Recent results from long-term FTIR monitoring activities at Jungfraujoch: some unexpected trends & new target species

Team members:

W. Bader, B. Bovy, P. Demoulin, O. Flock, B. Franco,
B. Lejeune, E. Mahieu, C. Servais, D. Zander
G. Roland (em.) and R. Zander (em.)

emmanuel.mahieu@ulg.ac.be

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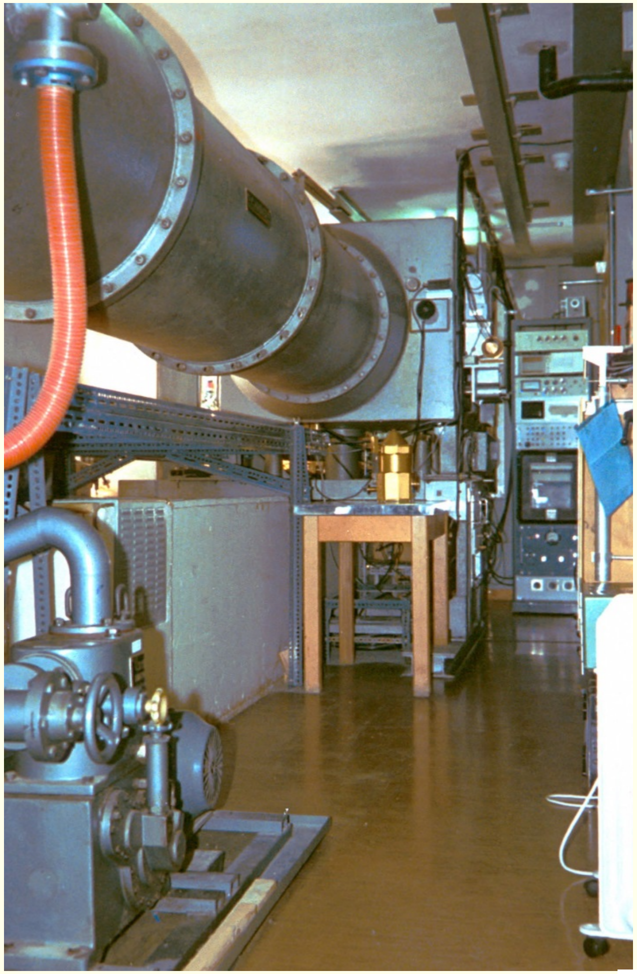
A bit of history…

Liège people at Jungfraujoch…
…since the early 1950s!



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The Jungfraujoch grating spectrometer

- A 7.3 m focal length Ebert/Fastie grating spectrometer was installed at the Jungfraujoch in the late 1950s, it was first exploited to record **solar atlases** (IR, vis and near-UV)
- As of 1976, the instrument was used in double-pass mode to record narrow ***atmospheric*** solar spectra (InSb detector), encompassing absorption lines of specific target gases, e.g. HF, HCl, N_2O, CH_4
- Various diffraction orders have been used over 1977 to 1989 => several observational subsets, with more than 10000 spectra available

The FTIR spectrometers

- Regular operation with Fourier Transform Spectrometer started in 1984, using a home-made interferometer
- It was backed -then progressively replaced- by a commercial Bruker instrument (IFS120HR), routine operation started in 1993
- For each transition (grating ↔ homemade ↔ Bruker), there was a significant overlap (several years) between the observational data sets, allowing robust intercalibration of the derived geophysical parameters ⇒ consistent time series
- Now, remote operation is possible, allowing to take advantage of most days with suitable observing conditions (clear-sky mandatory!) ⇒ current measurement density: >130 days/year
- Within the framework of the **Network for the Detection of Atmospheric Composition Change** (NDACC; see www.ndacc.org)

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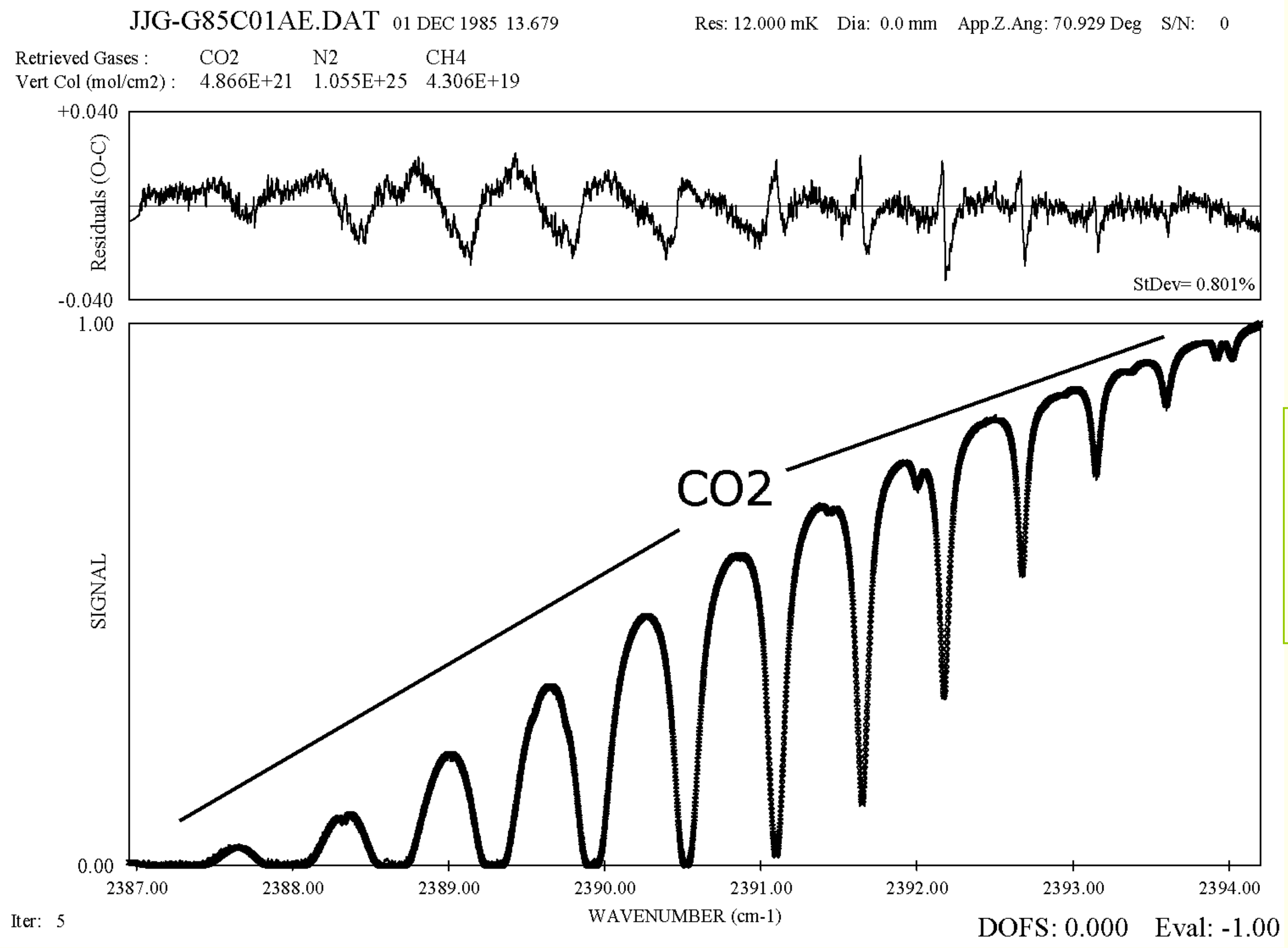
Sample “grating-spectrum”



- Medium resolution (here 0.012 cm^{-1})
- Narrow interval
- but unique!

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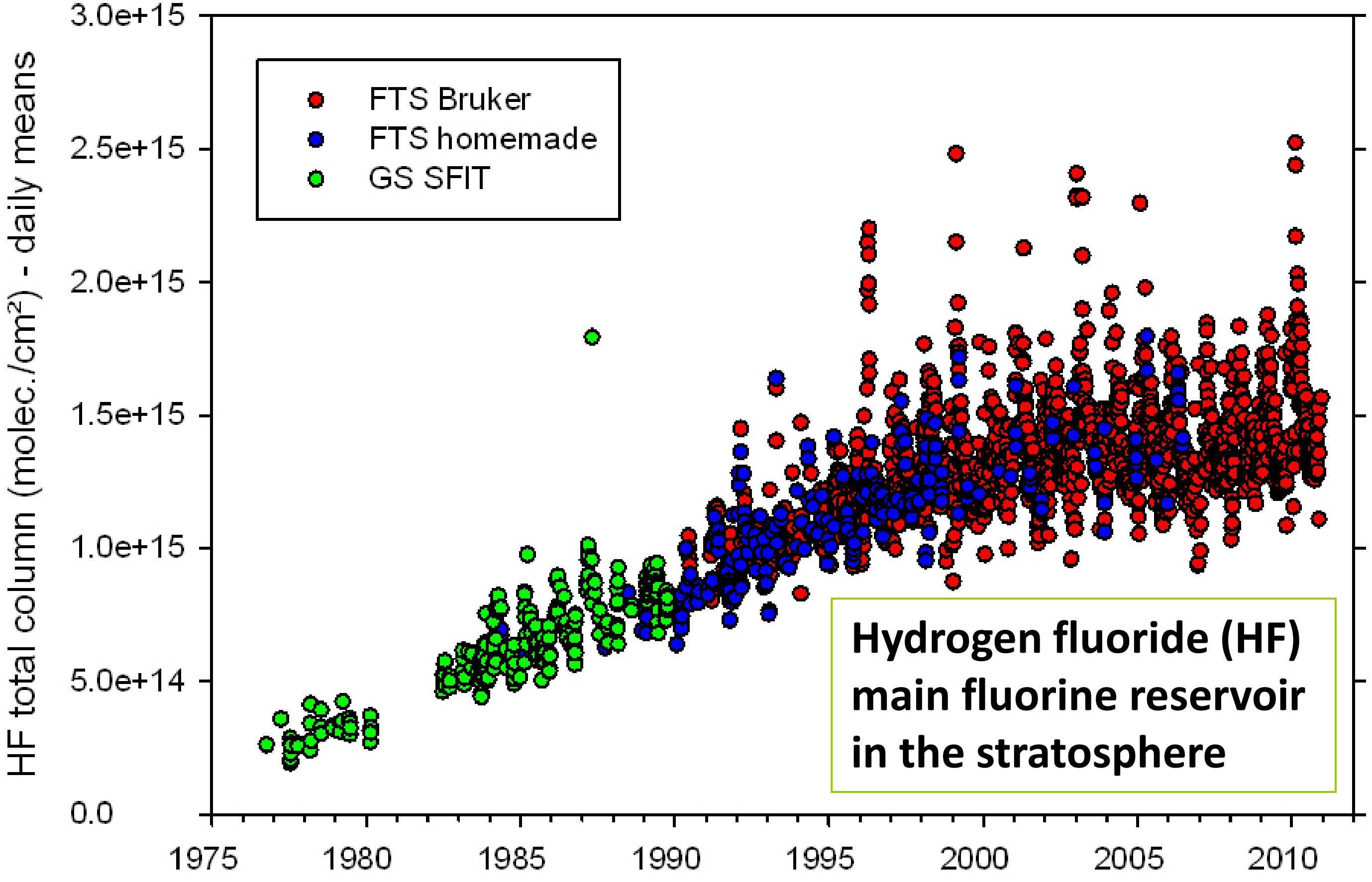
Harmonized time series: HF, since 1977

More than 35 years of continuous measurements!



