

# High precision FTIR measurements of atmospheric trace gases

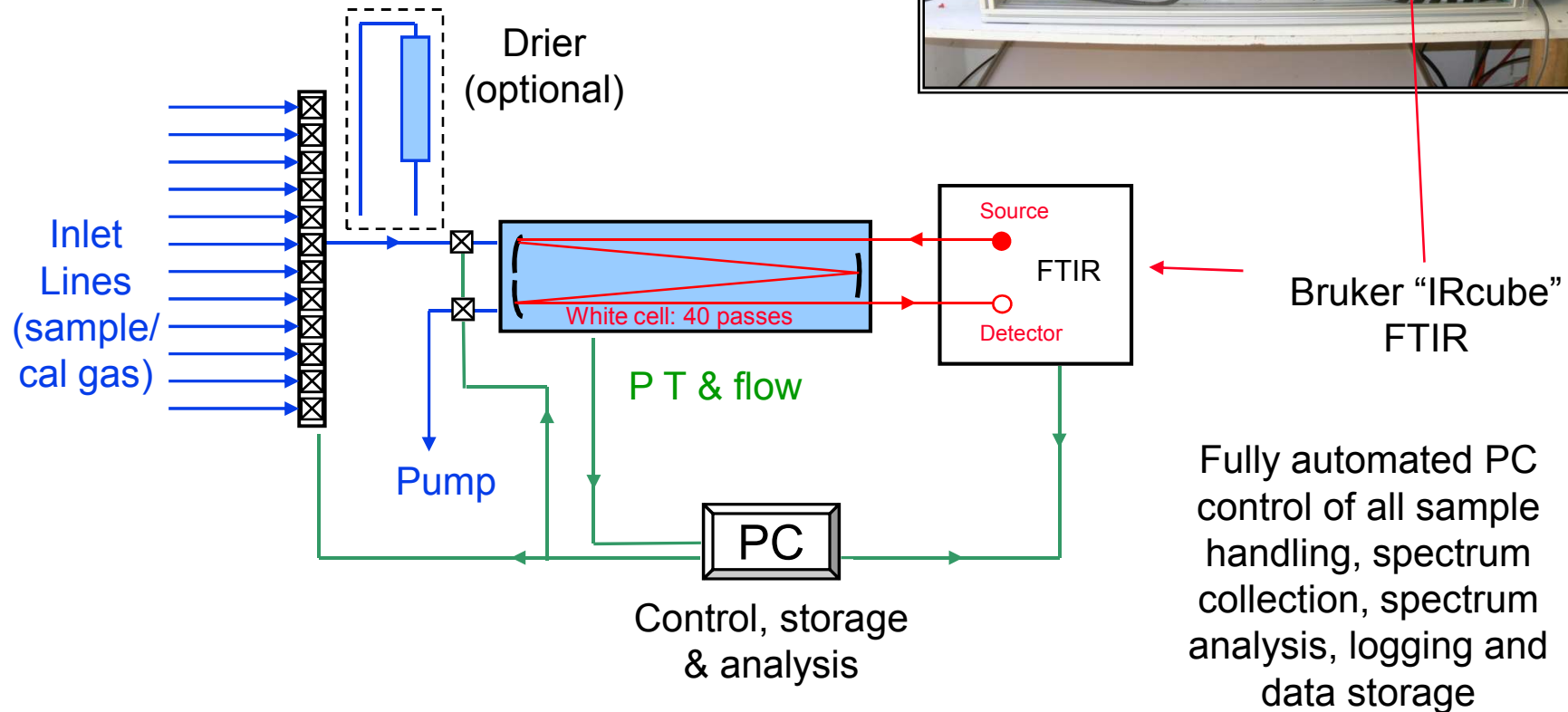
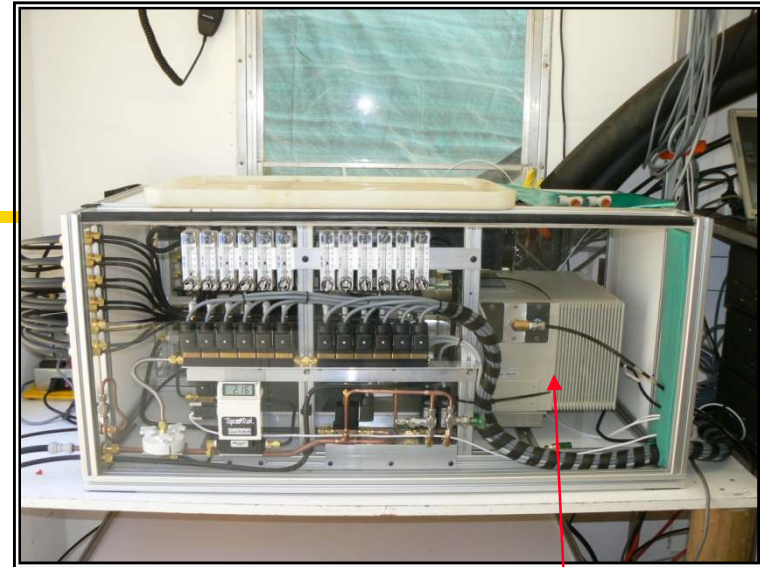
---

