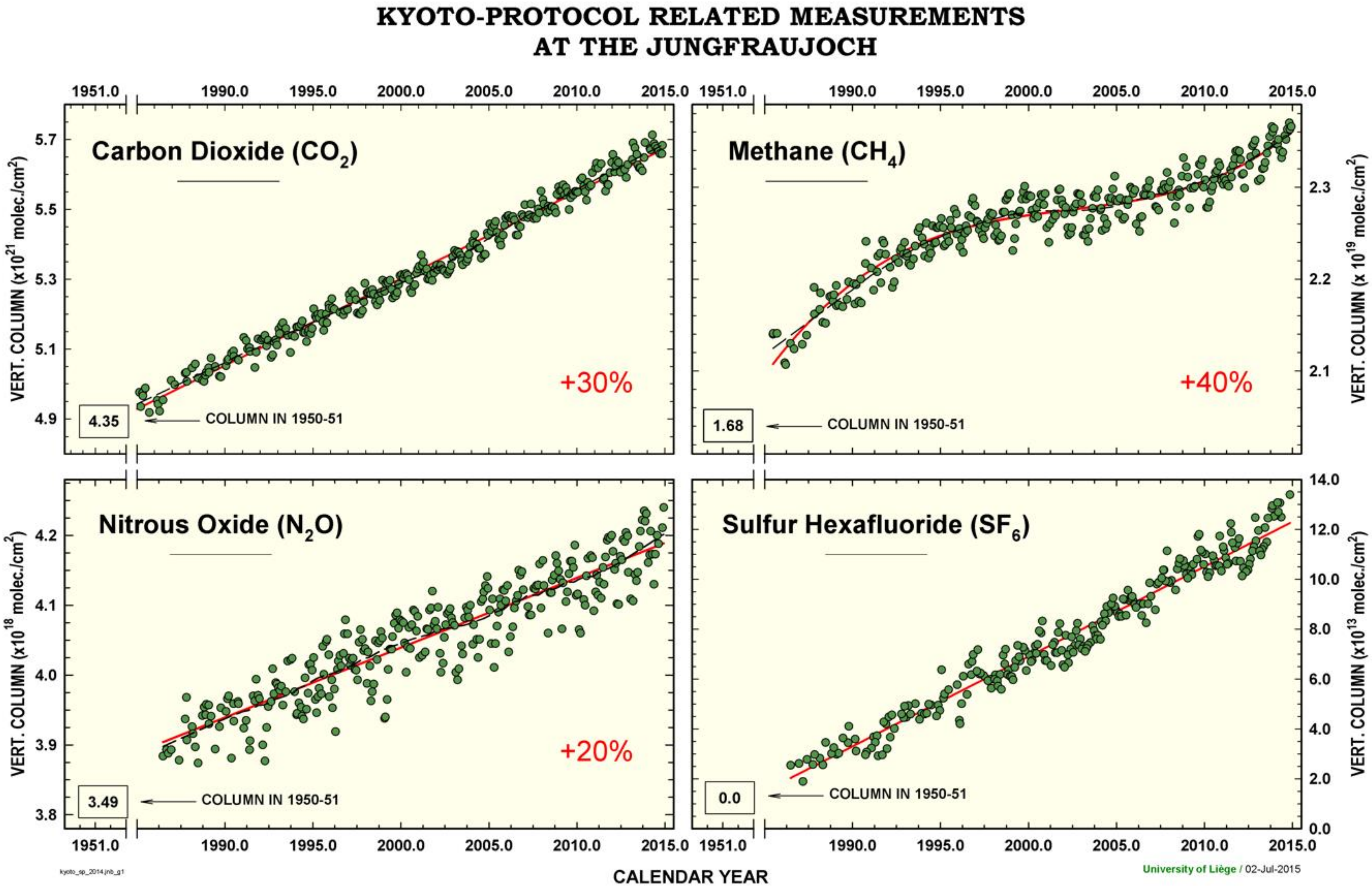
Over 20 FTIR sites around the world…

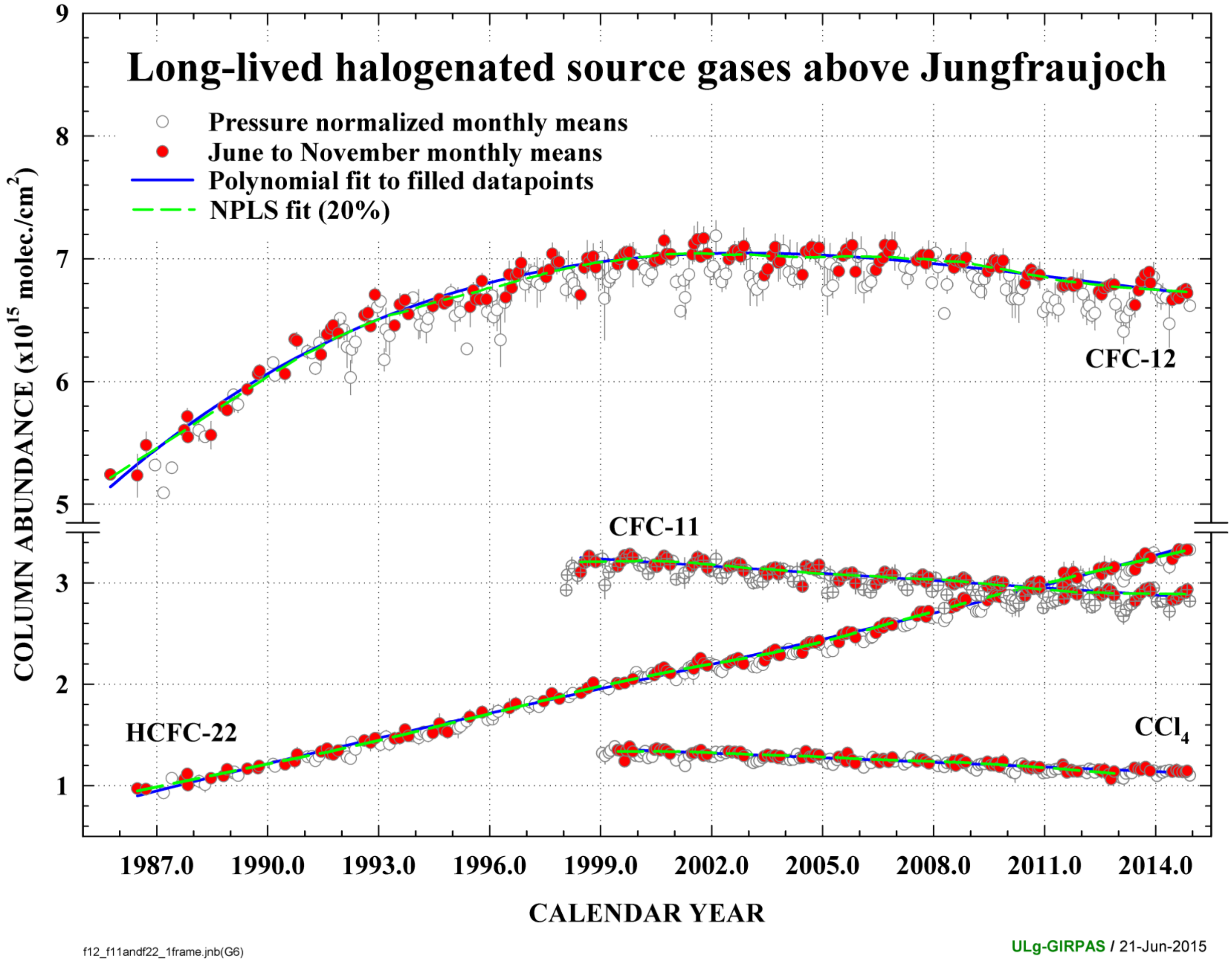


Around 30 species regularly retrieved from FTIR observations

Major greenhouse gases	H_2O, CO_2, CH_4, N_2O
Ozone (tropo and strato)	O_3
Halogenated compounds	CFC-11, CFC-12, HCFC-22, HCFC-142b, CCl_4, CF_4, SF_6, HCl, $ClONO_2$, HF, COF_2
Nitrogen compounds	N_2, N_2O, NO, NO_2, HNO_3, $ClONO_2$, NH_3
Organic compounds	CO, C_2H_2, C_2H_6, CH_3OH, HCN, HCHO, HCOOH, OCS
Many isotopologues of…	H_2O, CH_4, CO, O_3, …

=> *under development: C_2H_4, C_3H_8, PAN, CH_3Cl*


KYOTO-PROTOCOL RELATED MEASUREMENTS
AT THE JUNGFRAUJOCH
Carbon Dioxide (CO_2)
+30%
4.35
COLUMN IN 1950-51
VERT. COLUMN (x10^21 molec./cm^2)
Methane (CH_4)
+40%
1.68
COLUMN IN 1950-51
VERT. COLUMN (x 10^19 molec./cm^2)
Nitrous Oxide (N_2O)
+20%
3.49
COLUMN IN 1950-51
VERT. COLUMN (x10^18 molec./cm^2)
Sulfur Hexafluoride (SF_6)
0.0
COLUMN IN 1950-51
VERT. COLUMN (x10^13 molec./cm^2)
1951.0
1990.0
1995.0
2000.0
2005.0
2010.0
2015.0
CALENDAR YEAR
University of Liège / 02-Jul-2015



Long-lived halogenated source gases above Jungfraujoch
Pressure normalized monthly means
June to November monthly means
Polynomial fit to filled datapoints
NPLS fit (20%)
CFC-12
CFC-11
HCFC-22
CCl4
COLUMN ABUNDANCE (x10^15 molec./cm^2)
CALENDAR YEAR
9
8
7
6
5
3
2
1
1987.0
1990.0
1993.0
1996.0
1999.0
2002.0
2005.0
2008.0
2011.0
2014.0
f12_f11andf22_1frame.jnb(G6)
ULg-GIRPAS / 21-Jun-2015