Hydrogen fluoride (HF) main fluorine reservoir in the stratosphere

Mean trends:
~5%/yr for 1977-1999
~1%/yr for 2000-2010

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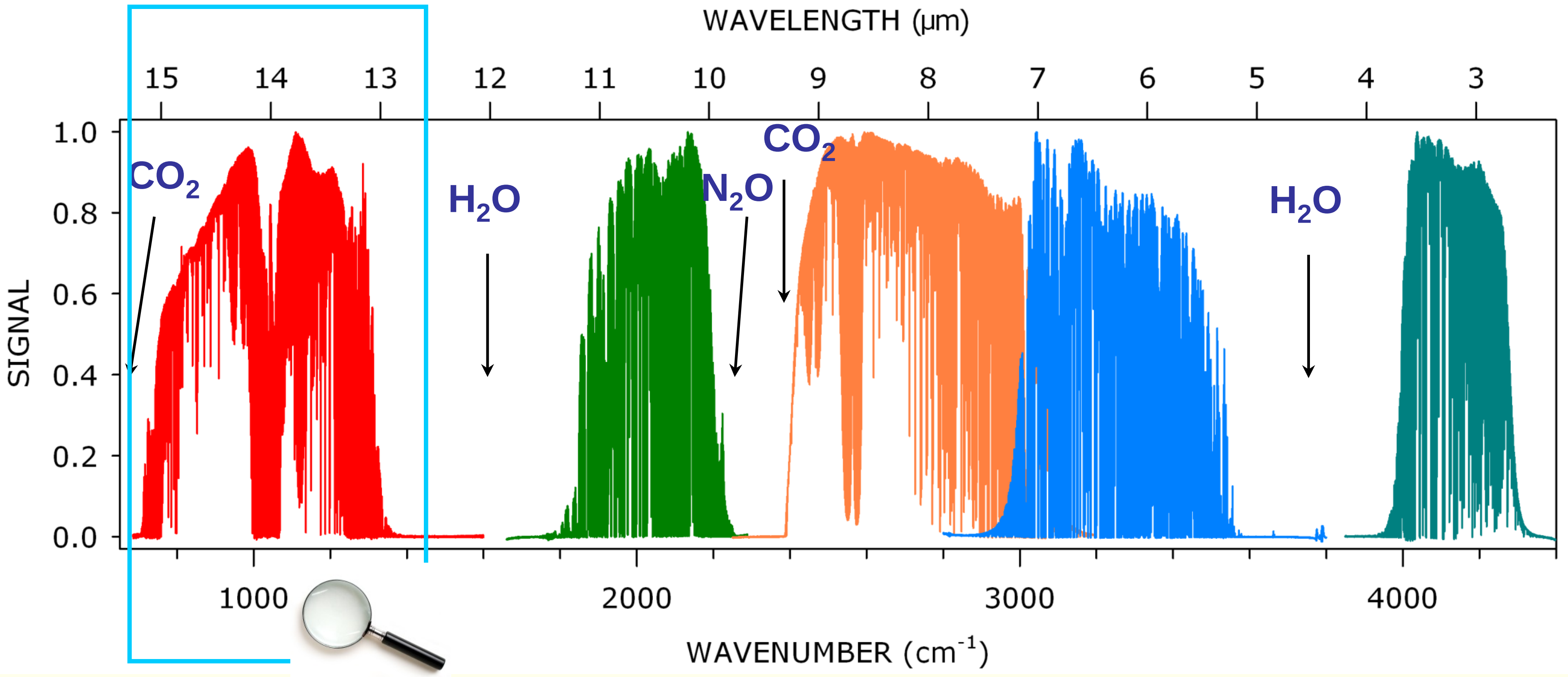
FTIR: 2 detectors + 5 optical filters

=> Broadband high-resolution spectra (<0.006 cm^{-1}), with high S/N (>1000)
=> Encompassing the signature of a large number of key atmospheric species



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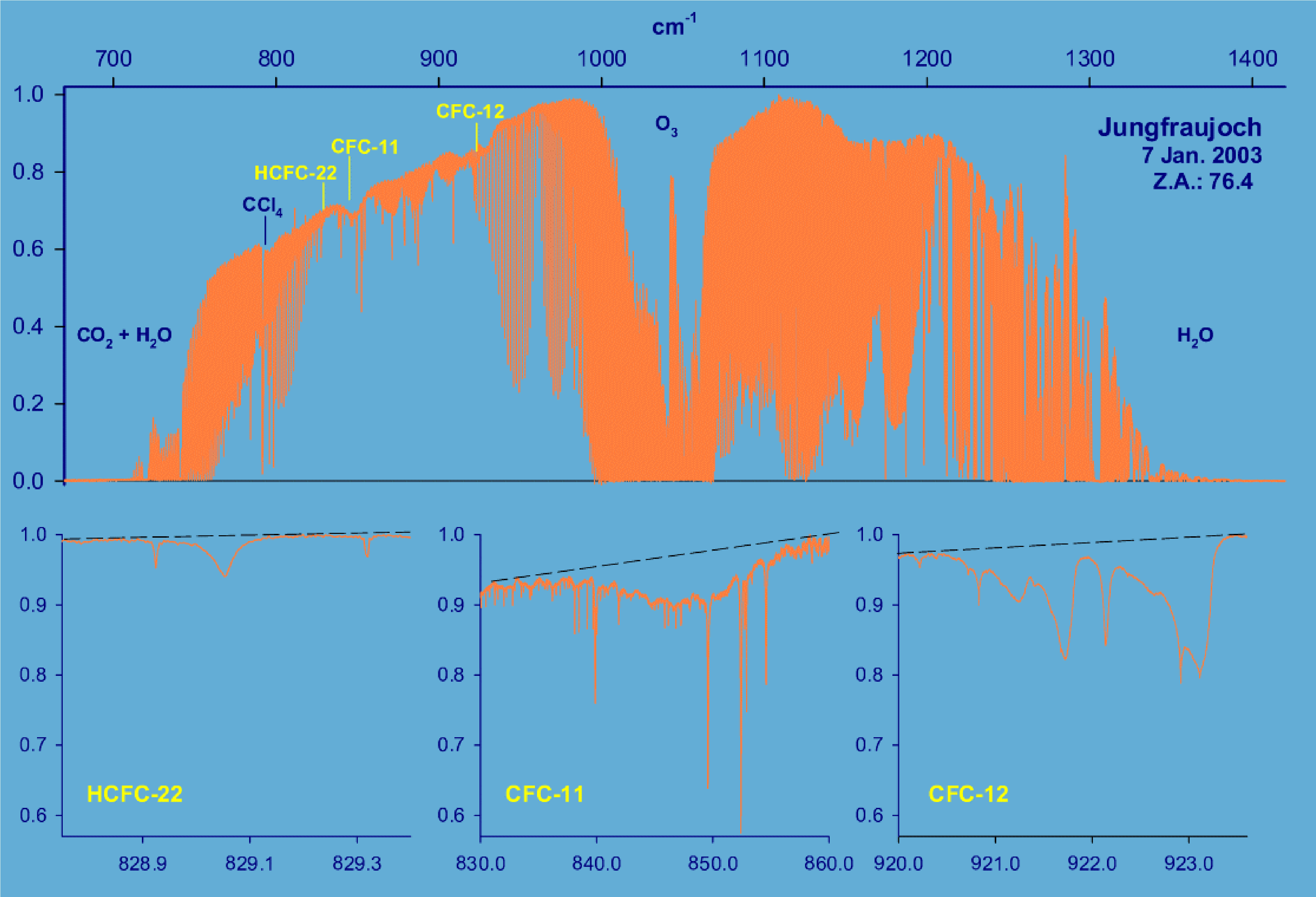

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Current FTIR targets (>25)

Climate-relevant (GHGs)	H_2O, CO_2, CH_4, N_2O, CF_4, SF_6	Support to the **Kyoto Protocol**
Ozone-relevant	O_3, NO, NO_2, HNO_3, $ClONO_2$, HCl, HF, COF_2, CFC-11, -12, HCFC-22, -142b, CCl_4	Support to the **Montreal Protocol** (tropo & strato)
Air quality, biomass burning…	CO, CH_3OH, C_2H_6, C_2H_2, HCN, H_2CO, HCOOH	Support e.g. to Copernicus The European Earth Observation Programme
Others	OCS, N_2, many isotopologues (HDO, CH_3D, ^{13}CH4, ^{13}CO…)	

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Retrieval algorithm and ancillary data

- For most species, the SFIT-2 algorithm (v3.91) is being used for the retrievals, this code is maintained and developed mainly at NCAR (Boulder, CO)
- SFIT-2 implements the **Optimal Estimation Method of Rodgers**, allowing to derive information on the vertical distribution of most species accessible to the ground-based FTIR technique (=> several independent pieces of information or partial columns, from 1 to 4)
- HITRAN-2004 and -2008 line-by-line spectroscopic parameter compilations are assumed in most retrievals, zpt info from NCEP daily data
- Cross-sections are not handled by SFIT-2, hence pseudolines produced by G.C. Toon (NASA-JPL) from laboratory spectra are used for numerous target or interfering species (e.g. CFCs, HCFCs, CCl_4, $ClONO_2$, C_2H_6)

emmanuel.mahieu@ Université de Liège

ULg involvement

Production of time series of high-level geophysical parameters (total and partial columns) for:

- Long-term monitoring and surveillance of the atmosphere for GHGs, O_3-related species, air quality (trend studies, atmospheric budgets, emissions…)
- Contribution to satellite validation (ACE-FTS, IASI, MIPAS, SCIAMACHY…)
- Comparison with model data (3D CTMs, CCMs): improvement of the models, interpretation of the data

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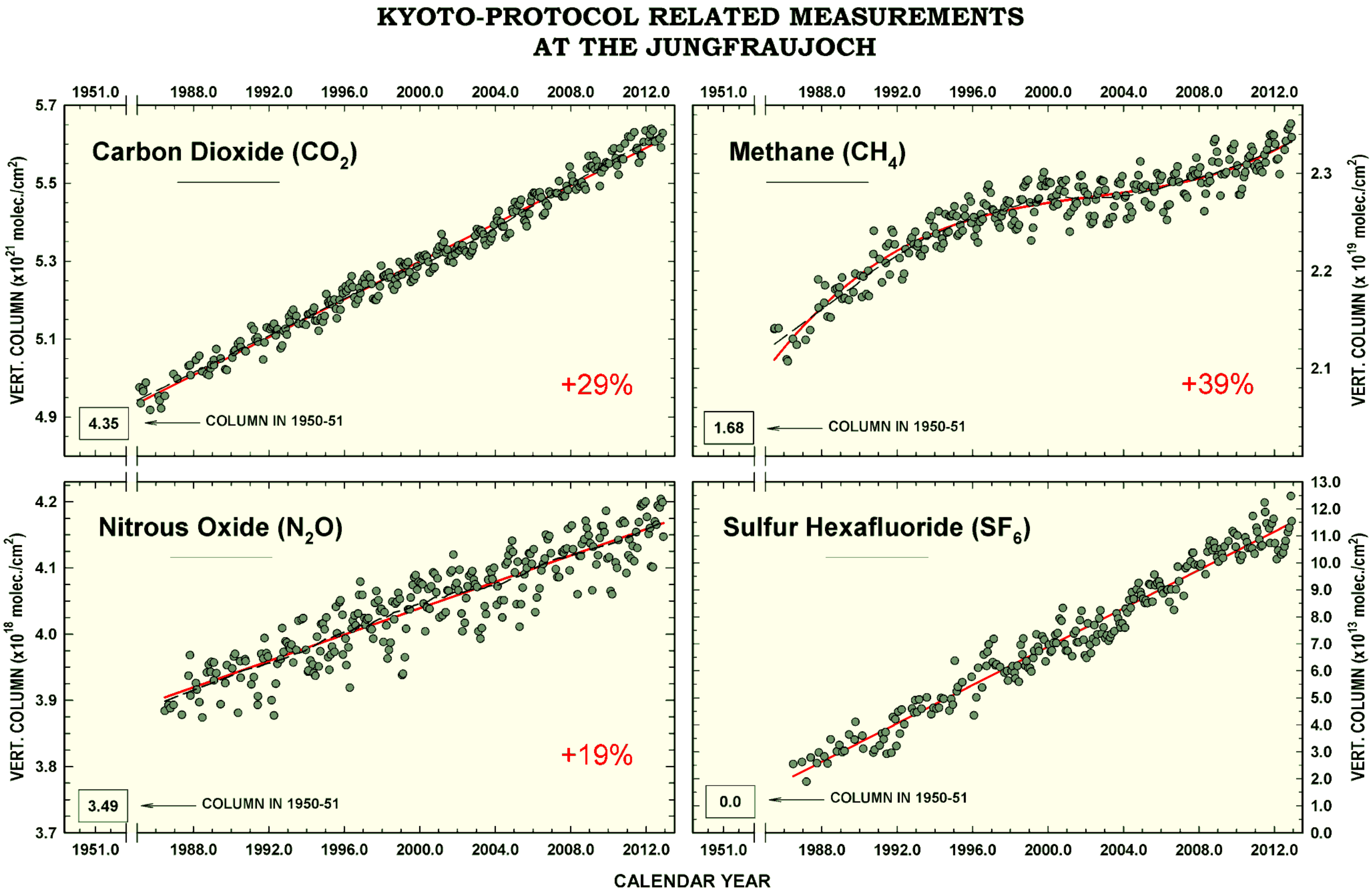