1. Multi-species in situ FTIR analyser
2. Total Carbon Column Observing Network (TCCON)

David Griffith

University of Wollongong  
Australia

# 1. FTIR trace gas analyser

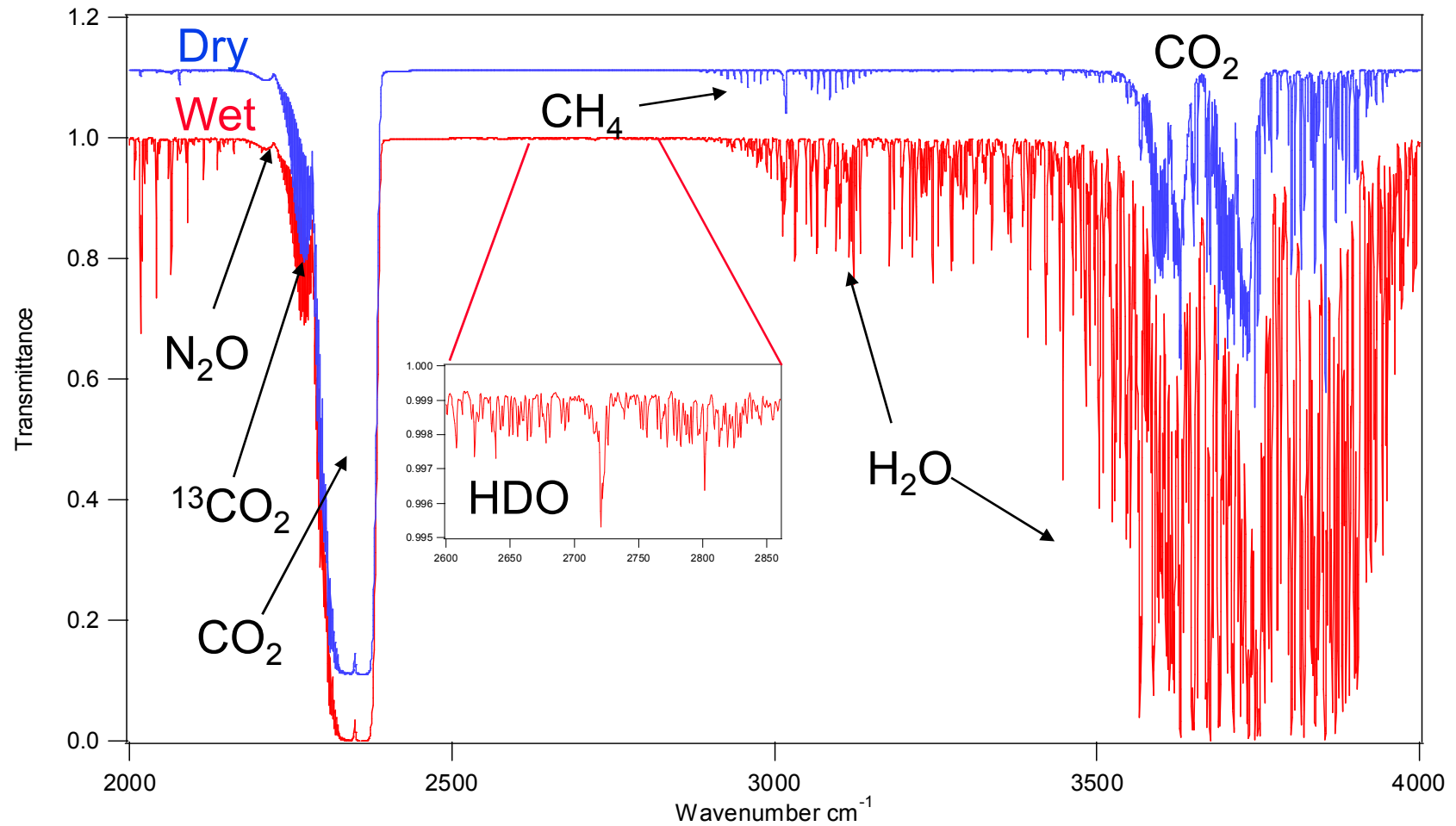


# FTIR and cell

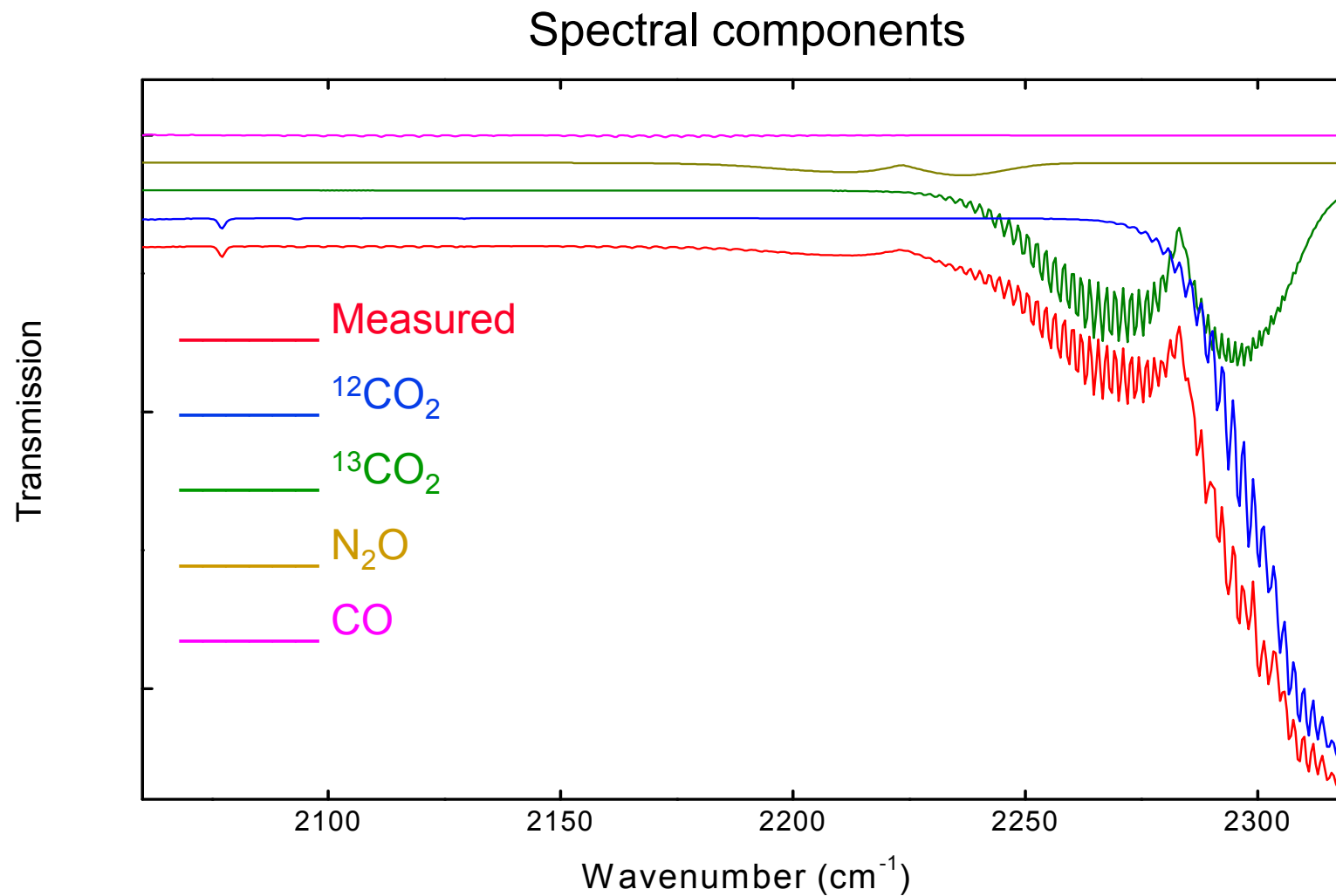
---



# Mid-infrared spectrum of clean air

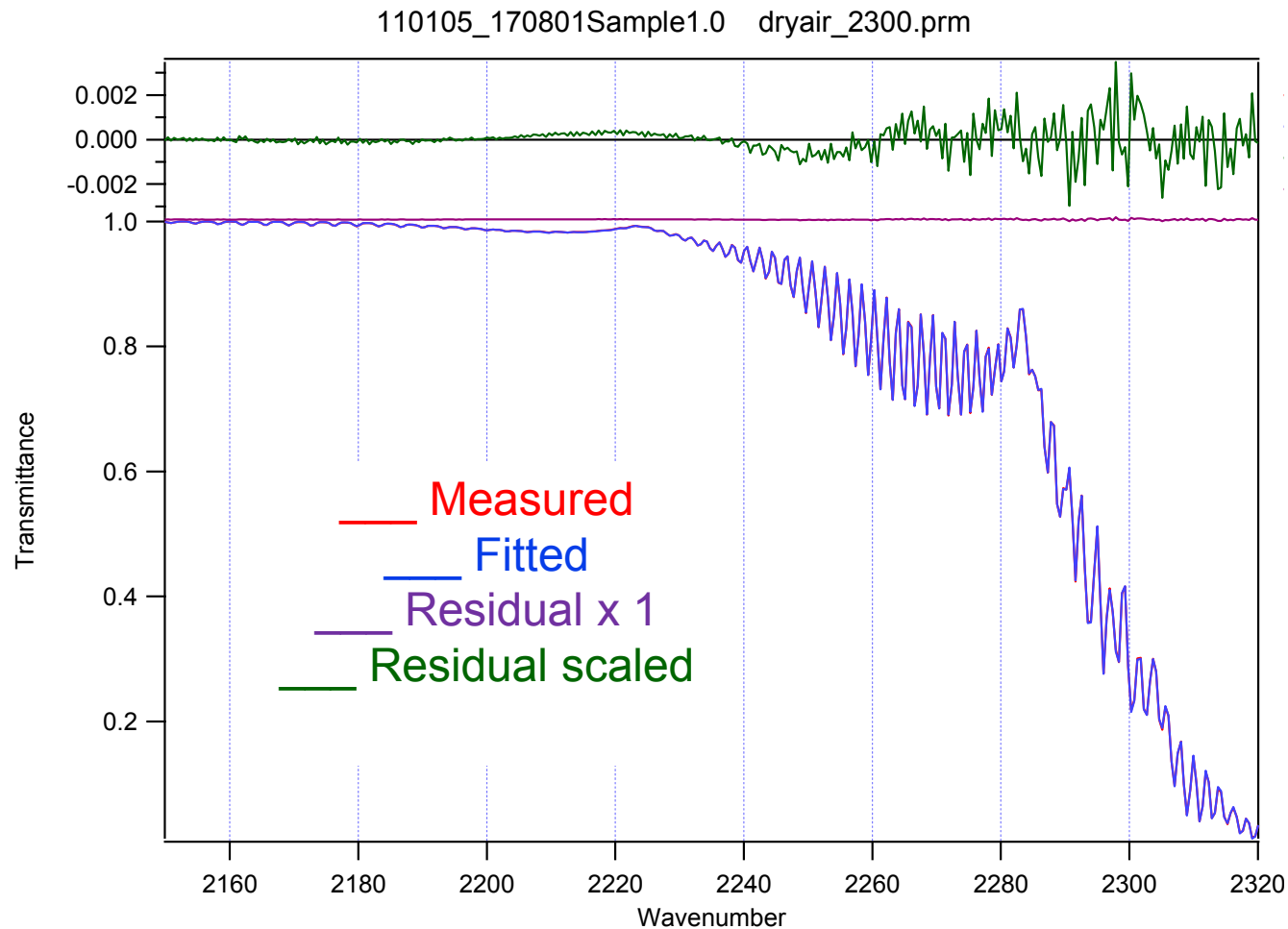


# IR spectrum of clean air $\sim 2200 \text{ cm}^{-1}$



# Spectrum analysis: least squares fitting

## MALT model, Hitran database

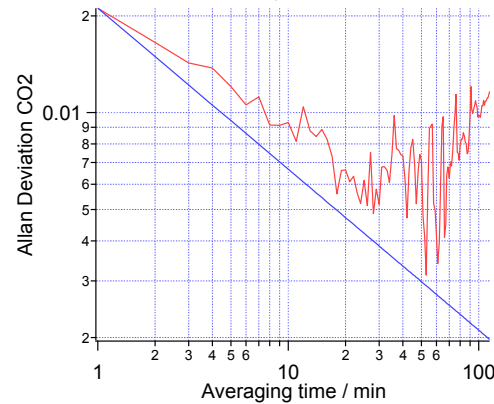
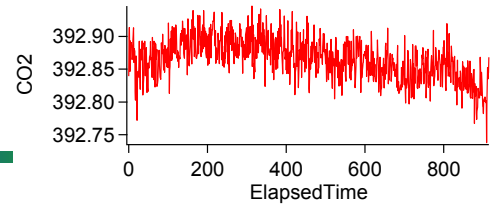


- ◆ Measured spectrum fitted with calculated spectrum for minimum residual (least squares)
- ◆ Different regions to fit for  $\text{CO}_2$ ,  $^{13}\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ , etc.
- ◆ Precision typically <0.1%

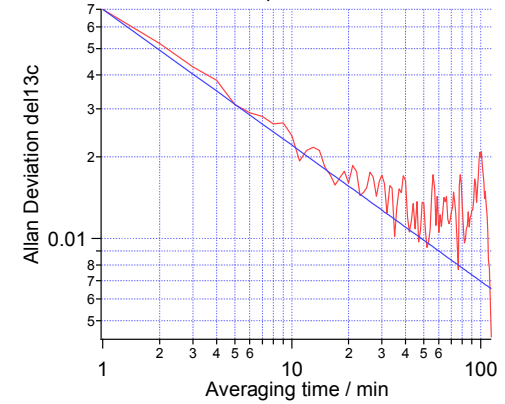
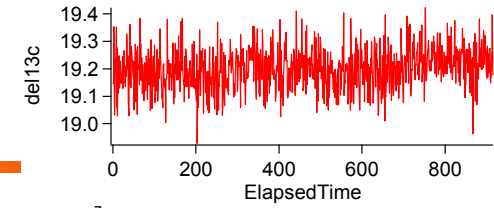
# Allan deviations

- ◆ Simultaneous determination of repeatability from a whole air sample

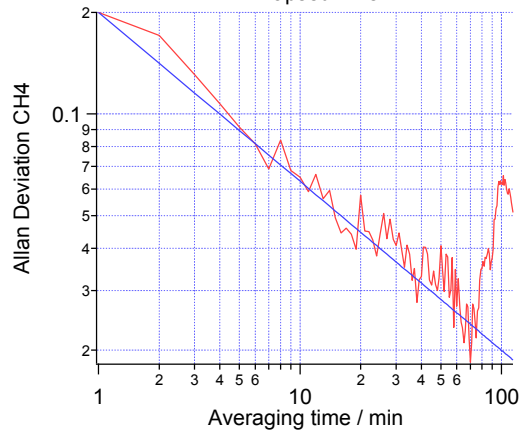
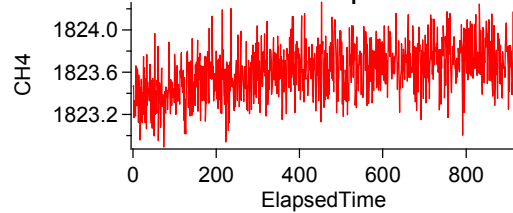
CO<sub>2</sub>



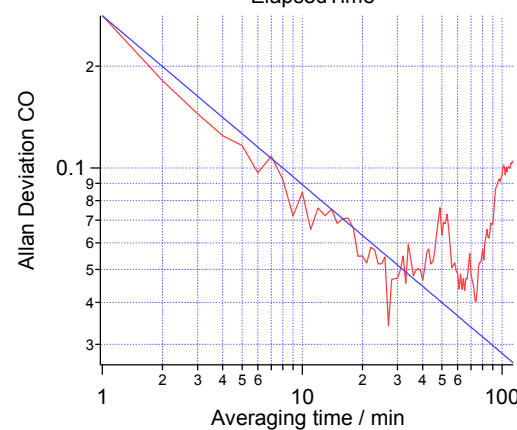
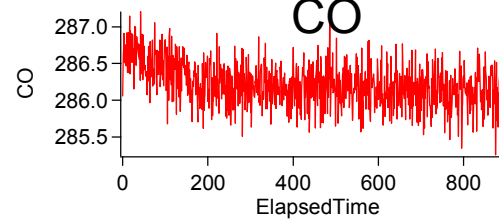
δ<sup>13</sup>C



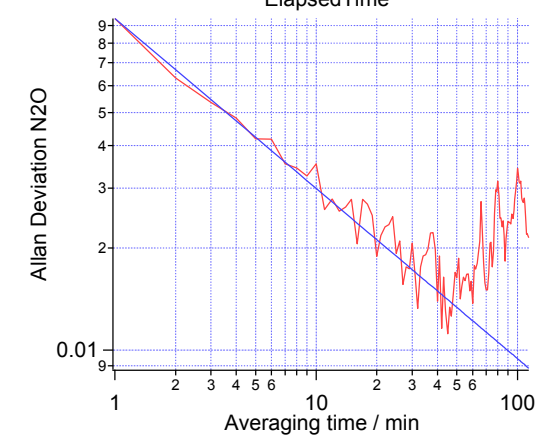
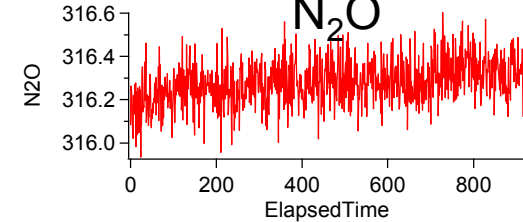
CH<sub>4</sub>



