40 years of observations of atmospheric methane from a remote European site
(among other things…)

Whitney Bader

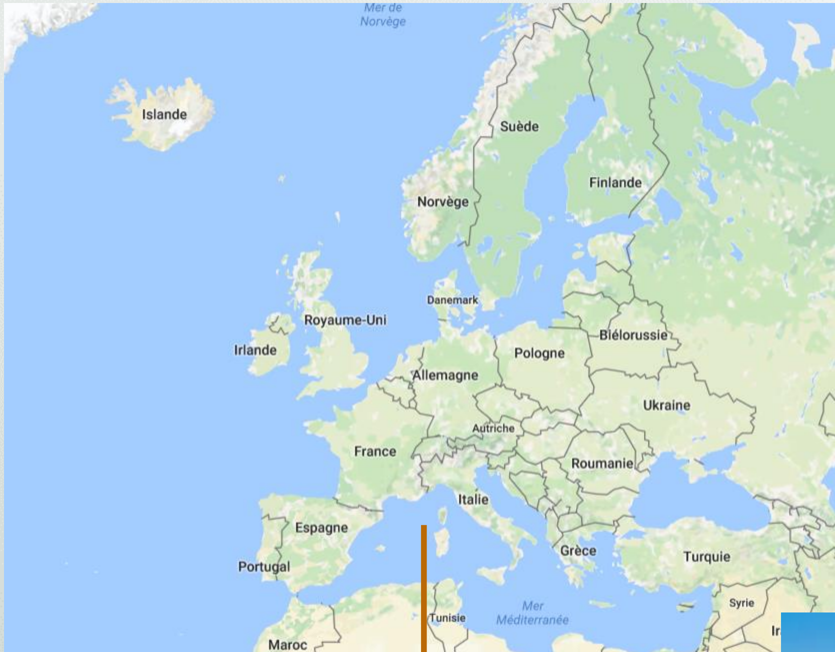
Brewer-Wilson Seminar

November 4th, 2016

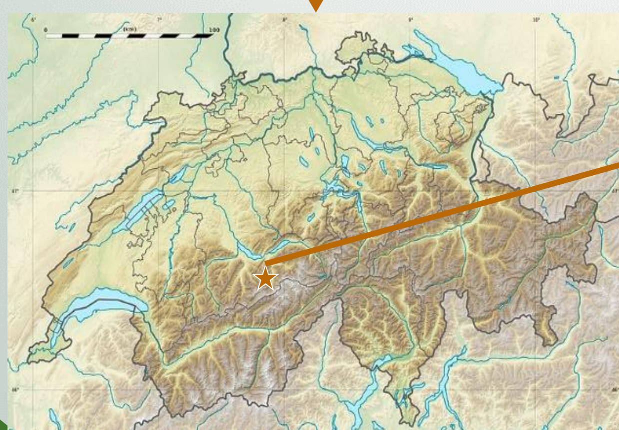
Overview

- Master's thesis : "Extension of the long-term total column time series of atmospheric methane above the Jungfraujoch station: analysis of grating infrared spectra between 1977 and 1989."
- PhD Thesis : "Long-term study of methane and two of its derivatives from solar observations recorded at the Jungfraujoch station."
  - Long-term evolution and seasonal modulation of CH_3OH above Jungfraujoch, AMT, 7, 3861-3872, 2014.
  - Retrieval of C_2H_6 from ground-based FTIR solar spectra : recent burden increase above Jungfraujoch, JQSRT, 160, 36-49, 2015.
  - Increase of CH_4 since 2005 based on FTIR observations and GEOS-Chem tagged simulation, ACPD, in review, 2016.
- Postdoc project : "Atmospheric content of the most abundant of $^{12}CH_4$ isotopologues from ground-based and satellite infrared solar observations and development of a methane isotopic GEOS-Chem module."

Jungfraujoch station



- Swiss Alps (46.5°N, 8.0°E)
- 3 580 m a.s.l.
- Weak local pollution : no major industries within 20 km
- Very high dryness : high-altitude + Aletsch Glacier in its immediate vicinity



Instrumentation and retrievals

Jungfraujoch station

Instrumentation timeline

1950'
1 m focal length grating spectrometer

→

1976 - 1989
7.3 m focal length Double Pass Grating Spectrometer

→

1985
Homemade Fourier Transform Spectrometer

→

1991
Bruker 120HR Fourier Transform Spectrometer

↓

Network for the Detection of Atmospheric Composition Change - NDACC

pioneering infrared solar observations
CH_4 : Nielsen and Migeotte, 1952
CO : Migeotte and Neven, 1950
+ solar atlas

1975
Detection of HF in the atmosphere by R. Zander
Zander *et al.*, 1989

Atmospheric observations resumed and haven't stopped since then.

Database of 45 000 spectra (grating + homemade + Bruker)
→ 40 years of continuous observations

Jungfraujoch station

Instrumentation timeline

1950' — 1 m focal length grating spectrometer → **1976 - 1989** — 7.3 m focal length Double Pass Grating Spectrometer → **1985** — Homemade Fourier Transform Spectrometer → **1991** — Bruker 120HR Fourier Transform Spectrometer

40+ atmospheric gases	
Kyoto protocol	H_2O, CO_2, CH_4, N_2O, CF_4, SF_6
Montreal protocol	O_3, NO, NO_2, HNO_3, $ClONO_2$, HCl, HF, COF_2, CFC-11, CFC-12, HCFC-22, HCFC-142b, CCl_4
Air quality, biomass burning	CO, CH_3OH, C_2H_6, C_2H_2, C_2H_4, HCN, HCHO, HCOOH, NH_3
Others	OCS, N_2, many isotopic forms (HDO, CH_3D, $^{13}CH_4$, ^{13}CO,…)

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Jungfraujoch station

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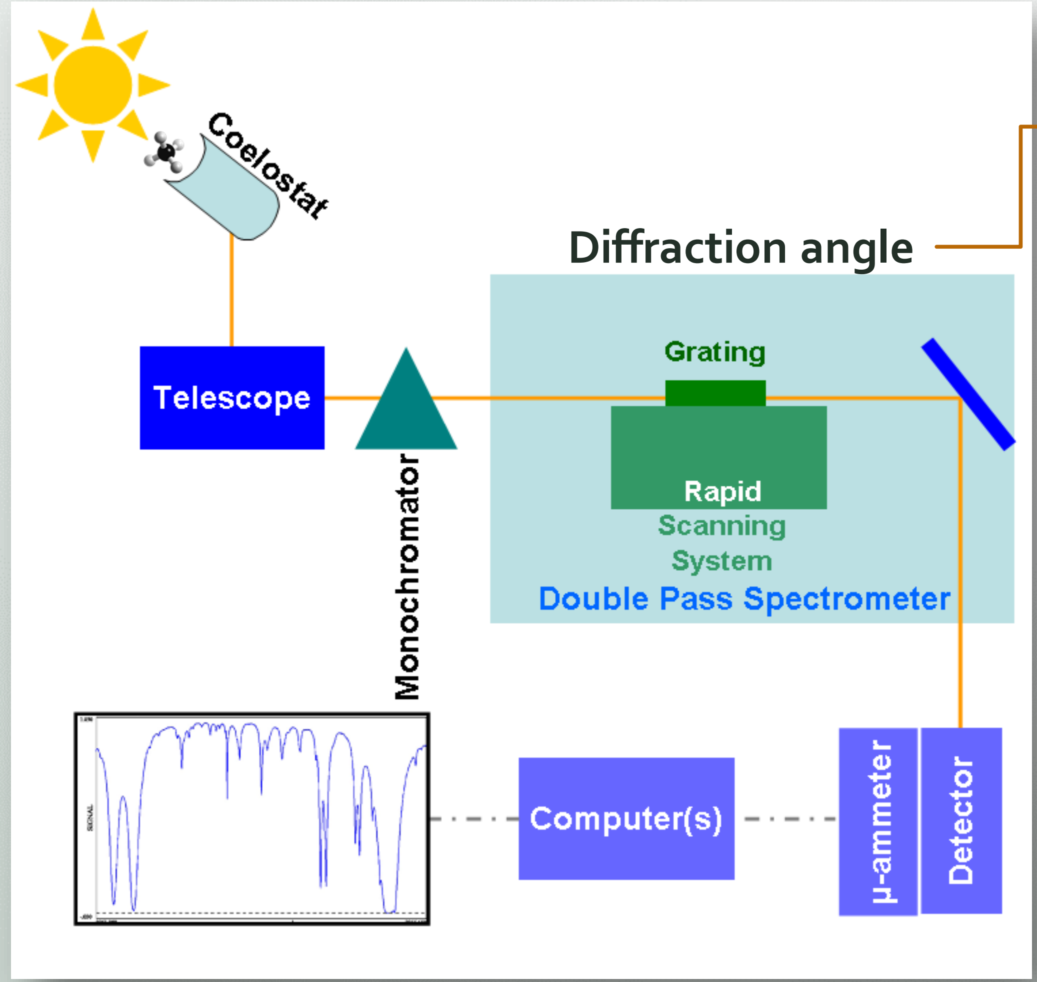
"Extension of the long-term total column time series of atmospheric methane above the Jungfraujoch station: analysis of grating infrared spectra between 1977 and 1989."