Updated from Zander et al., *Sci. Total Environ.*, *391*, 2008

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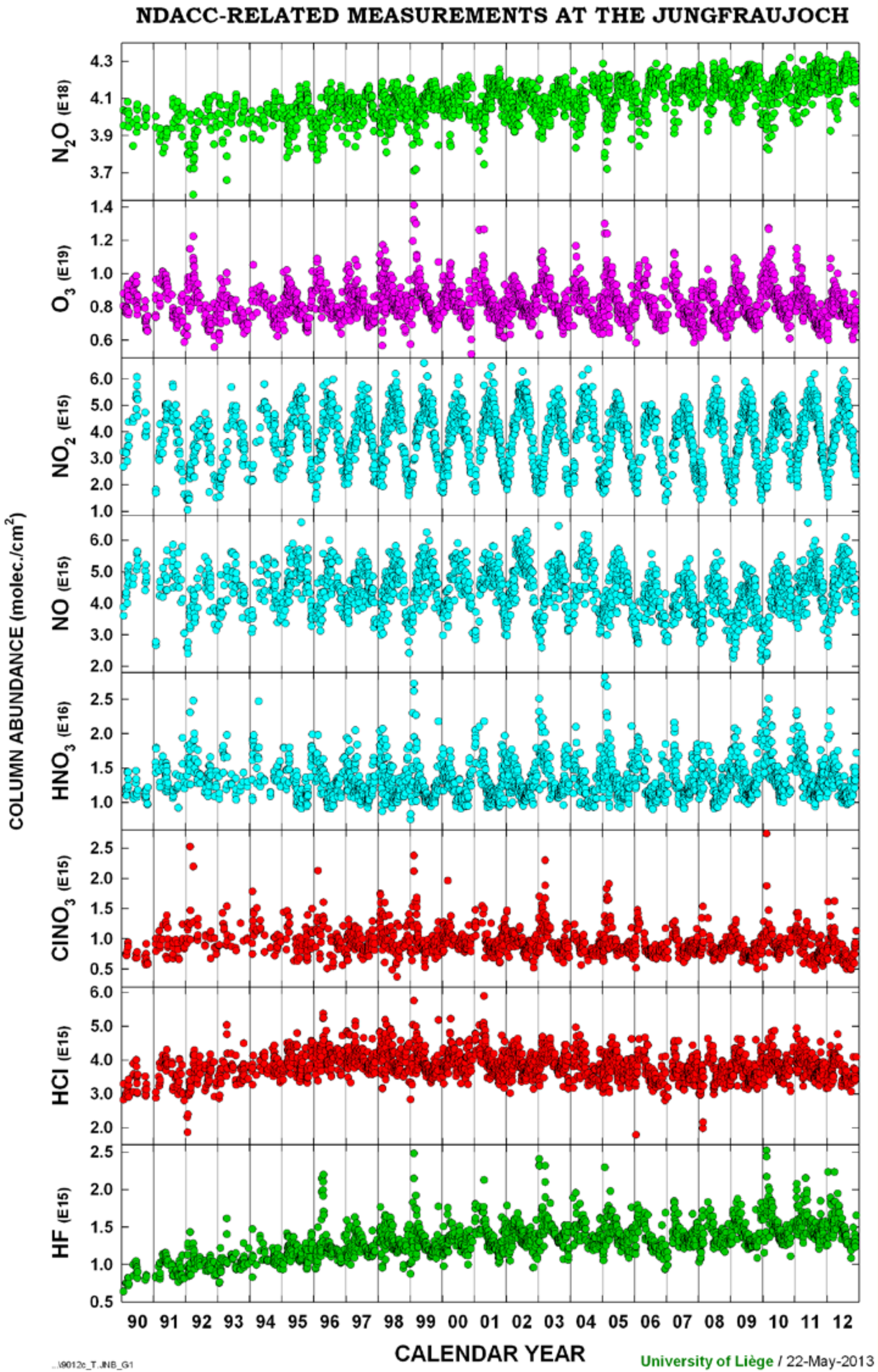

Our multi-decadal time series are appropriate for the determination/characterization of:

- **long-term trends**
- **year-to-year variations**
- **seasonal modulations**
- **daytime variations**
- **family partitioning (nitrogen, chlorine, fluorine)**
- **impact of volcanic eruptions**
- **impact of biomass burning (e.g. major fires)**

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New target species

- Continuously searching for exploitable signatures of additional atmospheric species (new anthropogenic gases, new/improved line parameters), to expand the scope of the ground-based FTIR technique
- Successful for **5 gases** over the last five years: **CCl_4, CF_4, HCFC-142b, CH_3OH, HCOOH**
- Under development: C_2H_4, CH_3Cl and other halogenated source gases…

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First retrievals of carbon tetrafluoride (CF_4) from ground-based FTIR spectra

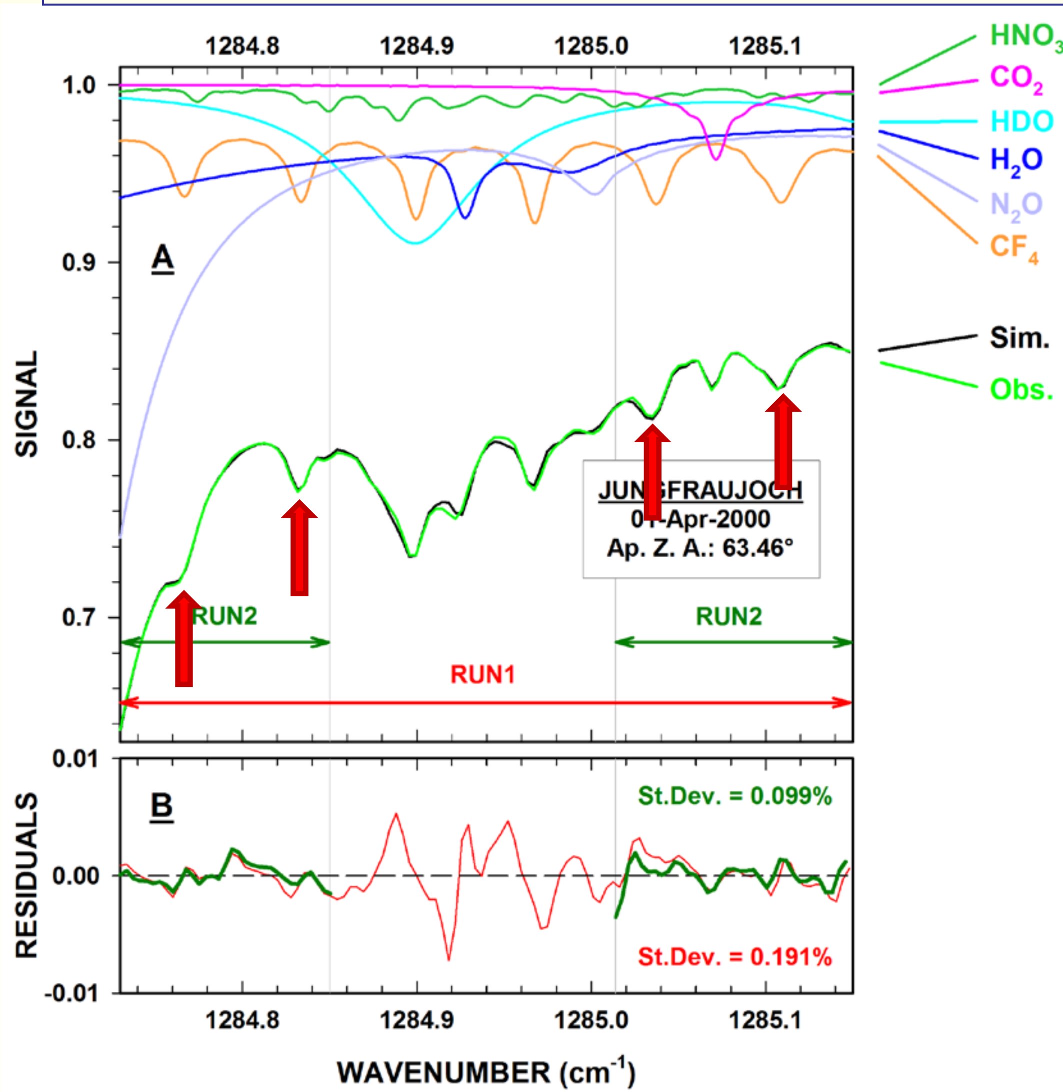
emmanuel.mahieu@ Université de Liège

CF_4 – motivation and background info

- Very strong (GWP 7390) and long-lived (>50000 years) greenhouse gas ⇒ targeted by Kyoto
- Emitted during anode effect episodes (Al-production), also released by manufacturing of semiconductors
- Natural source: degassing of the terrestrial crust
- On the rise: current rate of increase of ~1%/yr (0.8 ppt/yr)

emmanuel.mahieu@ Université de Liège

Carbon tetrafluoride – CF_4



- The retrieval strategy (simple scaling) is based on two consecutive runs allowing improving the precision of the retrievals; the 2nd window focuses on the most interference-free features of CF_4 (i.e. avoiding the center of the window (HDO & H_2O))
- A two-decade time series has been produced and analyzed, the "wet-spectra" are excluded
- Mean relative standard deviation around the daily averages (inv. ≥ 4 meas.): <u><1%</u>!

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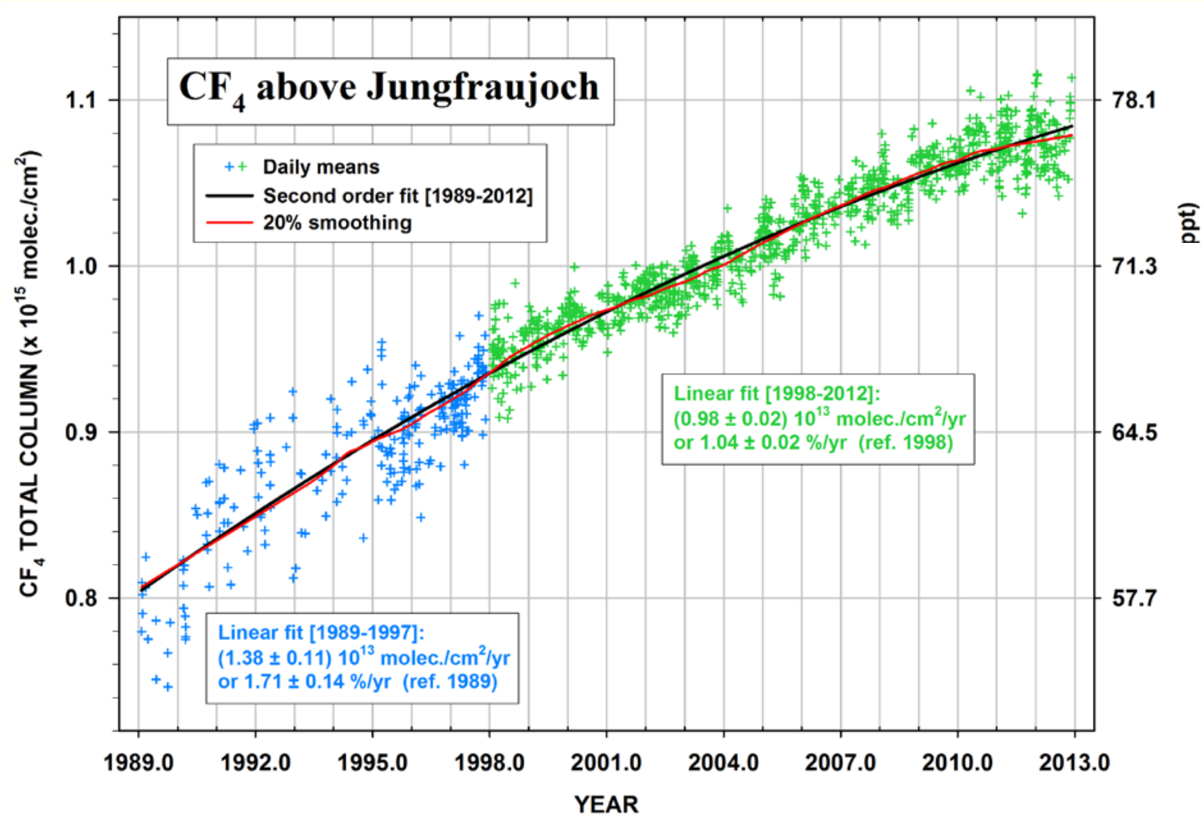
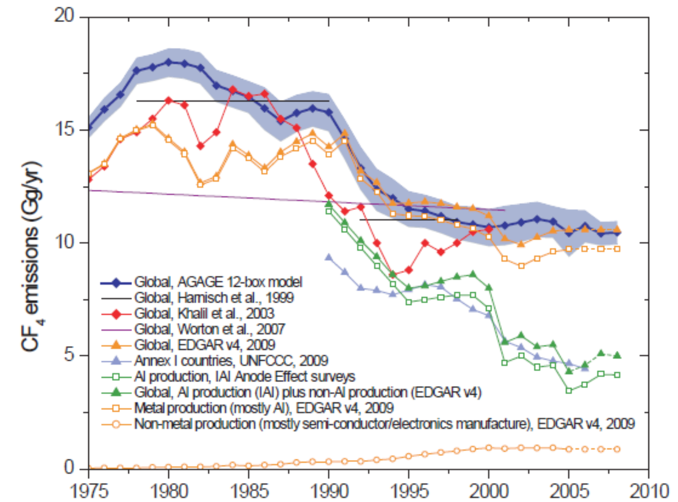
Carbon tetrafluoride – CF_4

- First FTIR time series for this very long-lived GHG
- Total column available from 1989 onwards