…with the archiving of the FTIR spectra offering the possibility to:

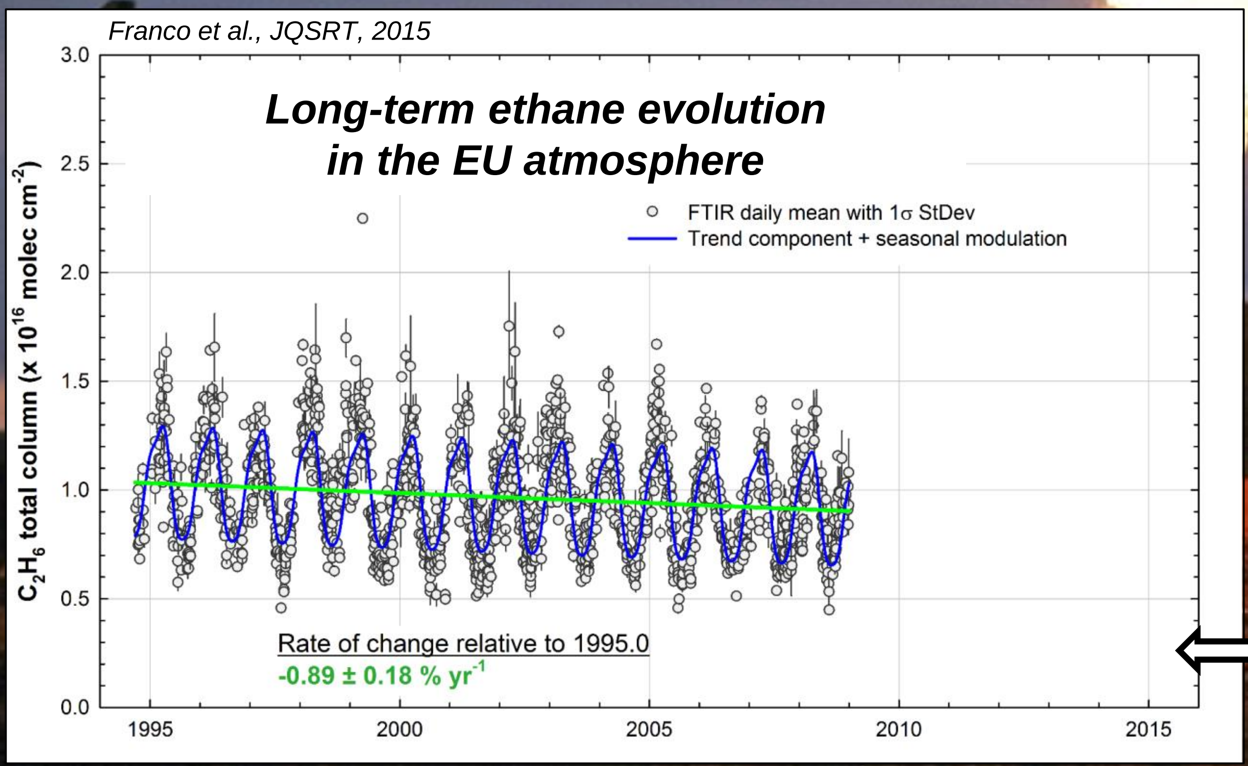
- improve the existing retrievals
- develop retrievals for new species

Thanks to new spectroscopic parameters…

→ improvement of the ethane retrieval

→ *improvement of the ethane retrieval*

→ *reanalysis of the ethane time series*



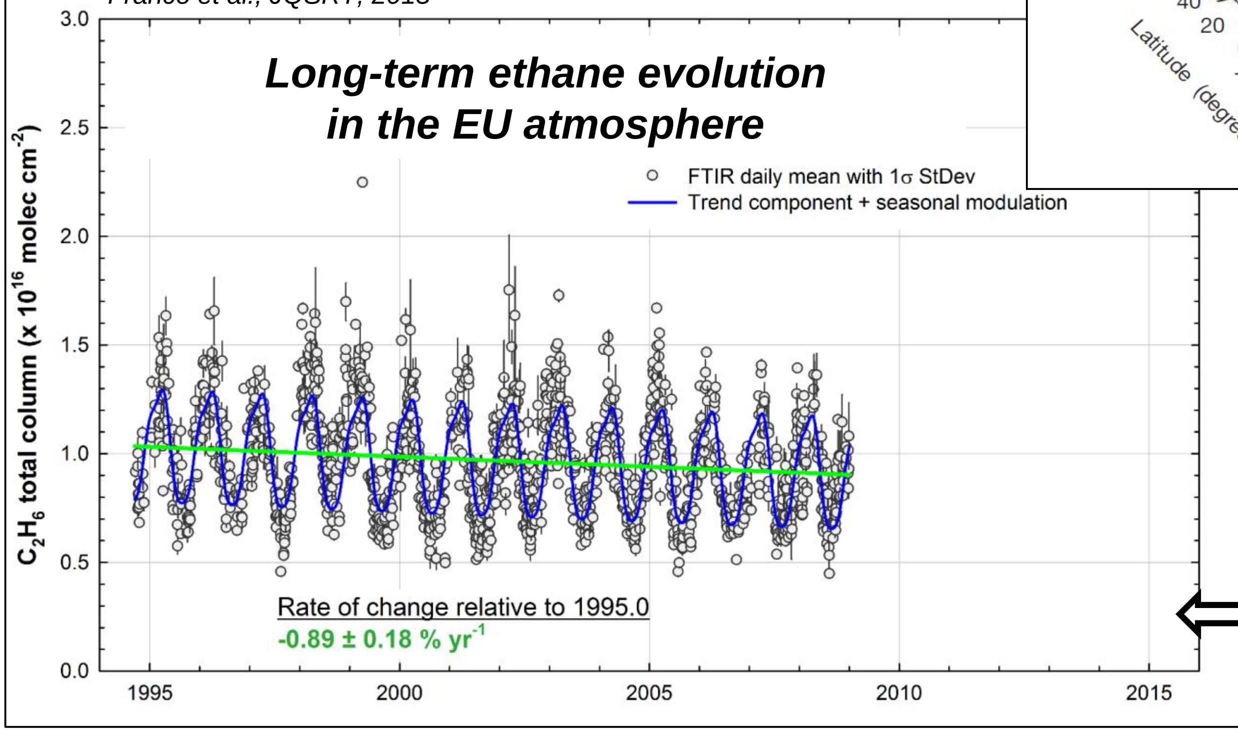
Total column time series from FTIR observations at Jungfraujoch

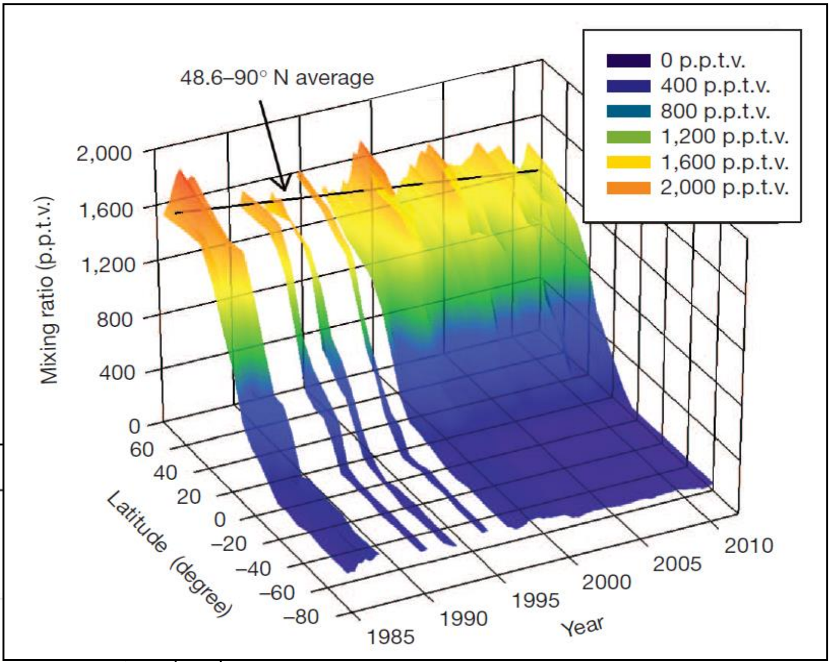
2. Reversal of long-term ethane trends

- Atmospheric ethane abundance has been declining in the -1 to -2.7 %/yr range since the mid-1980s
- Global emissions dropped from 14.3 to 11.3 Tg/yr over 1984-2010 (Simpson et al., 2012)

=> primarily due to reduced oil and gas fugitive emissions and to pollution abatement measures

