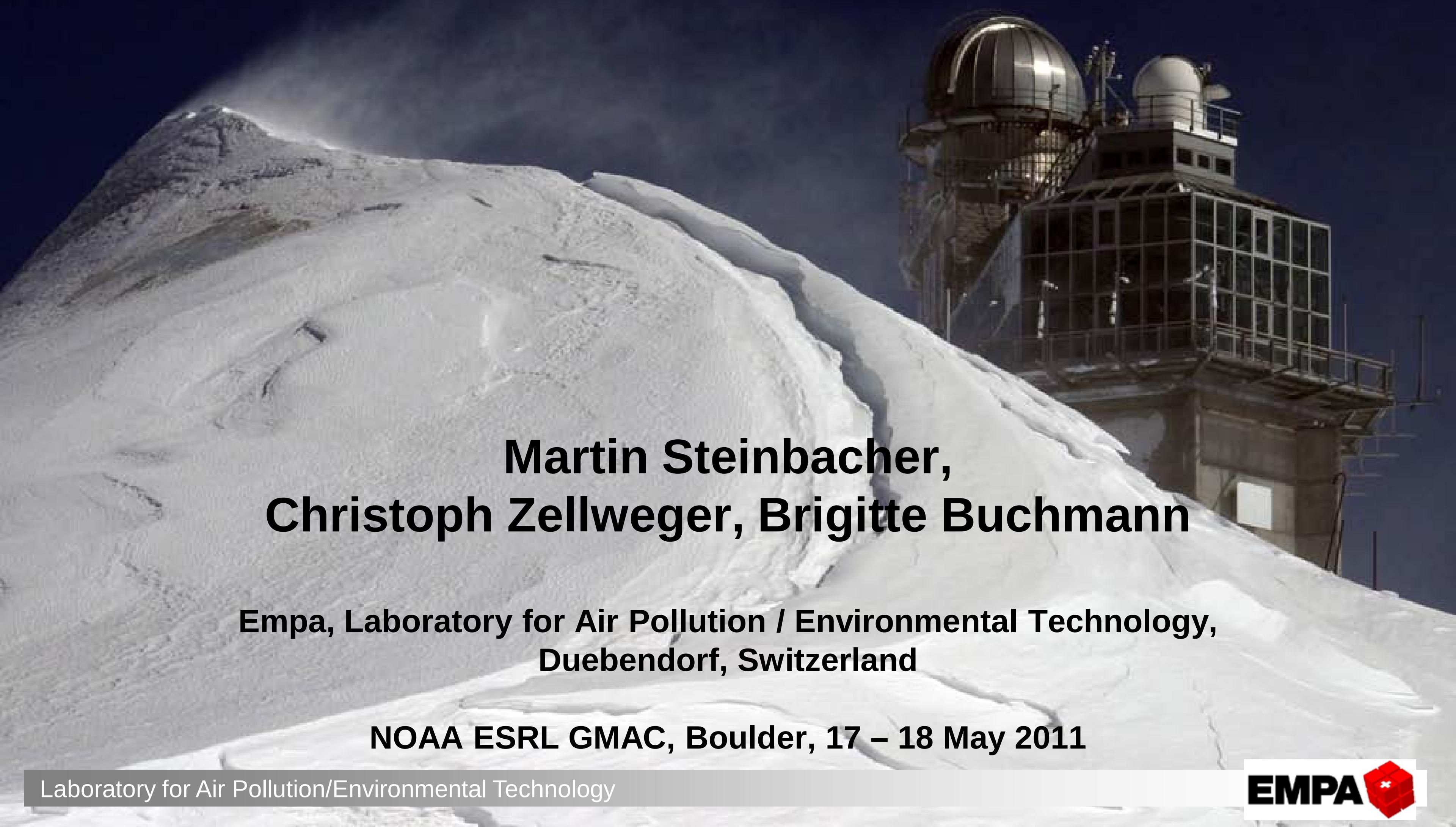
Long-term CH_4 Observations at the GAW site Jungfraujoch with Gas Chromatography and Cavity Ringdown Spectroscopy



Martin Steinbacher,
Christoph Zellweger, Brigitte Buchmann

Empa, Laboratory for Air Pollution / Environmental Technology,
Duebendorf, Switzerland