J. Mühle et al.: Perfluorocarbons in the global atmosphere
ACP, 10, 2010.



<u>Derived global emissions</u>: **15.8 ± 1.3 Gg/yr over 1989-1997**

11.1 ± 0.2 Gg/yr over 1998-2012

In very good agreement with evaluations based on AGAGE measurements

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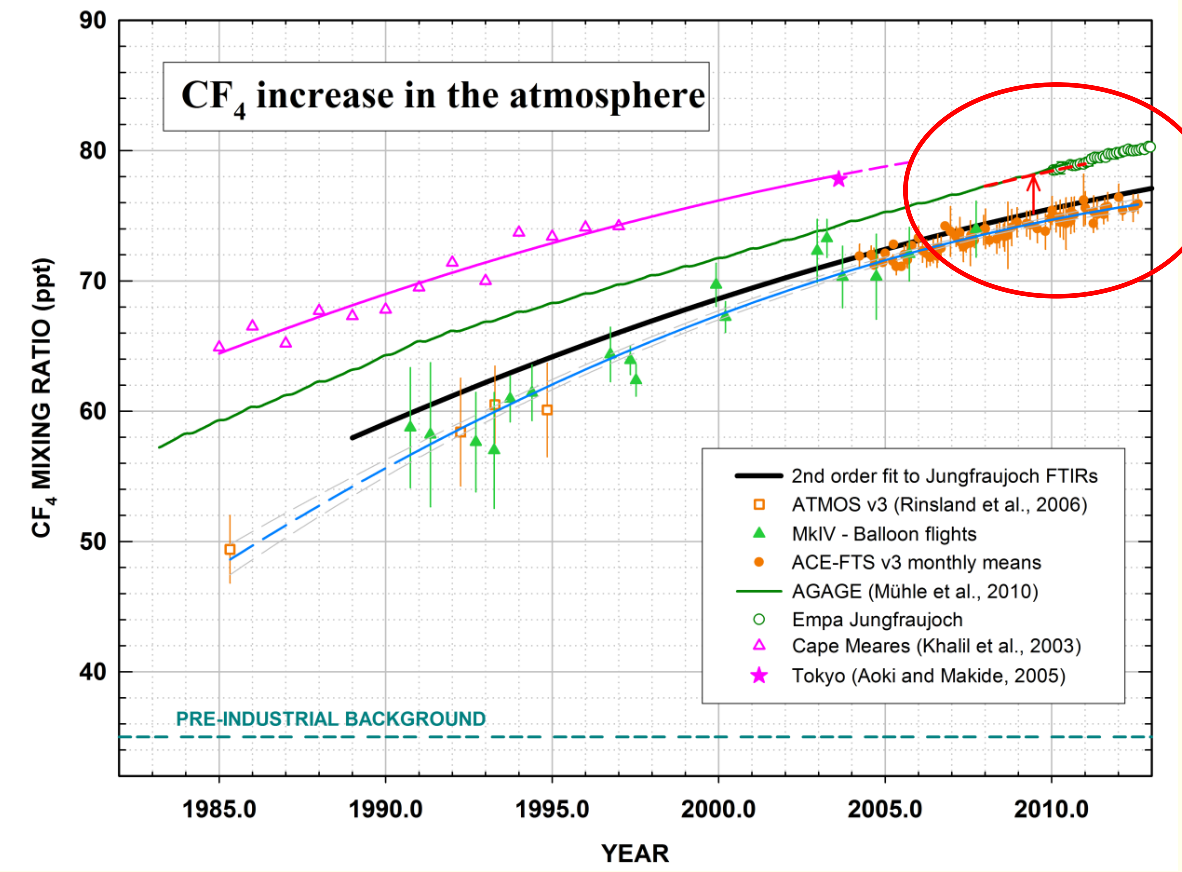
Carbon tetrafluoride – CF_4



- Good agreement with *in situ*, balloon and satellite data, when accounting for the uncertainties affecting the data sets and for the time needed for CF_4 to propagate and mix throughout the atmosphere
- Anthropogenic contribution larger than the natural background since about the late 90s

Mahieu *et al.*, Atmos. Meas. Tech., 7, 333-344, 2014

emmanuel.mahieu@ Université de Liège

CFC substitutes

First retrievals of HCFC-142b from ground-based FTIR spectra

emmanuel.mahieu@ Université de Liège

Retrieval of HCFC-142b (CH_3CClF_2)

- Lifetime of 18 years, GWP of 2310, targeted by the Montreal Protocol
- Its atmospheric content has been increasing to reach ≈ 21 ppt in 2011, with variable rates over the recent years: 1.1 ppt/yr in 2005-2008; 0.7 ppt/yr in 2009-2012, annual emissions on the order of 30-40 Gg
- Four candidate windows have been evaluated, around 903, 967, 1133 and 1193 cm^{-1} (used for ACE-FTS retrievals from space)
- HITRAN08 line parameters were assumed
- For HCFC-142b, pseudolines based on Clerbaux et al. (1993) cross-sections were assumed. Since then, improved laboratory measurements have been produced by Le Bris & Strong (2009), but no pseudolines available…

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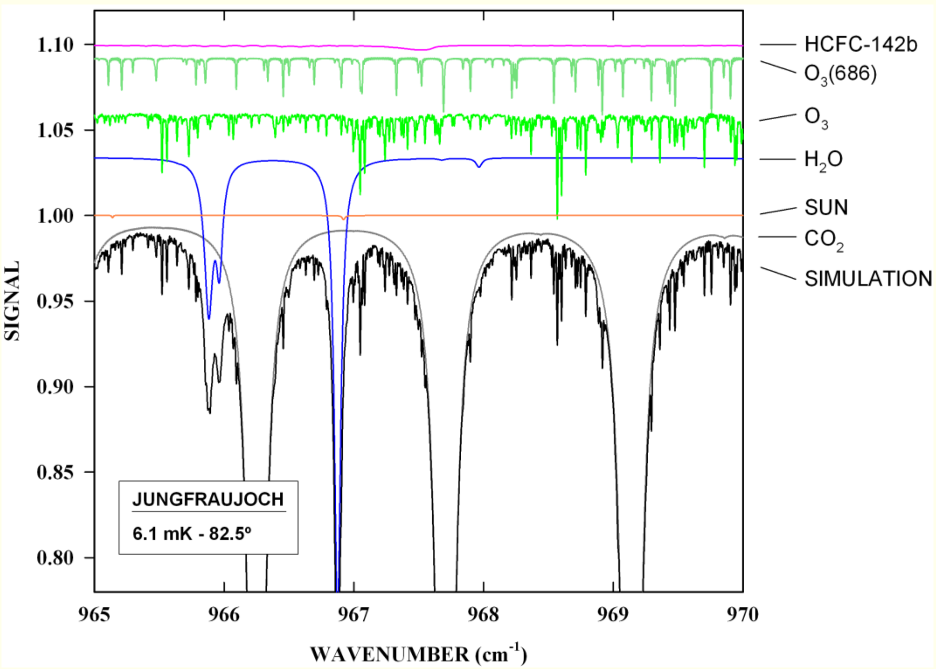
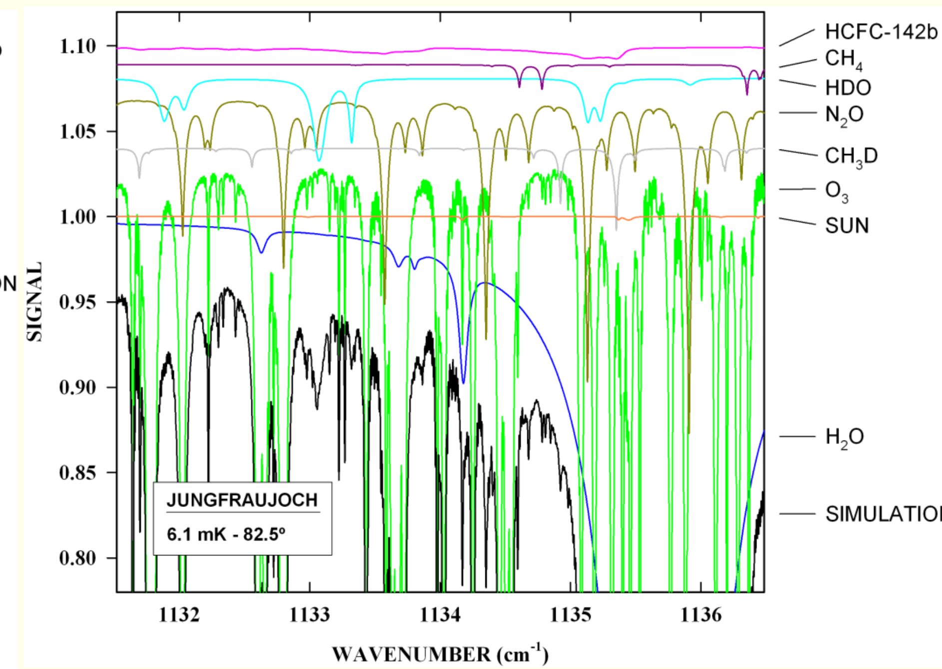
Two very unfavorable cases…





Here, strong CO_2 or H_2O lines prevent the retrieval of HCFC-142b from the ground…

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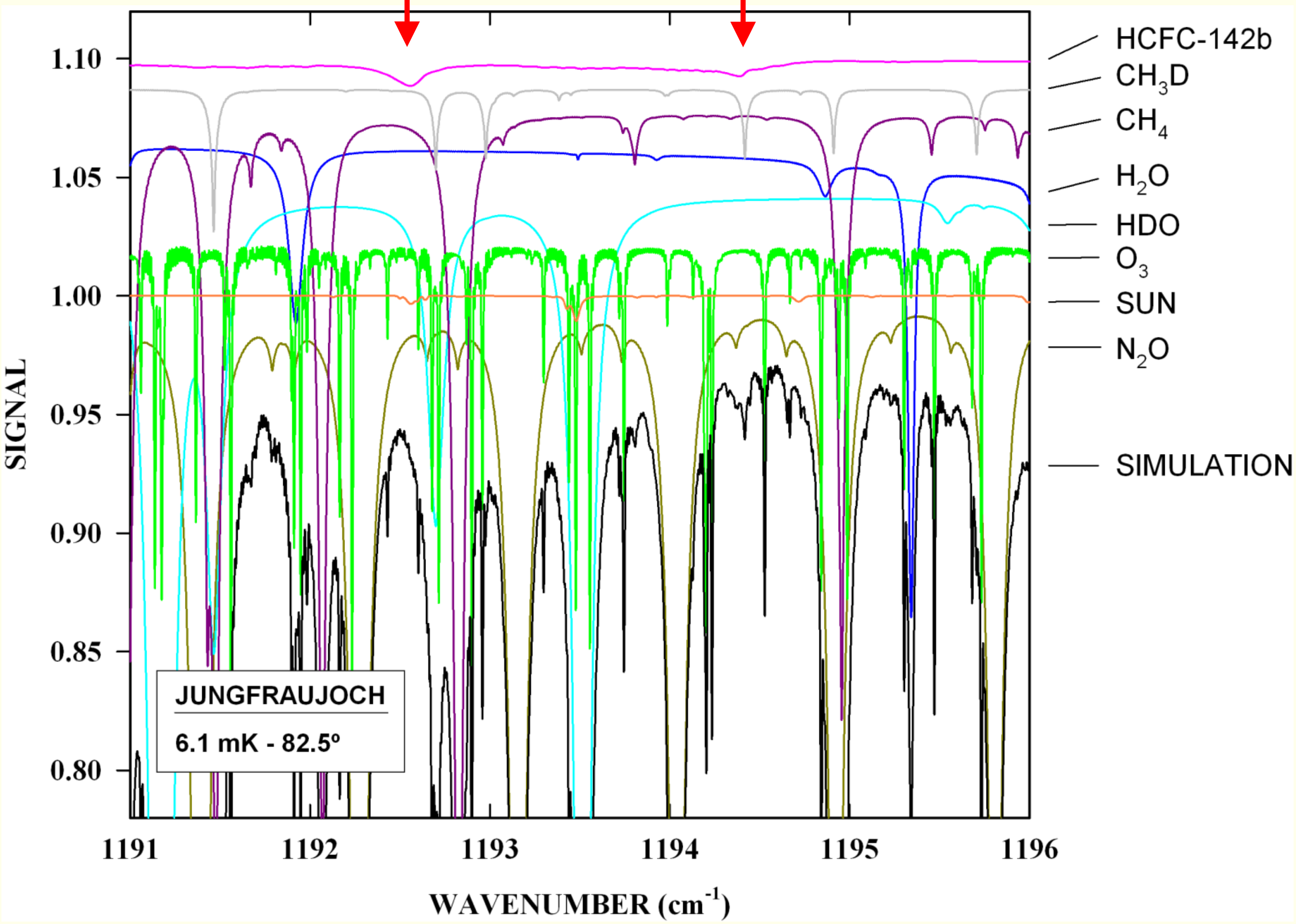
"Strong" signal, but HDO and N_2O…