Franco et al., JQSRT, 2015





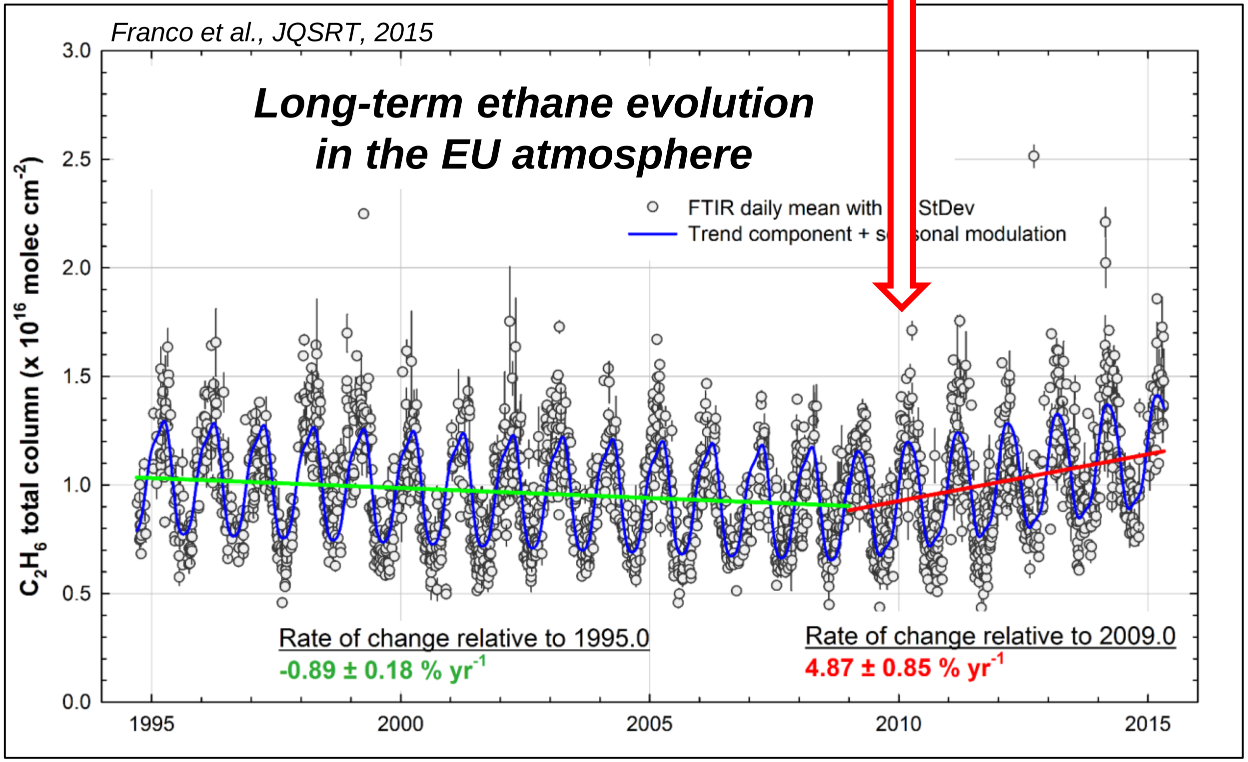
Simpson et al., Nature, 2012

Surface concentrations from air sampling of the UCI global trace gas monitoring network

Total column time series from FTIR observations at Jungfraujoch

- But a reversal in the long-term decline of ethane has been detected around 2009

- … as well as a sharp increase (**5 %/yr**) of the atmospheric ethane burden from 2009 onwards

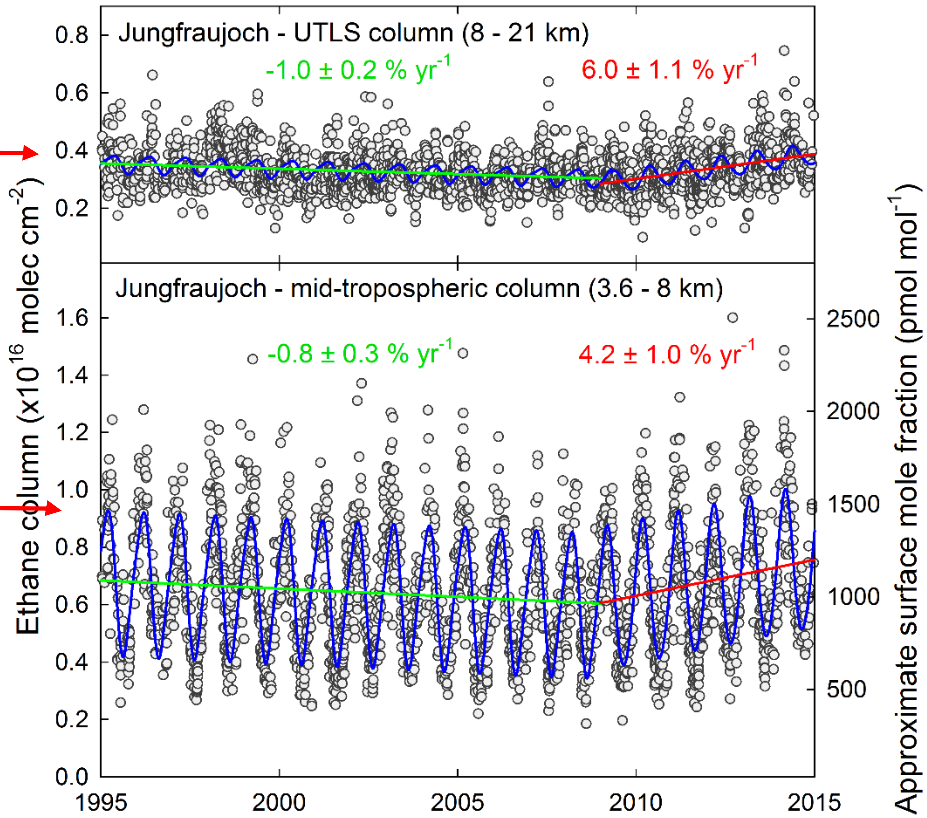


→ *"Monitoring is not boring"*

JÜLICH
FORSCHUNGSZENTRUM

Jungfraujoch (46° N)

UTLS partial columns



Mid-trop. partial columns

Based on Helmig et al. (2016), Nat. Geosc.

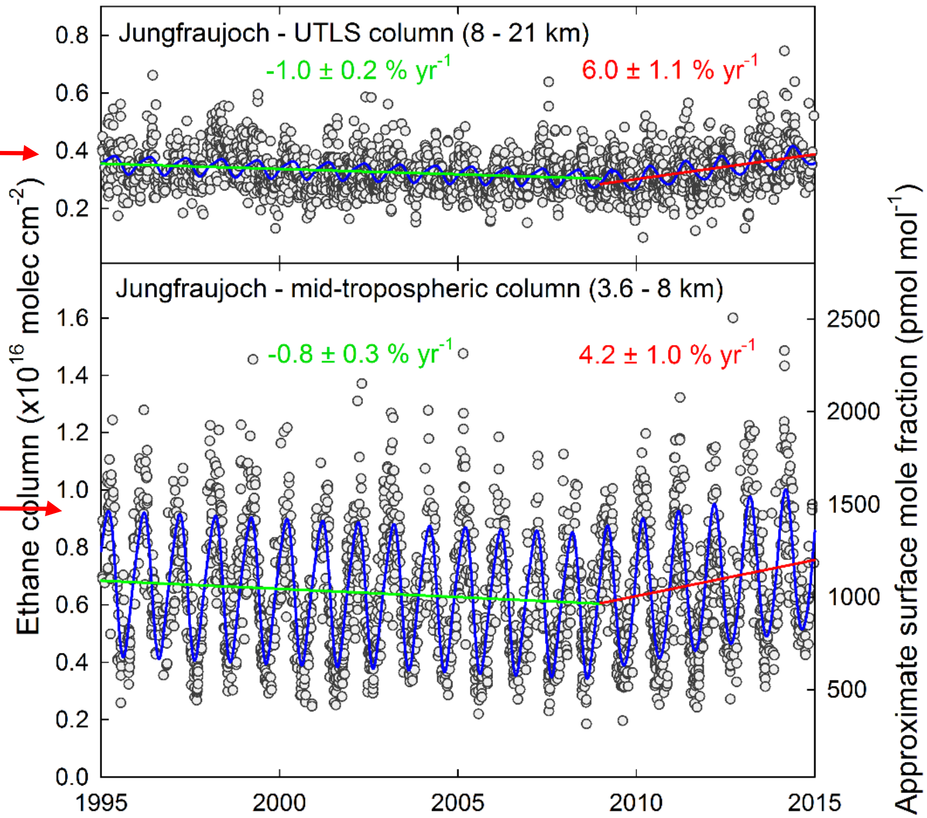
- → Jungfraujoch characterizes the free atmosphere over central EU
- → Reflecting continental background and long-range transport
- → Could be indicative of an hemispheric ethane increase

JÜLICH FORSCHUNGSZENTRUM

Jungfraujoch (46° N)

Lauder (45° S)