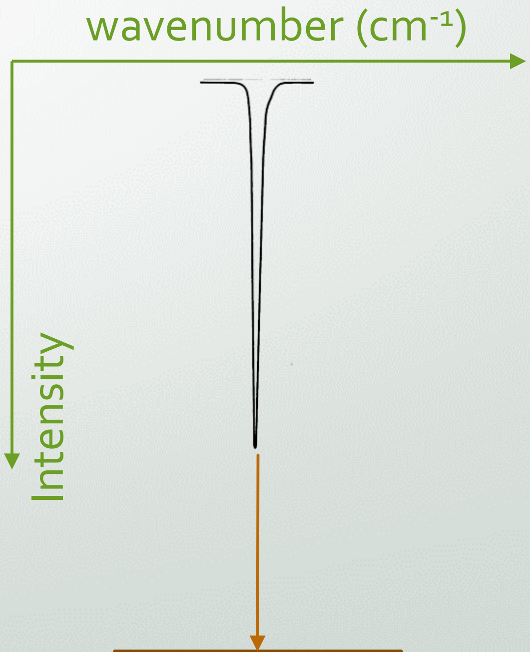
Master's thesis

Grating spectrometer



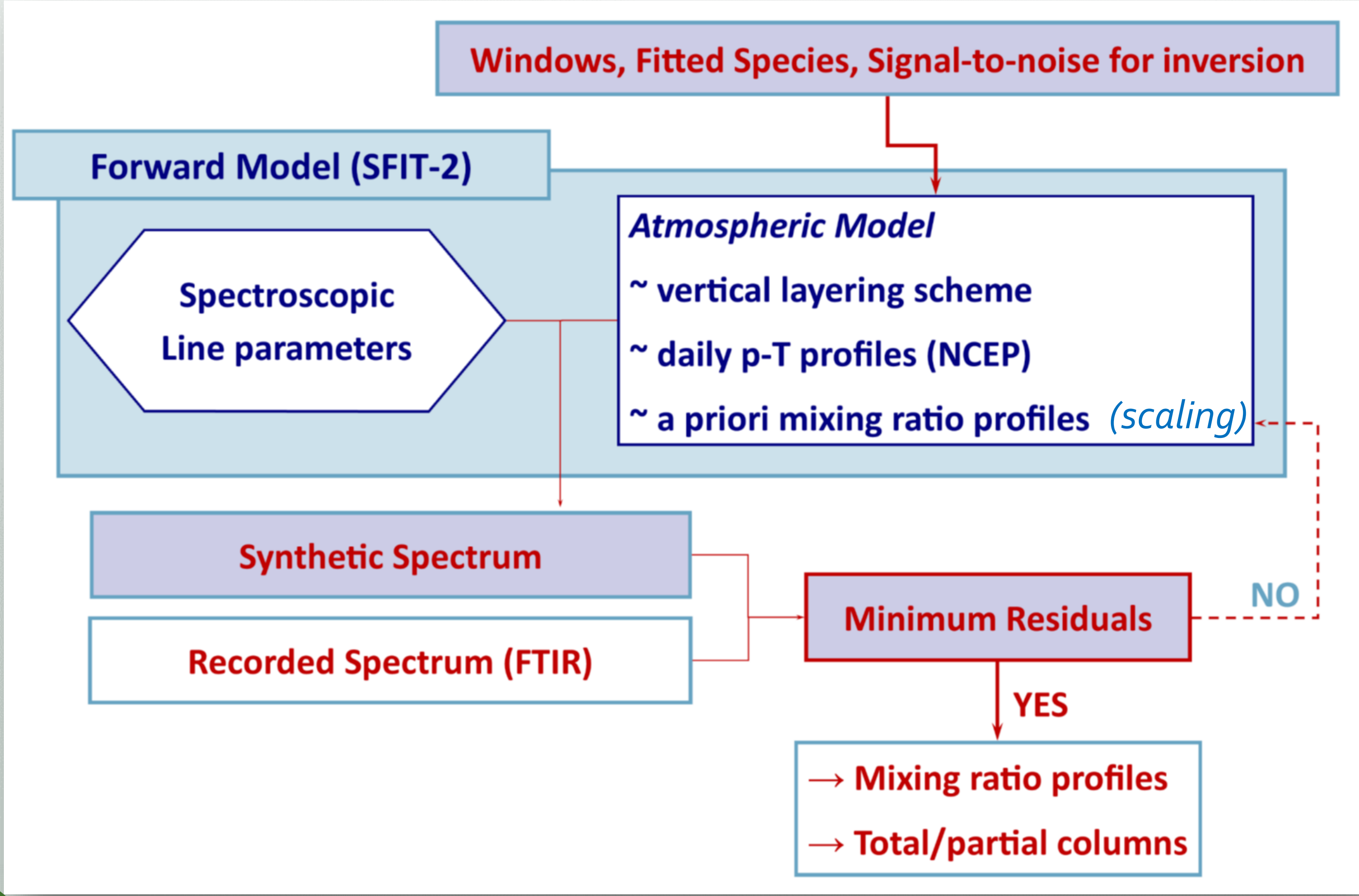
→ wavelength

→ diffraction order



Inversion

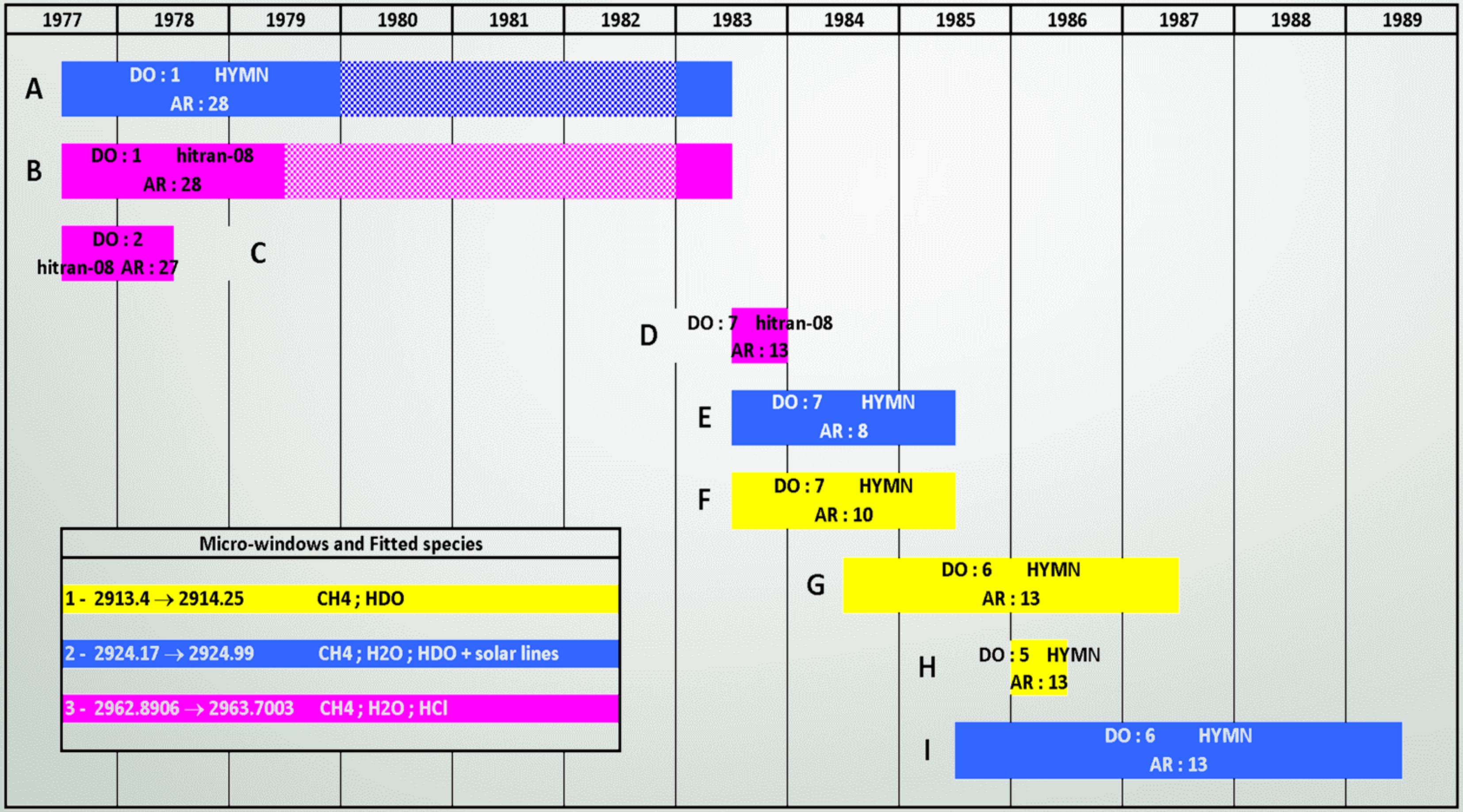
Inversion strategy (SFIT-2)



Datasets and harmonization

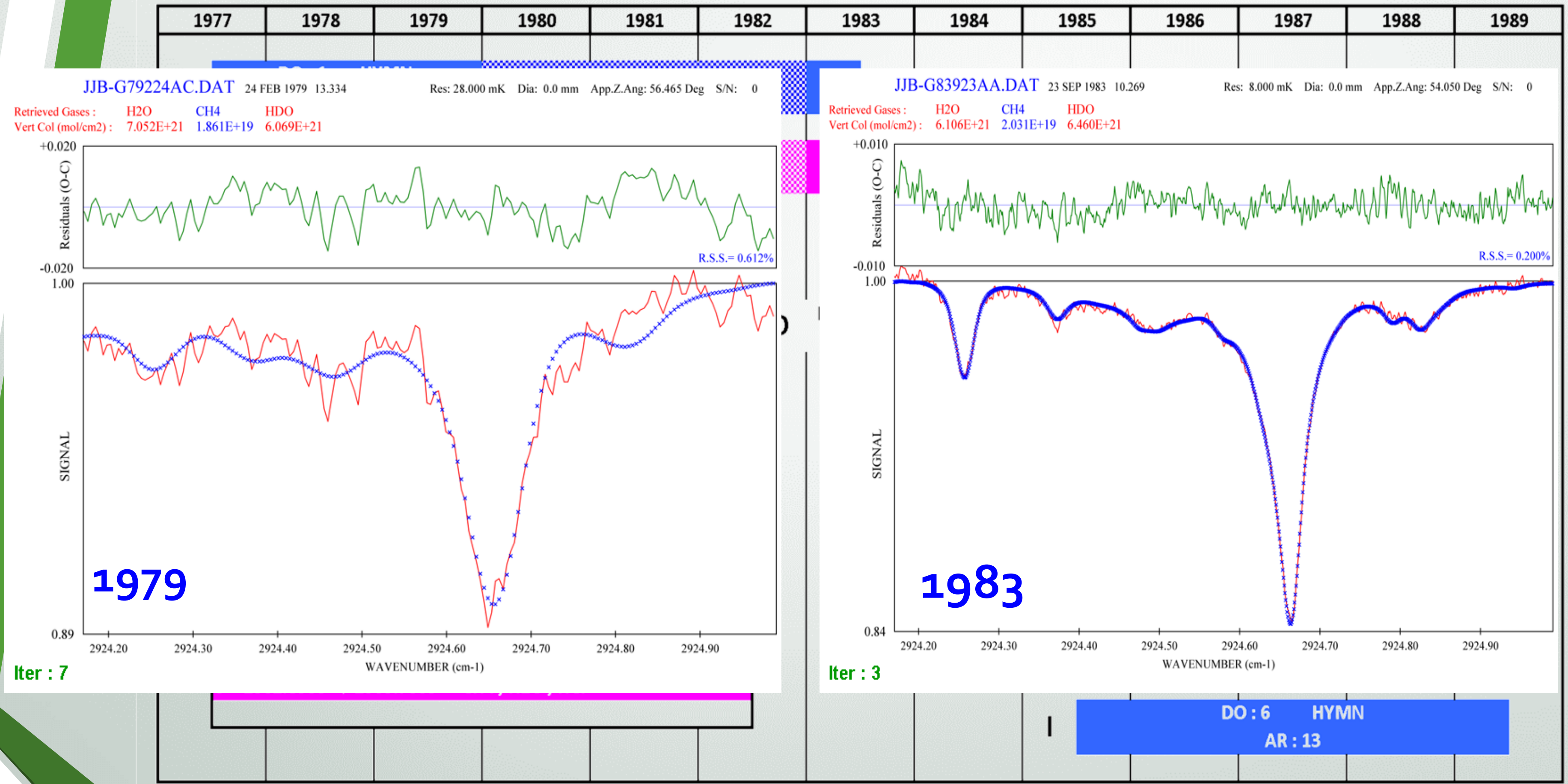
2700 spectra - 9 datasets

9 different combinations of diffraction orders, windows, spectroscopy,…

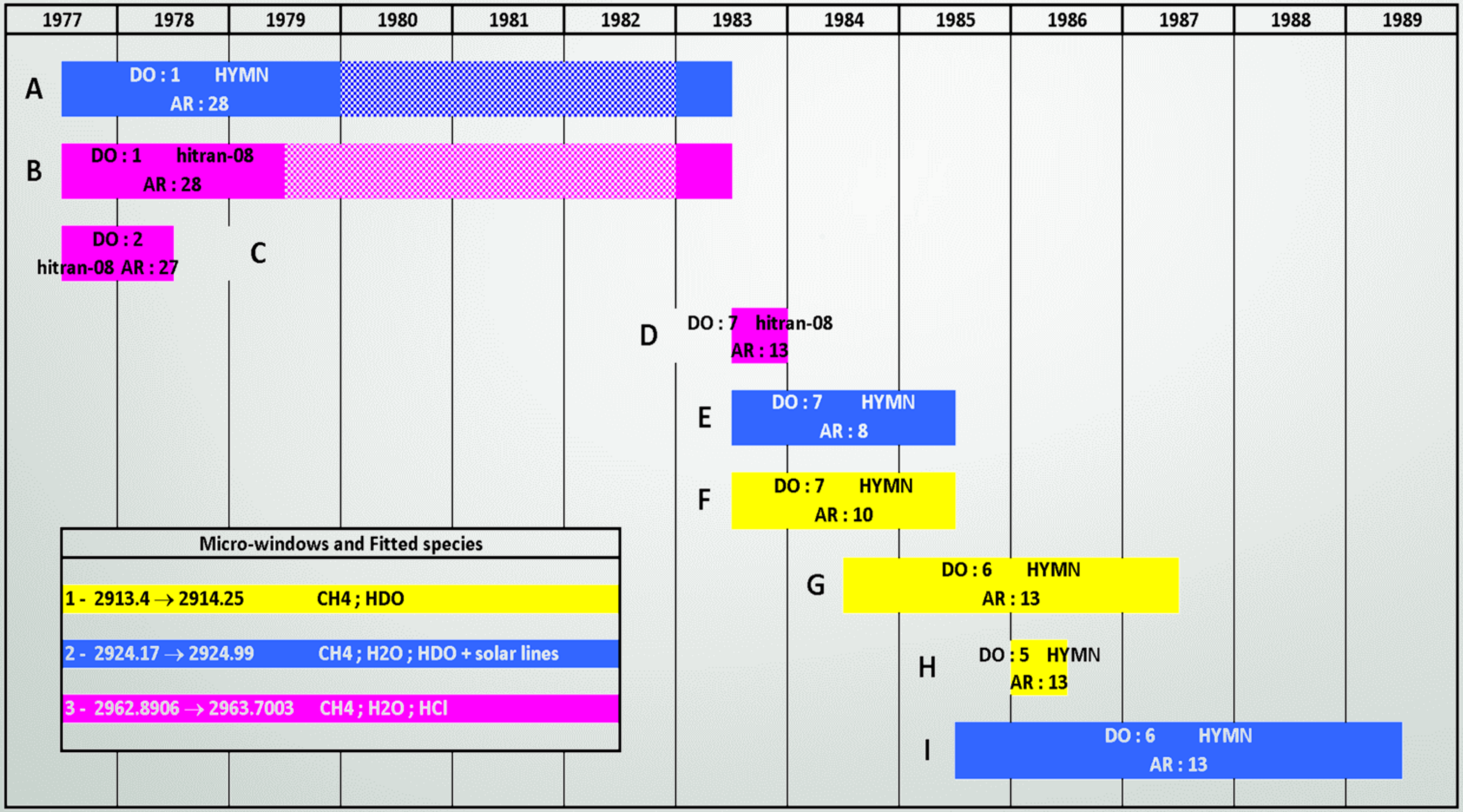


Datasets and harmonization

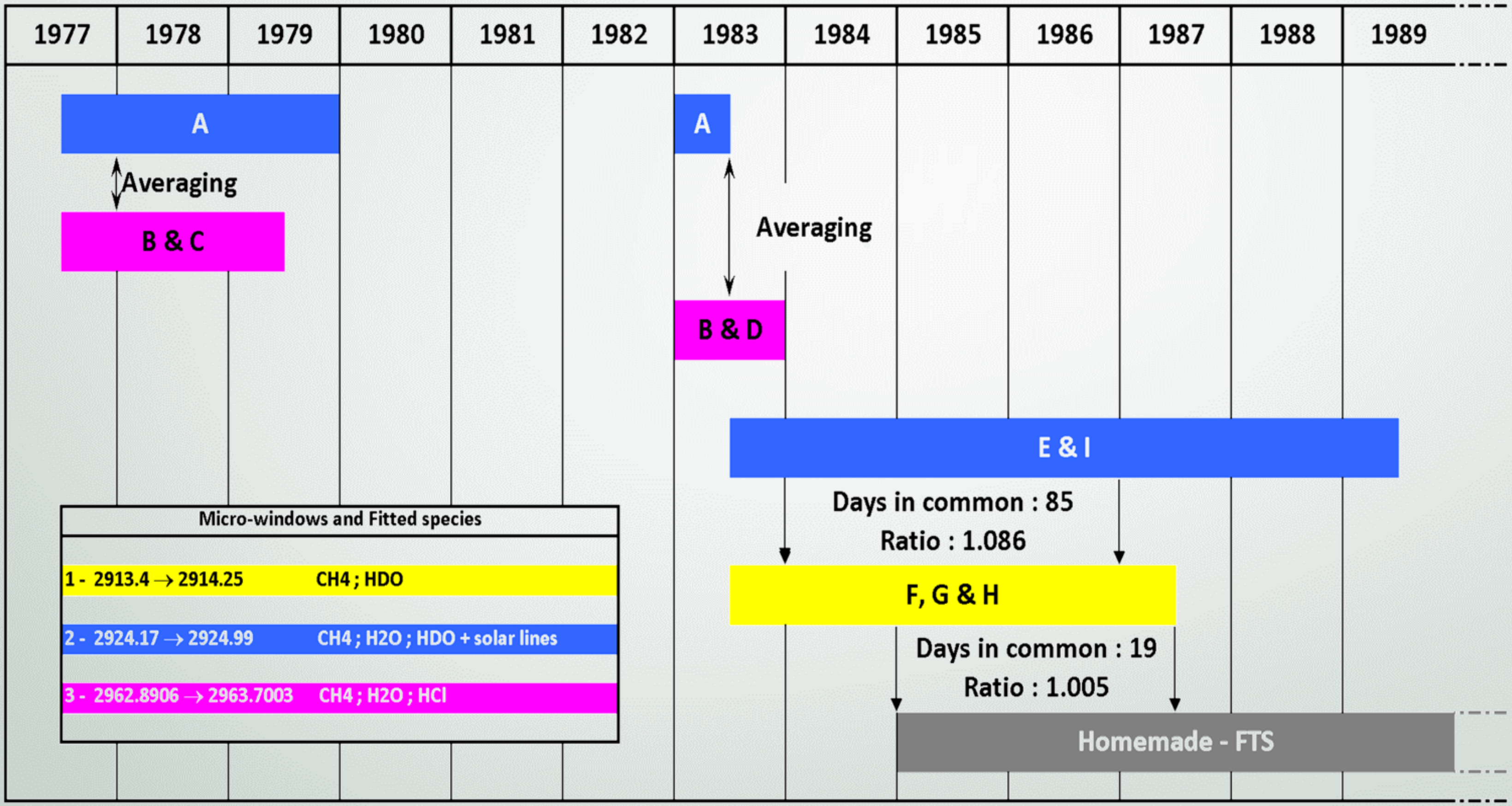
Different spectra quality, signal-to-noise ratio