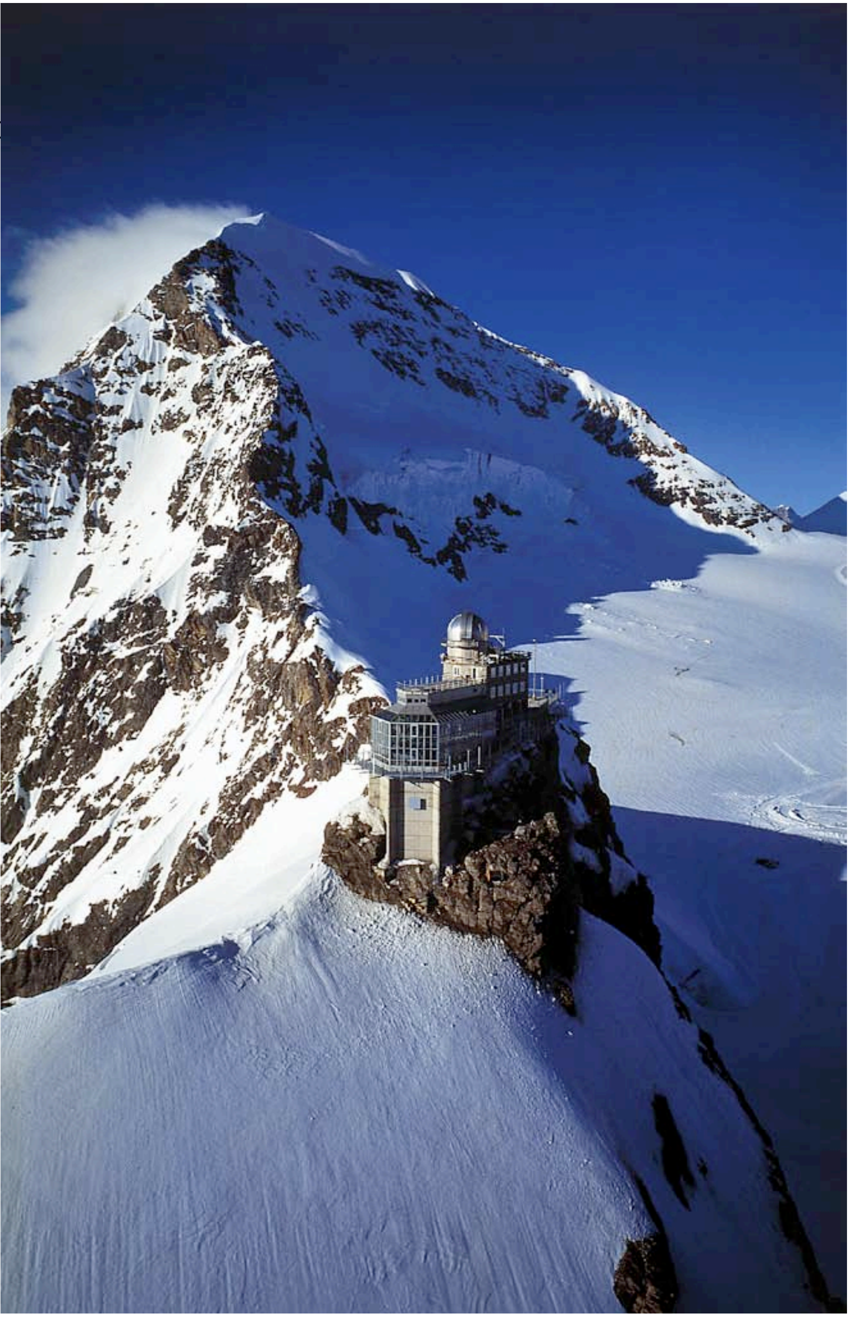
NOAA ESRL GMAC, Boulder, 17 – 18 May 2011

Jungfraujoch (JFJ)

3580 m asl, 7° 59' E, 46° 32' N

- part of the Swiss National Air Pollution Network
- one of the 28 Global GAW sites

well suited for
- monitoring the free troposphere
- European source allocations



Methane Measurements @ JFJ

GC-FID

Agilent 6890N
with
FID (CH_4, CO) and
ECD (N_2O, SF_6) detector

since February 2005

- length of run: 12min
- each ambient air sample is bracketed with calibration runs
- standards are traced back to NOAA/ESRL certified gas cylinders (NOAA04 scale)
- target gas measurements three times a week (3 subsequent analysis)
- samples are dried with a Nafion dryer
- precision based on recurrent working standard analyses: ~ 0.2% for CH_4

Methane Measurements @ JFJ

Cavity Ringdown Spectrometer

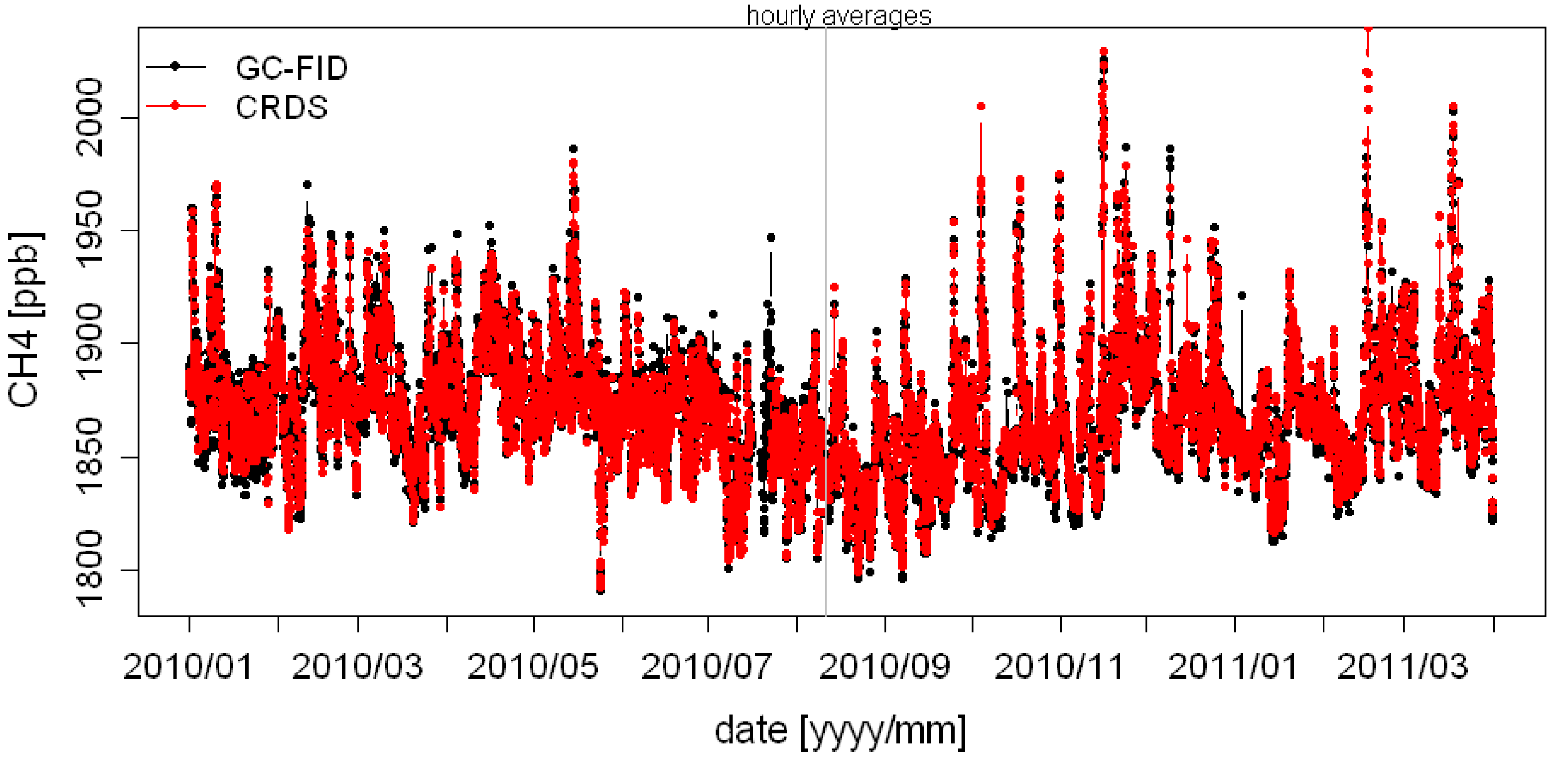
Picarro G1301
equipped with custom-built
calibration and drying unit