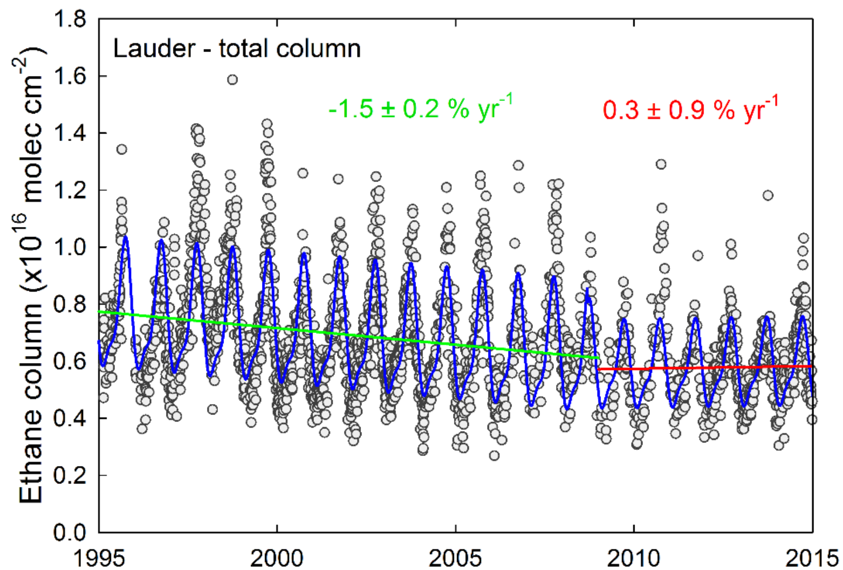
UTLS partial columns



Mid-trop. partial columns

→ No reversal in the Southern Hemisphere

Total columns

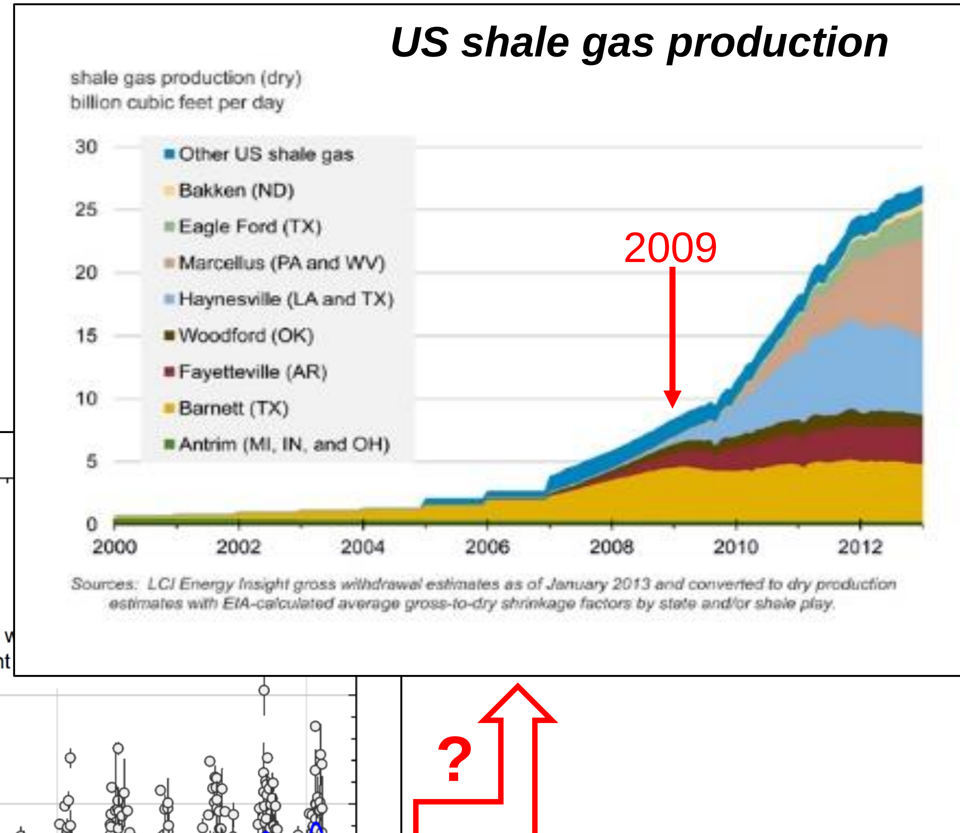


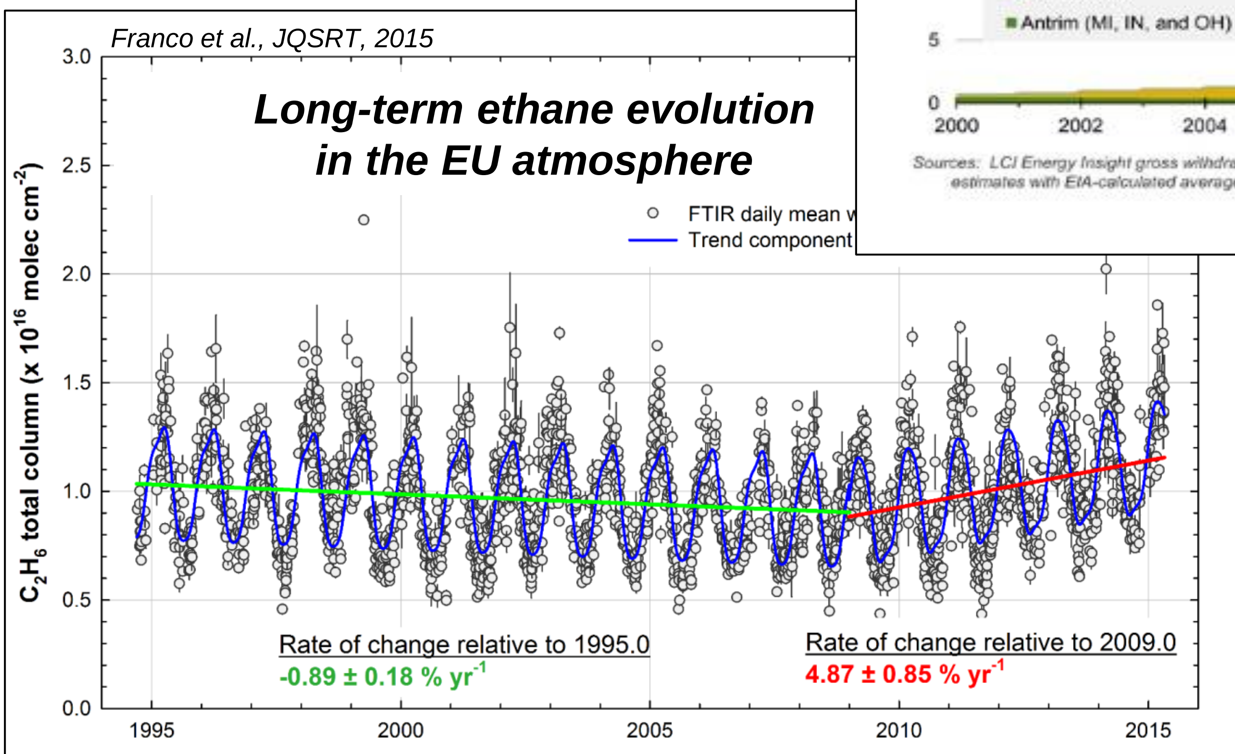
Based on Helmig et al. (2016), Nat. Geosc.

2. Reversal of long-term ethane trends

=> due to enhanced emissions associated with intense hydraulic fracturing and shale gas operations in North America?

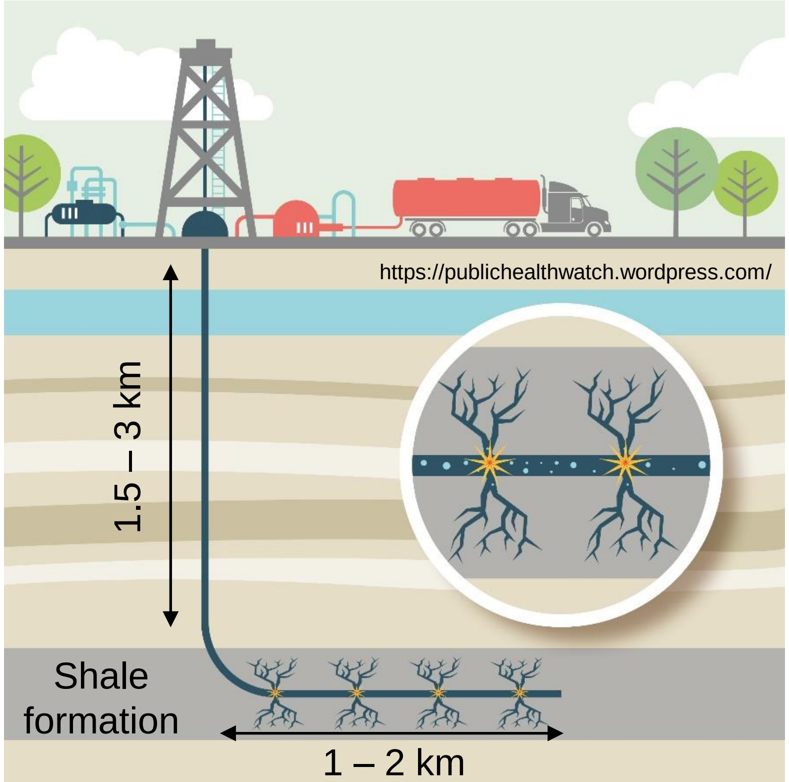
=> C_2H_6 lifetime = 2 months





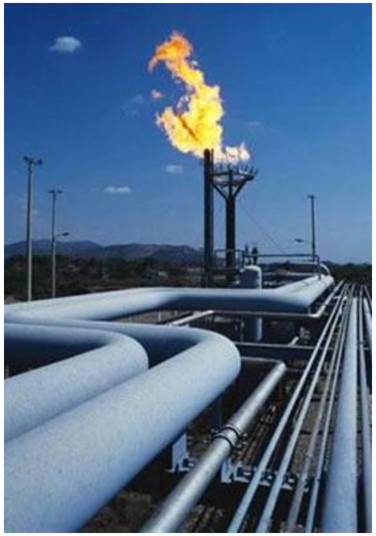
→ Enhanced fugitive emissions from shale gas operations?