CO



N<sub>2</sub>O



# Allan deviation - summary

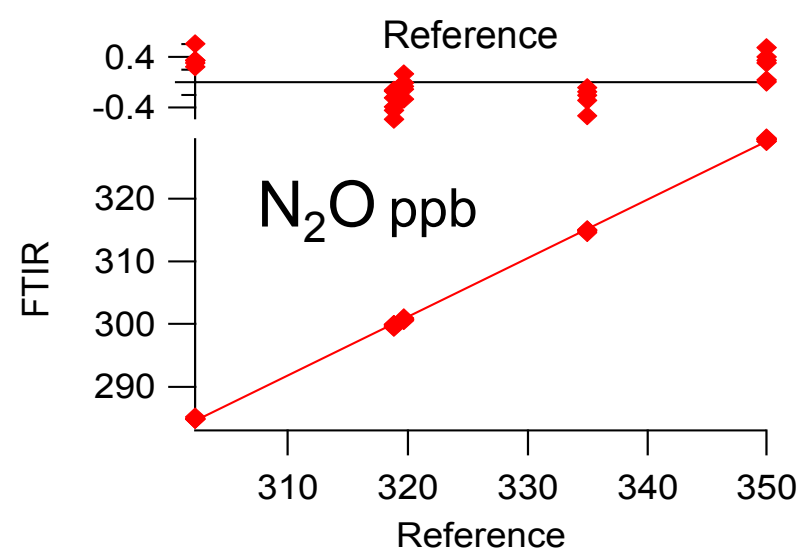
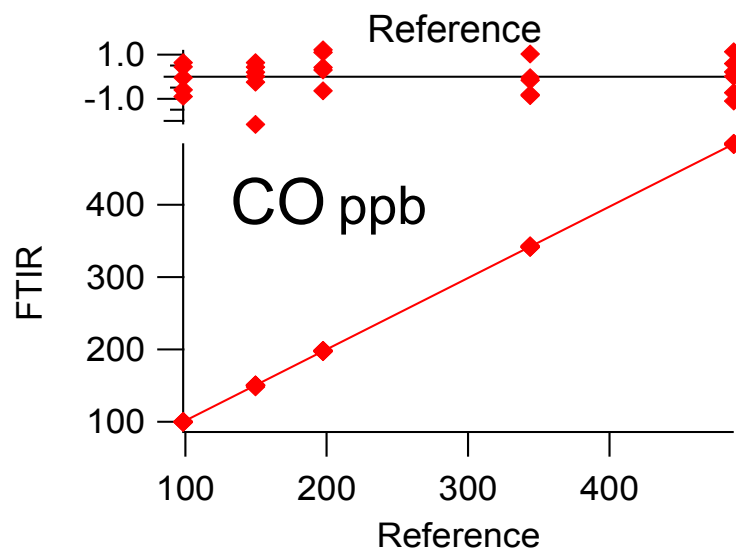
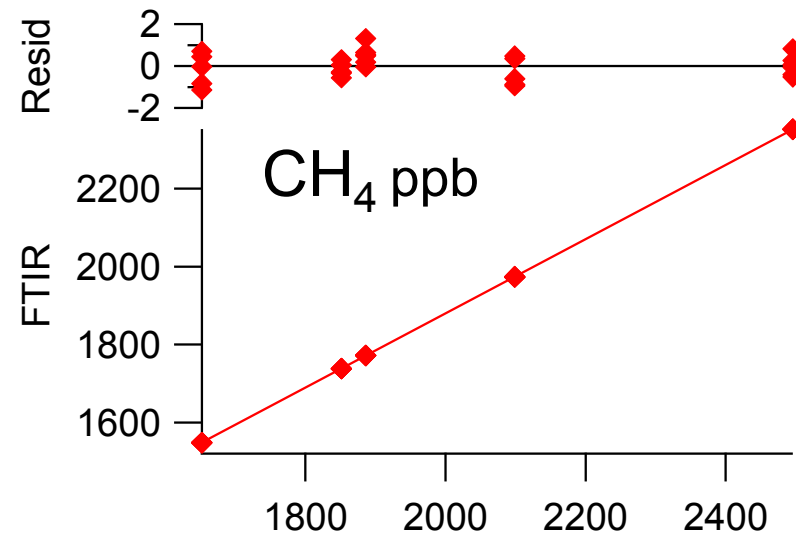
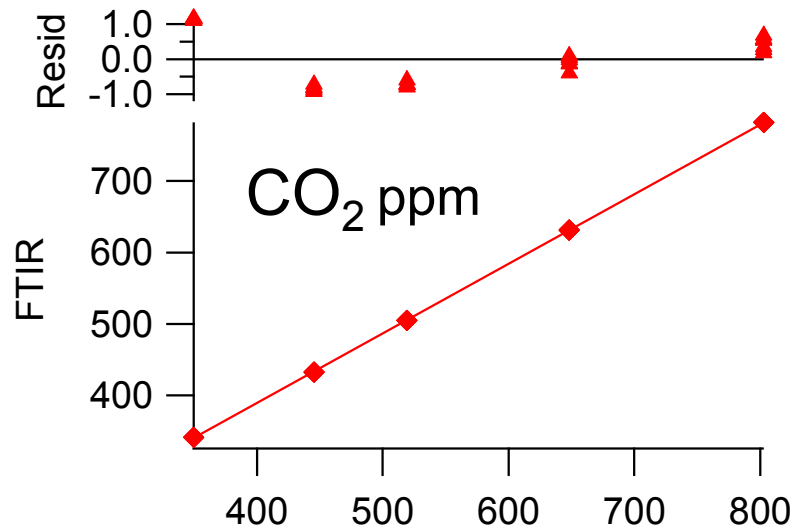
---

Species	FTIR		GAW recomm.
	1 min	10min	
CO <sub>2</sub> μmol mol <sup>-1</sup>	0.02	0.01	0.1 (0.05 in SH)
CH <sub>4</sub> nmol mol <sup>-1</sup>	0.2	0.1	2
CO nmol mol <sup>-1</sup>	0.3	0.1	2
N <sub>2</sub> O nmol mol <sup>-1</sup>	0.09	0.04	0.1
δ <sup>13</sup> C in CO <sub>2</sub> ‰	0.03	0.02	0.01
δD in H <sub>2</sub> O ‰	1.2	0.5	-
δ <sup>18</sup> O in H <sub>2</sub> O ‰	0.5	0.2	-