since December 2009

- continuous operation; CH_4 data every 4 seconds
- calibration runs (2 standards) every 46 hours
- data are reported on the NOAA04 scale
- target gas measured every 15 hours
- samples were dried with a Nafion dryer until August 2010
- mean precision for 20 mins of working standard analyses: < 0.02% for CH_4

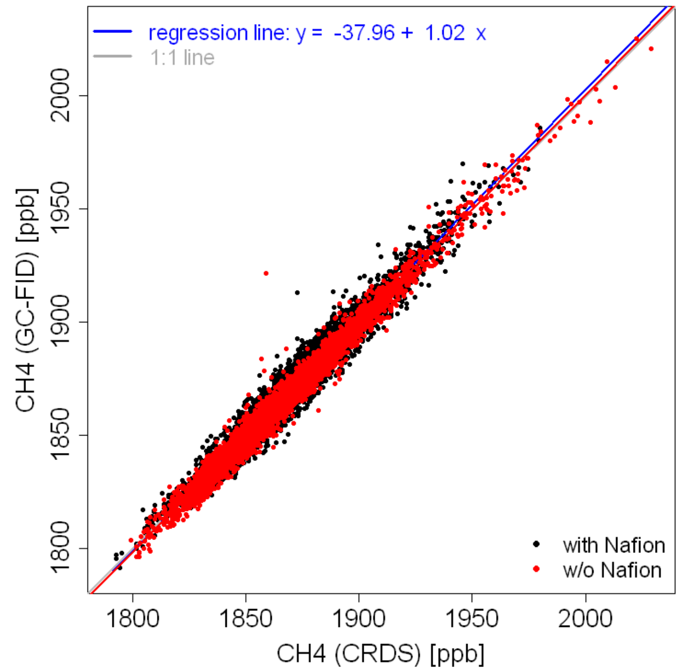
Methane comparison @ JFJ

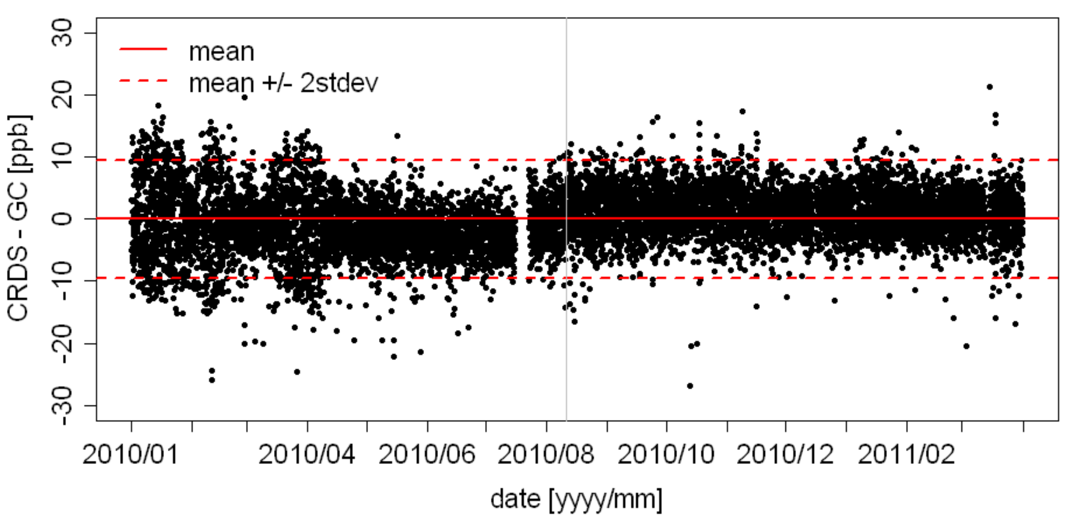
- Agilent 6890 (GC-FID) and Picarro G1301 (CRDS) are running in parallel since January 2010
- GC-FID: quasi-continuous (24-min); CRDS: continuous measurements