Hydraulic fracturing (« *fracking* »)



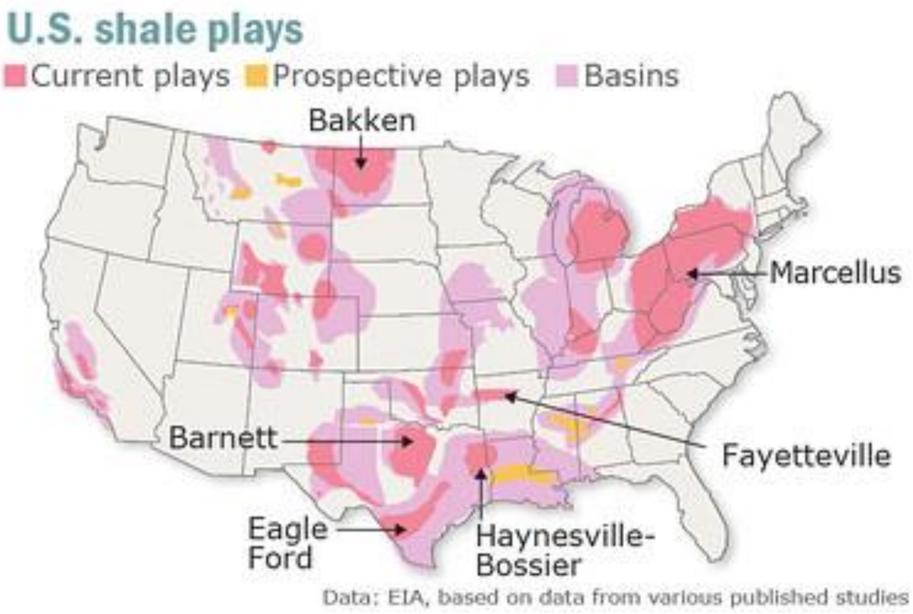
Directional drilling

Gas flaring and venting

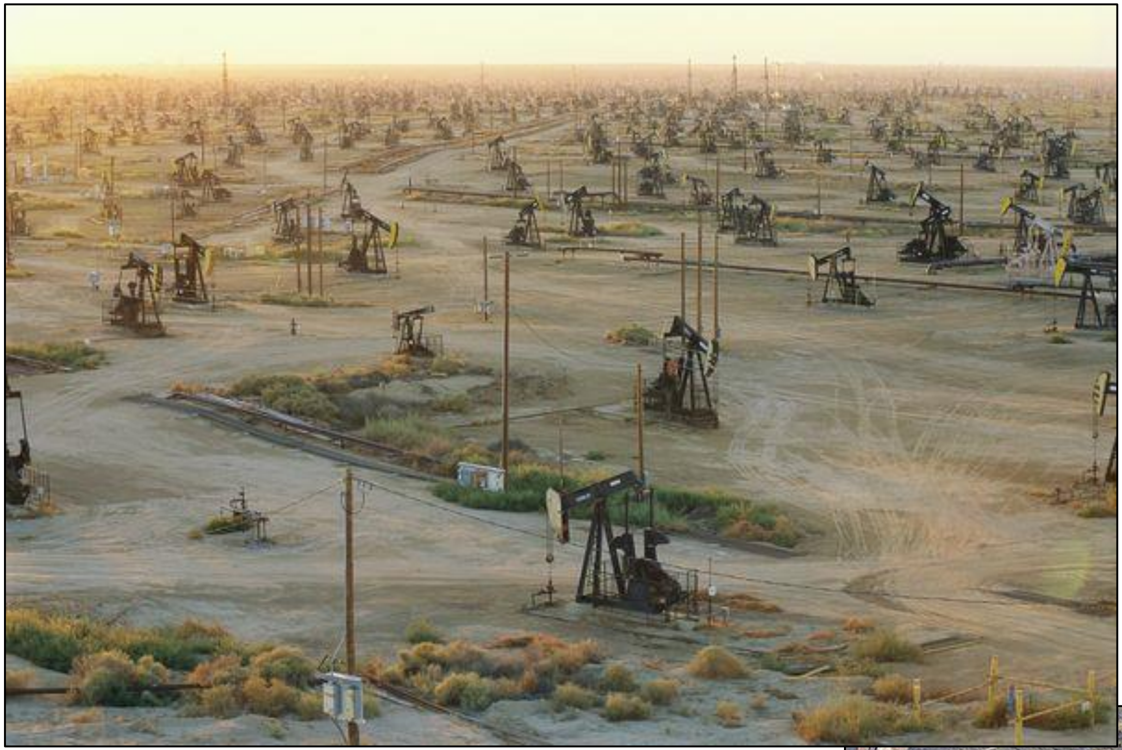


Distribution leakage

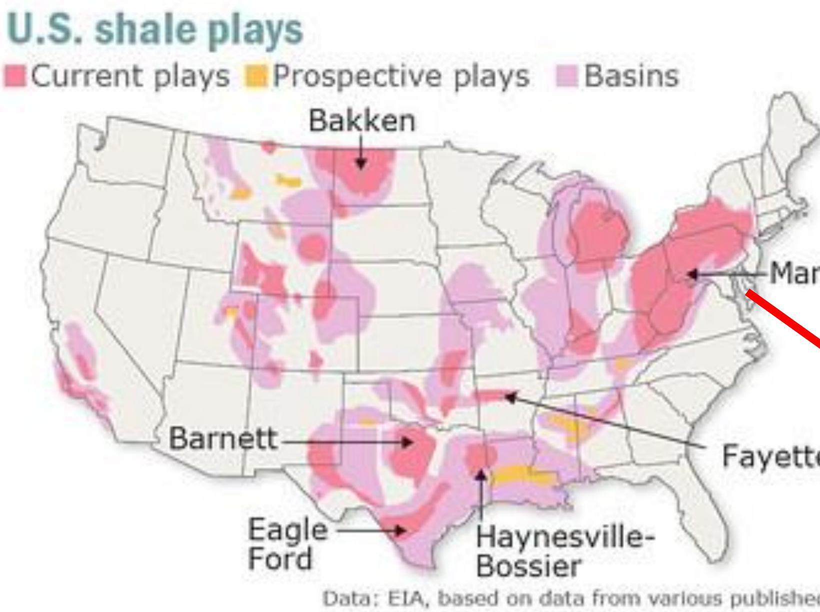
2. Reversal of long-term ethane trends



+ abandoned and orphaned wells

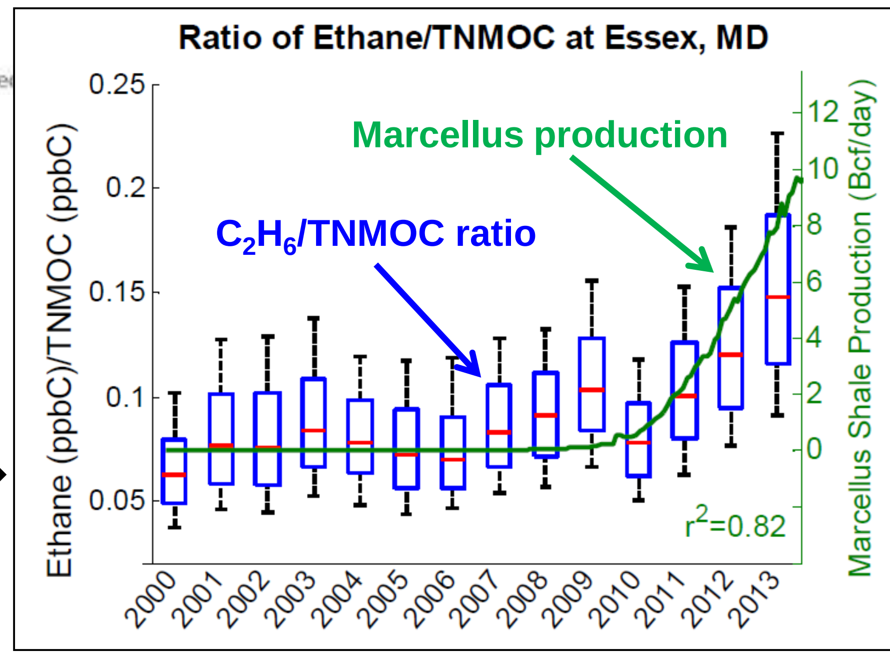


« *They're making of our ground a Swiss cheese!* » (E. Fischer, CSU)



=> Propane, with a lifetime 1/4 of ethane, is a more sensitive indicator for local/regional emissions

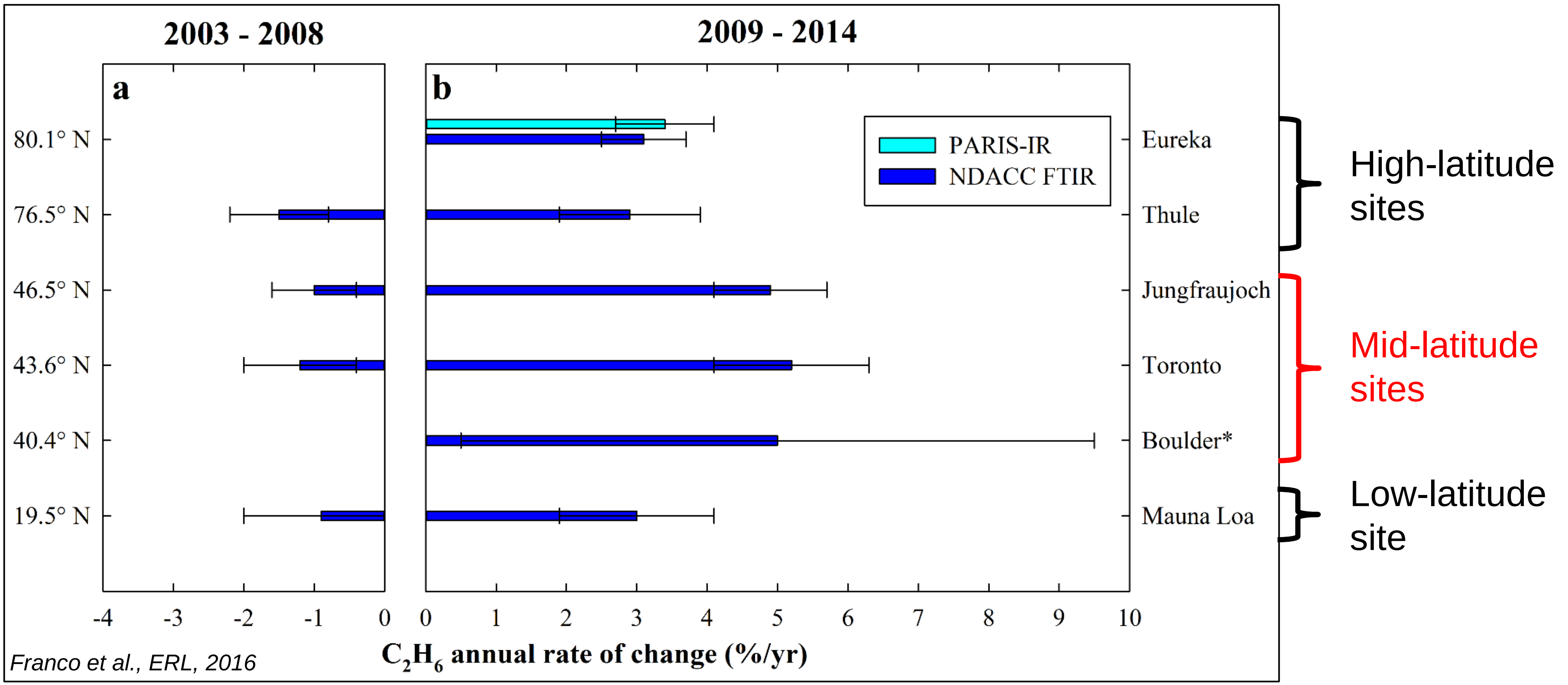
Vinciguerra et al., Atm. Chem., 2015



PAMS measurements at Essex, MD, located downwind from the giant Marcellus Shale play (WV, PA and NY)