Weaker signal, but less critical interferences…



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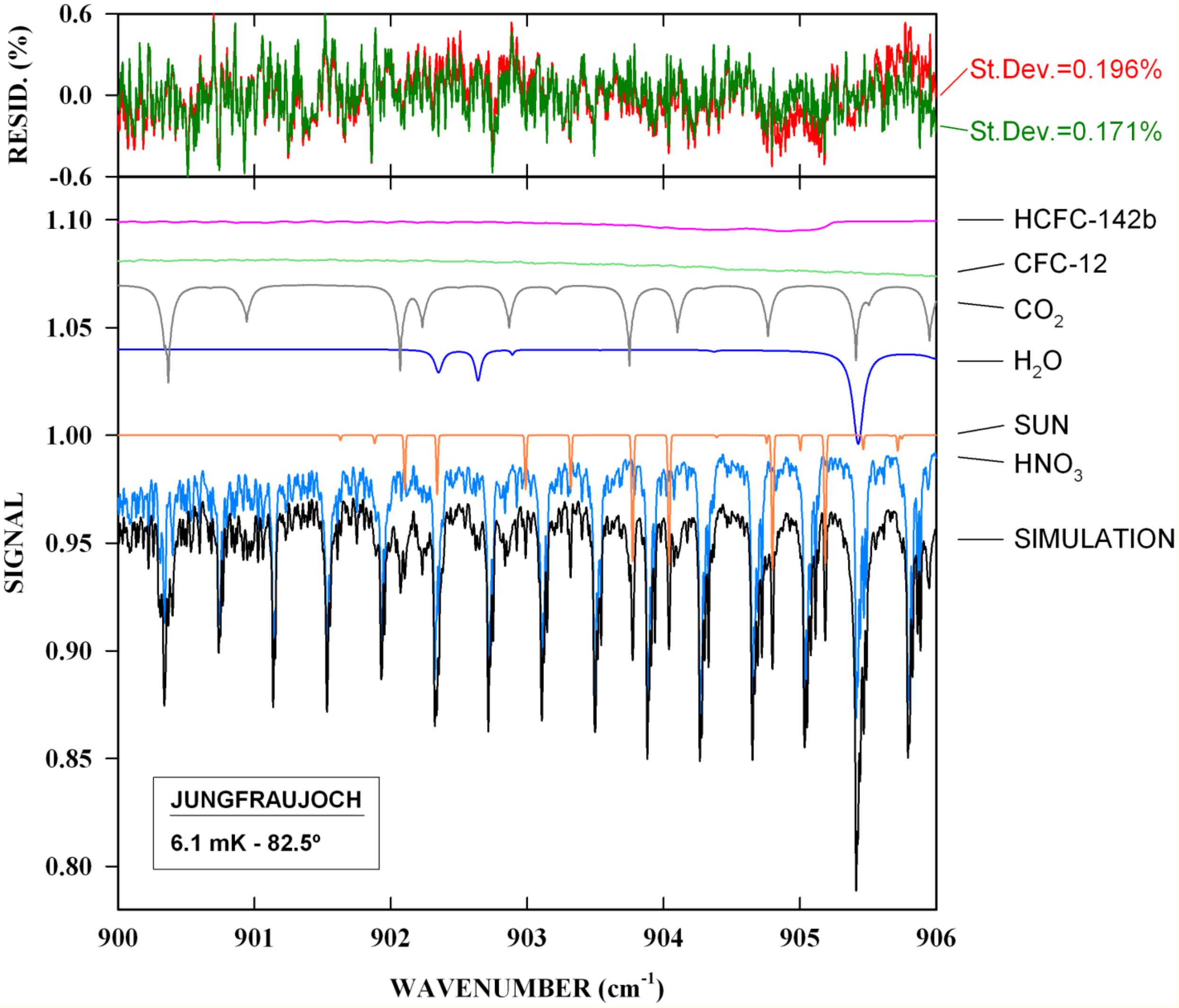
Simulation & fit for the 900-906 cm^{-1} window



- Weak absorption, even at low sun (0.5% for 85°), but relatively clean window
- Main interferences by HNO_3 manifolds, CO_2 and H_2O lines
- Red residuals when assuming no F142b in the atmosphere

emmanuel.mahieu@ Université de Liège

Retrieval of HCFC-142b

- The 900-906 cm^{-1} microwindow was selected despite a very weak absorption (0.5% on average)
- A time series has been produced for the Jungfraujoch, from 1990 onwards (daily mean data from 2000 onwards)
- Comparison with *in situ* surface data (Mace Head and Jungfraujoch) shows good overall agreement (absolute values and trend)

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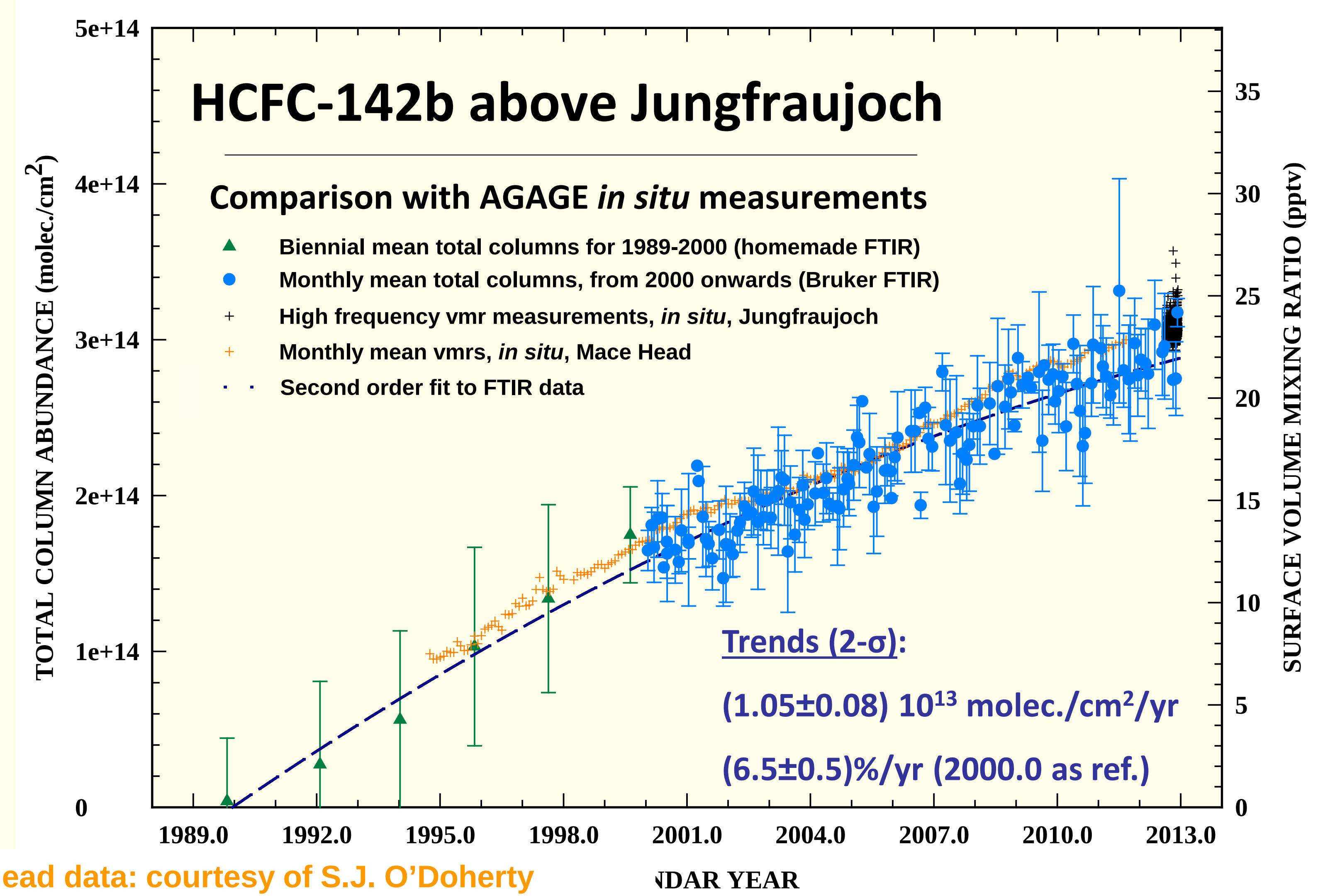
Jungfraujoch time series



Mace Head data: courtesy of S.J. O'Doherty

Empa data: courtesy of S. Reimann & M.K. Vollmer

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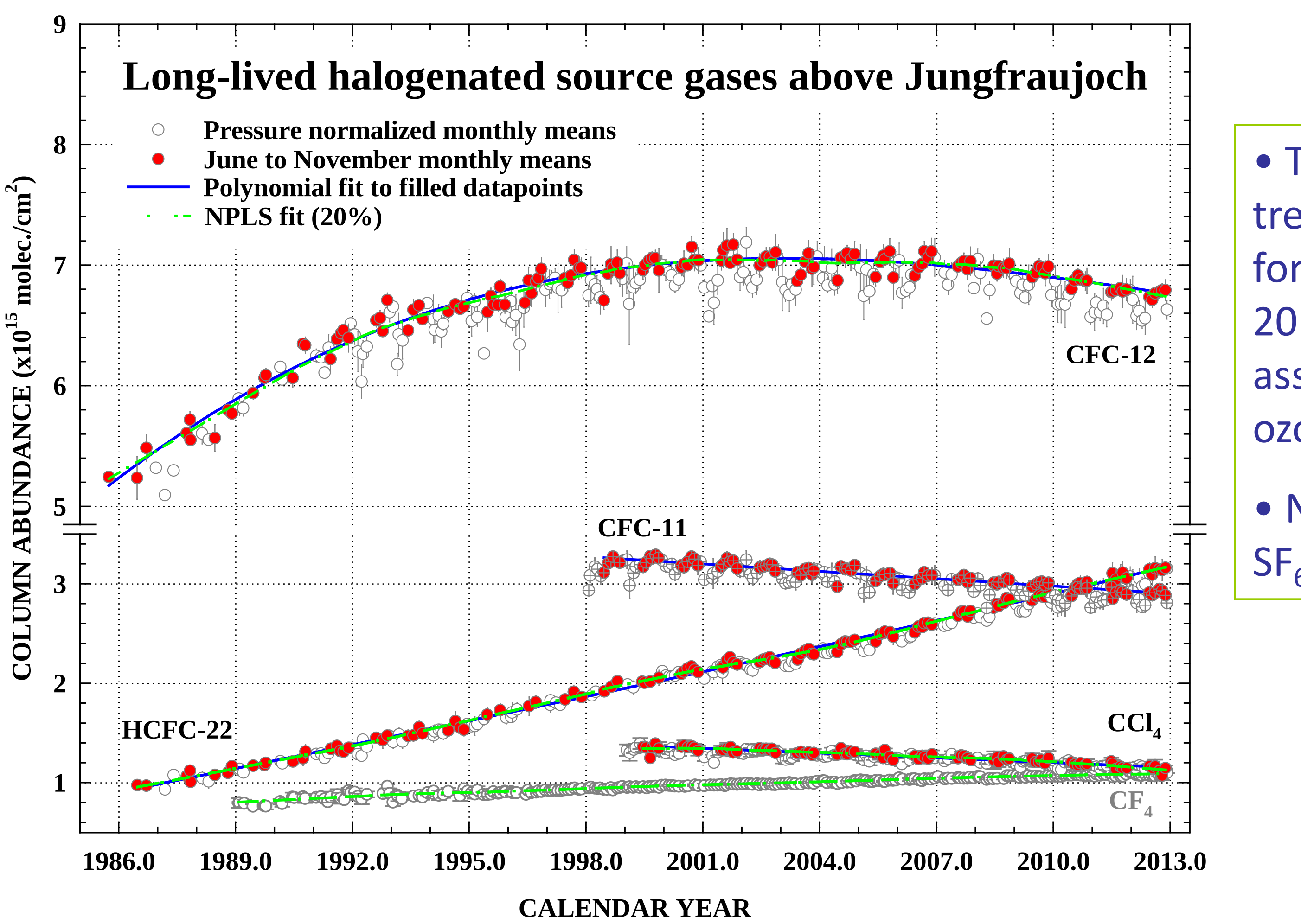
Long-term time series of (7) halogenated source gases above Jungfraujoch



- Time series and trends considered for inclusion in the 2014 WMO assessment on ozone depletion
- Not shown (scale): SF_6 and HCFC-142b