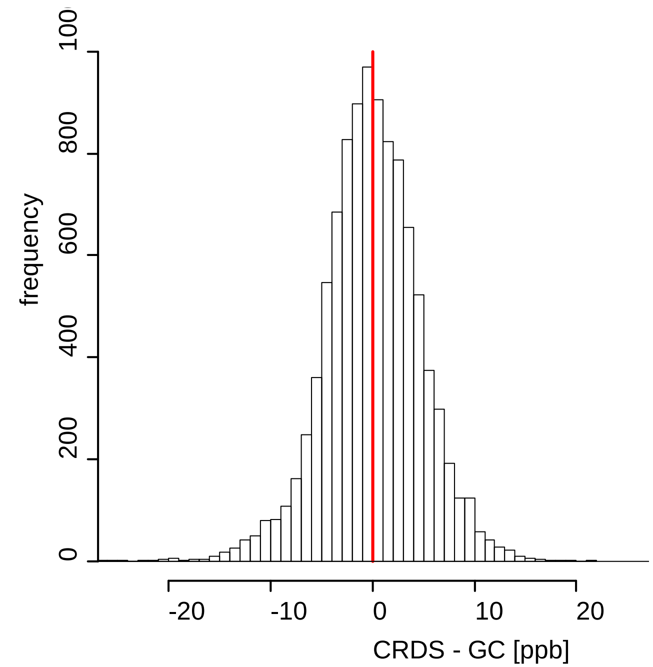


Methane comparison @ JFJ

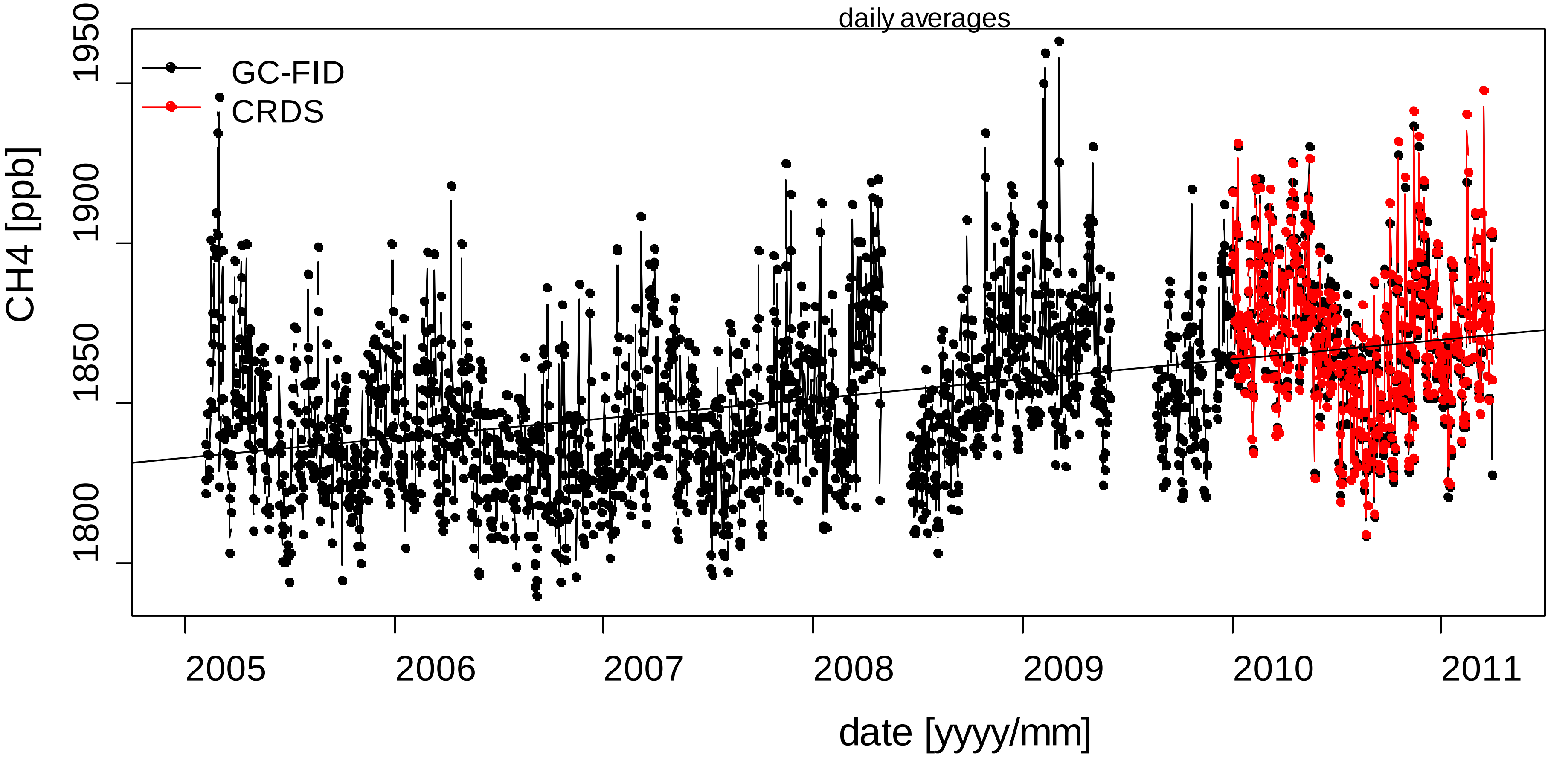
- main structures are well captured by both techniques
- mean difference (CRDS-GC) Jan 2010 to March 2011: -0.4 ± 4.7 ppb (1σ)
- periods with differences between the two techniques due to different temporal coverage