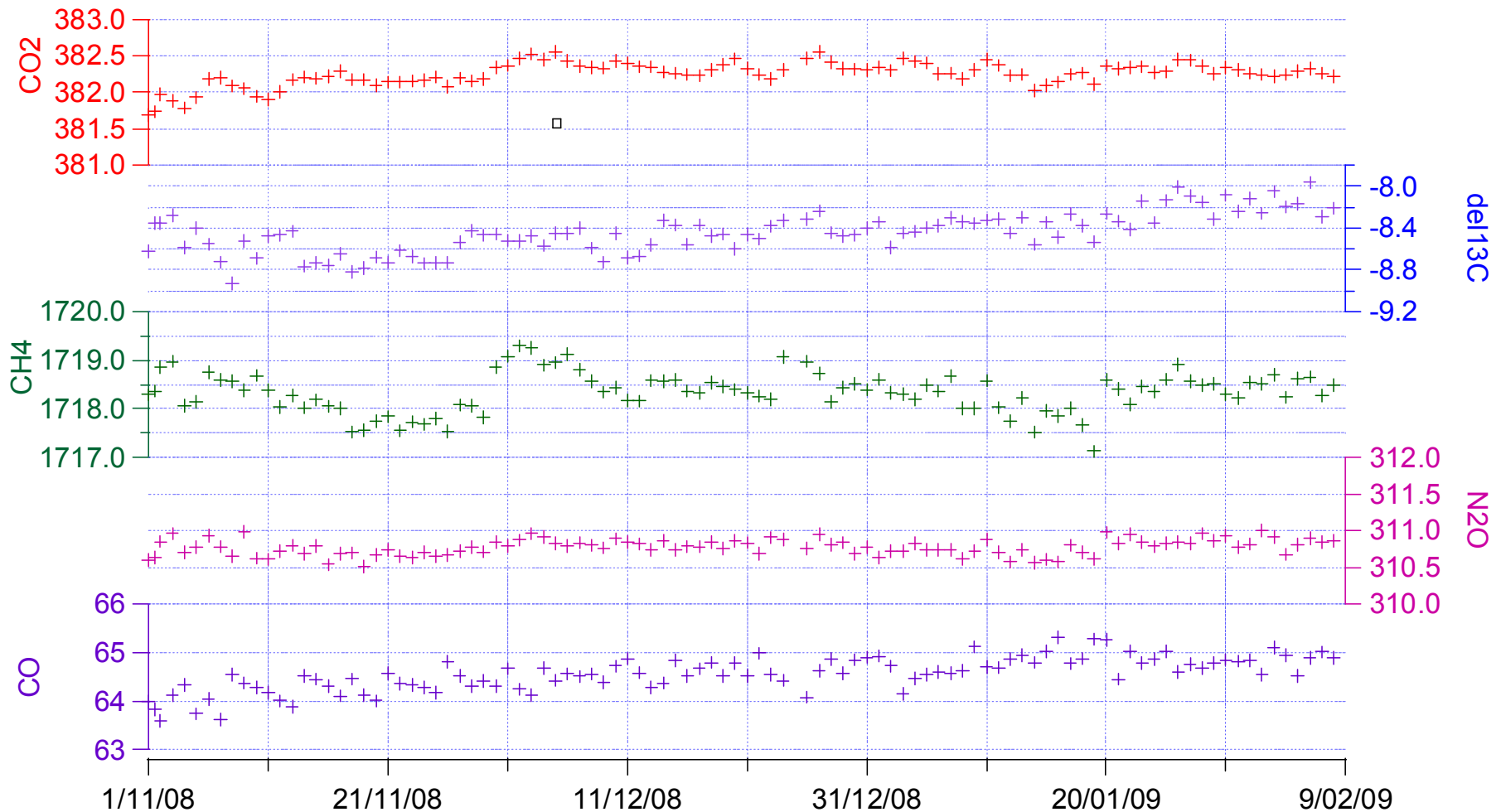
# Calibration

## FTIR vs reference gases (MPI-Jena)



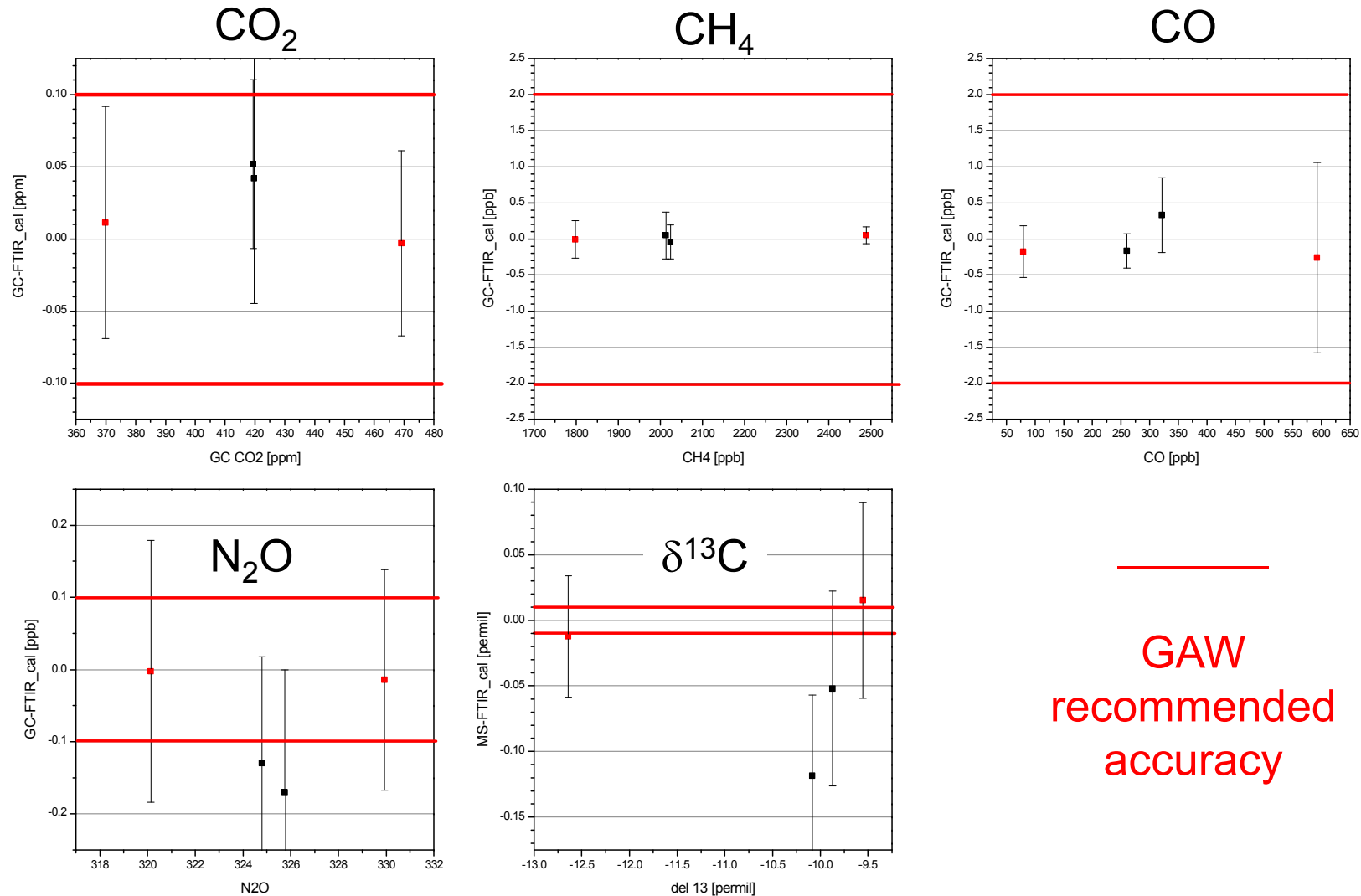
# Calibration: stability

## 100 daily target tank raw measurements



# ICOS reference tank measurements

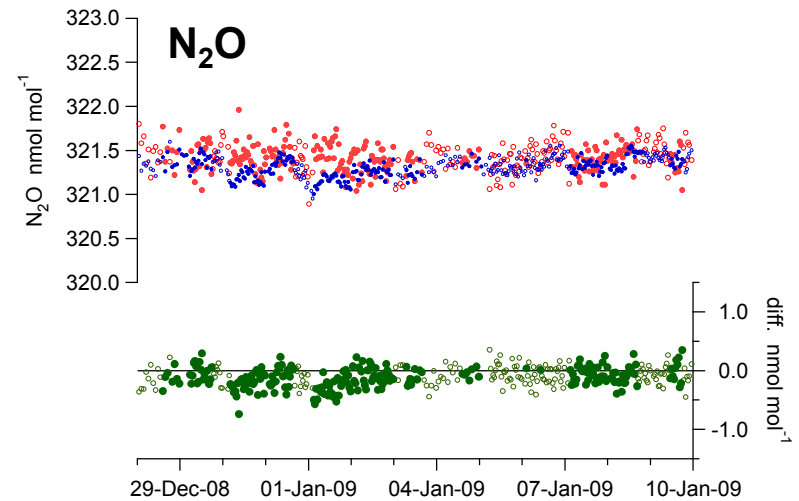
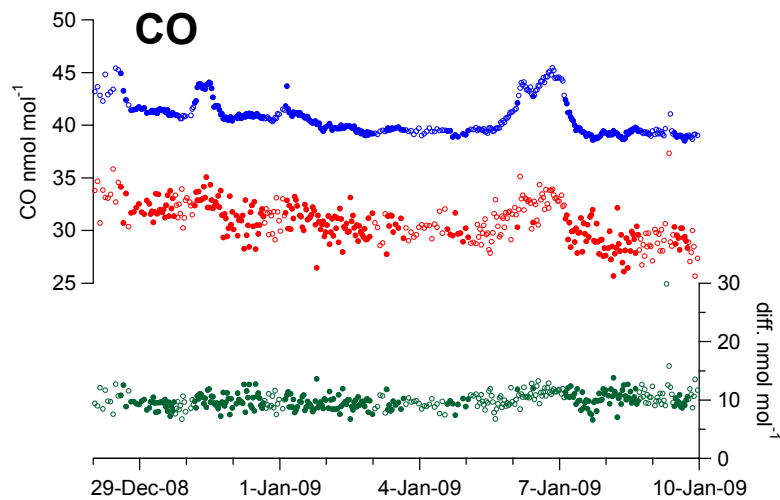
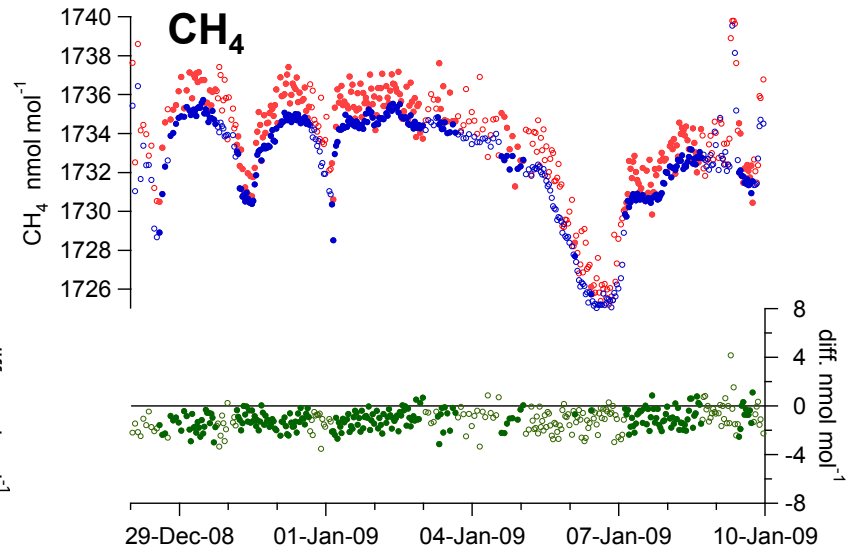
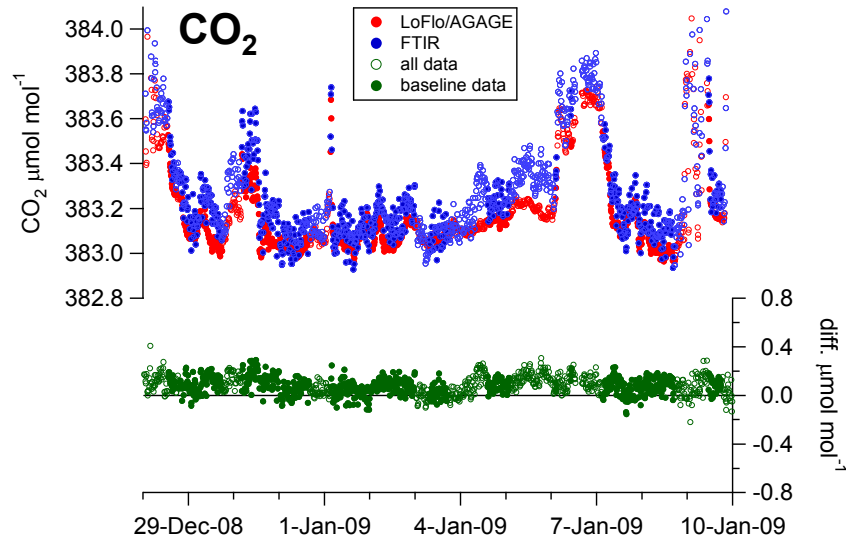
thanks to Sam Hammer, U. Heidelberg



GAW  
recommended  
accuracy

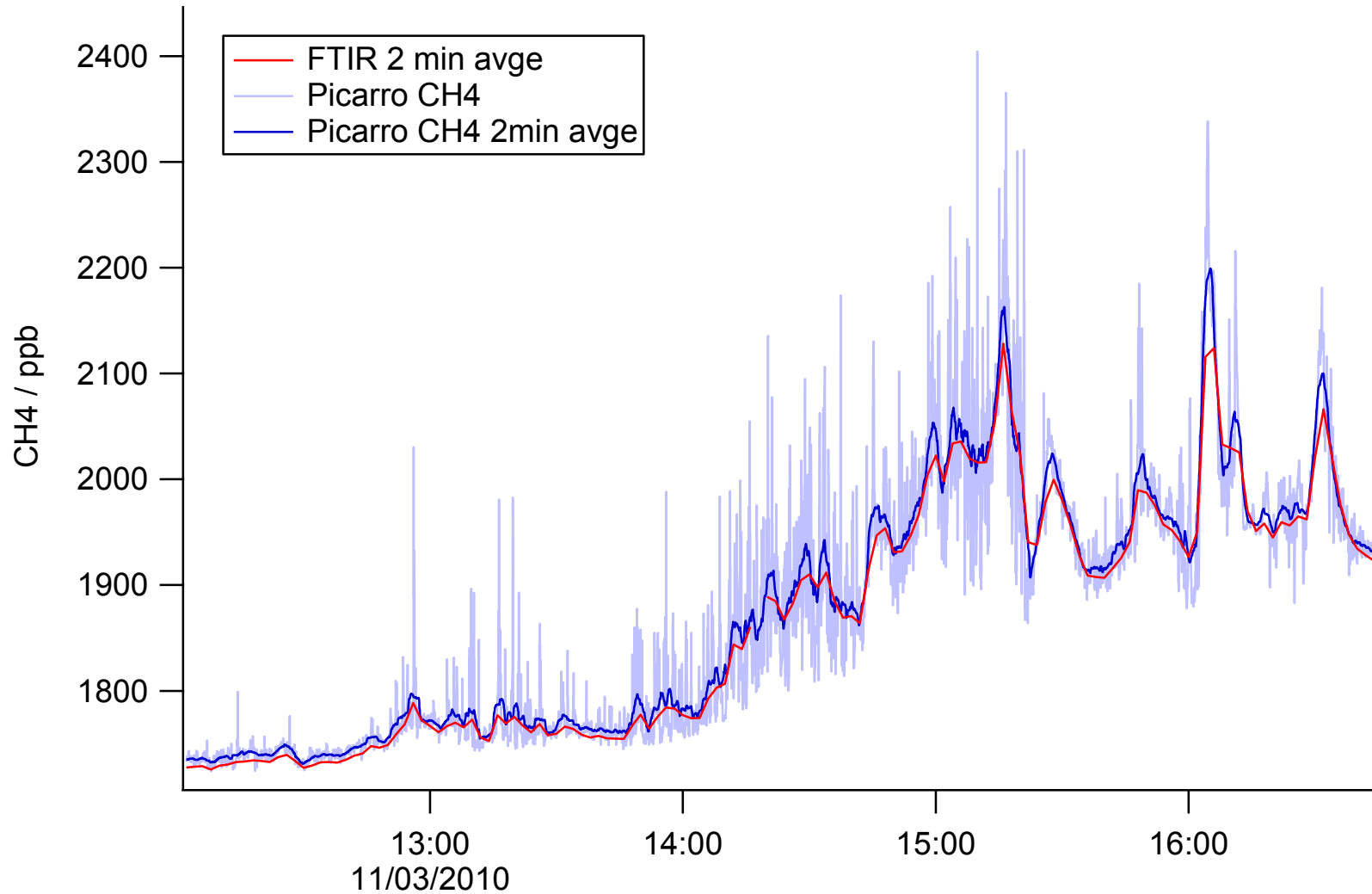
# FTIR vs LoFlo / AGAGE @ Cape Grim

\_\_\_\_\_ FTIR      \_\_\_\_\_ Loflo/AGAGE



# FTIR-Picarro comparison: CH<sub>4</sub>





## GASLAB March 2010






# FTIR vs laser

---

## FTIR

- ◆ Broadband spectrum 
  - Multiple components
  - Save spectra - reanalysable
- ◆ Thermal source - globar 
  - Low brightness
  - => best time resoln. ~ 1 sec
- ◆ Mid IR, atmospheric pressure 
  - Strong absorption
- ◆ Wide spectrum band fit 
  - more spectral information
  - Good stability

## Laser

- ◆ Narrowband, single lines
  - 1-3 species (per laser)
- ◆ Laser source 
  - High brightness
  - => high SNR, fast meas.
- ◆ Near IR, low pressure 
  - Weak absorption
  - MIR lasers becoming available
- ◆ Narrow band fit 
  - less spectral information
  - Drift, more freq. calib.