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Monitoring is not boring ☺

Recent HCl trend anomaly

emmanuel.mahieu@ Université de Liège

Global evolution of organic chlorine

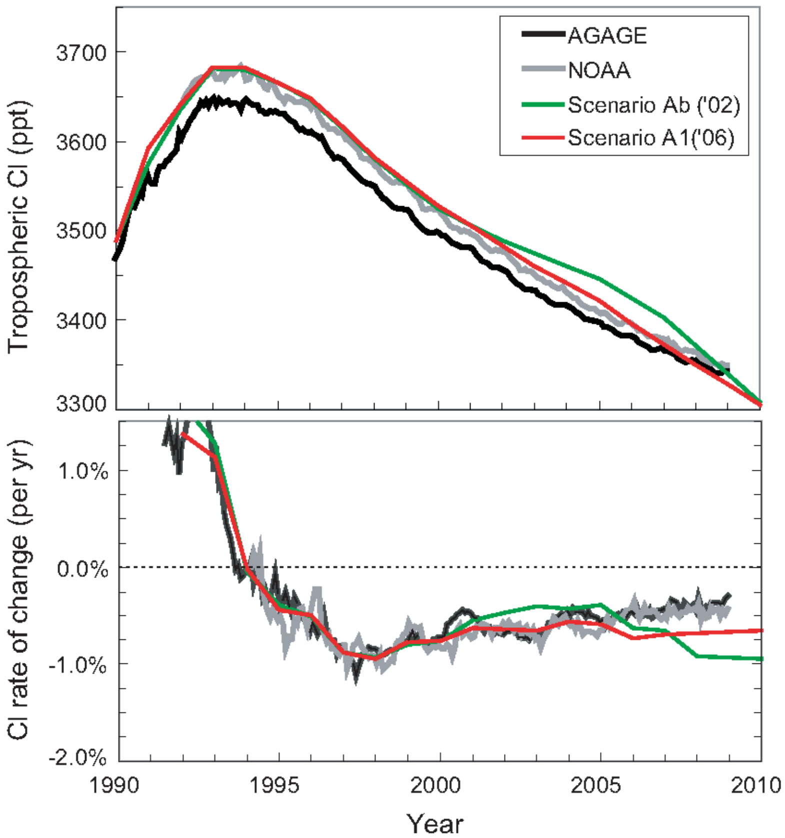
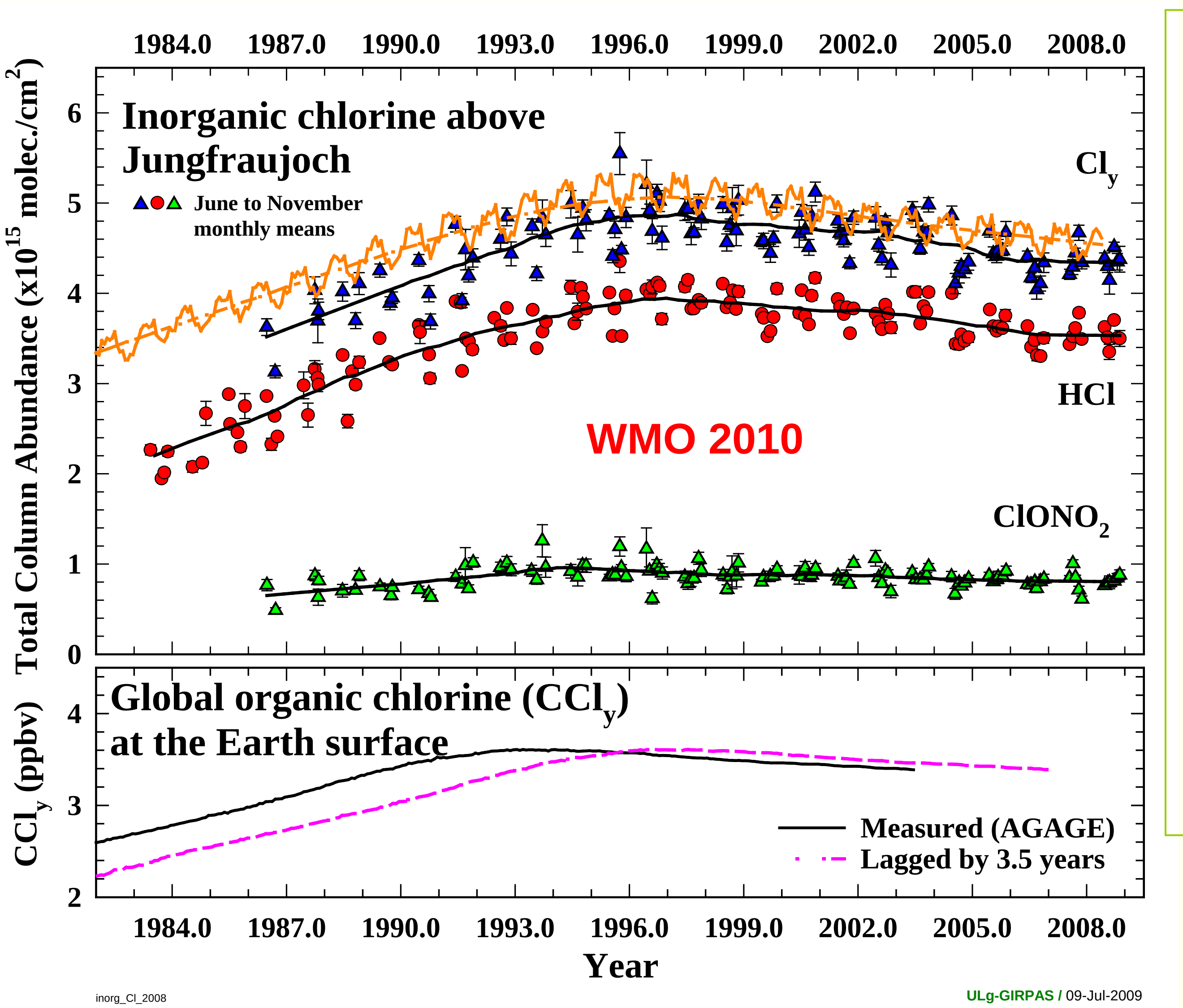


Figure 1-15. Top panel: The tropospheric abundance (ppt) of organic chlorine (CCl_y) from the NOAA (gray) and AGAGE (black) global measurement networks (updates of Montzka et al., 2003, and O'Doherty et al., 2004). Quantities are based upon independently measured mixing ratios of CFC-11, CFC-12, CFC-113, HCFC-22, HCFC-141b, HCFC-142b, methyl chloroform, carbon tetrachloride, and halon-1211. Results for CFC-114 and CFC-115 from Prinn et al. (2000) are used in both aggregations. An additional constant 550 ppt was added for CH_3Cl and 80 ppt was added for short-lived gases such as CH_2Cl_2, $CHCl_3$, CCl_2CCl_2, and $COCl_2$ (consistent with 40–130 ppt discussed in Section 1.3). Bottom panel: Annual rates of change (% per year) determined from 12-month differences. In both panels, observations are compared with the baseline scenario (Ab) from WMO 2002 (green line; Montzka and Fraser et al., 2003) and the baseline scenario A1 from WMO 2006 (red line; Daniel and Velders et al., 2007).

1.63

Long-term trend of chlorine (46.5°N)



HCl and $ClONO_2$, the two most abundant chlorine reservoirs in the stratopshere are accessible to the gb-FTIR technique, the long-term Jungfraujoch Cl_y time series shows:

-increase at ~4%/yr

-maximum load in 1996

-decrease at ~ -1%/yr

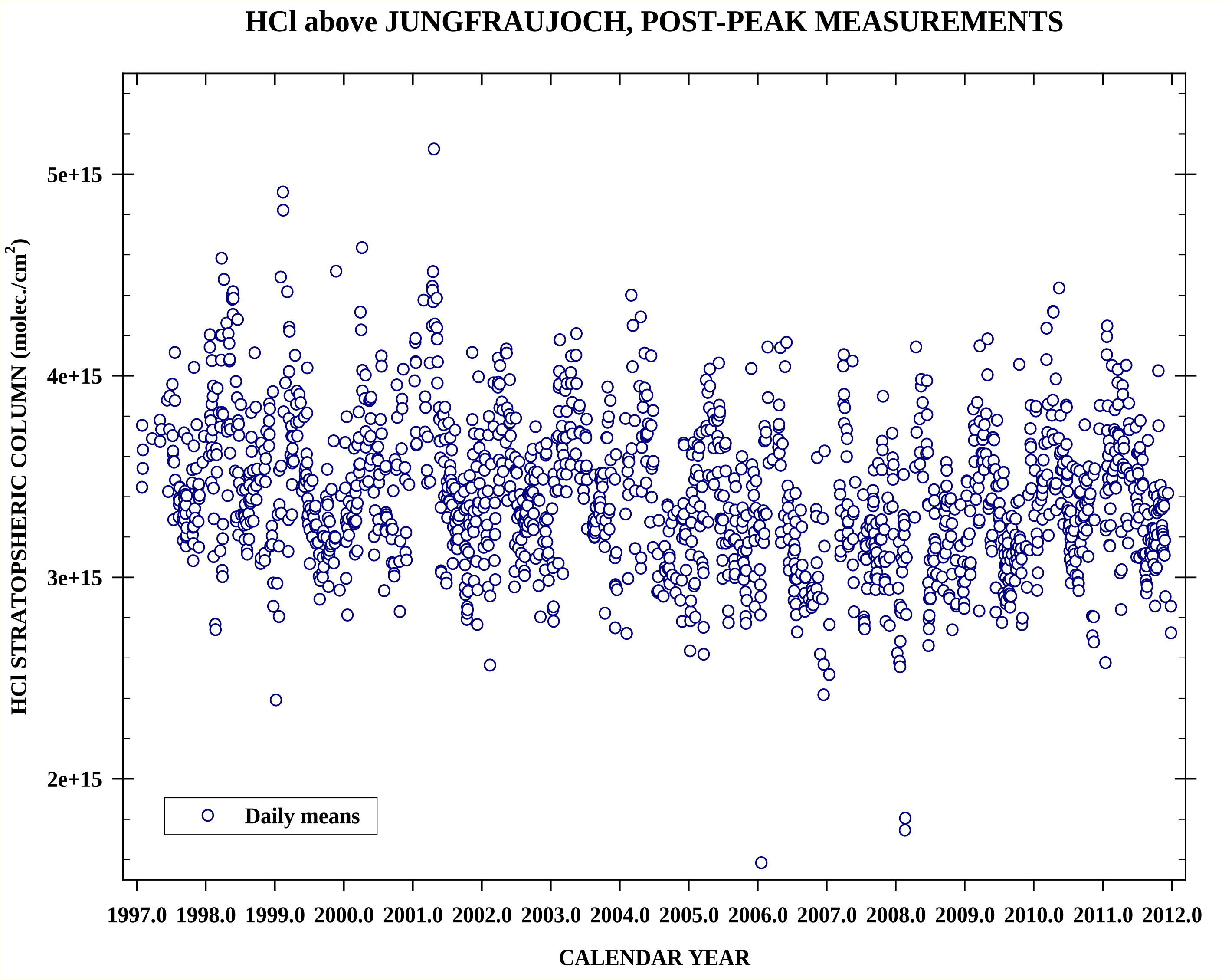
Good agreement with models and CCl_y build up in the troposphere

emmanuel.mahieu@ Université de Liège

Kohlhepp et al., ACP, 12, 2012

- NDACC-wide effort, involving **17 FTIR sites** from 80°N to 78°S, allowing a “near-global” coverage
- **2000-2009** time series of HCl, $ClONO_2$ (and HF) were compared to simulations performed by **5 models** (2 CTMs, 2 CCMs and a 2-D model)
- The decrease of inorganic chlorine is confirmed, at rates close to **-1%/yr**, in overall agreement with the model calculations
- There is however a larger spread in the measured trends than in the modeled ones