Datasets and harmonization

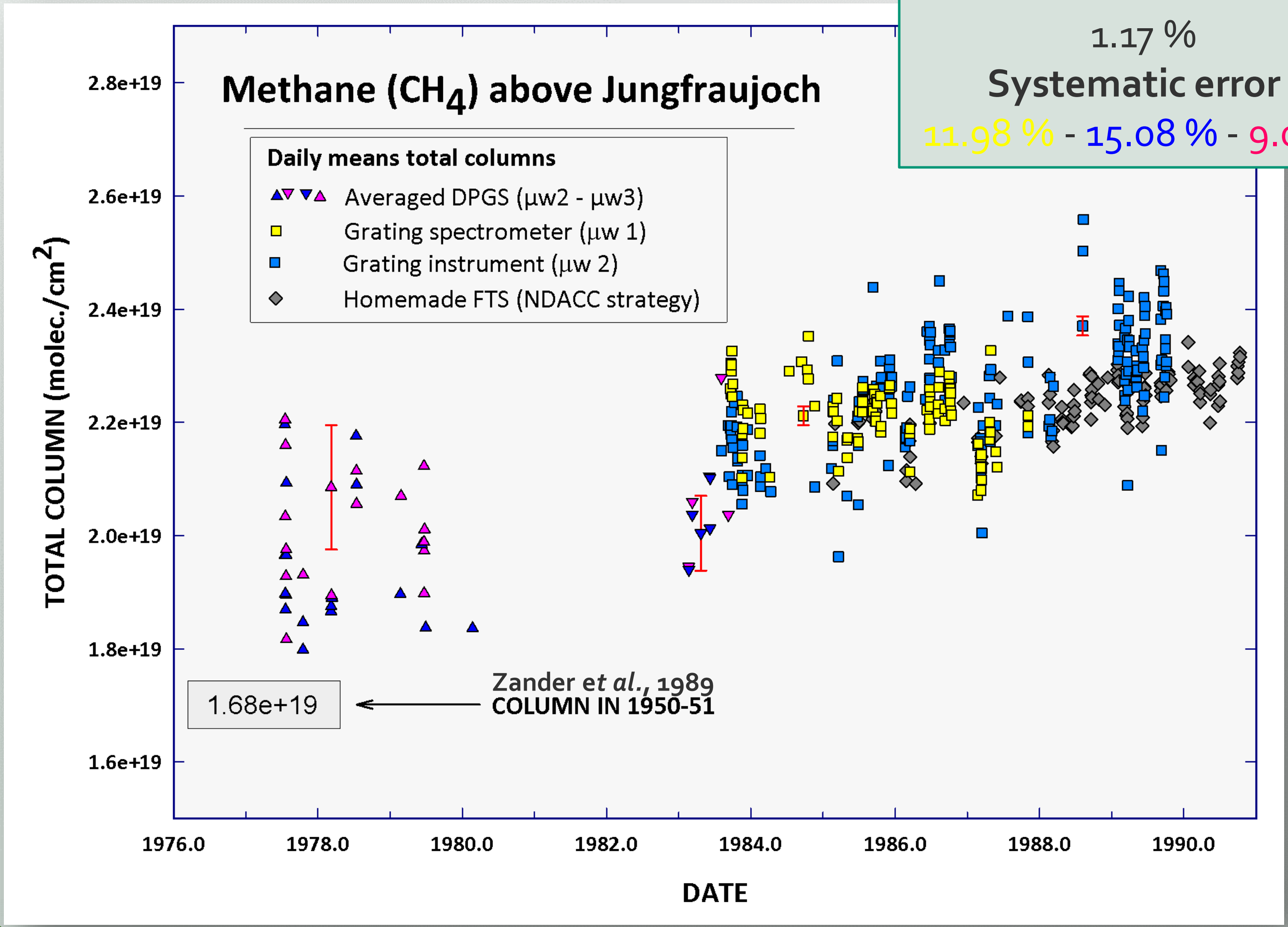


Datasets and harmonization



CH_4 : 1977 - 1989

Random error
1.17 %
Systematic error :
11.98 % - 15.08 % - 9.04 %



Jungfraujoch station

Instrumentation timeline

1950'	1976 - 1989	1985	1991
1 m focal length grating spectrometer	7.3 m focal length Double Pass Grating Spectrometer	**Homemade Fourier Transform Spectrometer**	**Bruker 120HR Fourier Transform Spectrometer**

- 1950': pioneering infrared solar observations
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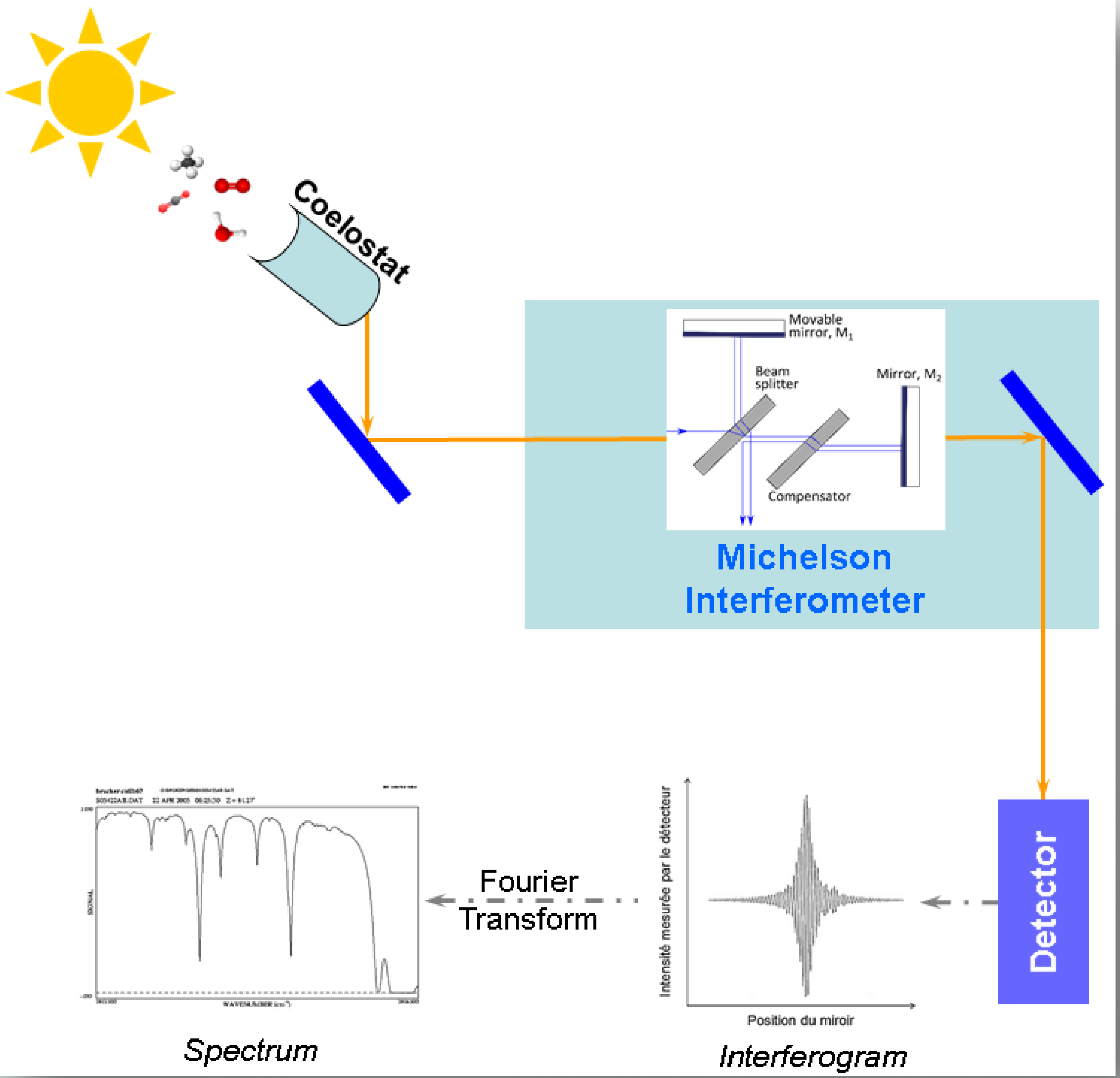
  + solar atlas
- 1976 - 1989: 1975
  Detection of HF in the atmosphere by R. Zander
  Zander *et al.*, 1989
- 1985: Atmospheric observations resumed and haven't stopped since then.
- 1991: Network for the Detection of Atmospheric Composition Change - NDACC

Database of 45 000 spectra (grating + homemade + Bruker)
→ 40 years of continuous observations

Fourier Transform Spectrometer



2 Detectors

HgCdTe and InSb

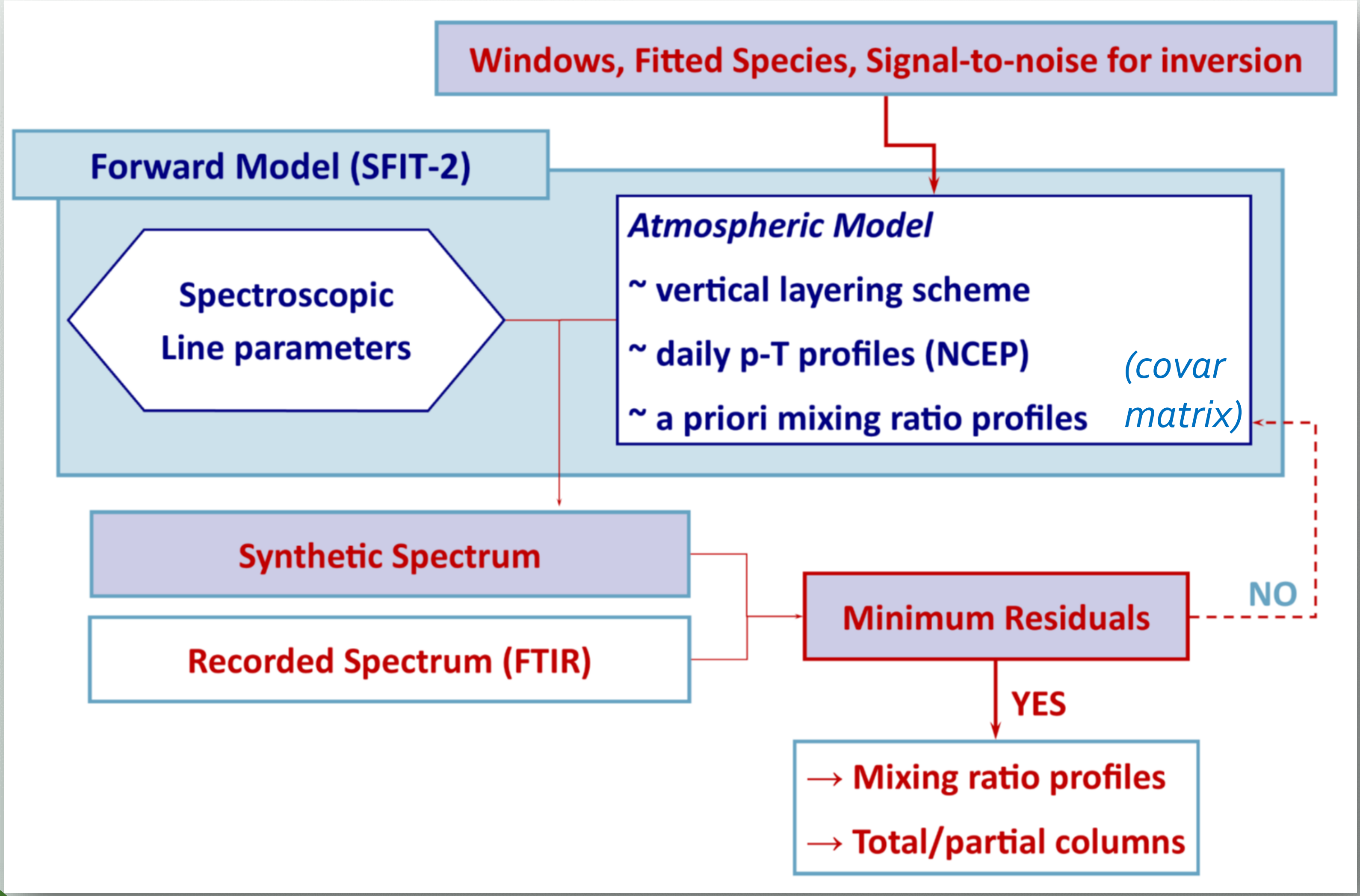
650 à 4500 cm^{-1}

High resolution

between 0.00285 cm^{-1}

and 0.006 cm^{-1}

Inversion strategy (SFIT-2)

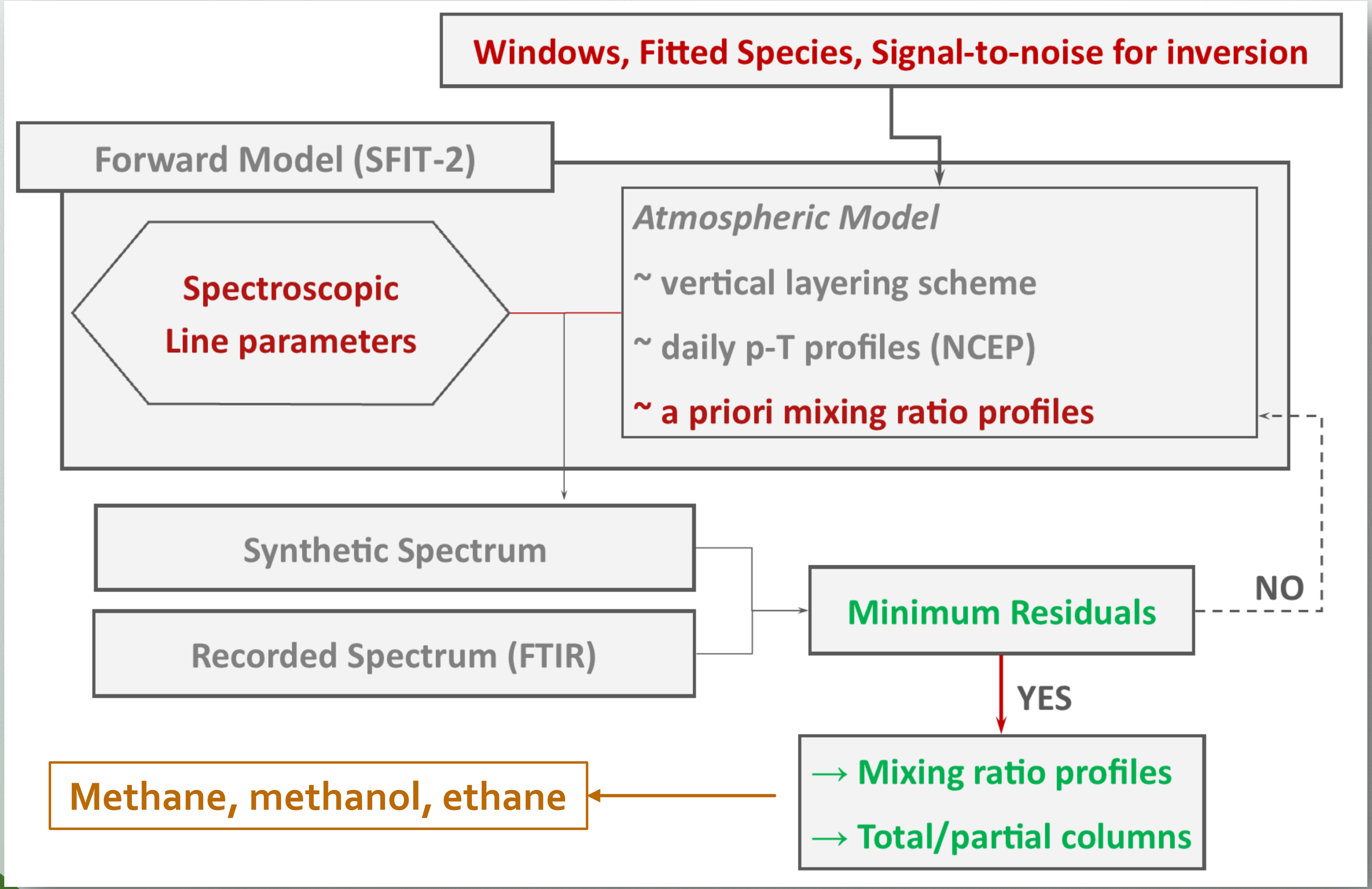


"Long-term study of methane and two of its derivatives from solar observations recorded at the Jungfraujoch station."