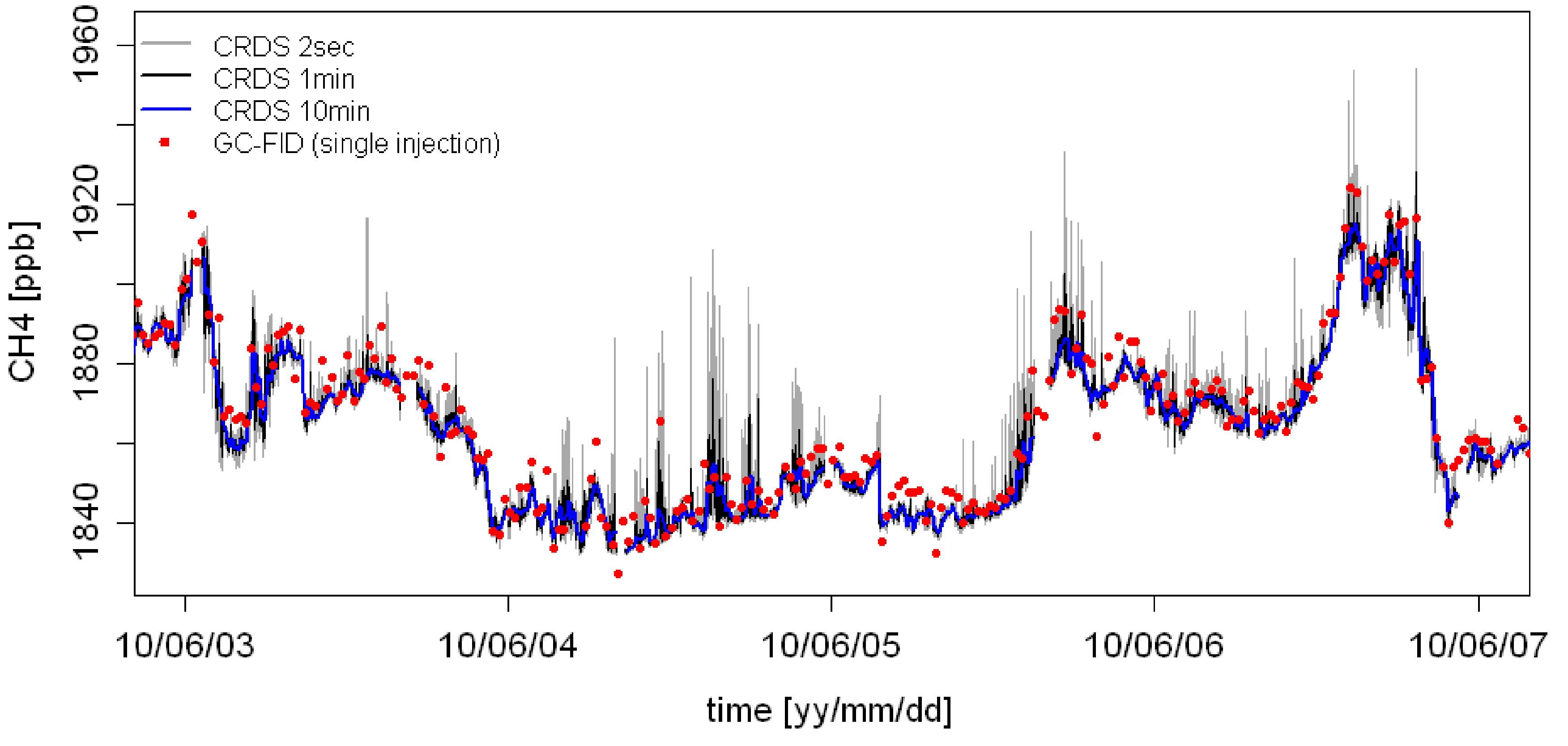


Complete Methane record @ JFJ



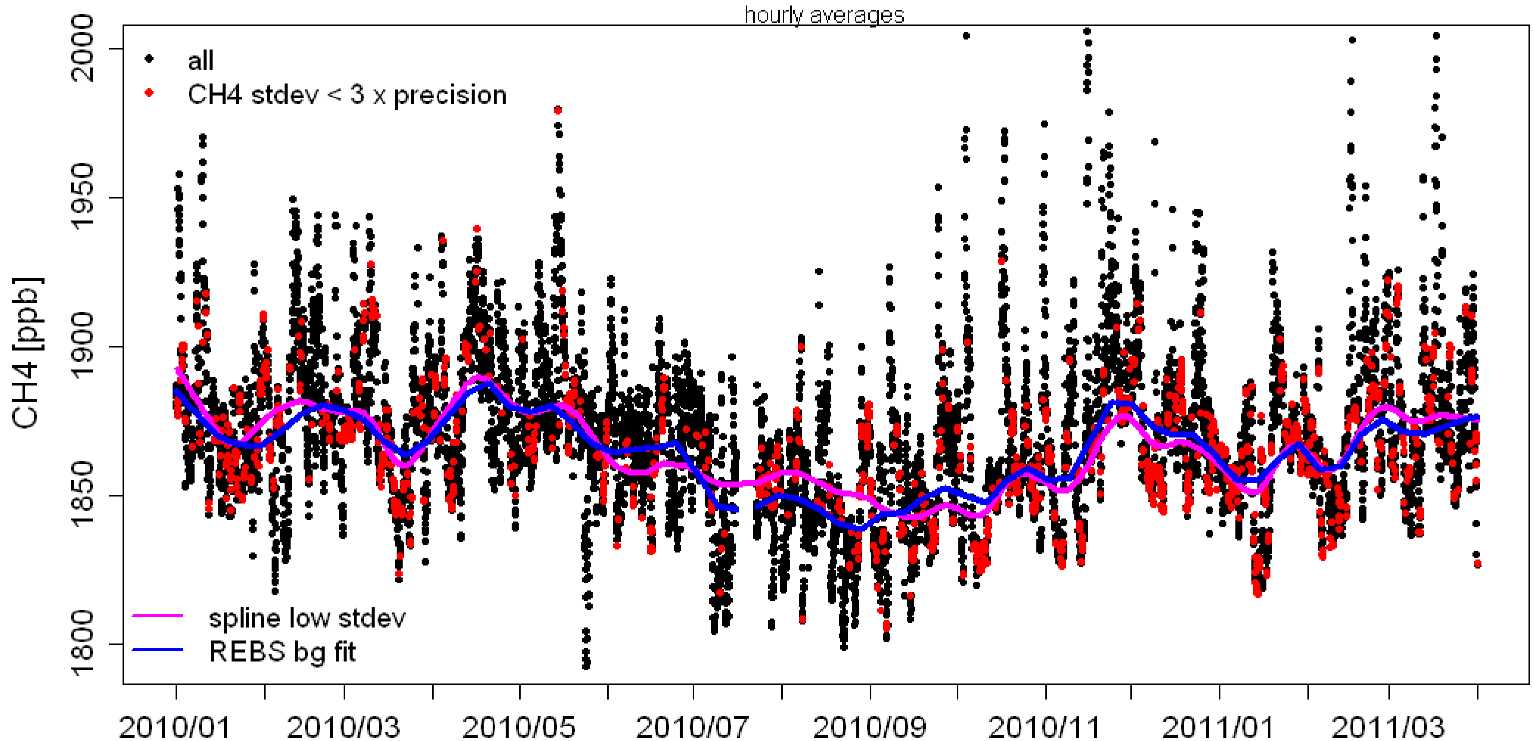
Methane comparison @ JFJ

- high-frequency CRDS data allow to identify periods with short-term fluctuations
- fluctuations usually show only little influence on aggregated data
- however, CRDS data might be useful to identify periods under local to regional influence