JÜLICH
FORSCHUNGSZENTRUM

- Slow decline of the C_2H_6 total columns between −1 and −1.5 %/yr prior to 2009, with consistent rates within the different latitudes
- Reversal around 2009 and growth rates of ~5 %/yr at mid-latitudes and of ~3%/yr at remote sites

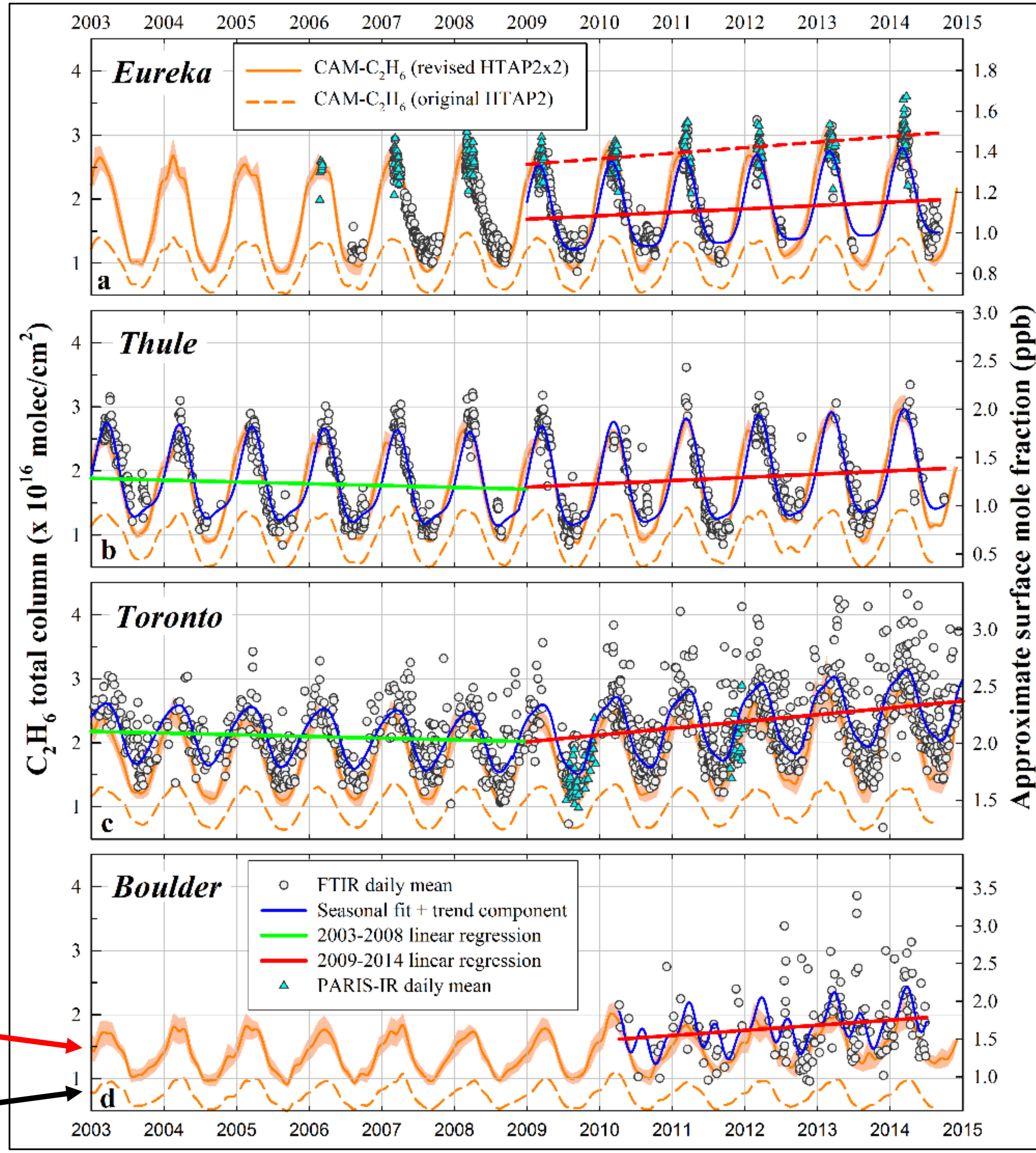


3. Ethane emissions from bottom-up inventories

- CHAM-chem simulation of ethane over 2003-2014, implementing the bottom-up anthropogenic inventory HTAP2
- C_2H_6 emissions from the oil and gas sector represent up to 80% of the total anthropogenic C_2H_6 emissions over North America
- The model underestimates the observed C_2H_6 abundances and does not reproduce the recent increase

=> Doubling global emissions is required to reconcile simulations and observations <u>prior to 2009</u>

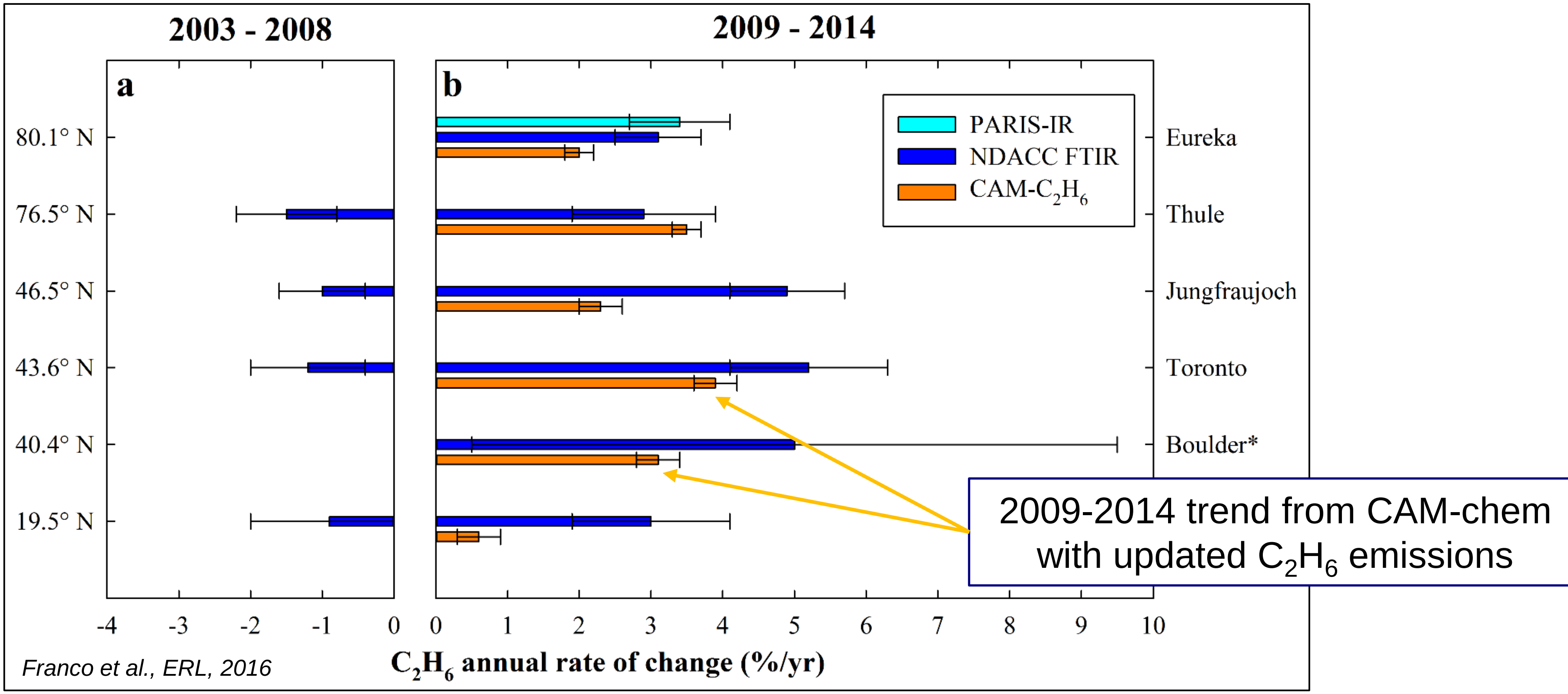
Franco et al., ERL, 2016



Doubled HTAP2 emissions

Original HTAP2 emissions

- An additional increase of the North American anthropogenic emissions (beyond the previous doubling emissions) is required to simulate the recent C_2H_6 rise
- … assuming that the missing emissions during this period resulted from the recent increase in oil and gas extraction in North America