PhD thesis

Part I – Optimization of retrieval strategies

Inversion strategy (SFIT-2)



Methanol – CH_3OH

Atmos. Meas. Tech., 7, 1–12, 2014
www.atmos-meas-tech.net/7/1/2014/
doi:10.5194/amt-7-1-2014

Atmospheric Measurement Techniques
Open Access

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

W. Bader[1], T. Stavrakou[2], J.-F. Muller[2], S. Reimann[3], C. D. Boone[4], J. J. Harrison[5], O. Flock[1], B. Bovy[1], B. Franco[1], B. Lejeune[1], C. Servais[1], and E. Mahieu[1]

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[2]Belgian Institute for Space Aeronomy, Avenue Circulaire 3, 1180, Brussels, Belgium
[3]Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland
[4]Department of Chemistry, University of Waterloo, Ontario, Canada
[5]Department of Chemistry, University of York, York, UK

Inversion strategy

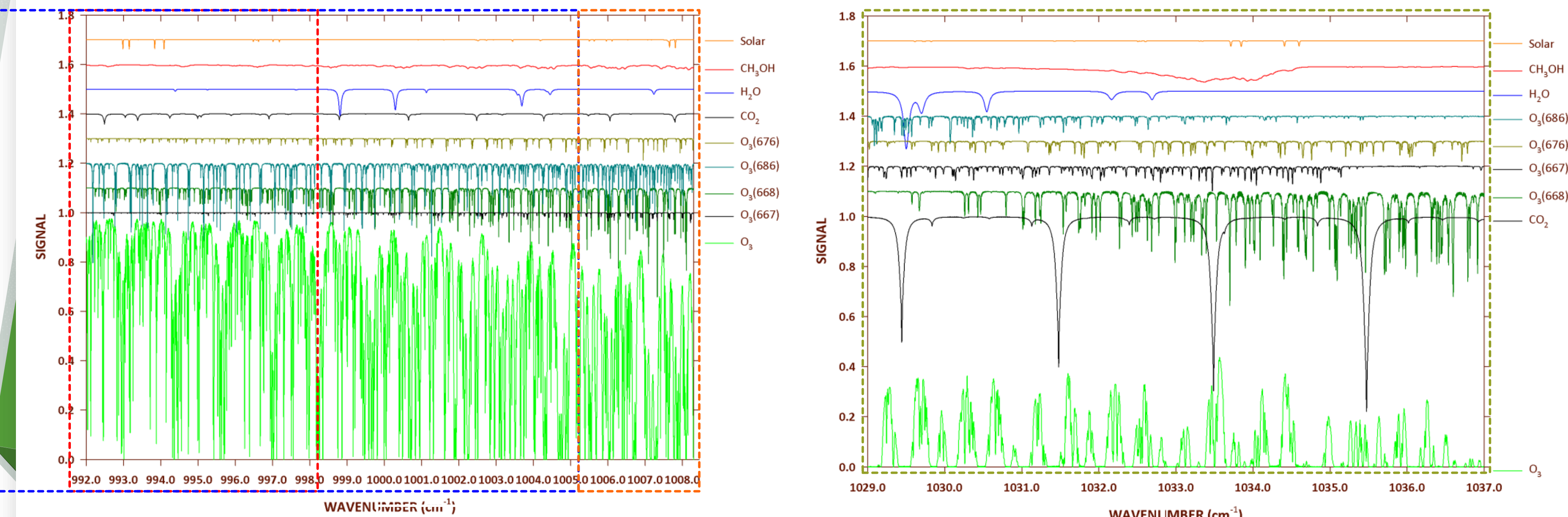
Mahieu *et al.*, 2012

Rinsland *et al.*, 2009 → 992 – 998.7 cm^{-1}

+ Atmospheric Chemistry Experiment, 2011 → 984.9 – 1005.1 cm^{-1}

+ CH_3OH

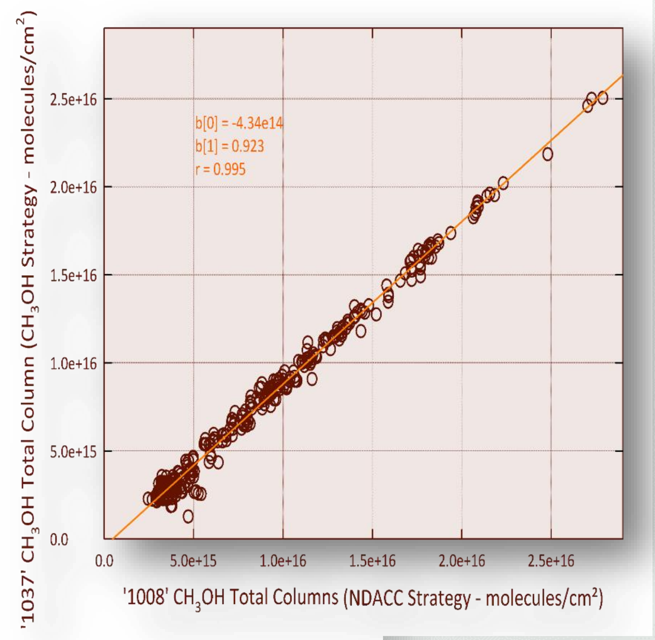
Stavrakou *et al.*, 2011 → 1029 – 1037 cm^{-1}

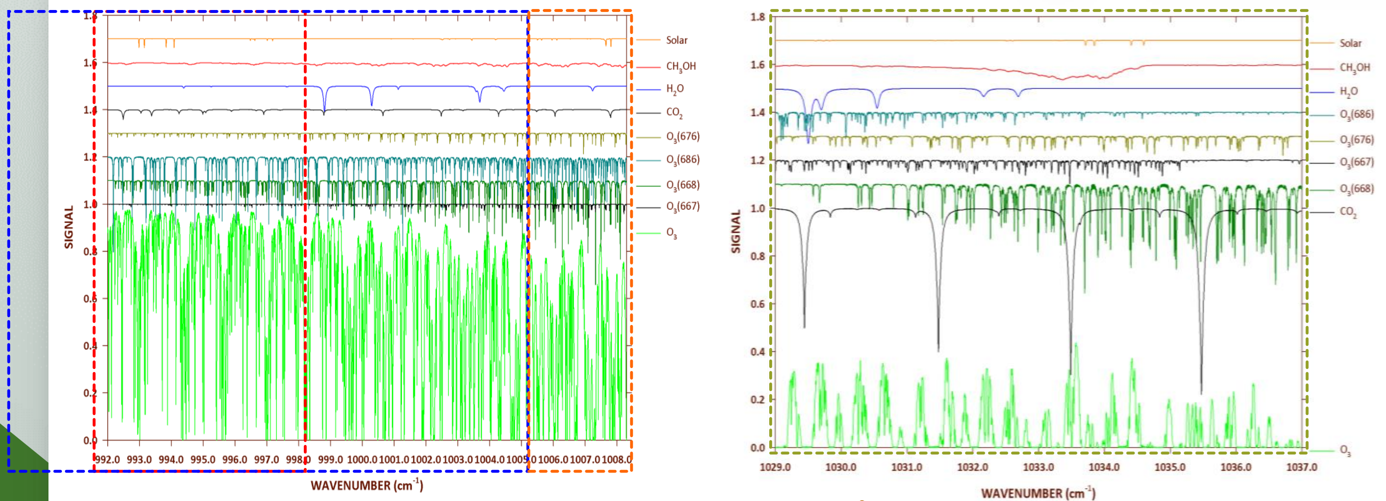


Simulated windows for Jungfraujoch, SZA : 80°, 6.1 mK, HITRAN08

Inversion strategy

- Solar zenith angle
  65 et 80°
- Contrasting absorptions features
  O_3 93% and 98 %
  CH_3OH 1.7% and 1.8 %
- Improved vertical sensitivity range
  Low troposphere [surface - 7 km]
  UTLS [7 - 15 km]





Simulated windows for Jungfraujoch, SZA : 80°, 6.1 mK, HITRAN08

Ethane – C_2H_6

Retrieval of ethane from ground-based FTIR solar spectra using improved spectroscopy: recent burden increase above Jungfraujoch

B. Franco[a,*], W. Bader[a], G. C. Toon[b], C. Bray[c], A. Perrin[d], E. V. Fischer[e], K. Sudo[f,g], C. D. Boone[h], B. Bovy[a], B. Lejeune[a], C. Servais[a], E. Mahieu[a]

[a] *Institute of Astrophysics and Geophysics, University of Liège, B-4000 Liège (Sart-Tilman), Belgium*
[b] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena California, 91109, USA*
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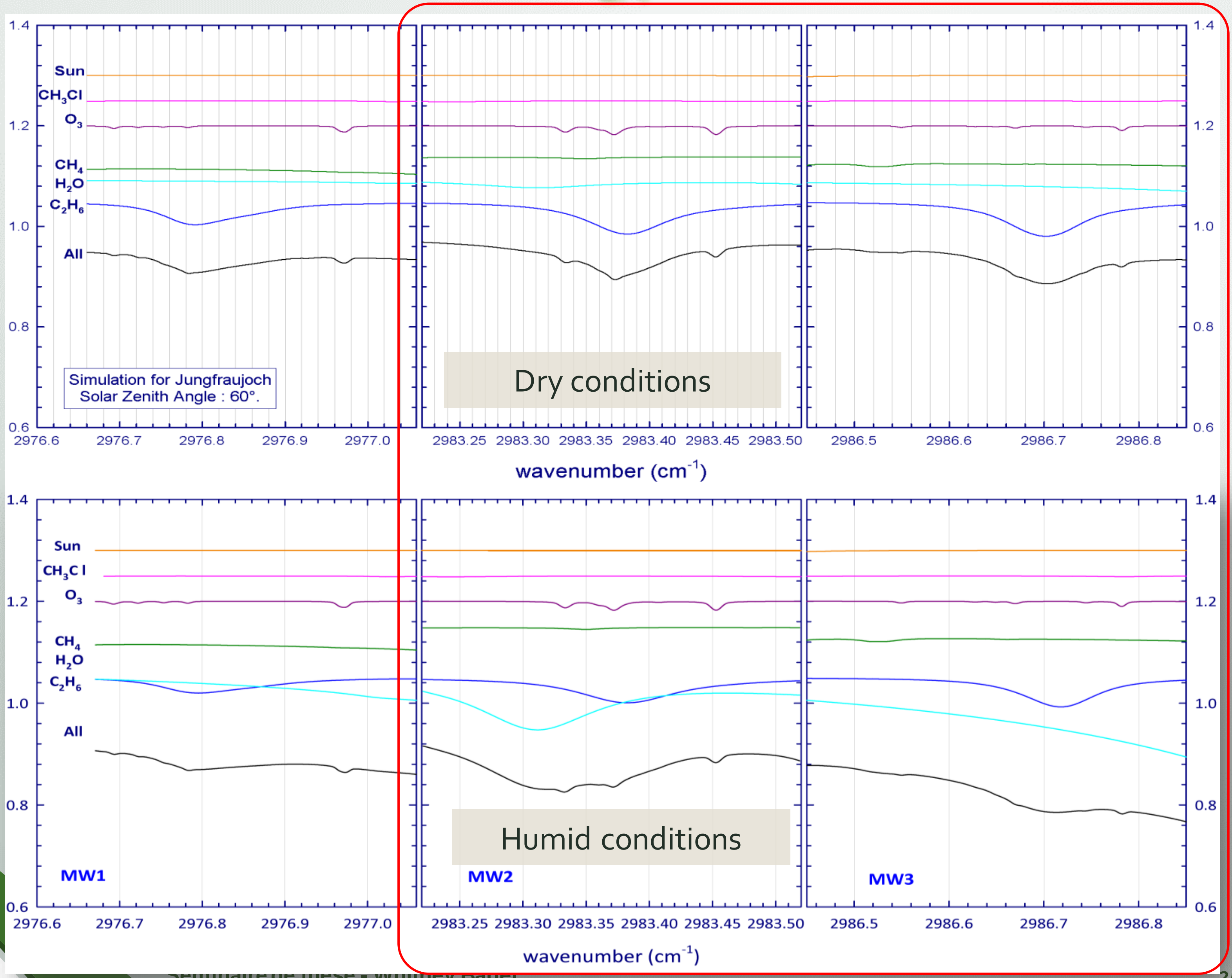
[d] *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA-UMR7583) CNRS, Universités Paris Est Créteil and Paris 7 Diderot (IPSL), F-94010 Créteil cedex, France*
[e] *Department of Atmospheric Science, Colorado State University, Fort Collins, CO USA*
[f] *Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan*
[g] *Department of Environmental Geochemical Cycle Research, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan*
[h] *Department of Chemistry, University of Waterloo, Ontario, Canada*

Inversion strategy - Interferences



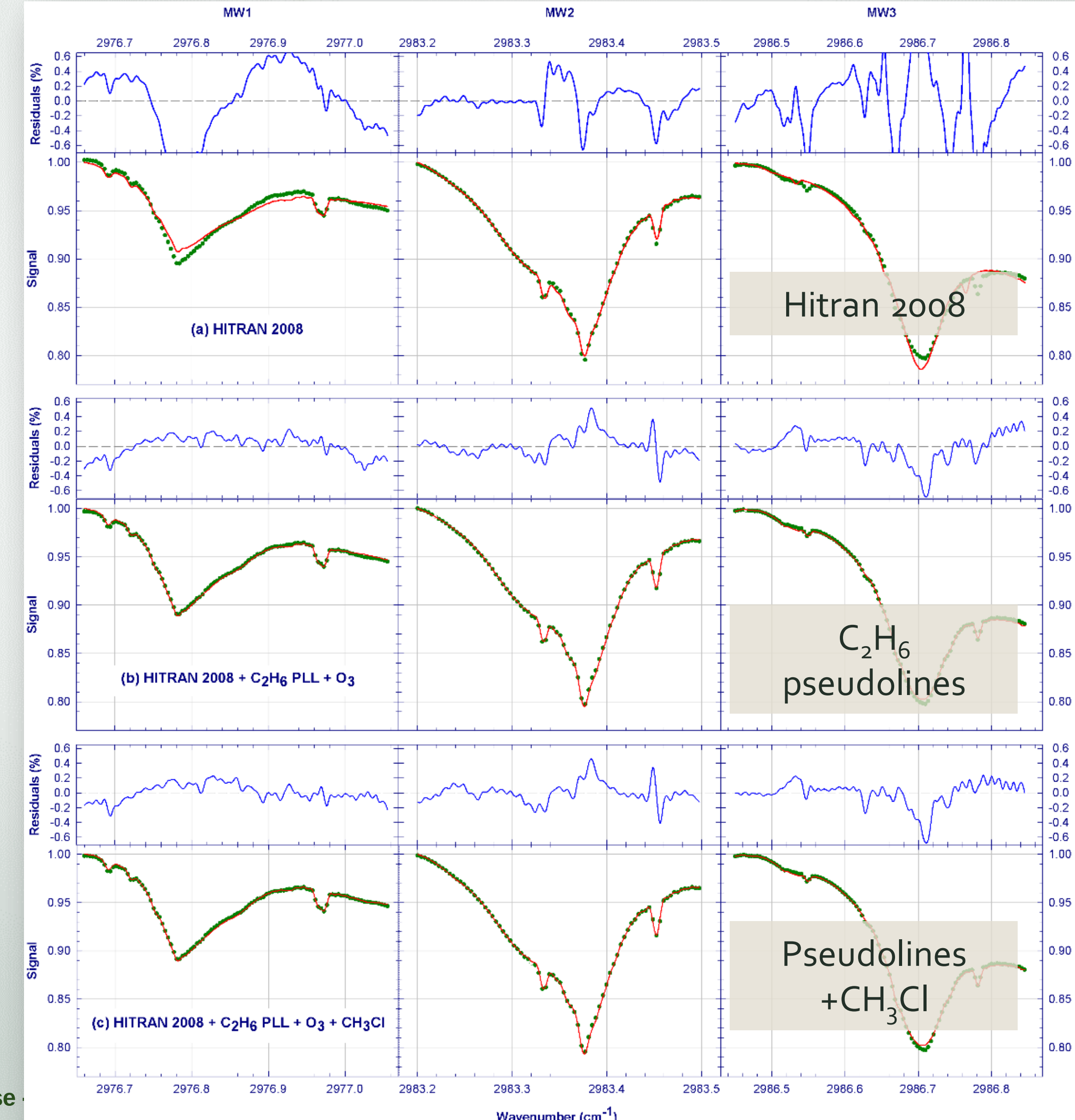
Inversion strategy - Spectroscopy

- Combination of 3 windows & updated spectroscopic parameters included
- Improved vertical sensitivity range