When extending to more recent data…



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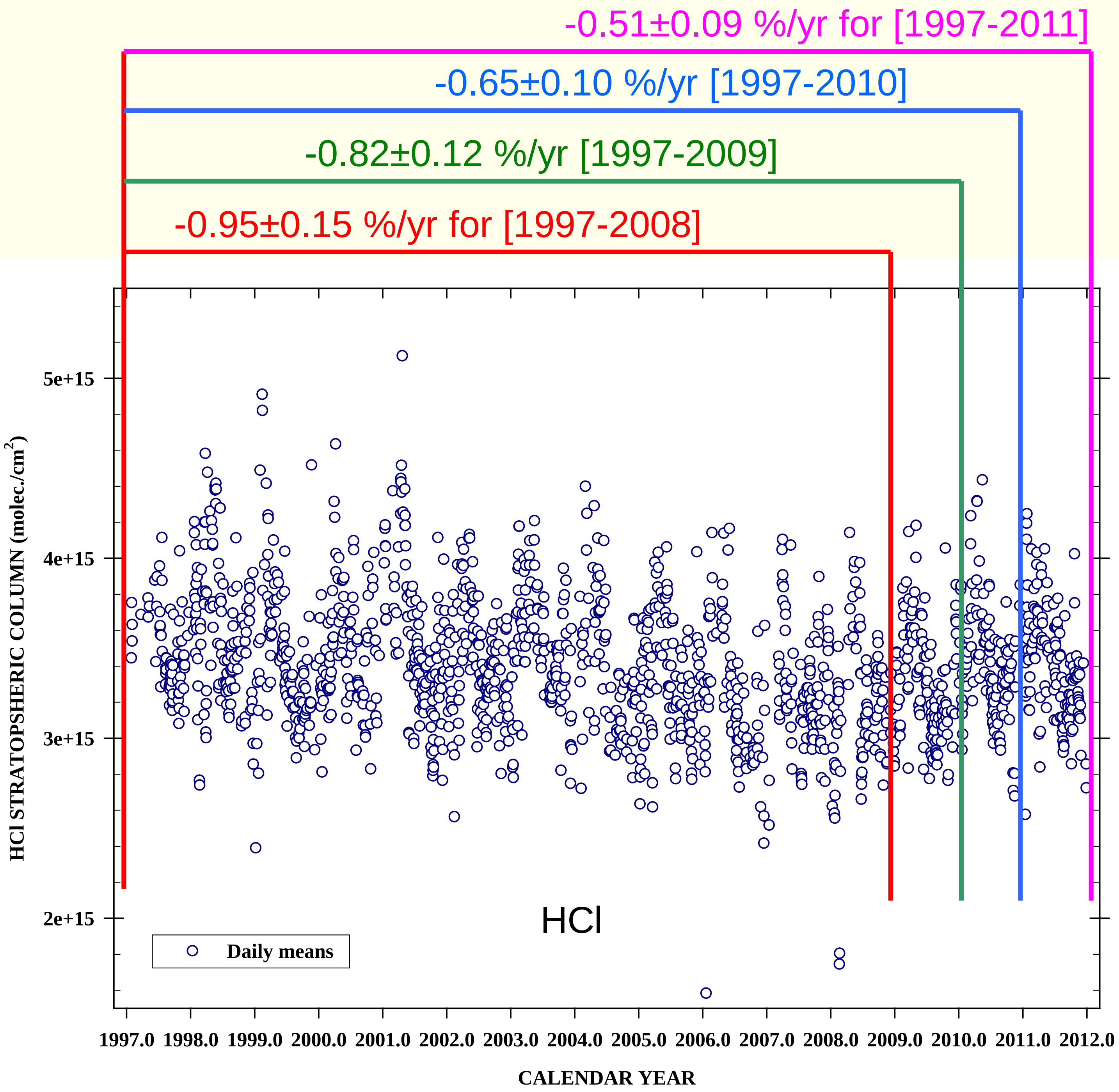

- Trend analyses performed with the bootstrap resampling tool developed by Gardiner et al. (ACP, 8, 2008)

- 2-sigma confidence levels are provided

- Although still significantly negative, the **HCl** trend is nearly <u>divided by 2</u> when adding the last three years…

- Consistent findings when considering the HCl + $ClONO_2$ data set

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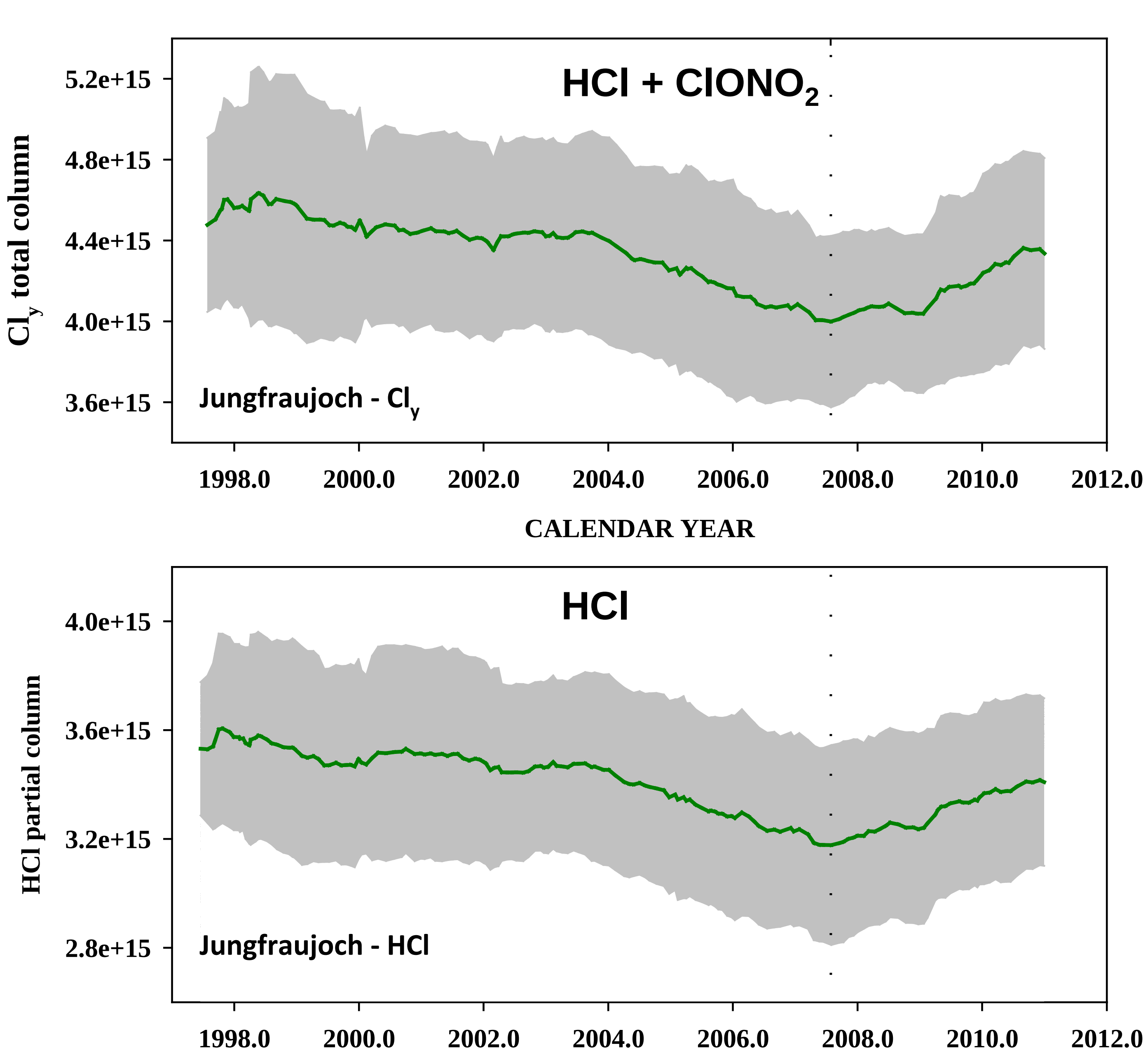

- **Running mean analyses** on the Cl_y and HCl time series indicate minimum columns around July 2007
- Since then, both sets show steady increase of the local means

➢ There is no redistribution of chlorine among the main reservoirs!

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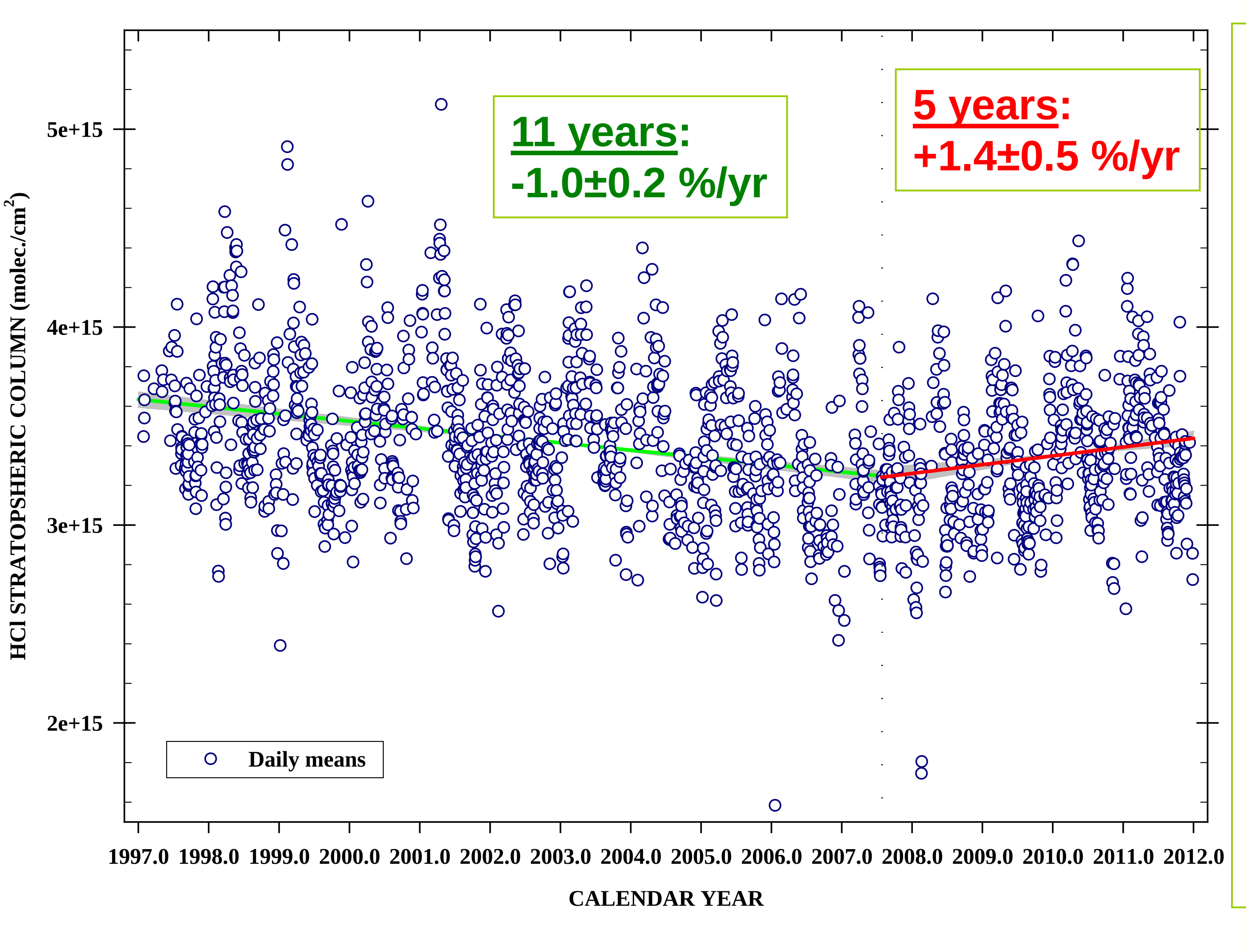
When considering the two regimes separately…



- Decrease over 1997-2007, with a rate of -3.7x10^{13} molec./cm^2/yr
- Followed by a significant increase of 4.4x10^{13} molec./cm^2/yr
- The upward trend is almost three times larger in magnitude than its 2-sigma uncertainty
- Mean levels at the end of 2011 = those of early 2002
- But short time period of only 5 years

What about satellite observations?