Franco et al., ERL, 2016

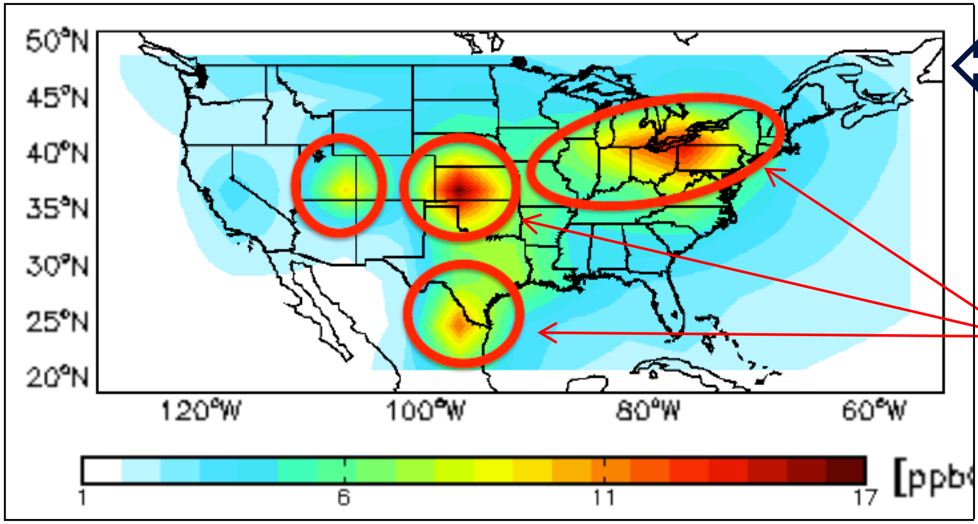
⇒ Increase of the North American anthropogenic C_2H_6 emissions by 75% (from 1.6 Tg/yr in 2008 to 2.8 Tg/yr in 2014)

Top-down emissions of ethane

- Based on CH_4 fluxes inferred from 50 x 50 km GOSAT measurements (Turner et al., *ACP*, 2015) and subsequently evaluated by surface and aircraft data
- By applying C_2H_6/CH_4 emission ratios to satellite-derived CH_4 emissions for the oil and natural gas, biofuel consumption and biomass burning categories

Preliminary results…

Tzompa-Sosa et al., in preparation



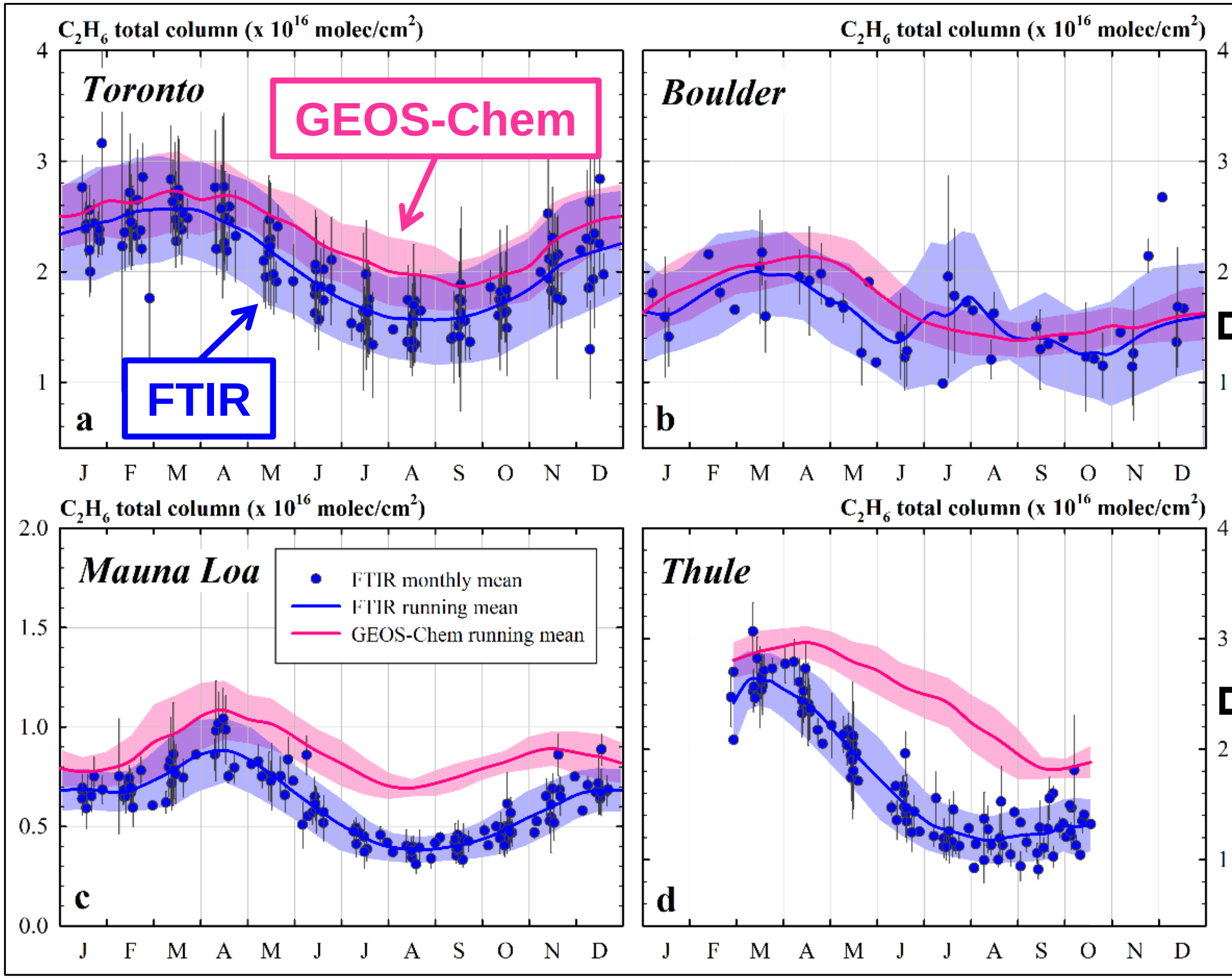
GEOS-Chem simulation of C_2H_6 surface concentrations

Major oil and gas basins

GEOS-Chem C_2H_6 surface concentration for December 2010, derived from GOSAT CH_4

JÜLICH FORSCHUNGSZENTRUM

Comparison between FTIR and GEOS-Chem implementing new top-down emissions



Franco et al., ERL, 2016

- Good agreement at the mid-latitudinal sites (close to regions with high drilling productivity)
- High-bias of summertime ethane at remote sites (too low OH levels in the model)

- Good agreement between the inventory-based (1.9 Tg/yr) and GOSAT-derived (1.8 Tg/yr) ethane emissions
- … and the top-down approach allows to allocate the ethane emissions on the basis of measurements

Annual ethane emissions from North America

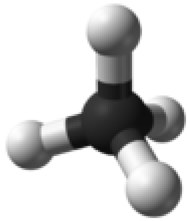
Region—sector	CAM-C_2H_6 (original HTAP2)	CAM-C_2H_6 (revised HTAP2x2)			GEOS-Chem
	2008–2014	2008	2010	2014	2010
Globe—all sectors	9.7–10.2	17.3	17.9	18.7	13.2
Globe—anthropogenic	7.5	15.0	15.3	16.2	10.5
Globe—biomass burning	1.8–2.3	1.9	2.2	2.2	2.7
Globe—biogenic	0.4	0.4	0.4	0.4	Not included
North America—anthropogenic	0.8	1.6	1.9	2.8	1.8

Franco et al., ERL, 2016

Updated bottom-up emissions

Inferred top-down emissions

… and about methane?



→ Realistic C_2H_6 emissions can be used as proxies to decipher the anthropogenic emission changes of CH_4 from the growth of oil and natural gas development

5. Conclusions

JÜLICH
FORSCHUNGSZENTRUM

→ Realistic C_2H_6 emissions can be used as proxies to decipher the anthropogenic emission changes of CH_4 from the growth of oil and natural gas development

C_2H_6/CH_4 emission ratios ⇒ Increase of C_2H_6 emissions based on FTIR measurements

5. Conclusions

→ Realistic C_2H_6 emissions can be used as proxies to decipher the anthropogenic emission changes of CH_4 from the growth of oil and natural gas development

C_2H_6/CH_4 emission ratios

Increase of C_2H_6 emissions based on FTIR measurements

North American CH_4 emissions from oil and gas have increased from <u>20 Tg/yr</u> in 2008 to <u>35 Tg/yr</u> in 2014

See also:

- Helmig et al. (2016), Nat. Geosc.
- Turner et al. (2016), GRL

→ Realistic C_2H_6 emissions can be used as proxies to decipher the anthropogenic emission changes of CH_4 from the growth of oil and natural gas development

C_2H_6/CH_4 emission ratios ⇒ Increase of C_2H_6 emissions based on FTIR measurements → North American CH_4 emissions from oil and gas have increased from <u>20 Tg/yr</u> in 2008 to <u>35 Tg/yr</u> in 2014

See also:

- Helmig et al. (2016), Nat. Geosc.
- Turner et al. (2016), GRL

But… ⇒

Many uncertainties!!!