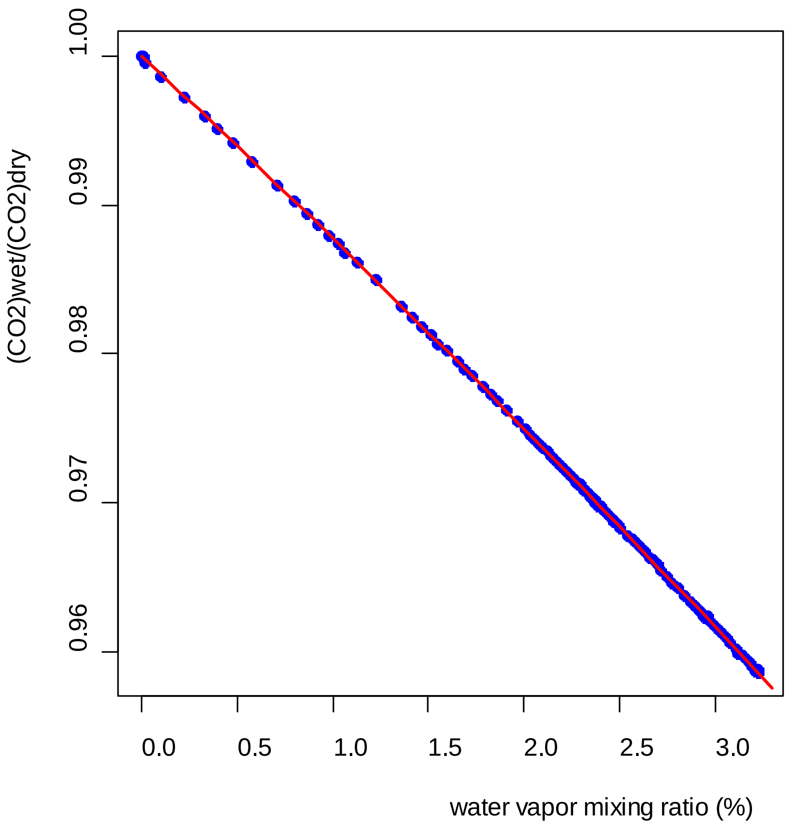


Background determination with high-resolution data

- as first guess, hourly averages with standard deviation < (3 x instrument precision) are considered as data recorded during background (here: free troposphere) conditions
- spline fit through these data compares reasonable well with background fit based on an advanced statistical approach (robust local regression; REBS (Ruckstuhl et al., 2010, AMTD)