- **HALOE** (1991-2005), version 19 (netcdf files)
- **ACE-FTS**, version 3 (from 2004 onwards)
- *Also available: AURA/MLS data (Froidevaux et al., GRL, 33, 2006), not considered thus far*
- But these time series cannot be combined directly to form a consistent set due to a known bias between them, as noticed in ACE validation studies (McHugh et al., GRL, 32, 2005; Mahieu et al., ACP, 8, 2008) as well as in Lary et al., GRL, 34, 2007)
- This bias is obvious when displaying both time series, HALOE being low

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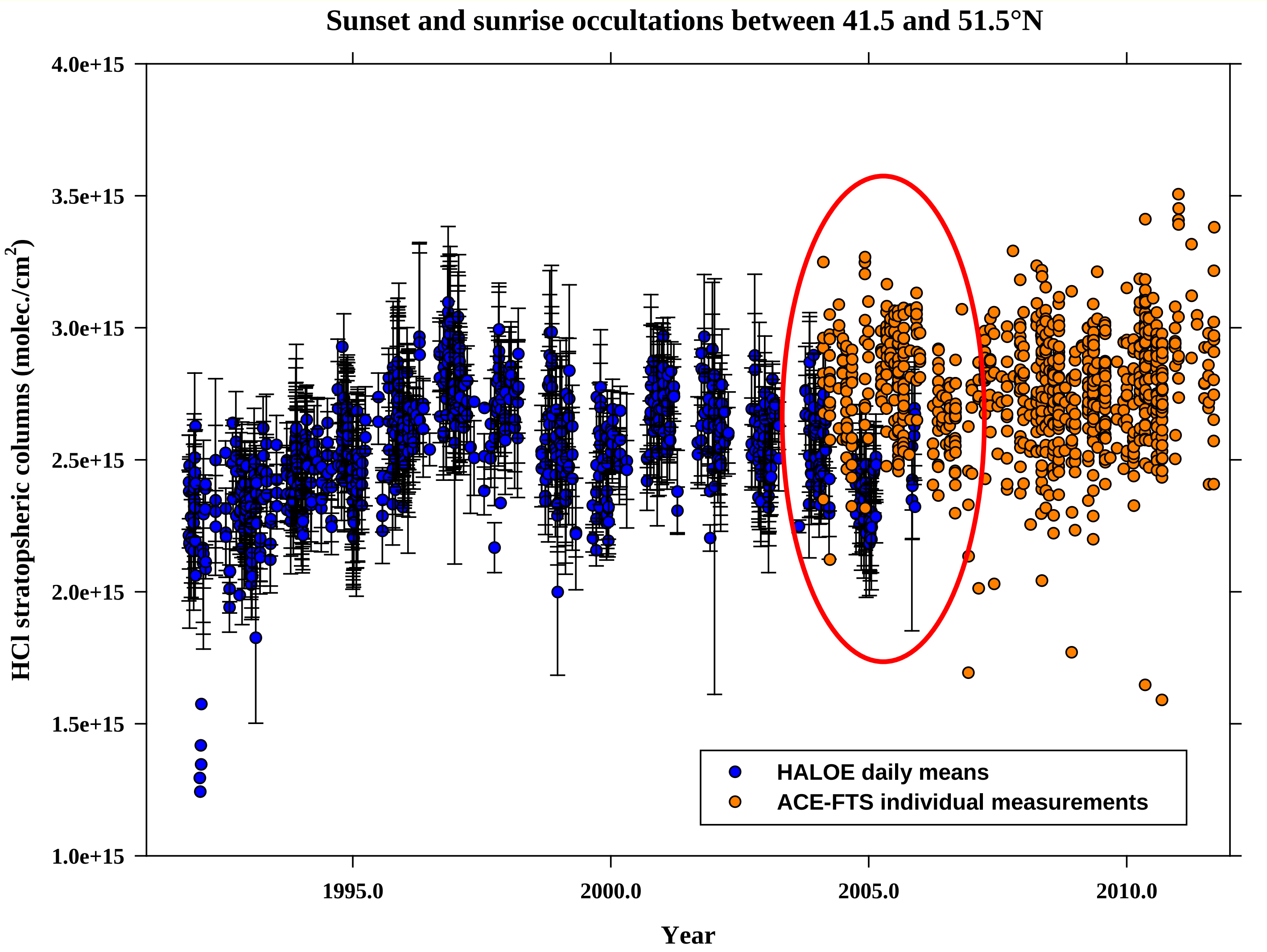
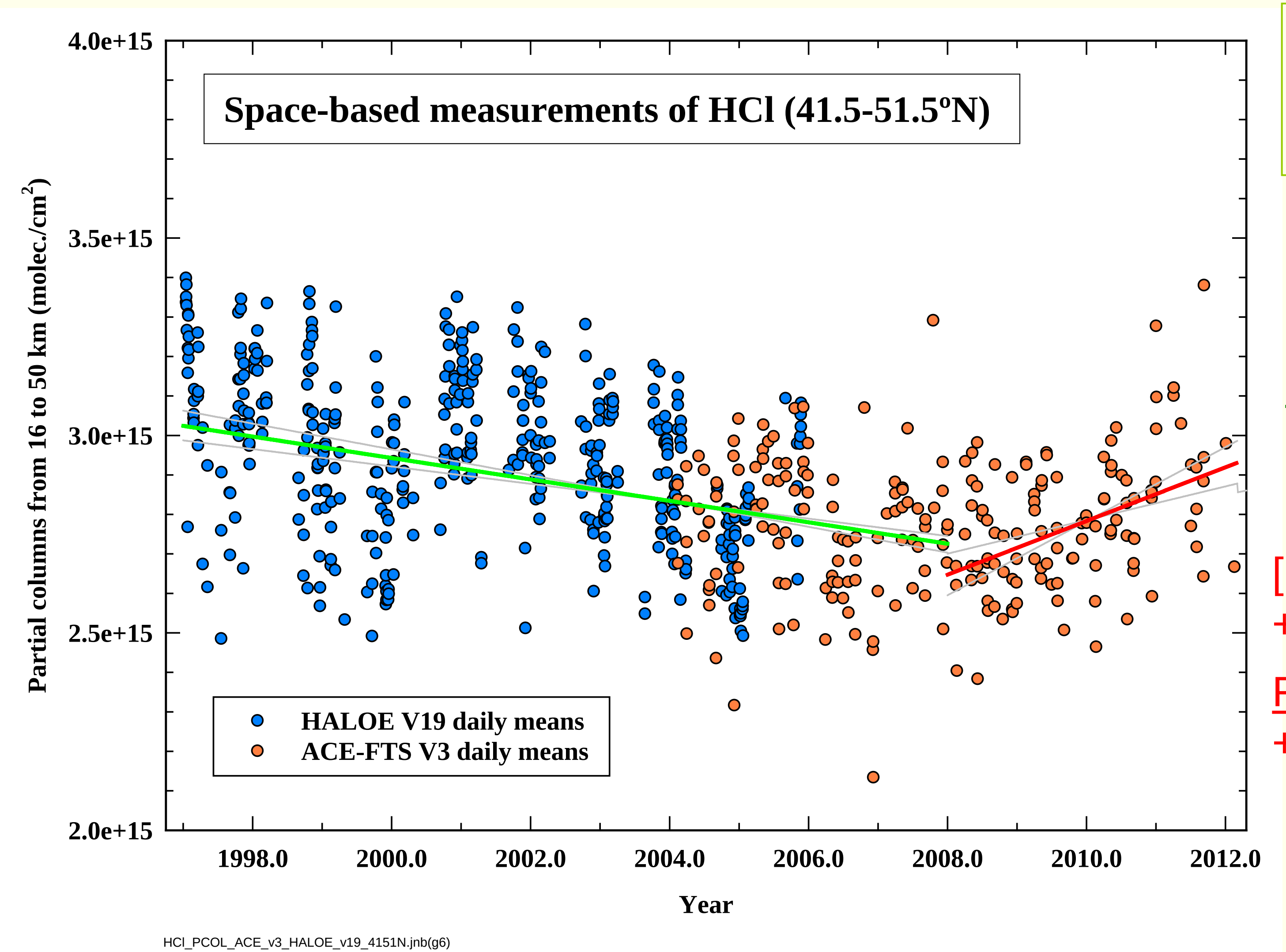
HALOE V19 and ACE-FTS V3



Accounting for the bias

- The relative bias has been re-evaluated, considering all available coincidences (within 2h and 500 km) as well as the mean difference between both sets in the 41.5-51.5°N zone
- Both approaches led to the determination of a relative bias of 14 %, with ACE higher than HALOE, in agreement with previous studies (bias of 10-20% quoted by McHugh et al., 2005; 10-15% by Mahieu et al., 2008).
- HALOE was therefore scaled high by 14% to match ACE-FTS

Harmonized satellite time series



All trends in 10^{13} molec./cm^2 or in % per year

[1997-2007] trend:
-3.4±2.5 (-1.1%/yr)

From the ground:
-3.7±0.6 (-1.0%/yr)

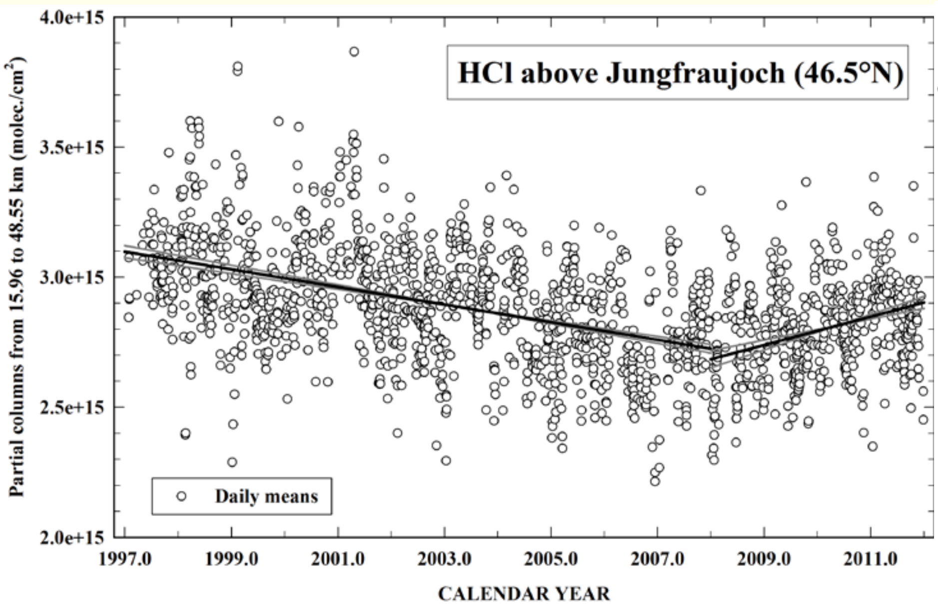
[2008-2011] trend:
+6.8±2.6 (+2.6%/yr)

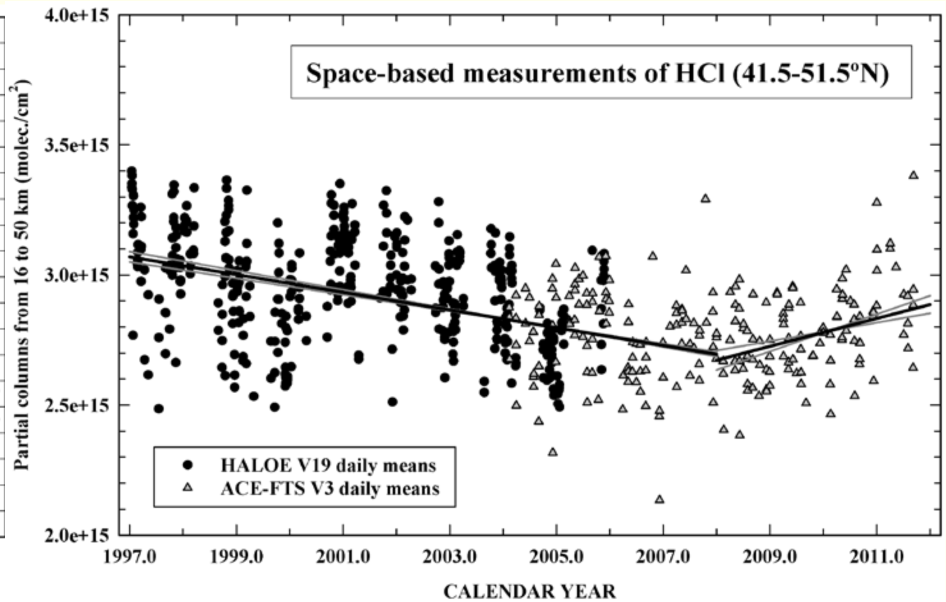
From the ground:
+4.4±1.8 (+1.4%/yr)

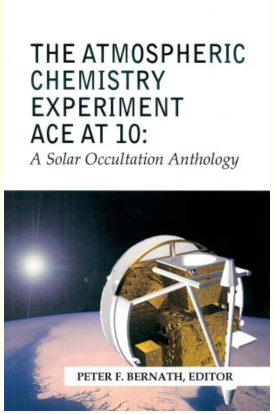
Uncertainty:
2-sigma level

emmanuel.mahieu@ulg.ac.be

Very consistent picture…







Mahieu *et al.*, 2013, in the ACE Book (ISBN-978-0-937194-54-9)

emmanuel.mahieu@ Université de Liège

Current conclusions

- Good agreement between trends derived from the Jungfraujoch and composite satellite time series, suggesting at least a recent and significant slowing down of HCl (and of Cl_y) at Northern mid-latitudes, *or even a positive trend over the last 5 years*
- This new feature in the HCl and Cl_y time series is unexpected: chlorine has steadily decreased in the troposphere over the 1993-2008 time frame, as shown by the AGAGE & NOAA ins situ measurements, at rates between about -0.4 and -1%/yr
- **The data are being compared with dedicated model results from the 3D-CTM SLIMCAT (M.P. Chipperfield, Leeds)**

⇒ more to come soon!

emmanuel.mahieu@ Université de Liège

With support from BELSPO (PRODEX and SSD programs), F.R.S. – FNRS, Fédération Wallonie-Bruxelles, Meteoswiss (GAW-CH)… and HFS**JG**.

Thank you!

Including contributions/data from Empa (CH) colleagues, from ACE-science team members (UWaterloo, ON) and from AGAGE. Pseudolines from G.C. Toon (NASA-JPL, CA).

Jungfraujoch FTIR data are available (in hdf) from the NDACC-DHF:

ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/jungfrau/hdf/ftir/

or upon request by email:

emmanuel.mahieu@ulg.ac.be

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