- assuming that the added C_2H_6 emission is entirely from oil and gas
- C_2H_6/CH_4 ratios largely vary in space and time

Some inconsistencies with:

- surface and aircraft observations of CH_4 stable isotopes

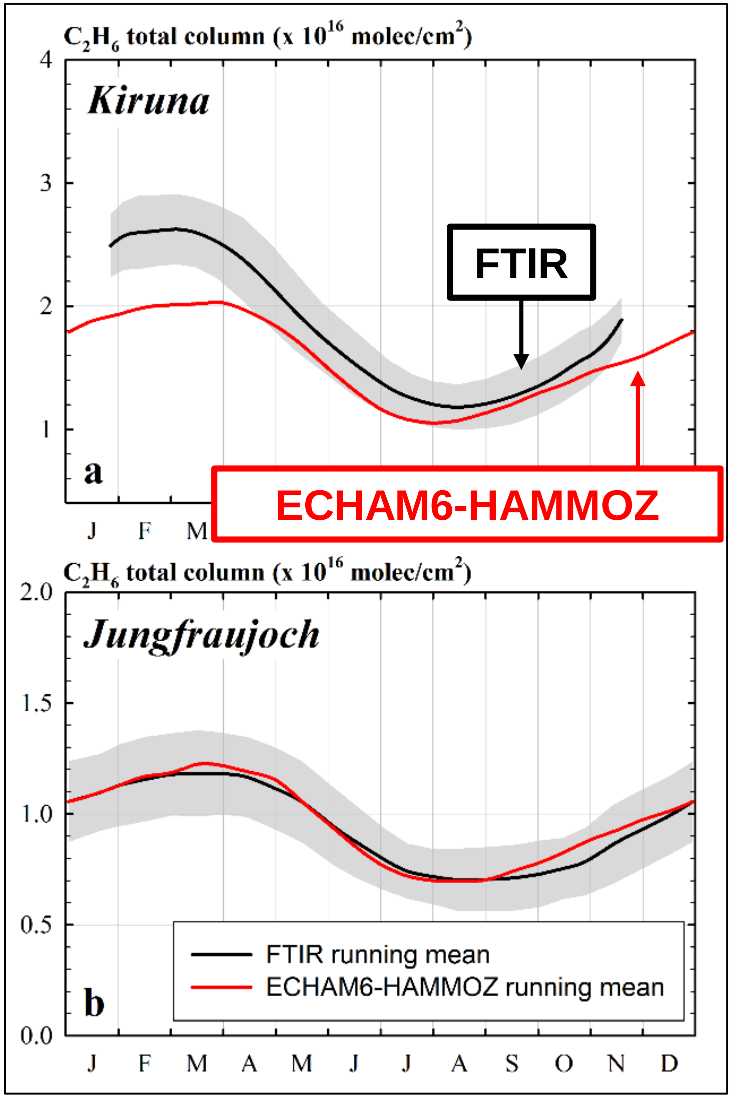
There is a need to:

- Characterize the recent C_2H_6 (and other NMHC) evolution at the global scale
  - ✓ Development of C_3H_8 retrieval from FTIR
- To refine the source attribution and identification of missing C_2H_6 emissions
  - ✓ Unidentified increasing sources for NMHC emissions independent of CH_4?
  - ✓ Potential emission increases outside North America?

<u>There is a need to:</u>

- Characterize the recent C_2H_6 (and other NMHC) evolution at the global scale
  - ✓ Development of C_3H_8 retrieval from FTIR
- To refine the source attribution and identification of missing C_2H_6 emissions
  - ✓ Unidentified increasing sources for NMHC emissions independent of CH_4?
  - ✓ Potential emission increases outside North America?

⇒ Application to the recently developed ECHAM6-HAMMOZ atmospheric chemistry-climate model: sensitivity runs with updated C_2H_6 emissions

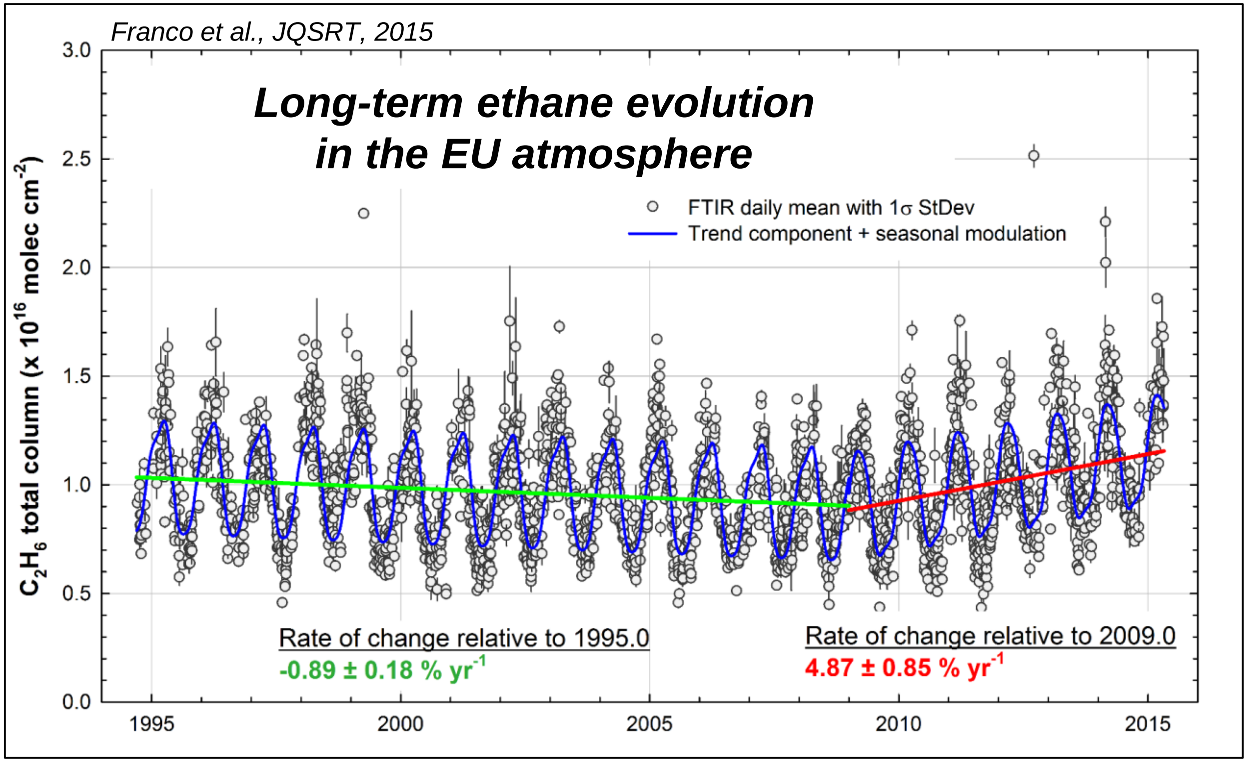


Thank you for your attention

JÜLICH
FORSCHUNGSZENTRUM

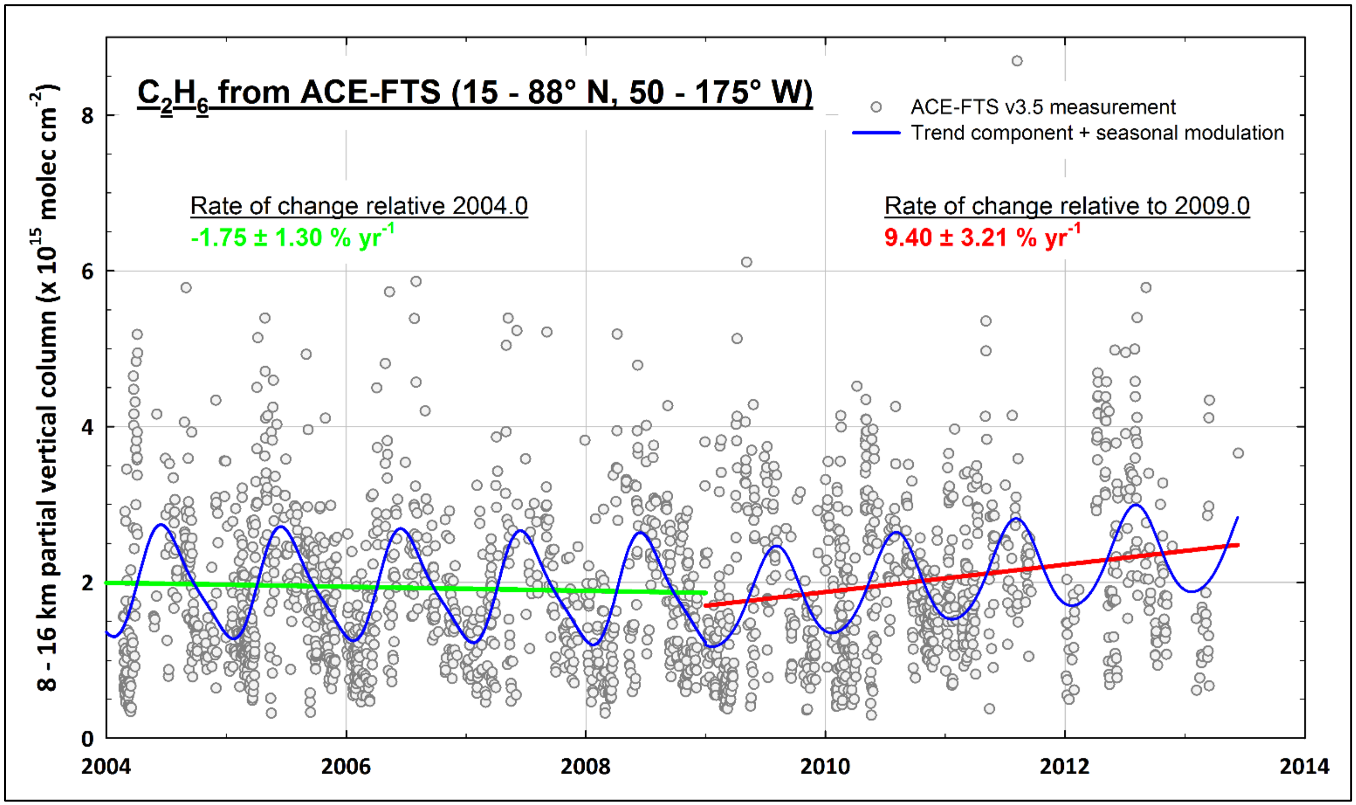
Knowing that…

- ✓ The gobal OH levels have not exhibited large interannual variability since the end of the 20th century (*Montzka et al., Science, 2011*)
- ✓ Neither CO nor other species that have oxidation by OH as their major removal pathway, present such reversal



JÜLICH FORSCHUNGSZENTRUM

→ From satellite (ACE-FTS) over the North American continent



Preliminary results… (thanks to C. Boone, U. of Waterloo)