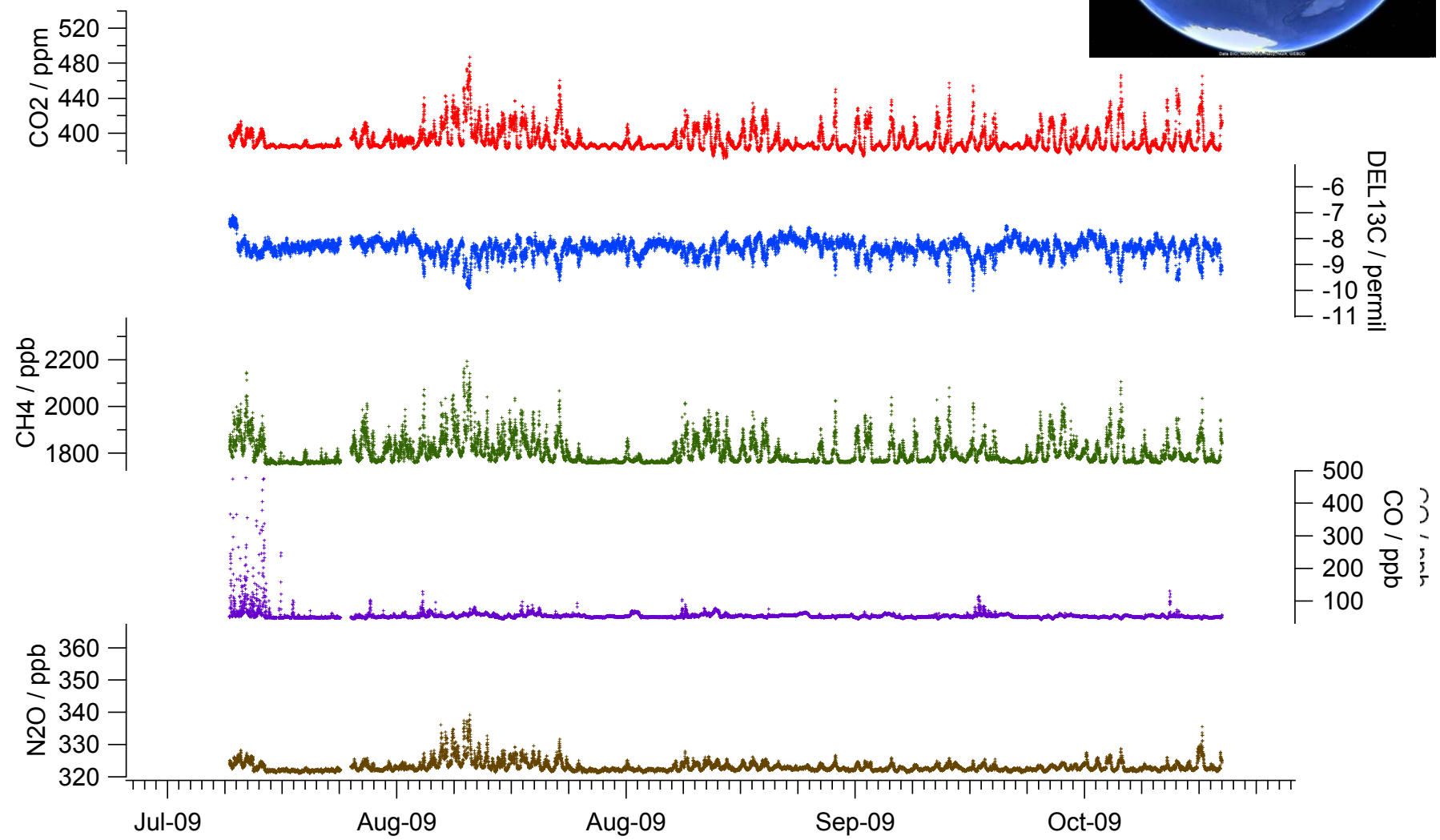
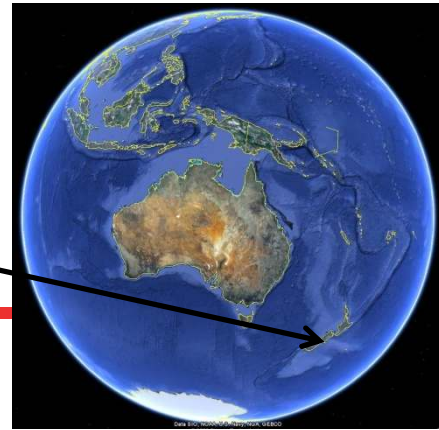
Net result: similar precision

# Applications

---

- ◆ Continuous multispecies trace gas measurement
  - Clean, urban, agricultural air
  - Limestone caves
  - Mobile platforms (e.g. train)
- ◆ Flux measurements (esp. agriculture)
  - Tower profiles
  - Micromet. methods
  - Automated soil flux chambers
- ◆ Open path FTIR spectrometer
  - Tracer methods (multicomponent measurements)

# Long term clean air measurements Lauder NZ



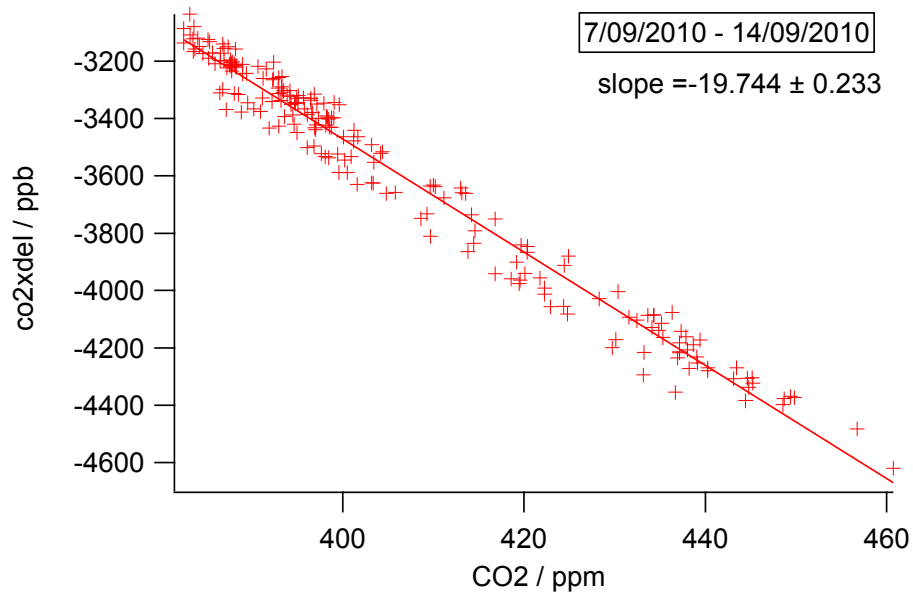


# Trace gas correlations

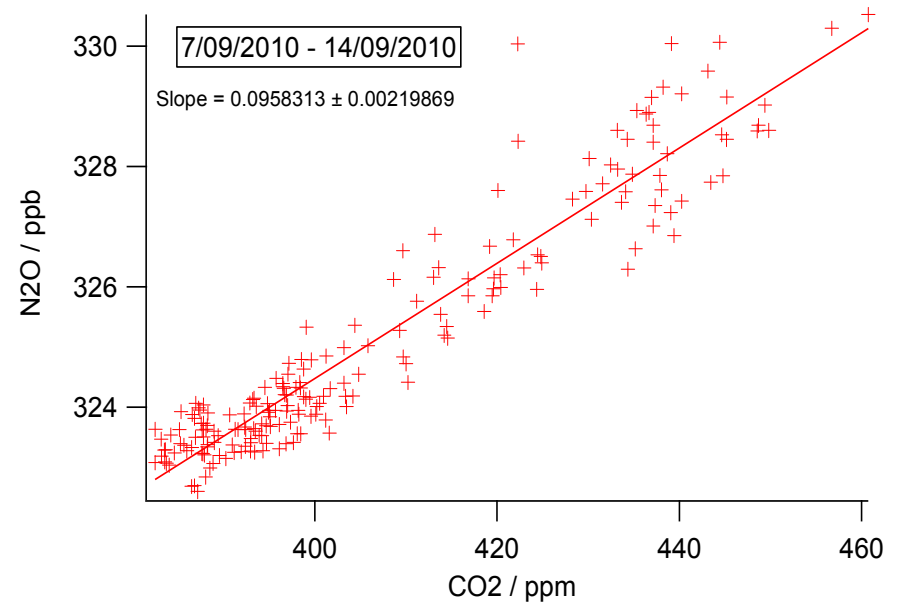
## Utilising the multi-component advantage