  Low tropospheric

  < 8.5 km

  UTLS 8.5 - 22 km



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Whitney Bader

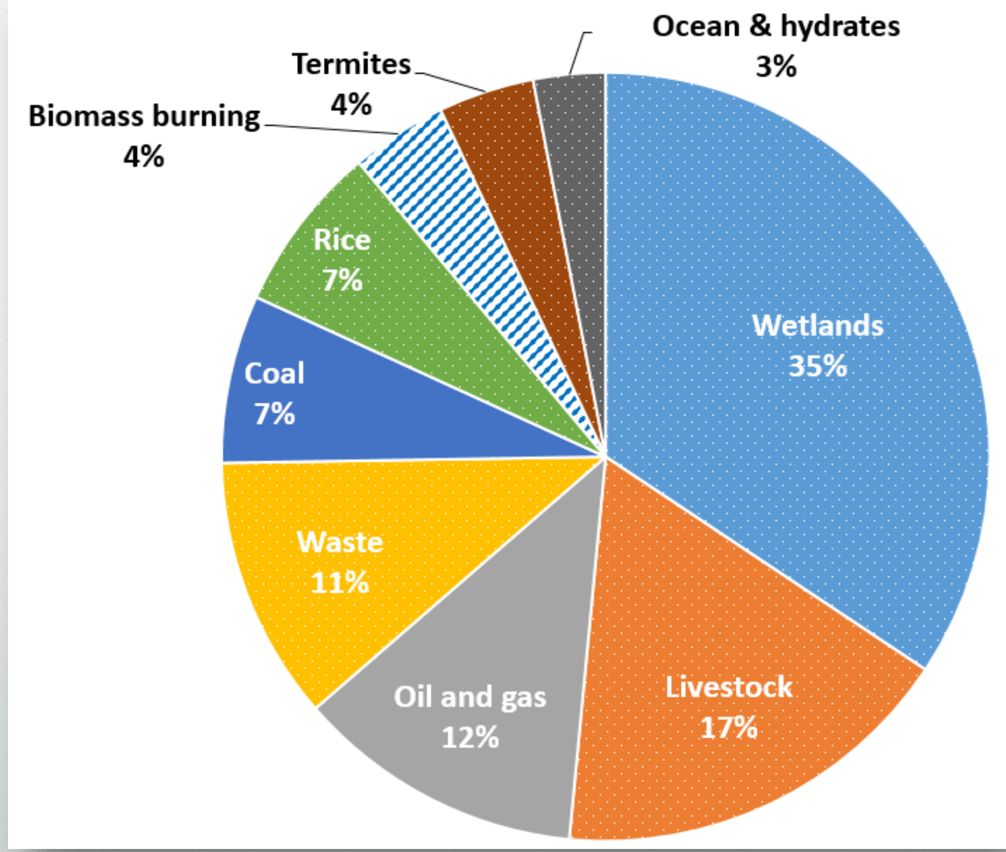
Brewer-Wilson Seminar

November 4th, 2016

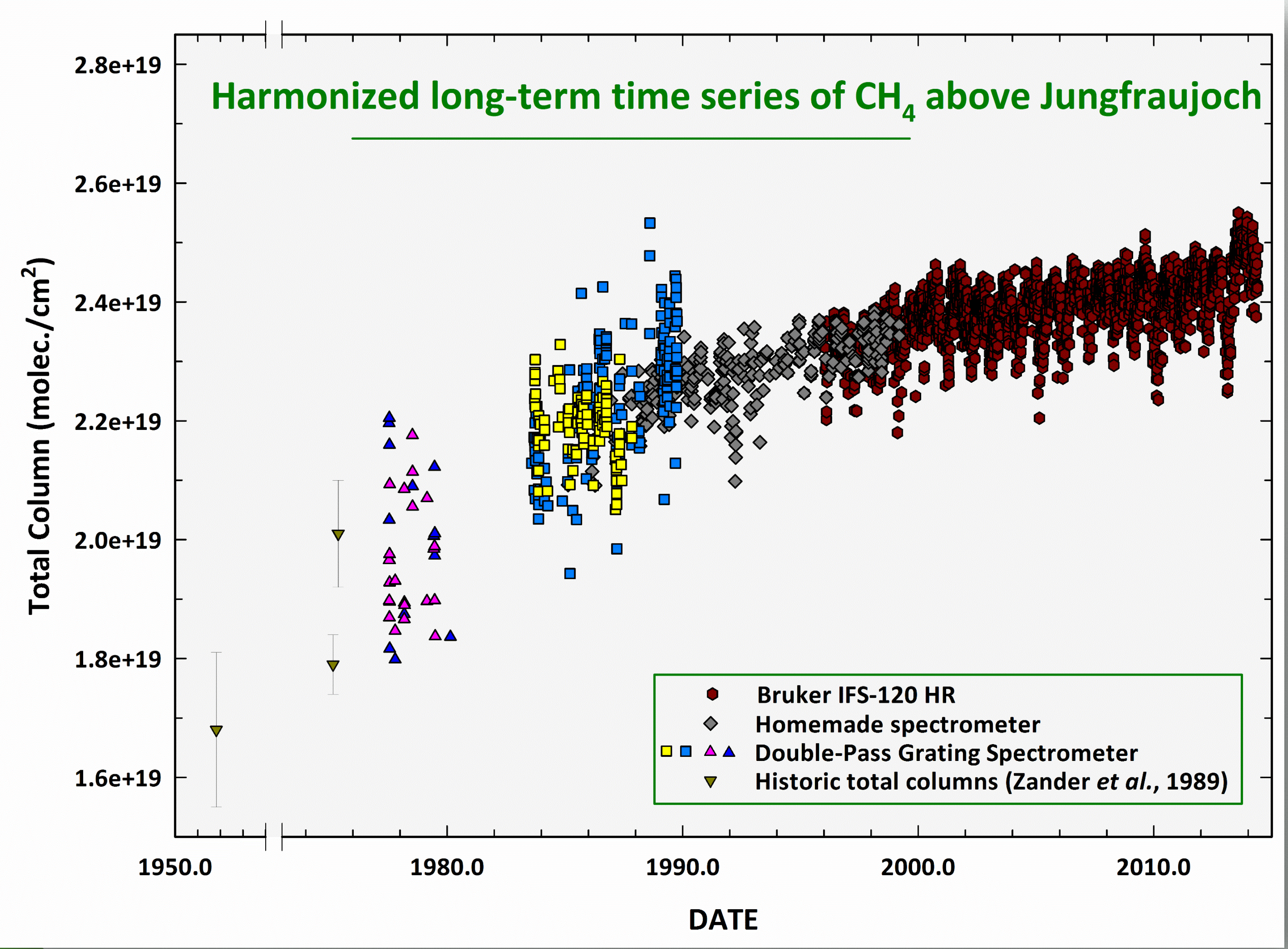
Atmospheric methane

- 2nd most important anthropogenic greenhouse gas
- 1/5 of anthropogenic radiative forcing since 1750 is due to methane
- 3 types of emission processes :
  - biogenic (dotted)
  - thermogenic (plain)
  - pyrogenic (hatched)
- 1 major sink
  - oxidation by OH

+ 260% since 1750



CH_4 : 1977 - 2015



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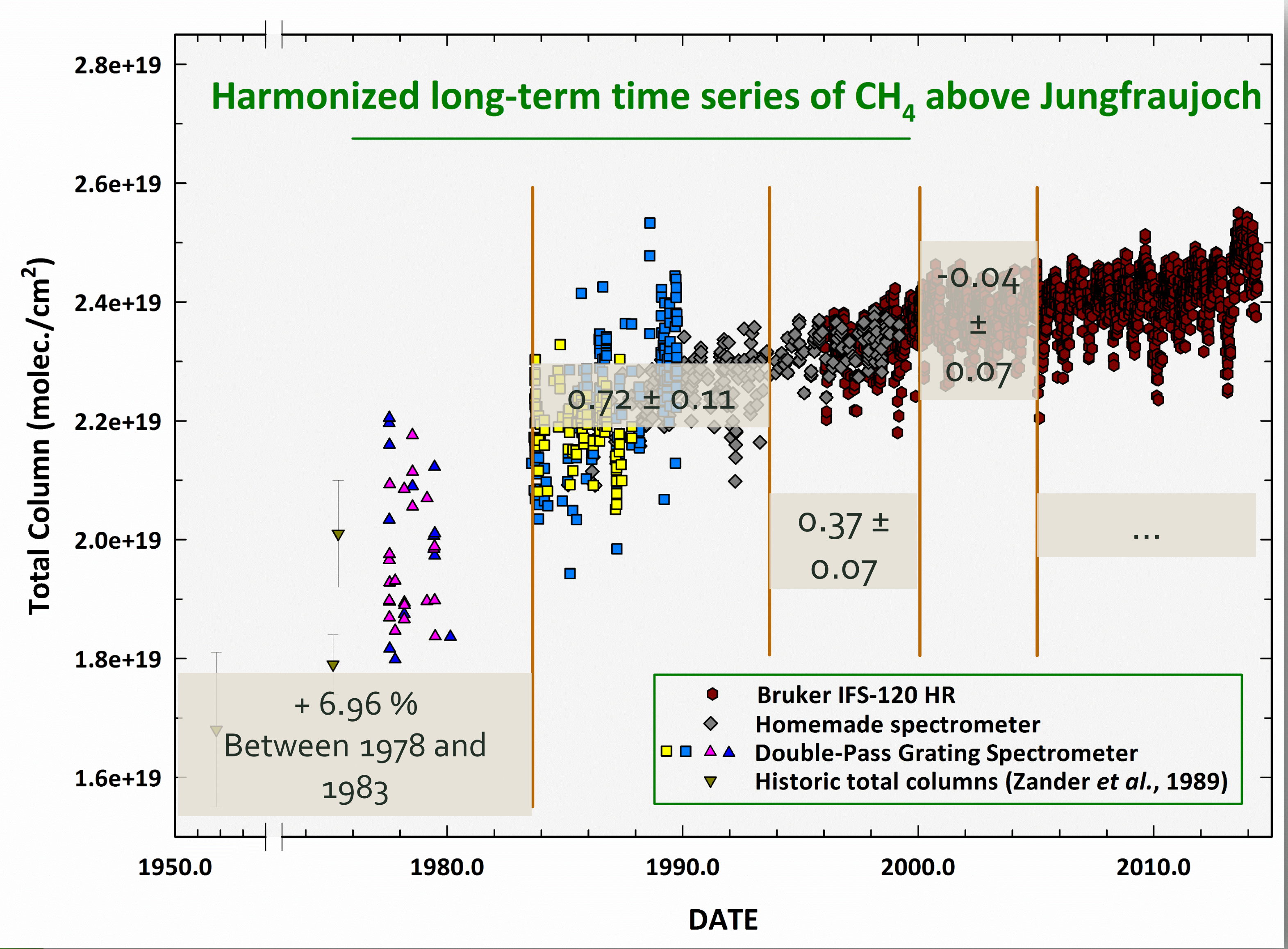

"The recent increase of methane from 10 years of NDACC ground-based FTIR observations."

Bader, W. et al., Ten years of atmospheric methane from ground-based NDACC FTIR observations, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-699, in review, 2016.

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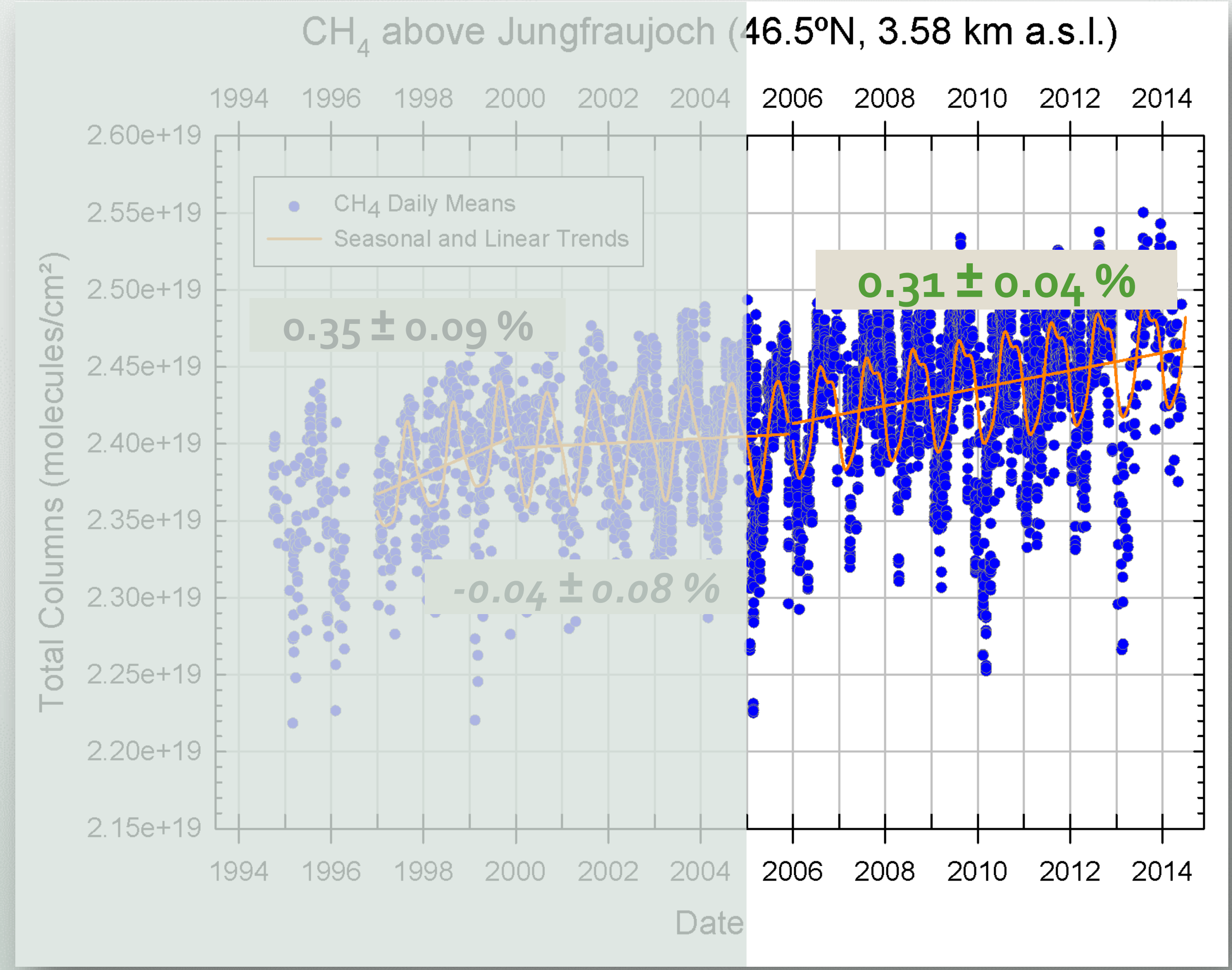
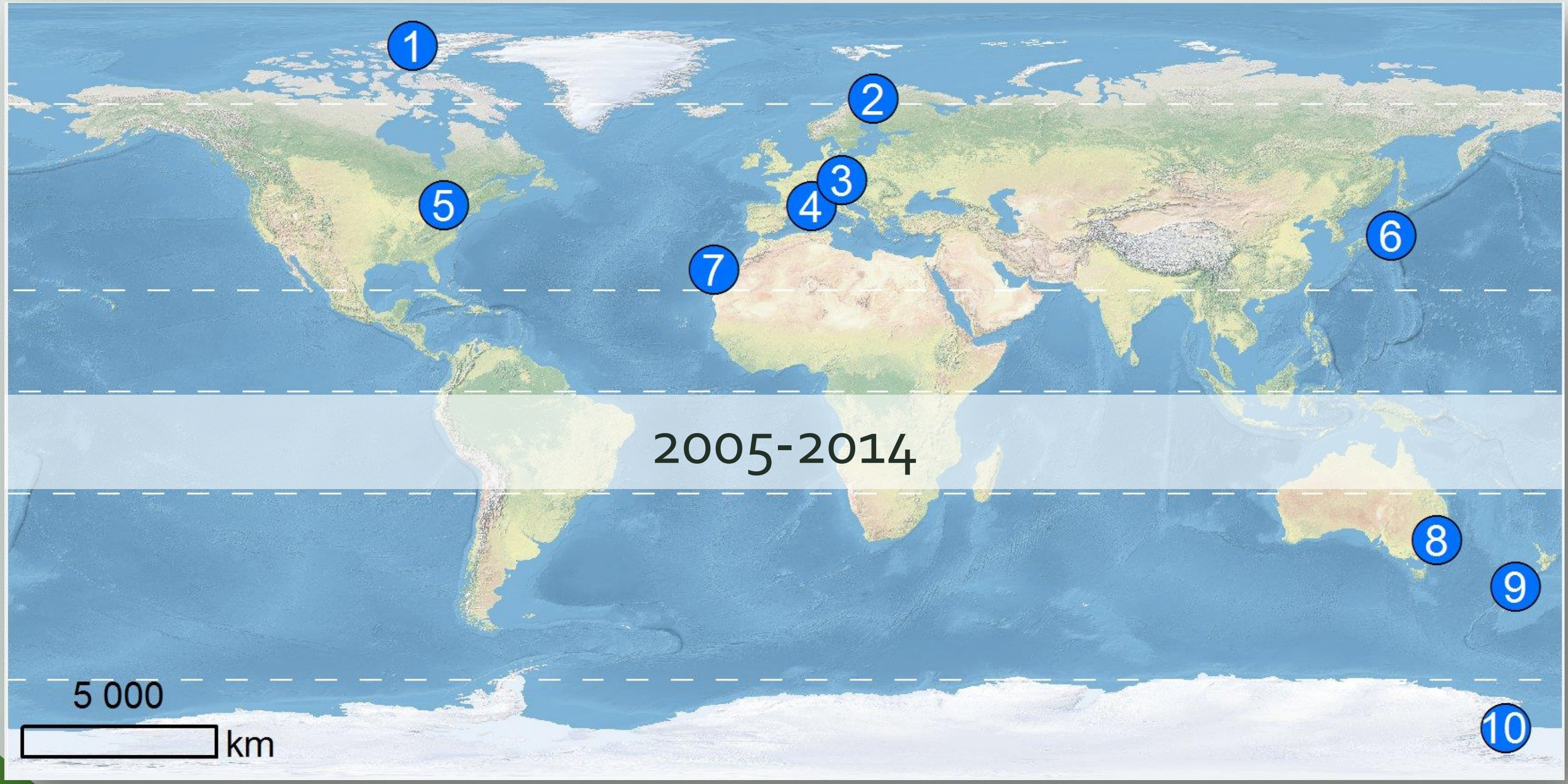
Unexplained increase since ~2005