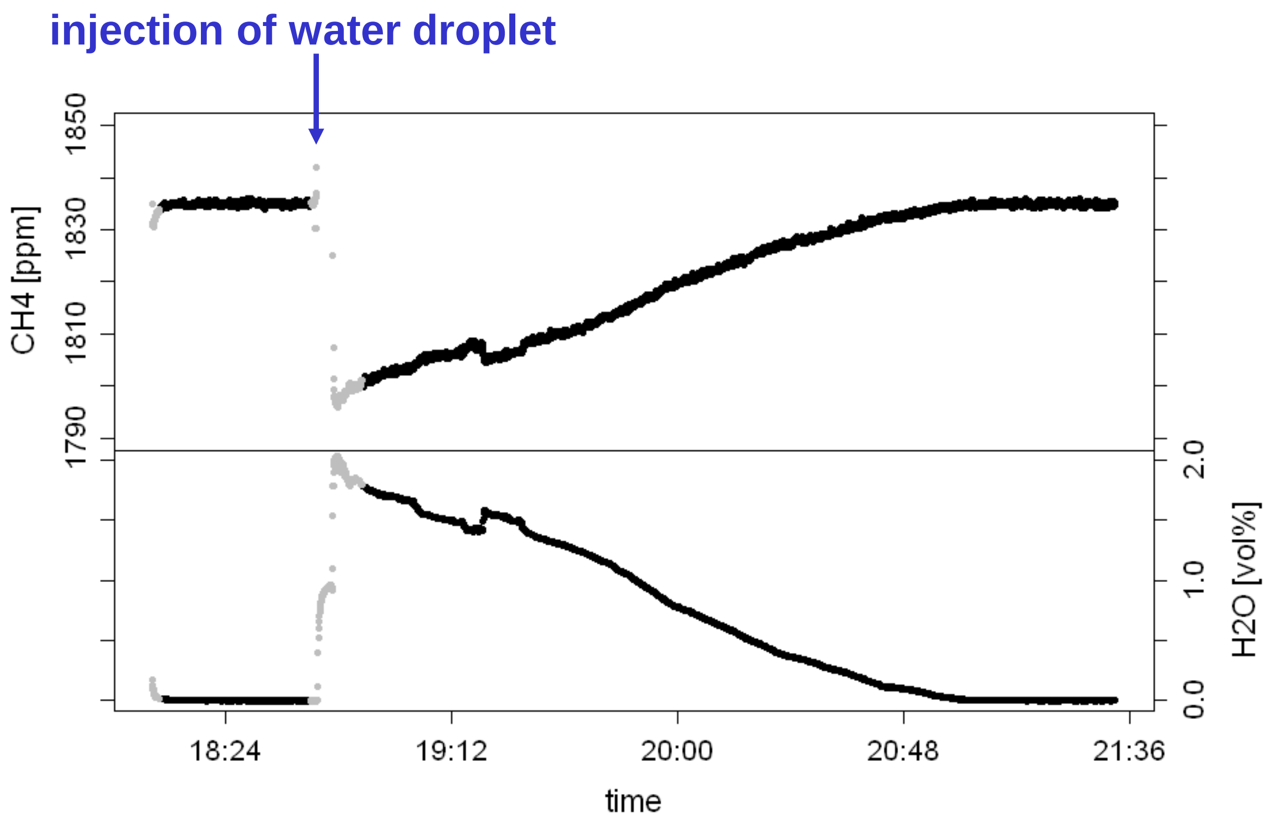


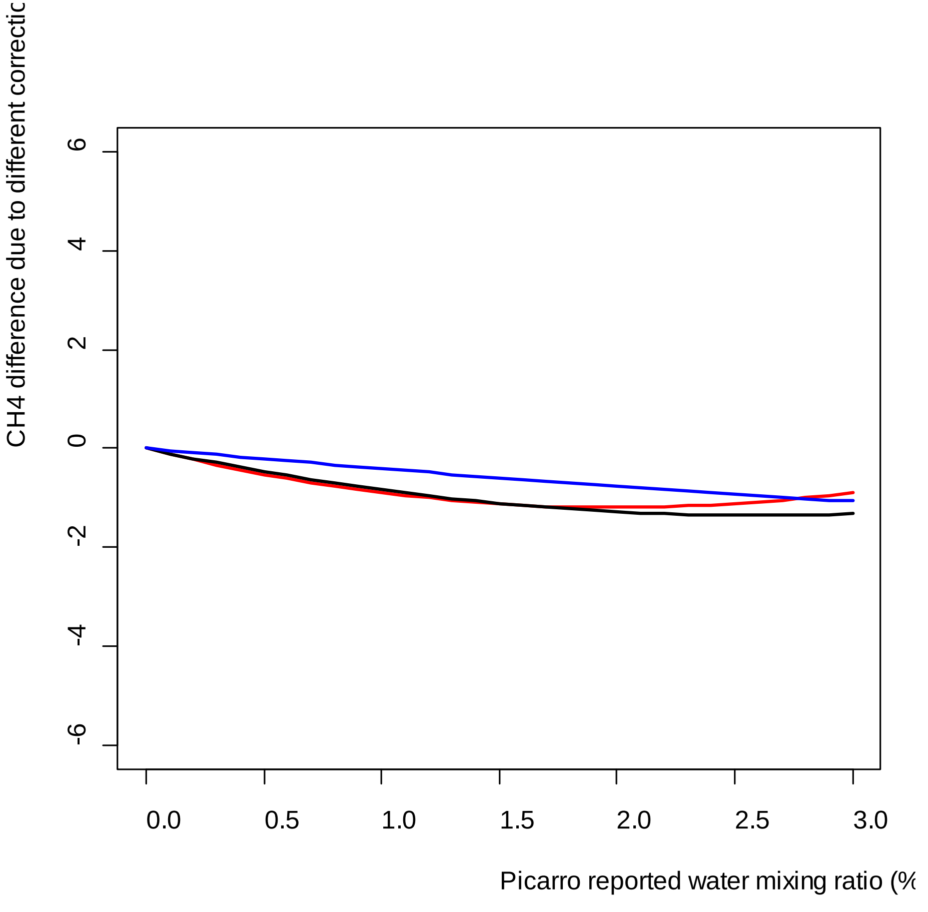
- water vapor correction instead of sample drying (= less maintenance, no potential interaction of the sample with the drying system)
- correction accounts for both **dilution** and **spectroscopic** effects
- water vapor measurements are available as an additional parameter!



Advantage of simultaneous H_2O measurements

- water vapor correction instead of sample drying (= less maintenance, no potential interaction of the sample with the drying system)
- correction accounts for both **dilution** and **spectroscopic** effects
- water vapor measurements are available as an additional parameter!