---

$\delta^{13}\text{C}.\text{CO}_2$  vs  $\text{CO}_2$

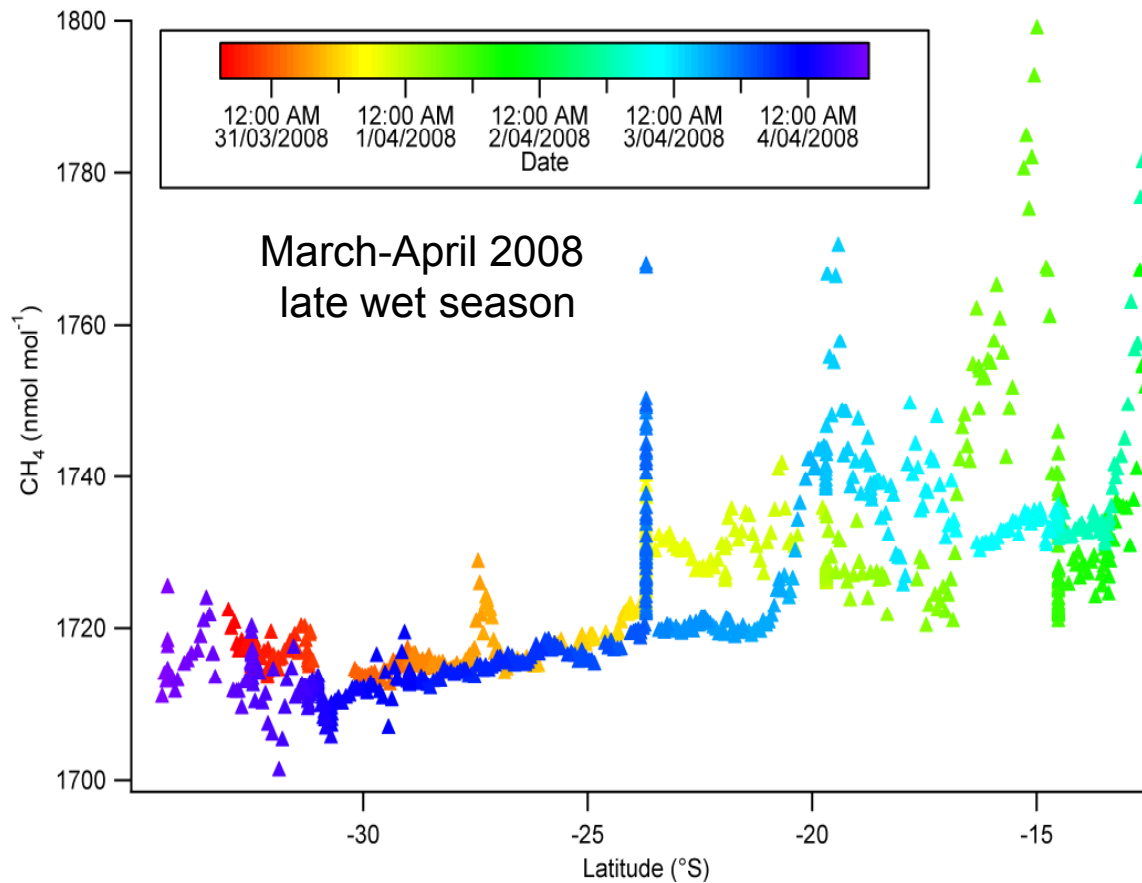


$\text{N}_2\text{O}$  vs  $\text{CO}_2$

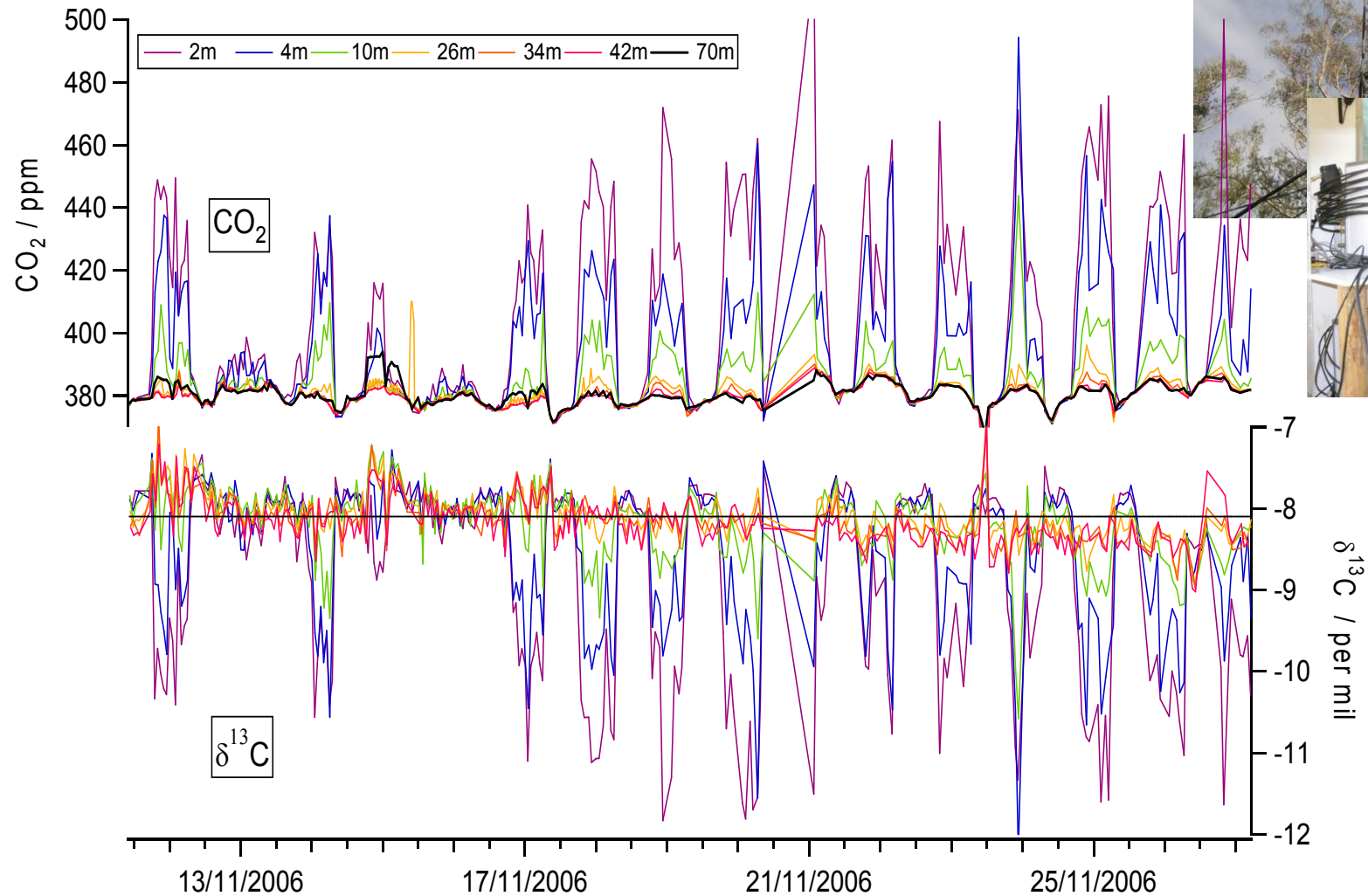


# Mobile measurements: Transects of the Australian continent

Enhanced methane concentrations in  
the tropical wet season

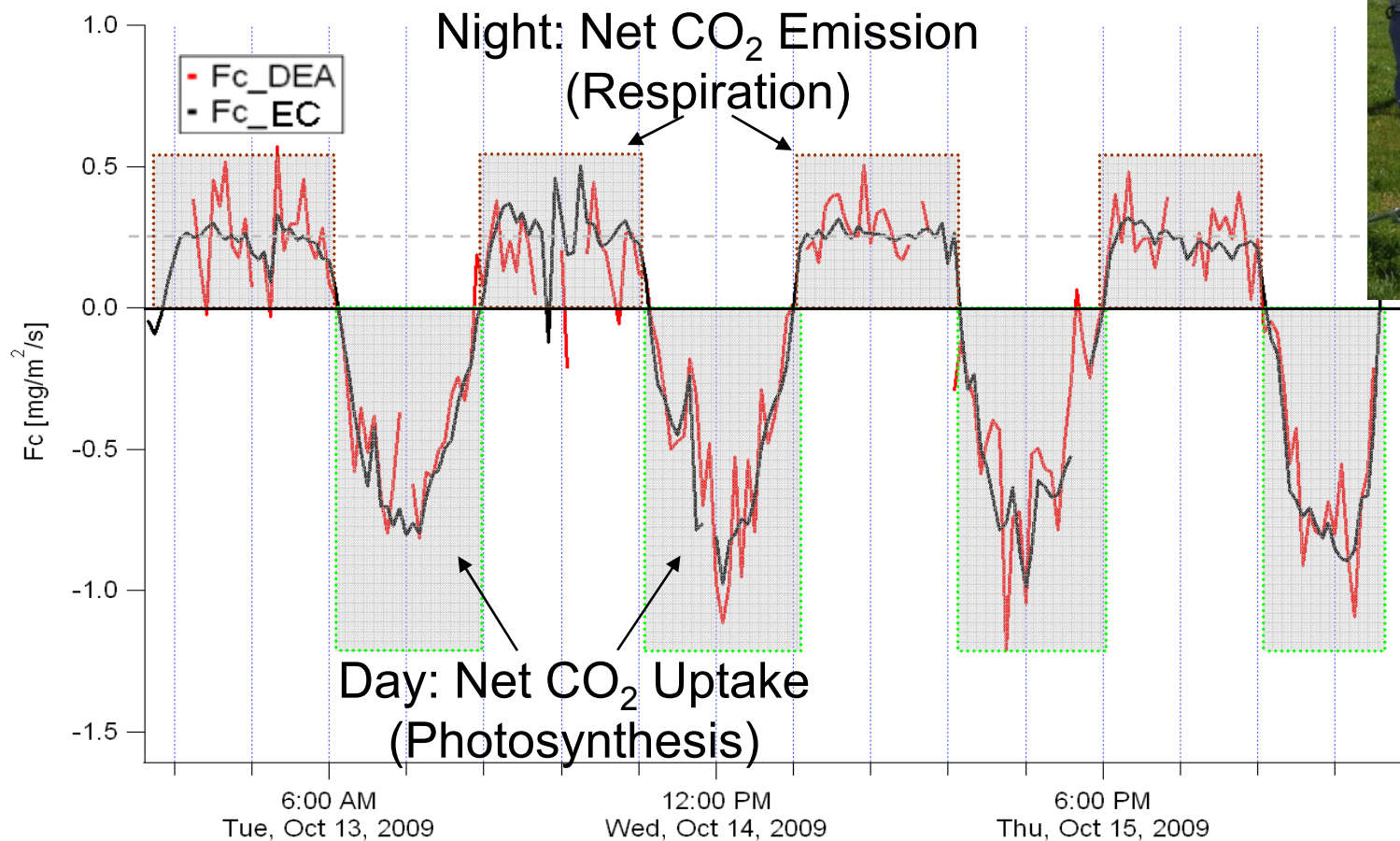
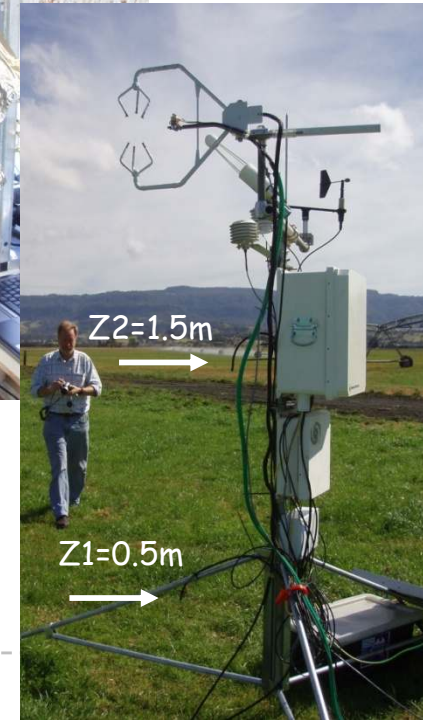


# Forests: using vertical profiles of trace gases and isotopic fractionation to partition C and H<sub>2</sub>O exchange



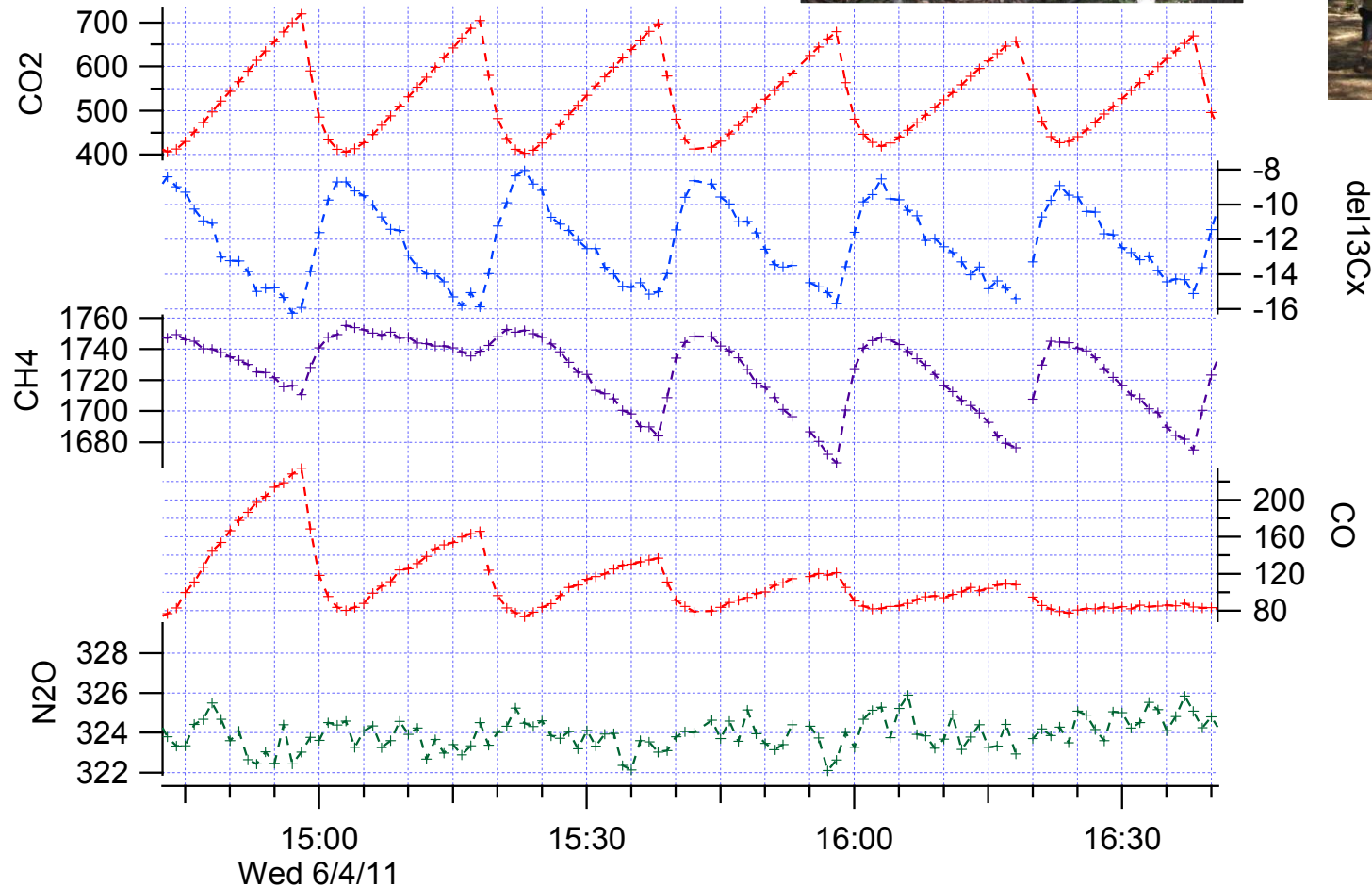
# Fluxes: flux gradient and eddy accumulation methods