10 years of NDACC FTIR observations

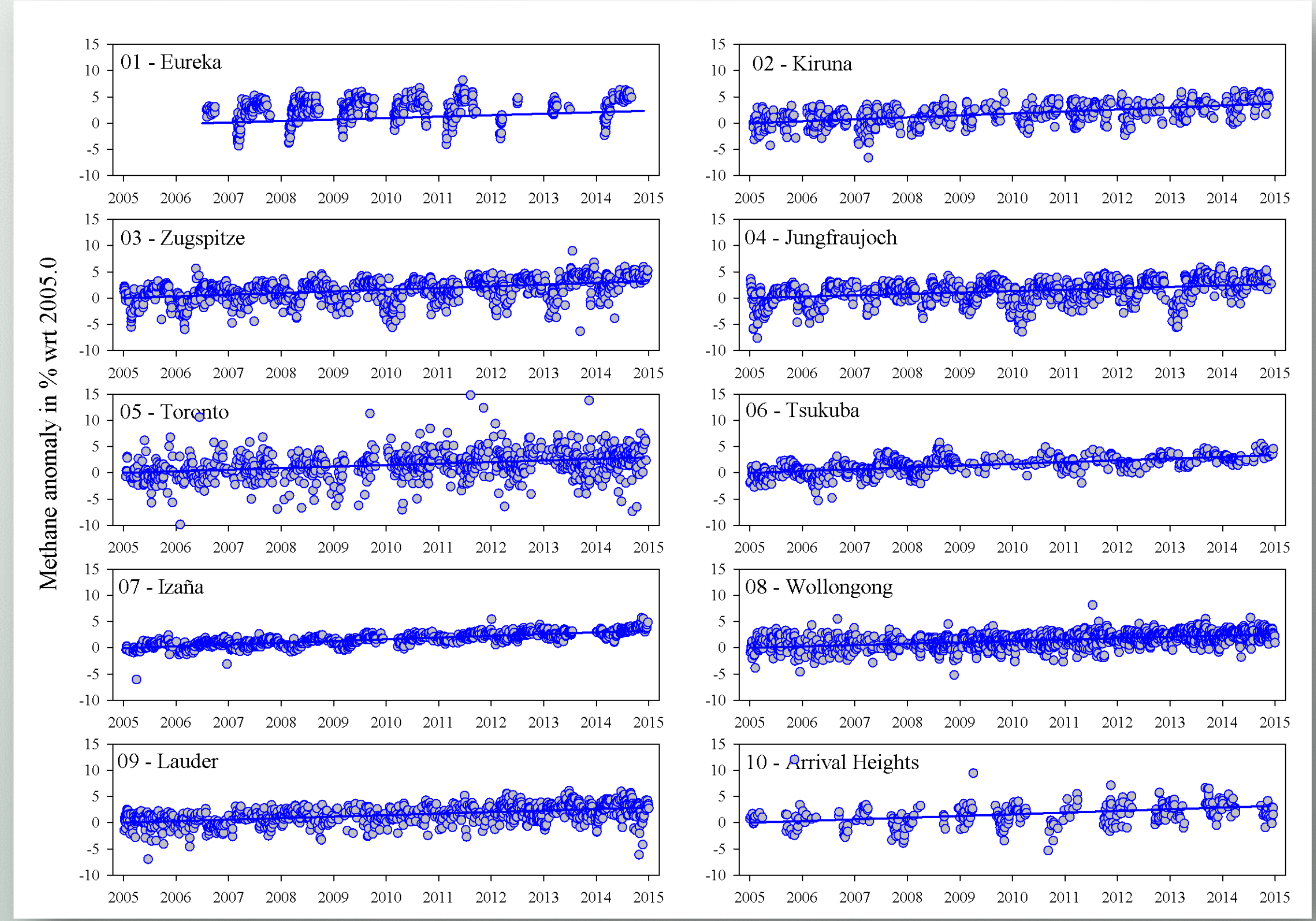
1- Eureka (80 °N)
2- Kiruna (68 °N)
3- Zugspitze (47 °N)
4- Jungfraujoch (47 °N)
5- Toronto (44 °N)
6- Tsukuba (37 °N)
7- Izaña (28 °N)
8- Wollongong (34 °S)
9- Lauder (45 °S)
10- Arrival Heights (78 °S)



10 years of NDACC FTIR observations

Anomaly with respect to 2005.0
Averaged increase : 0.31 ± 0.03 %/year

0.26 ± 0.02 %/year : Wollongong
0.39 ± 0.09 %/year : Toronto



GEOS-Chem v9-02. Tagged simulation

- Resolution : 2° x 2.5° and 4° x 5°
- 47 vertical levels - Output : 3 hours
- Meteo fields : GEOS5
  (Dec 2003 - May 2013)
- Spin-up over 2004
  (70 spins for initialization)
- Emission inventories
  - Anthropogenic emissions : EDGAR v4.2
  - Biomass burning : GFED3 (8h)
  - Wetland model [Pikett-Heaps, 2011]
  - Termites [Fung et al., 1991]
  - Biofuels [Yevich and Logan, 2003]
  - Soil absorption [Fung et al., 1991]
- Main sink : 3D OH monthly
  [Park et al., 2004]
- Lifetime : 8.9 years

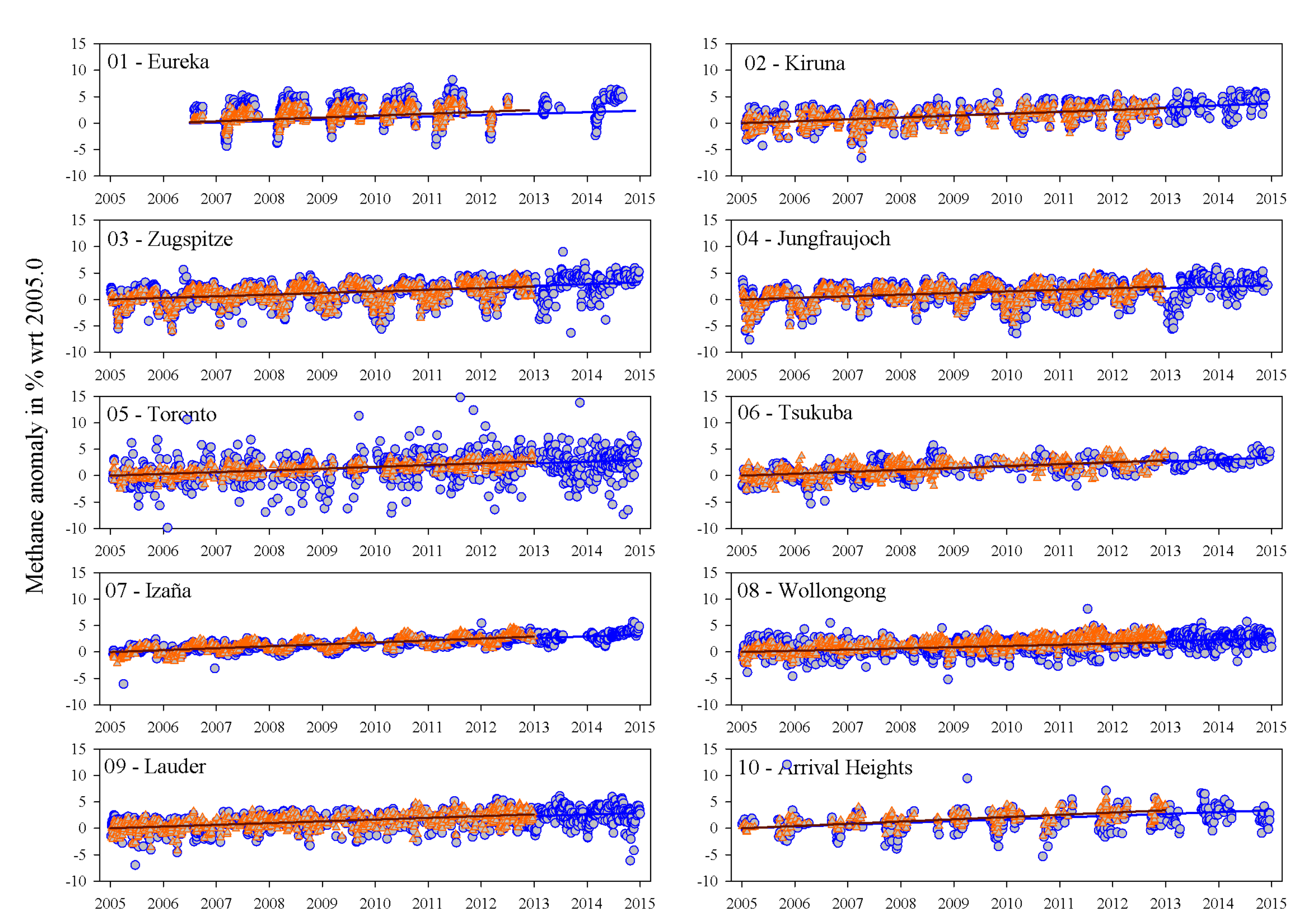
- ***Each tracer represents the contribution of each source to the simulated total column of methane***

Tracers
1- Total
2- Gas and oil
3- Coal
4- Livestock
5- Waste management
6- Biofuels
7- Rice cultures
8- Biomass burning
9- Wetlands
10- Other natural
11- Other anthropogenic
12- Soil absorption