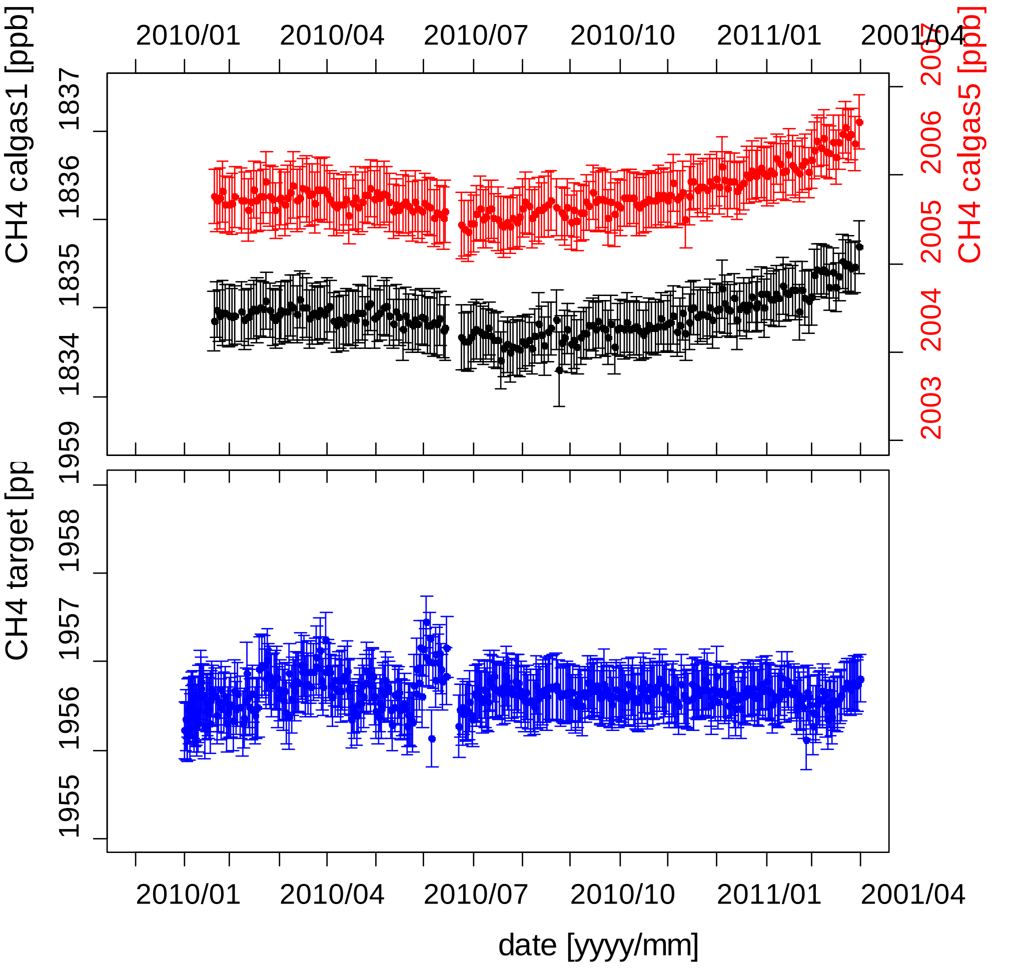




CH4 difference due to different correctic
6
4
2
0
-2
-4
-6
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Picarro reported water mixing ratio (%

EMPA

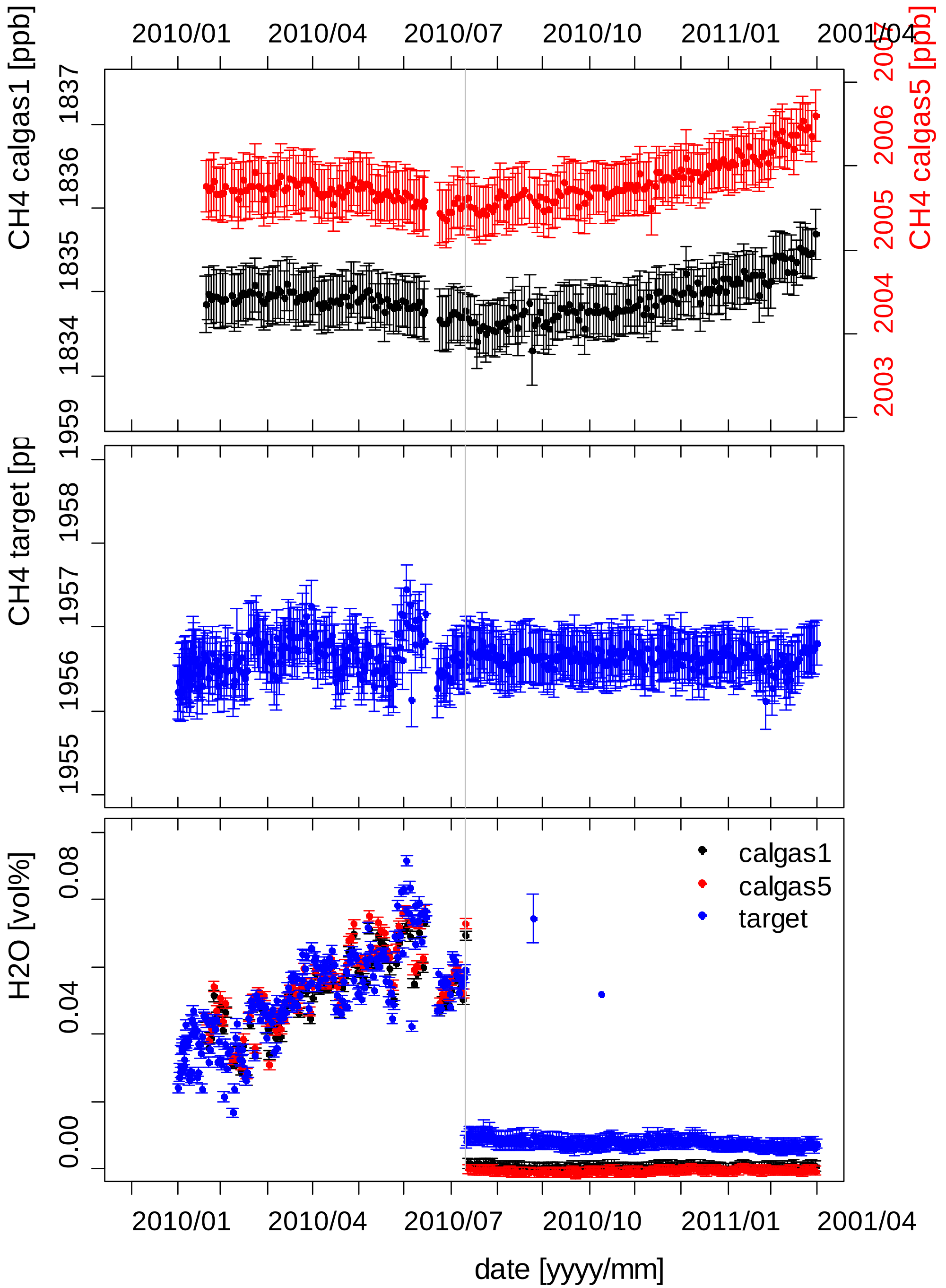
Stability of calibration



EMPA

Stability of calibration

- influence of Nafion dryer
- drying system humidifies standards
- amount of humidification depends on ambient air humidity
- at least for CO_2: non-negligible losses in the drying system standards have to be treated as ambient air



Conclusions

- CRDS and GC-FID data show a very good agreement
- high time resolution data provides information to be used as background condition identifier
- humidity correction function for CRDS easily experimentally determinable, pretty stable over time
- application of humidity correction allows to measure humid air streams and to calculate dry air mixing ratios