Here: Disjunct Eddy Accumulation





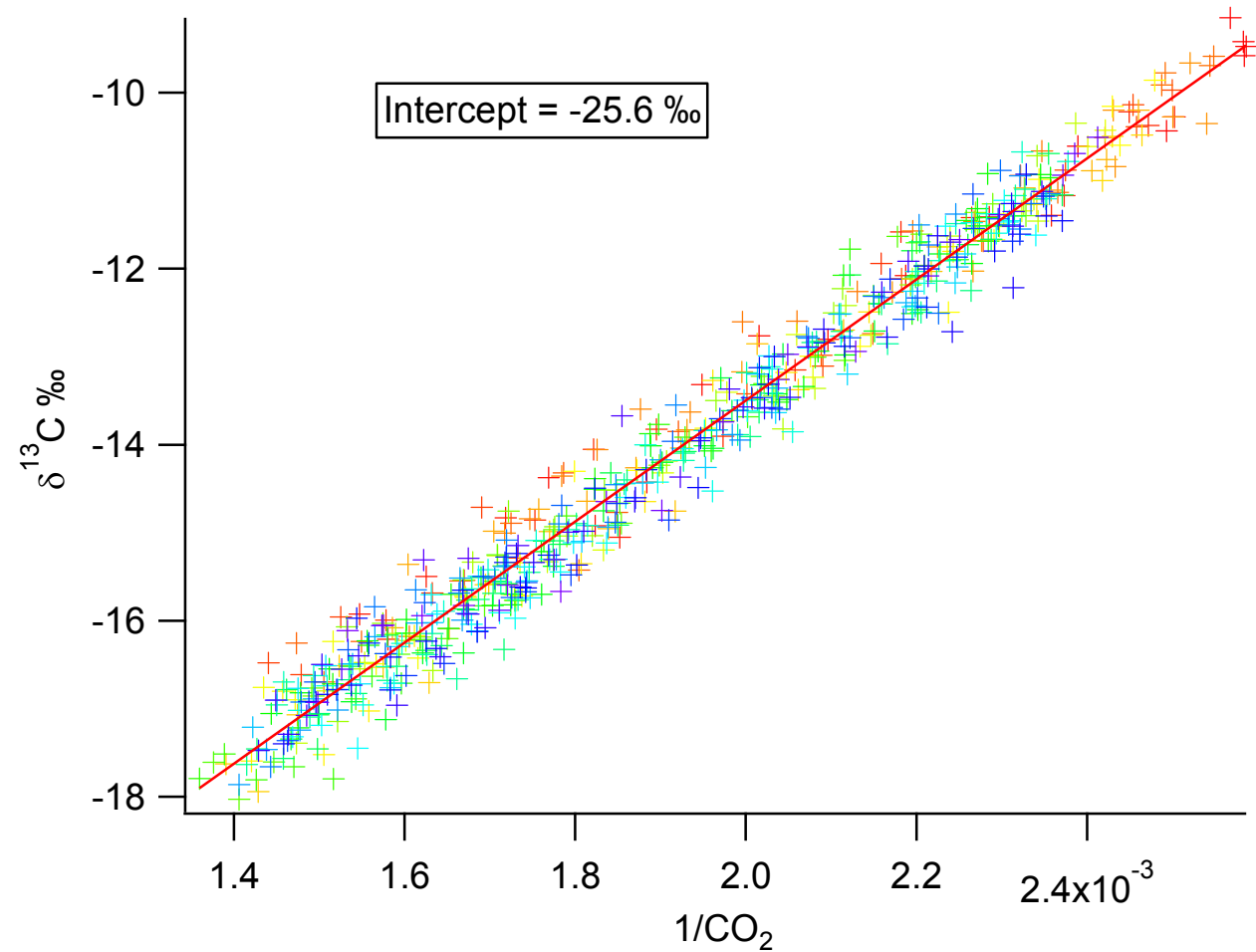
# Chamber fluxes: Forest soils, agriculture



Steve Livesley, Stefan Arndt, Benedikt Fest, Nina Hinko-Najera, Uni Melbourne

# Keeling plot, all chambers, 12 hours

---



# Summary: FTIR analyser

---

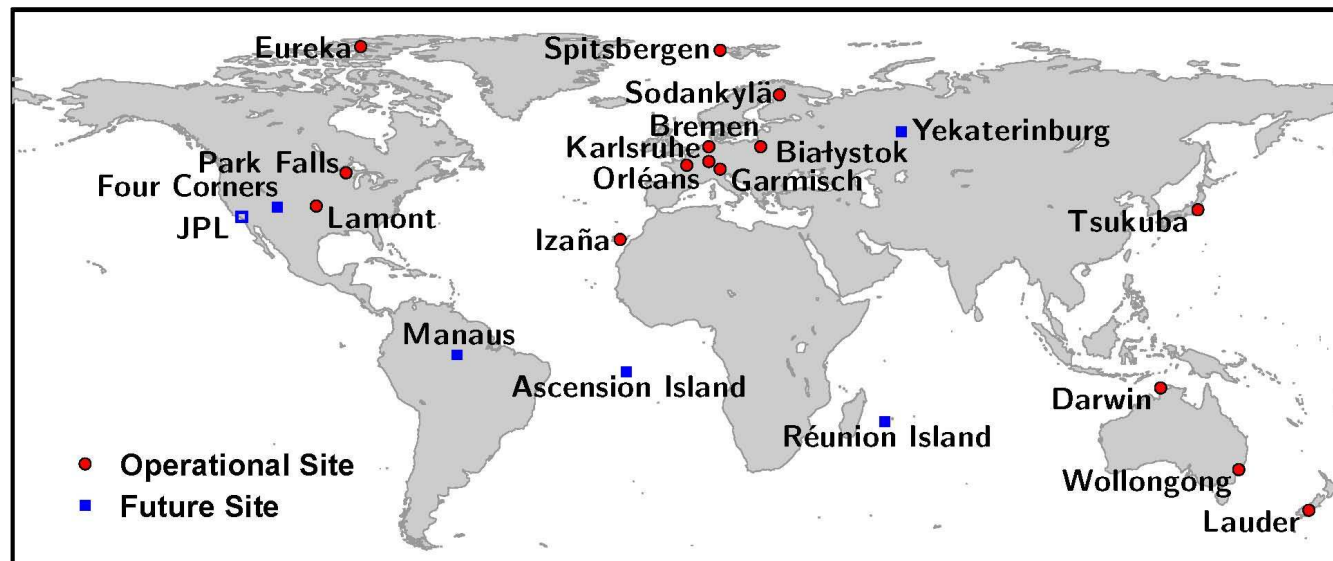
- ◆ Continuous, simultaneous, multispecies analyser
- ◆  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\delta^{13}\text{C}$
- ◆ High precision and accuracy
- ◆ Low maintenance
- ◆ Now available from Ecotech, Australia
  - [www.ecotech.com](http://www.ecotech.com)
  - [www.knj-eng.co.kr](http://www.knj-eng.co.kr) in Korea

... now to TCCON...

# TCCON: Total Carbon Column Observing Network



- ◆ Remote sensing of total column  $CO_2$ ,  $CH_4$ ,  $N_2O$ ,  $CO$  ...
  - Direct-sun solar absorption spectroscopy in the near IR
- ◆ Derive column average dry air mole fractions (e.g.  $X_{CO_2}$ )
  - Using column  $O_2$  as internal standard
- ◆ Calibrated against NOAA/WMO in situ reference scales
- ◆ Currently ~15 sites





# Why TCCON?

---

- ◆ Total columns measurements :
  - Are less susceptible to local sources and sinks than in situ
  - Are less sensitive to vertical transport errors in models
    - Do not alias diurnal and seasonal boundary layer transport into the measured column amount
  - Can be used for satellite validation
    - GOSAT
    - OCO-2
    - CarbonSat

# Southern Hemisphere & Asia TCCON stations

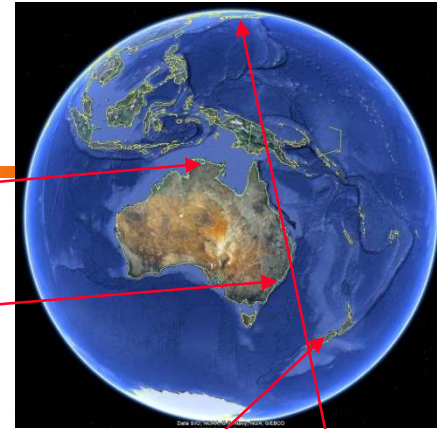
Darwin



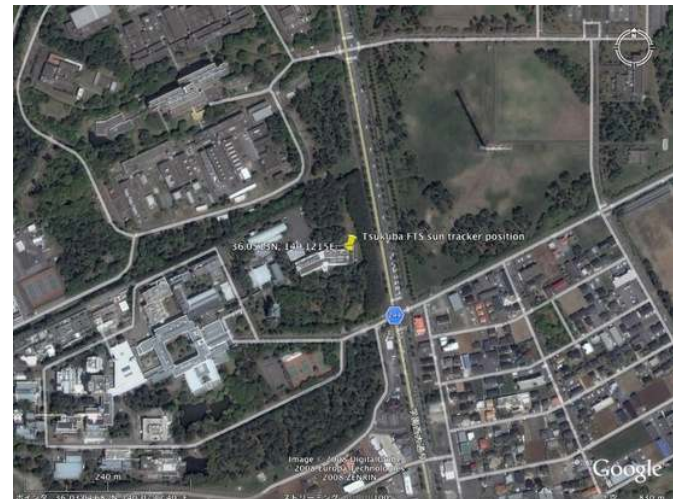
Wollongong



Lauder



Tsukuba



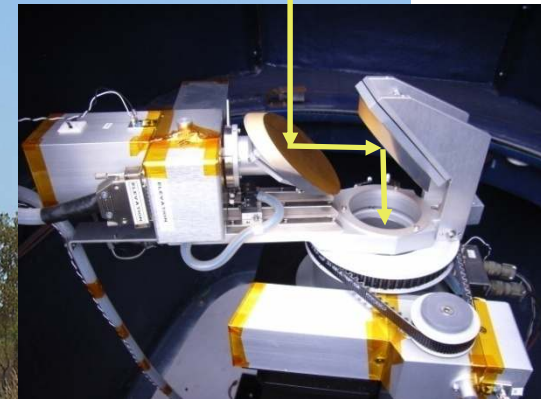
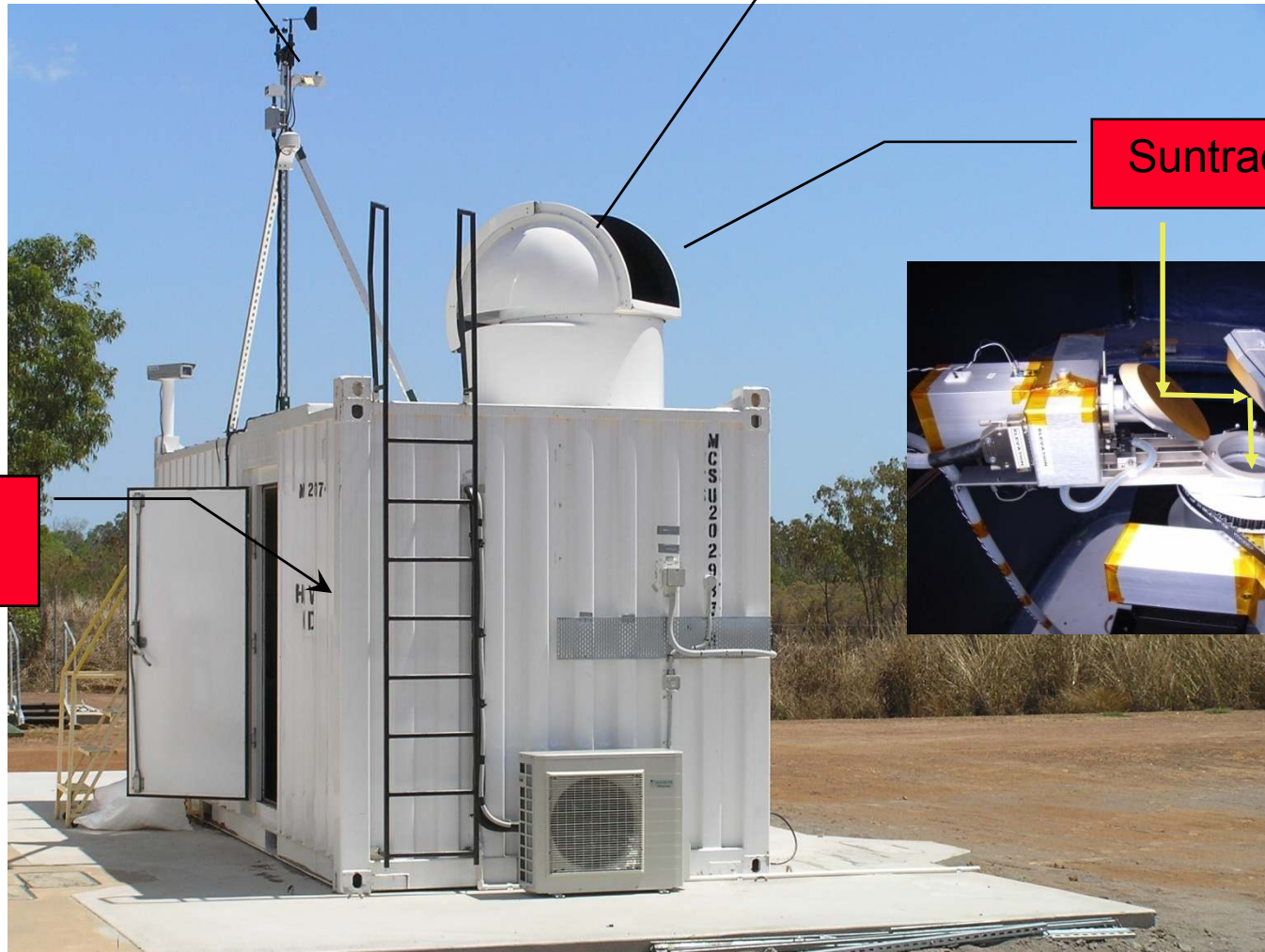
# Darwin TCCON container