FTIR vs GEOS-Chem

- Maximum bias 4.8 ± 3.5 % (Arrival Heights) ≈ FTIR systematic error

> Anomaly with respect to 2005.0

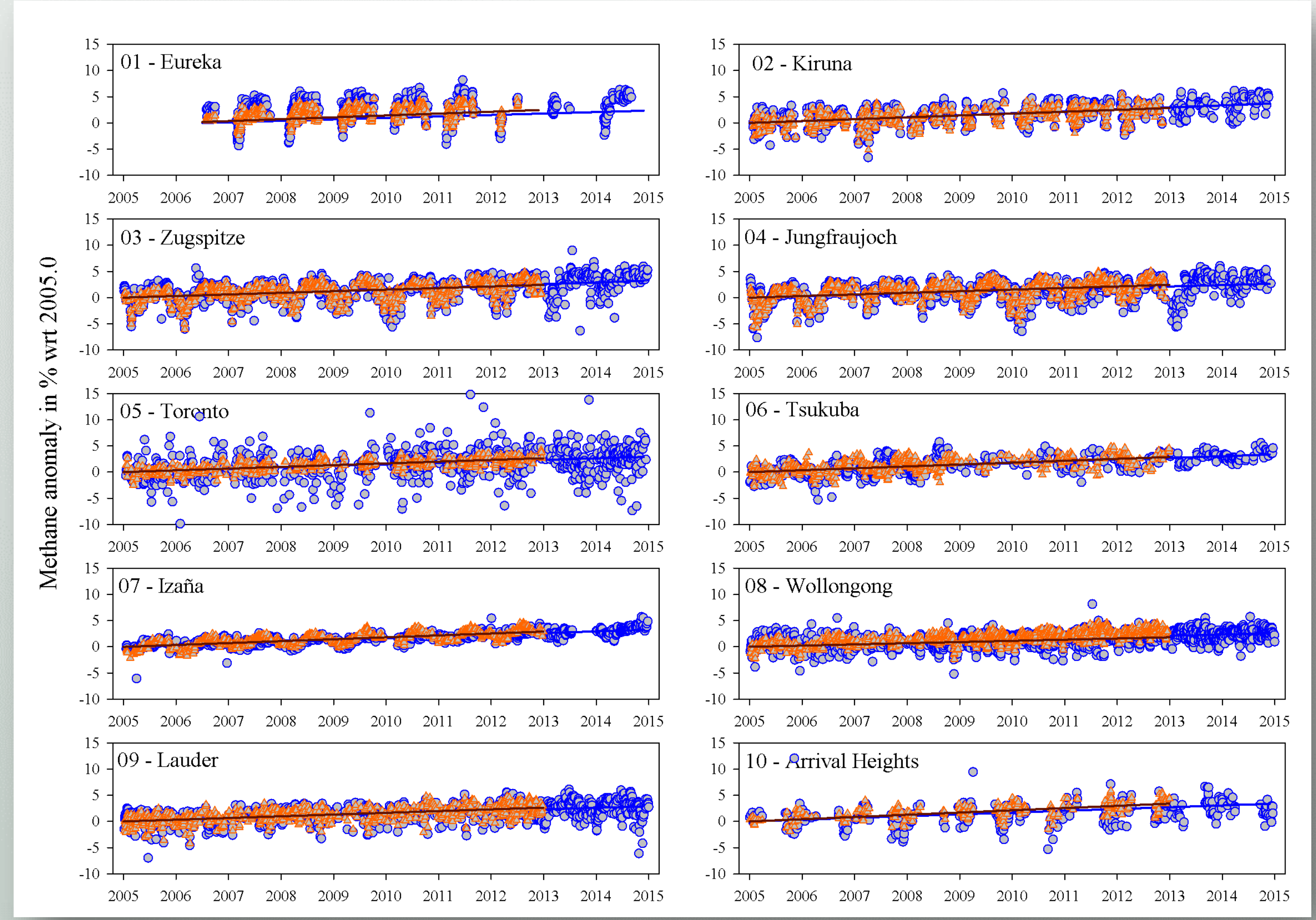


FTIR vs GEOS-Chem

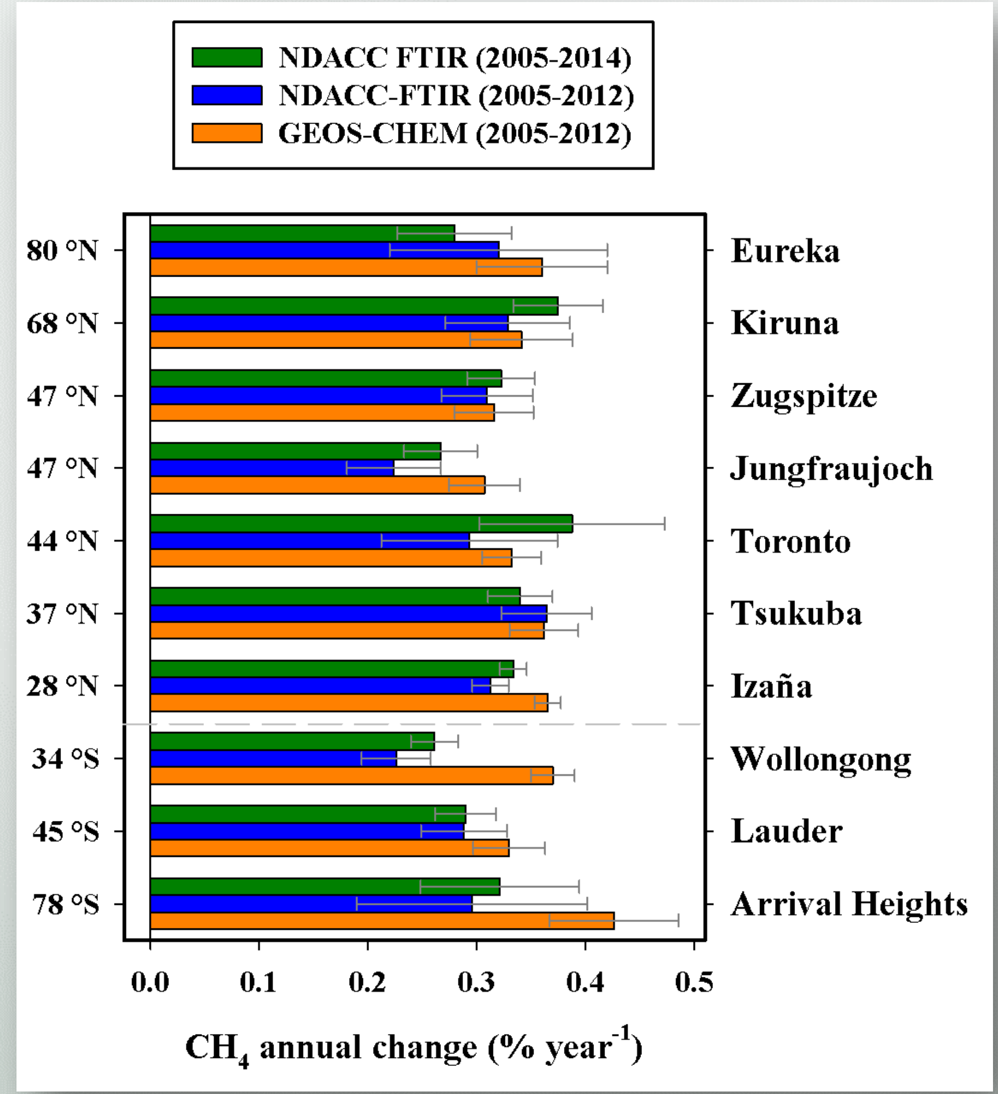
Averaged increase over 2005-2012

FTIR : 0.30 ± 0.04 %/year

GEOS-Chem : 0.35 ± 0.03 %/year



Methane since 2005



GC tagged simulation : Analysis

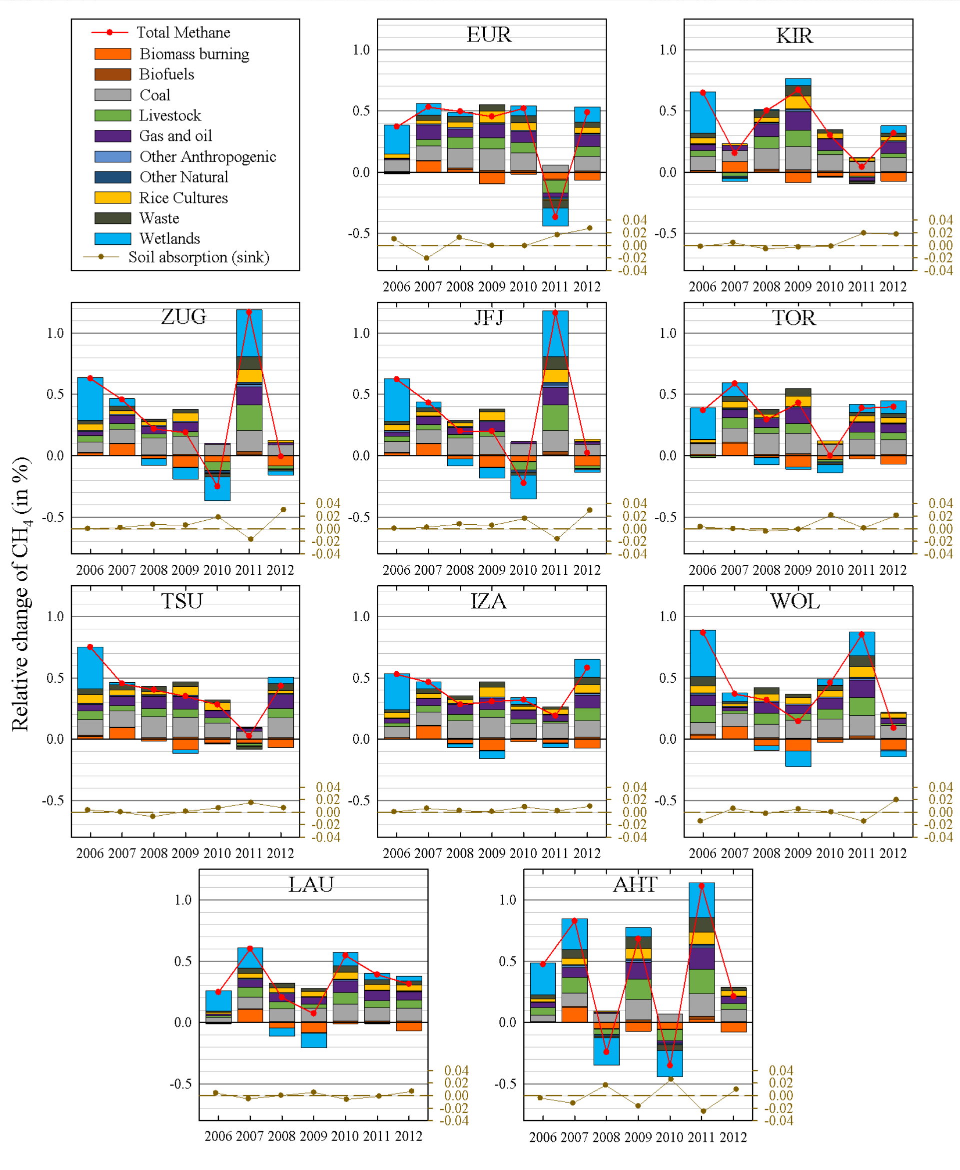
Yearly relative change in %.

$$YC\ (in\ \%) = \frac{(\mu_n - \mu_{n-1})}{\mu_{tot,n-1}}$$

μ_n : annual mean of CH_4, year n.

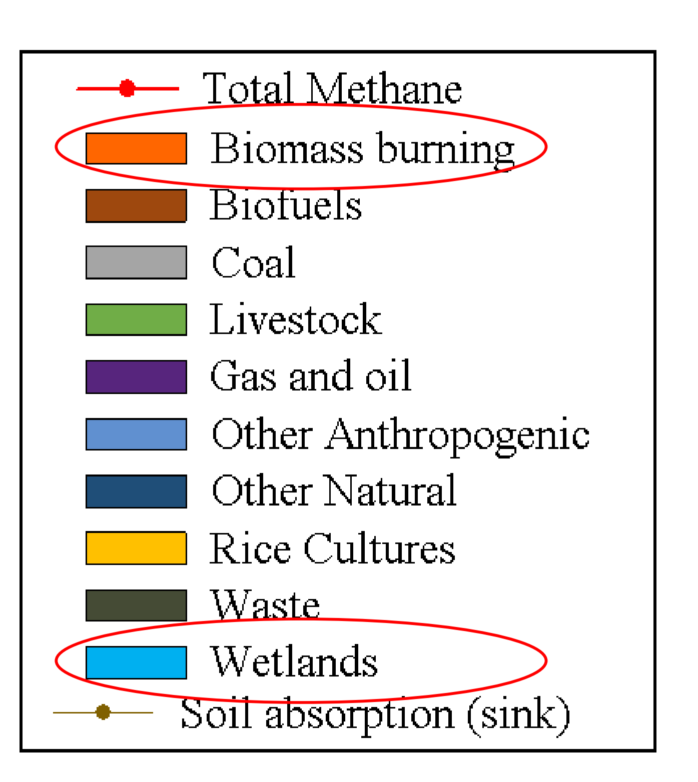
The year-to-year relative changes are computed so that when we assume a relative change of a tracer for the year n, it is expressed wrt to the previous year (n-1) as reference.

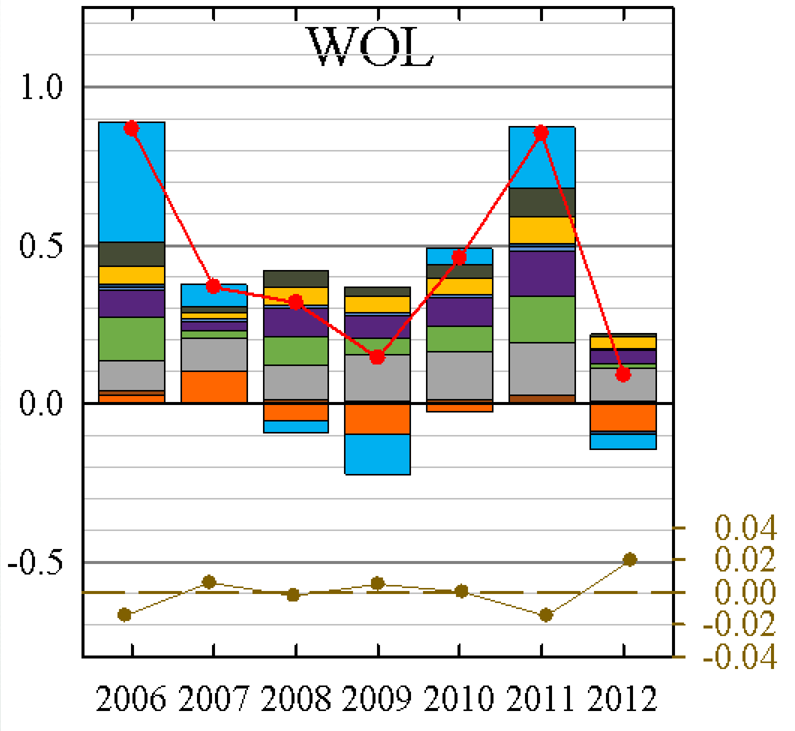
$\mu_{tot,\ n-1}$: annual mean of the simulated cumulative methane for the year (n-1)



GC tagged simulation : Analysis

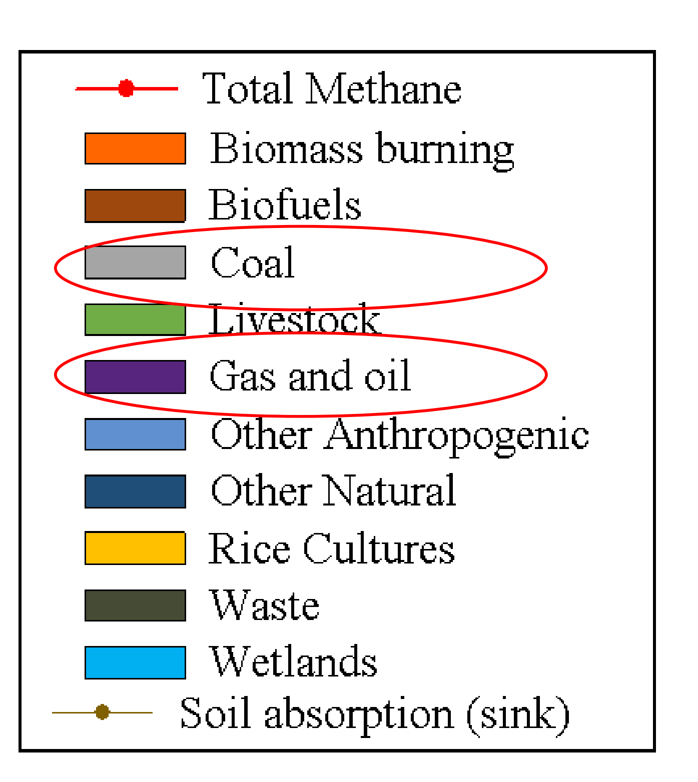
- Yearly relative change (%)
- Natural sources mainly responsible for the interannual variation
- e.g. Wollongong

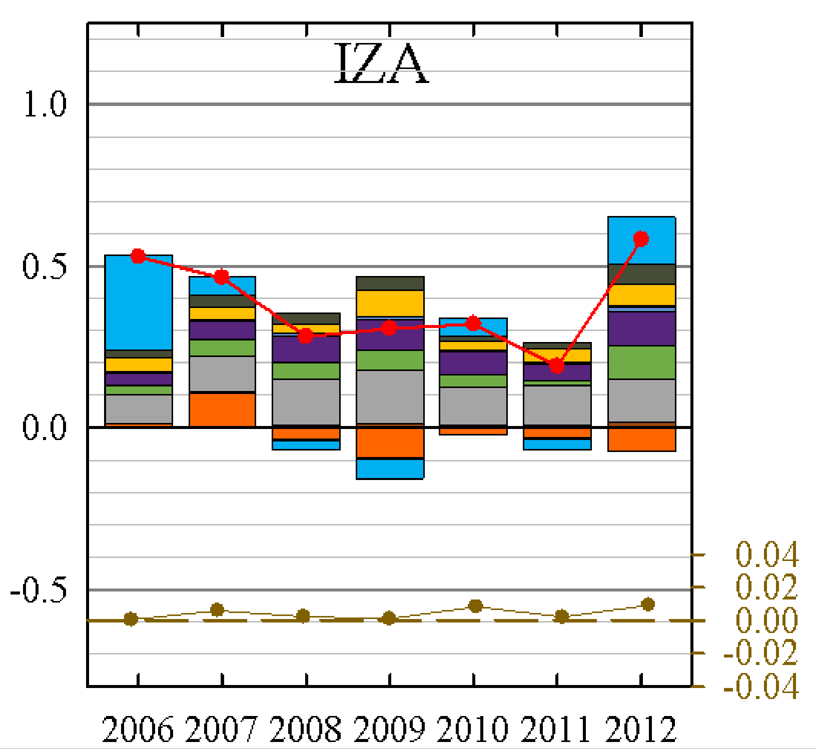




GC tagged simulation : Analysis

- Yearly relative change (%)
- Secondary contributors such as coal or gas and oil contribute to the overall increase
- e.g. Izaña

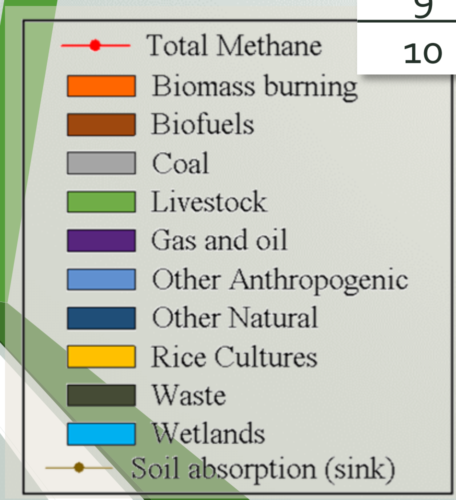




GC tagged simulation : Analysis

- Contributors to the cumulative increase : tracer ranking

	EUR	KIR	ZUG	JFJ	TOR	TSU	IZA	WOL	LAU	AHT
1	co	co	co	co	co	co	co	co	co	co
2	gao	gao	wl	gao	gao	gao	gao	li	gao	gao
3	wl	wl	gao	wl	wl	wl	wl	gao	li	li
4	ri	li	ri	ri	ri	li	li	wl	wl	wl
5	li	ri	li	li	li	ri	ri	ri	ri	ri
6	wa	wa	wa	wa	wa	wa	wa	wa	wa	wa
7	bf	bf	oa	oa	bf	bf	bf	bf	bf	bf
8	oa	oa	bf	bf	oa	oa	oa	oa	oa	oa
9	on	on	on	on	on	on	on	on	on	on
10	bb	bb	bb	bb	bb	bb	bb	bb	bb	bb



Methane increase : Discussion

Source attribution ?

Many studies…

Rigby et al., 2008
Ringeval et al., 2010
Bloom et al., 2010
Aydin et al., 2011
Dlugokencky et al., 2009
Sussmann et al., 2012
Kirschke et al., 2013
Nisbet et al., 2014
Hausmann et al., 2016
Schaefer et al., 2016

Methane increase : Discussion

Source attribution ?

From GEOS-Chem tagged simulation

Secondary contributors to the global budget of methane play a major role in the increase of methane observed since 2005.

→ coal mining, gas and oil transport and exploitation

Methane increase : Discussion

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From GEOS-Chem tagged simulation

Secondary contributors to the global budget of methane play a major role in the increase of methane observed since 2005.

→ coal mining, gas and oil transport and exploitation

Best emission inventories available → limitations

EDGAR v4.2

- Overestimates the recent emission growth in Asia (Schwietzke et al. 2014, Bergamaschi et al. 2013 and Bruhwiler et al. 2014).
- Chinese coal mining emissions are too large by a factor of 2 (Turner et al. 2015, from a global GOSAT inversion)
- EDGAR v4.2 vs global GOSAT inversion (Turner et al., 2015)
    - increase in wetland emissions in South America
    - increase in rice emissions in Southeast Asia

Methane increase : Discussion

Source attribution ?

Gas and oil use and exploitation (GAO)

underestimated by current emission inventories (incl. EDGAR)

Franco et al., 2015, 2016; Turner et al., 2015, 2016

Methane increase : Discussion

Source attribution ?

Gas and oil emissions : the use of C_2H_6 as a proxy

CH_4 and C_2H_6 share a source of emissions

Production, transport and use of natural gas and the leakage associated to it amounts at ~ 62 % of ethane's atmospheric budget (**Logan et al., 1981; Rudolph, 1995**)

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Source attribution ?

Gas and oil emissions : the use of C_2H_6 as a proxy

CH_4 and C_2H_6 share a source of emissions

Production, transport and use of natural gas and the leakage associated to it amounts at ~ 62 % of ethane's atmospheric budget (Logan et al., 1981; Rudolph, 1995)

Franco et al., 2016

- Observations : sharp increase of C_2H_6 since 2009 × GEOS-Chem
  → ~5 %/year at mid-latitudes, ~3 %/year at remote sites
- Massive growth of oil and gas exploitation in the North American continent, confirmed by **Helmig et al. 2016**

Methane increase : Discussion

Source attribution ?

Gas and oil emissions : the use of C_2H_6 as a proxy

Production, transport and use of natural gas and the leakage associated to it amounts at ~ 62 % of ethane's atmospheric budget (**Logan et al., 1981; Rudolph, 1995**)

Franco et al., 2016

- Observations : sharp increase of C_2H_6 since 2009 × GEOS-Chem
  → ~5 %/year at mid-latitudes, ~3 %/year at remote sites
- Massive growth of oil and gas exploitation in the North American continent, confirmed by **Helmig et al. 2016**

Methane increase ? From C_2H_6/CH_4 ratio derived from GOSAT measurements

→ from 20 Tg in 2008, to 35 Tg in 2014

Confirming the influence of GAO on the observed methane increase

Methane increase : Discussion

Source attribution ?

Gas and oil emissions : the use of C_2H_6 as a proxy → C_2H_6/CH_4

Hausmann et al. 2016 : GAO contribution of 39 % to the renewed methane in Zugspitze between 2007 and 2014

BUT

The strength of the C_2H_6/CH_4 relationship associated to GAO strongly depends on the studied region and/or production basin

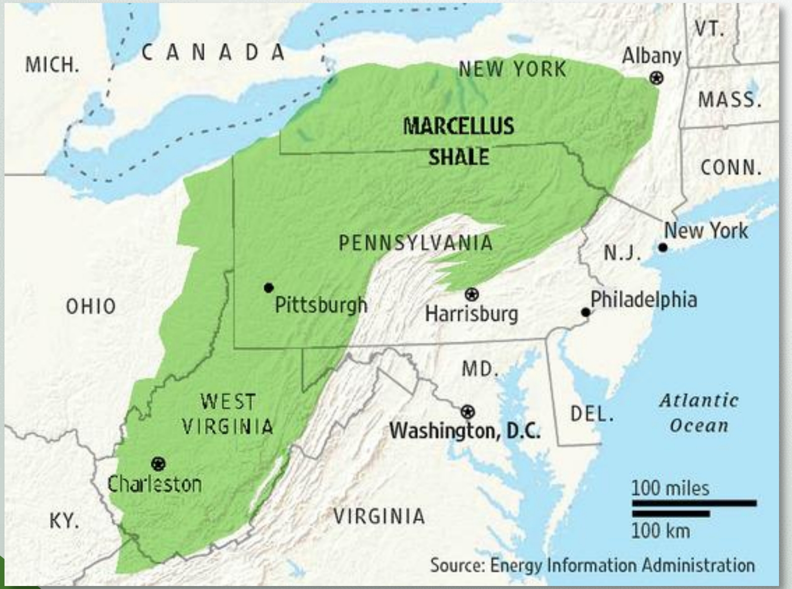
Variability rarely taken into account (Kort et al. 2016, Peischl et al. 2016)

Methane increase : Discussion

Source attribution ?

The problem of the use of C_2H_6 as a proxy → C_2H_6/CH_4

- Emissions from GAO well pads may be missing from most bottom-up emission inventories. Lyon et al. (2016)
- A horizontal drilling rig for natural gas in the Marcellus formation in eastern, Pennsylvania.



- Emissions differ from one well pad to another and even within the same pad depending on the depth of the extraction.
- e.g. Marcellus Basin that is actually two different overlapping basins.

Methane increase : Conclusion

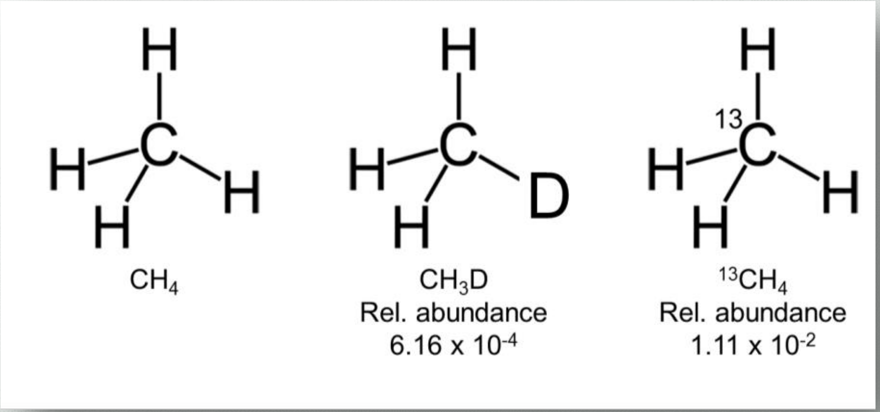
- FTIR ground-based measurements : 0.31 ± 0.03 %/year wrt 2005.0

Source attribution ?

- GEOS-Chem : 0.35 ± 0.03 %/year vs 0.30 ± 0.04 %/year (FTIR)
- Anthropogenic sources, secondary contributors to the global CH_4 budget, are first contributors to the observed increase
  - coal mining, gas and oil exploitation, livestock

- While GEOS-Chem agrees with our observations, the repartition between the different sources of methane would greatly benefit from an improvement of the global emission inventories. e.g. EDGAR
  - US oil and gas and livestock are underestimated.
  - Coal emissions are overestimated.

What's the next step ?



Postdoc project

How can isotopologues help ?

Source attribution ?

In situ $^{13}CH_4$ observations

NOAA Earth System Research Laboratory & Global Atmospheric Watch

Schwietzke et al. (2016)

Total fossil fuel = industry activities + natural geological seepage

"*Methane emissions from natural gas, oil and coal production and their usage are 20 to 60 percent greater than inventories.*"

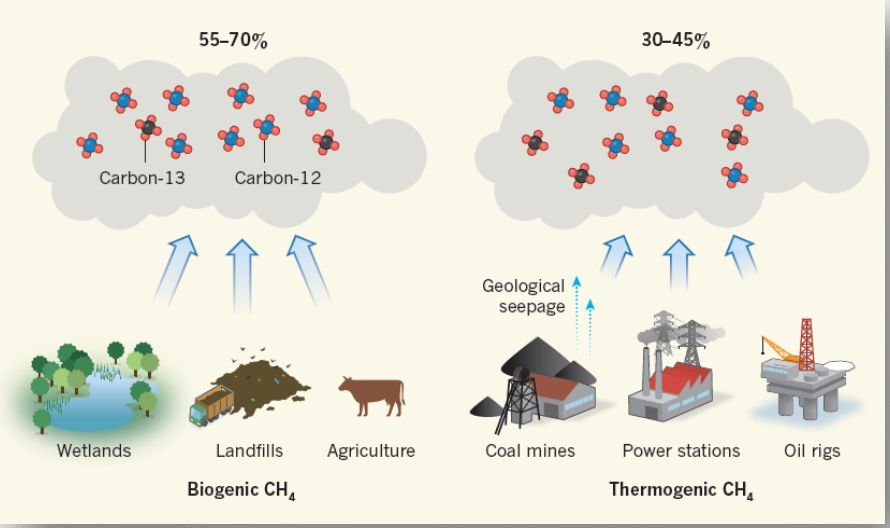
No upward trend of industrial fossil fuel emissions in global CH_4 inventories → natural-gas industry improvements

Nisbet et al. (2016)

"*A major cause of increased tropical wetland and tropical agricultural methane emissions, the likely major contributors to growth, may be their responses to meteorological change.*"

How can isotopologues help ?

- Both isotopologues show distinctive $^{13}C/^{12}C$ (and D/H) signature depending on the emission process



Allen, Rebalancing the global methane budget, Nature, 46, 538, 2016. (Fig. 1)

- ***Kinetic Isotope Effect (KIE)*** **:** Each isotopologue will react at a specific rate constant depending on the removal pathway. KIE = Ratio of the rate constants. (Saueressig et al., 2001 & Snover and Quay, 2000).

- Determining the $^{13}C/^{12}C$ and D/H content of atmospheric methane is therefore a unique tracer of its budget.

Two year project – Part I

- Development of a retrieval strategy for $^{13}CH_4$ and CH_3D from infrared observations

- **Instrumentation & Database**
- *Fourier Transform Spectrometers*
    - *Toronto :* ~1430 days since 2002, resolution : 0.004 cm^{-1})
    - *Eureka :* ~760 days since 2006 (0.0035 cm^{-1})
    - *Jungfraujoch, Switzerland : 2590 days since 1990* (0.004 cm-1)

- *PARIS-IR (0.02 cm^{-1}) ~240 days since 2004*
    - Portable Atmospheric Research Interferometric Spectrometer for the InfraRed

- *Complementary : ACE-FTS solar occultations*
    - ~35 000 occultations since February 2004

Two year project - Part II

- Development of an isotopic module for GEOS-Chem
- CH_4 GEOS-Chem tagged simulation as a starting point
- Supported by the best available emission inventories of CH_4
- + Emission ratios for each isotopologues and source type + KIE

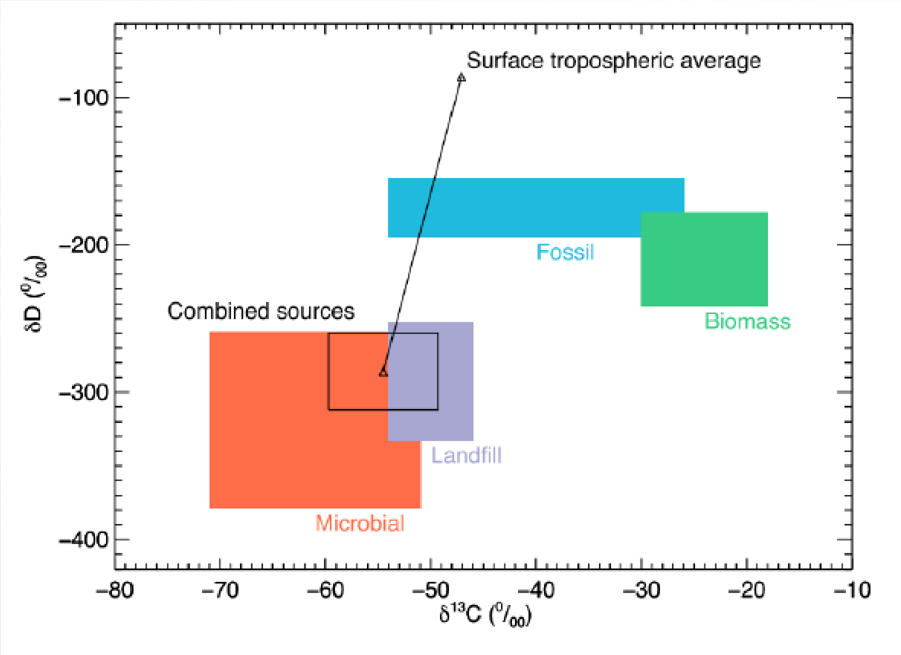


Figure 2 from Rigby et al., 2012

- The model will provide a spatially global answer to the question of the methane budget.

Thank you !

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