Weather station

Protective Dome

Suntracker

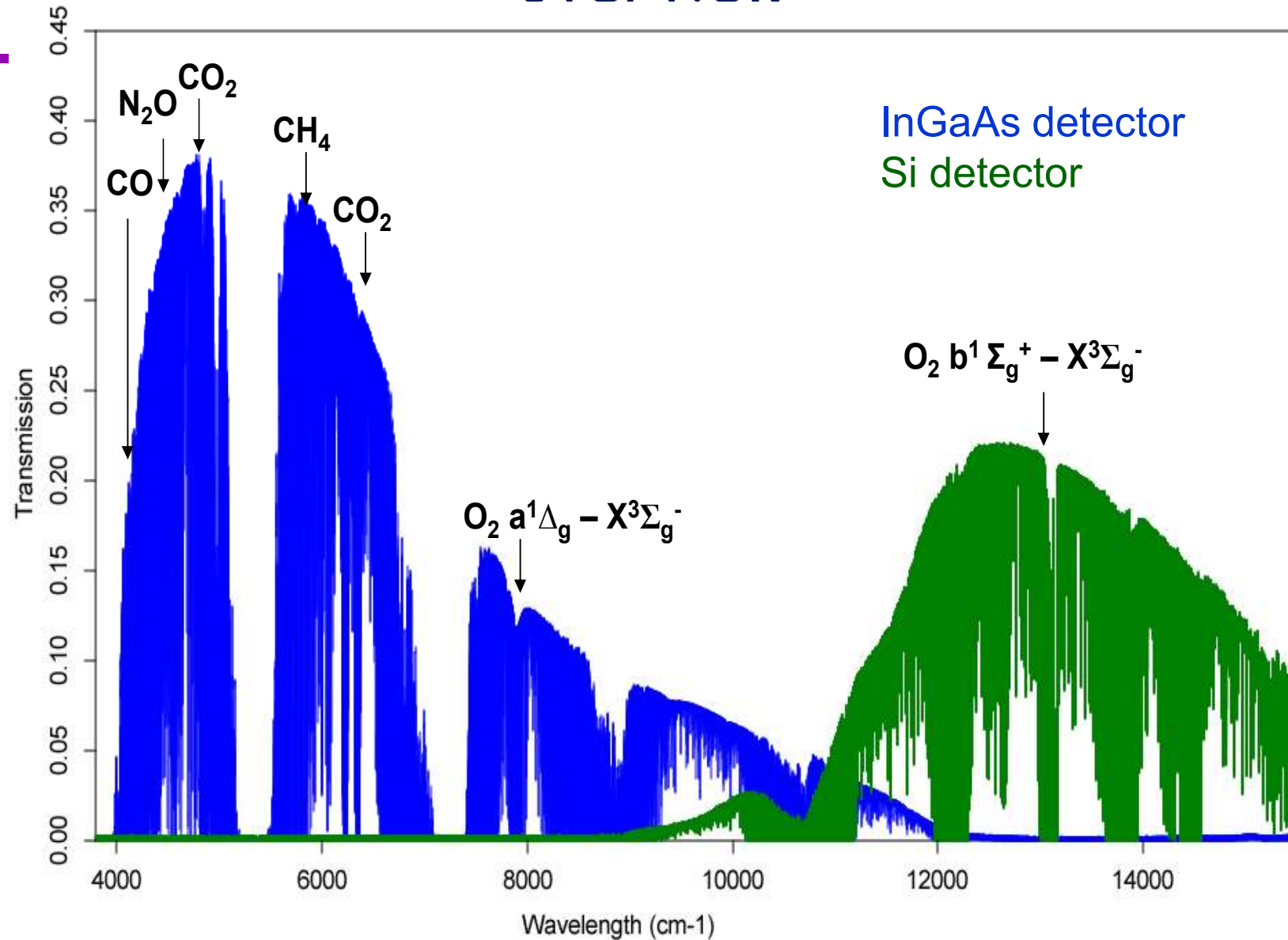
Bruker IFS125





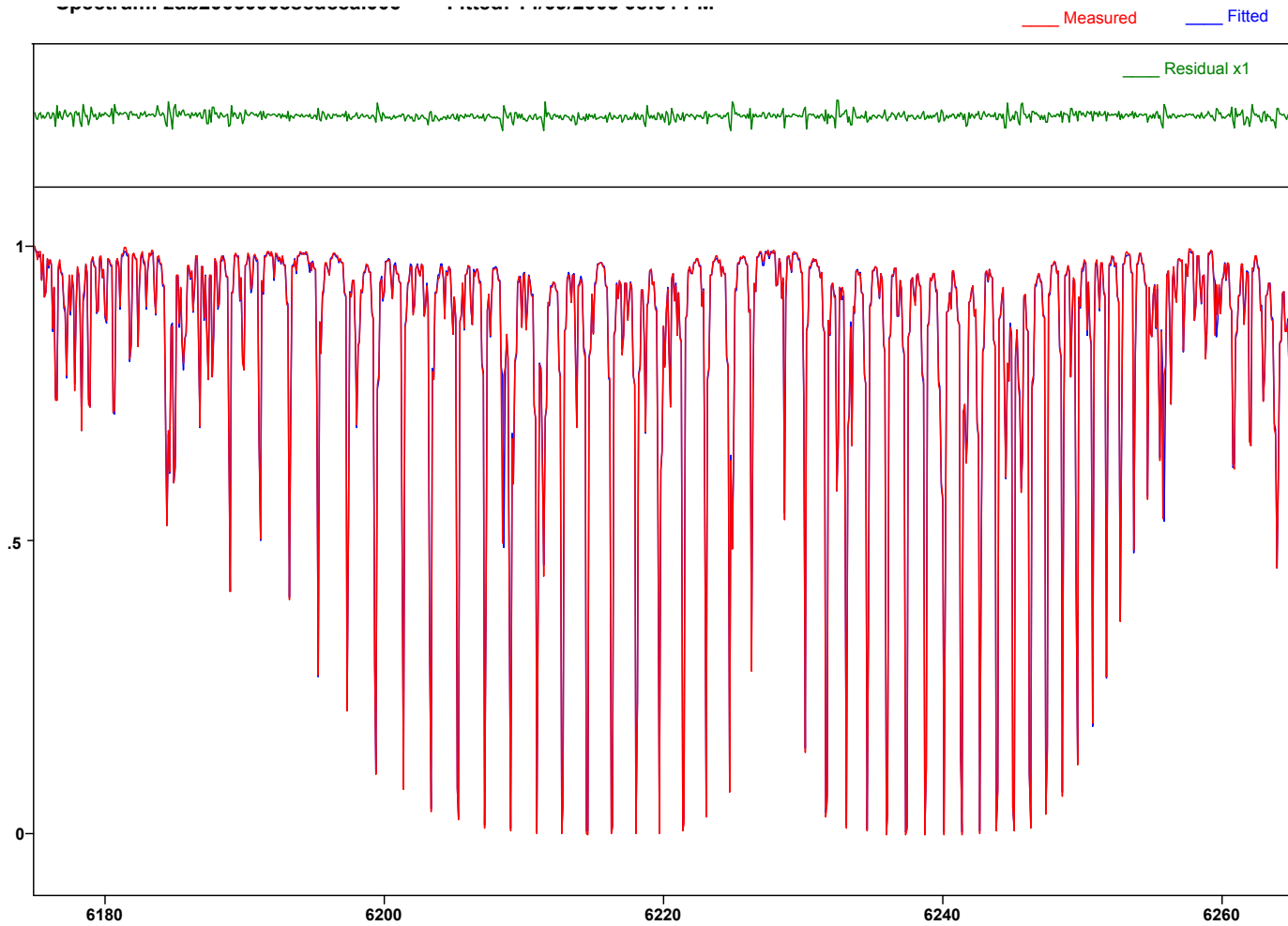


# Near IR solar absorption spectrum overview



# Analysis by spectrum fitting

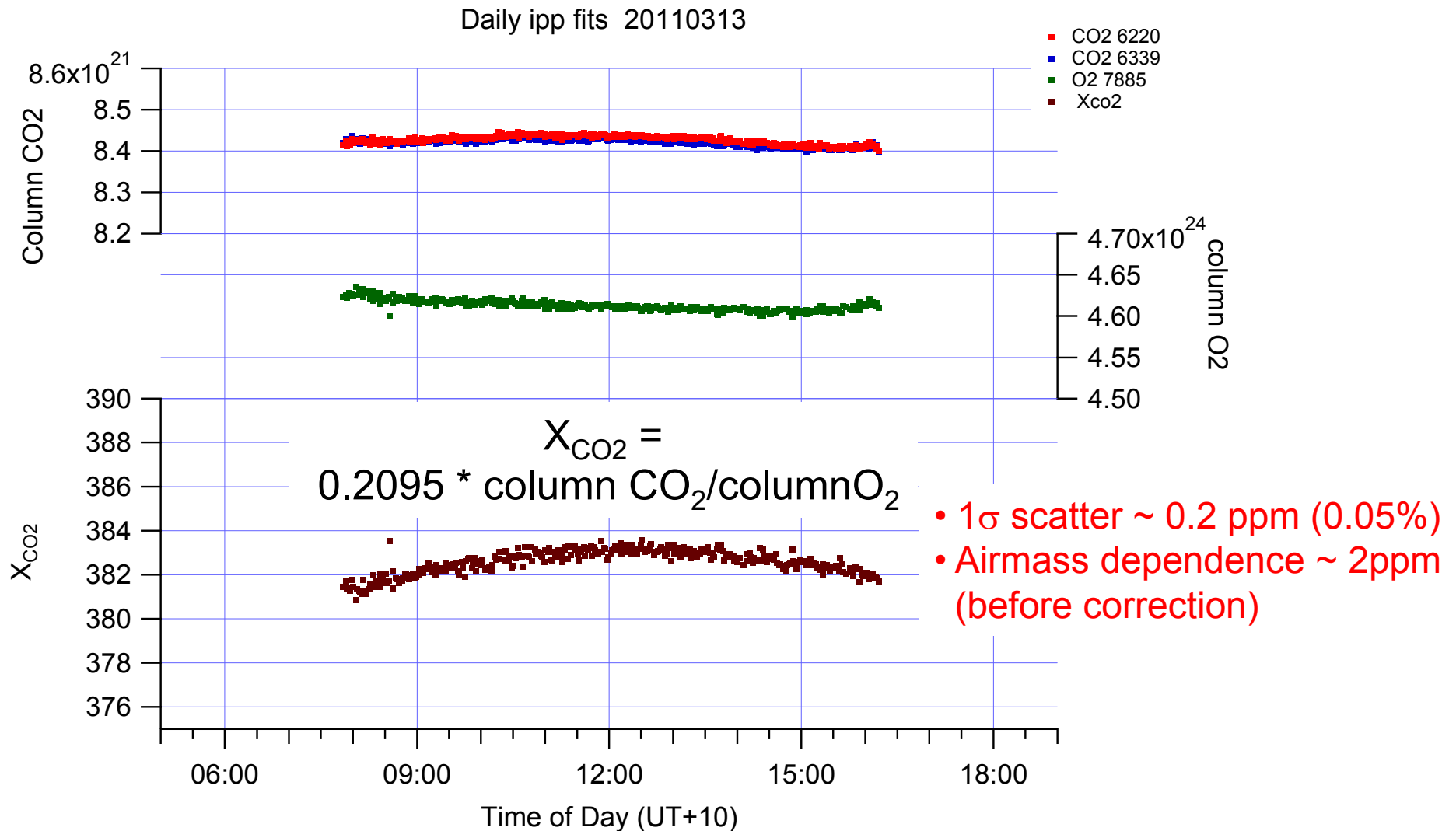
e.g. 6230  $\text{cm}^{-1}$   $\text{CO}_2$  band



co2 = 8.16E+21 (1.09E+20)

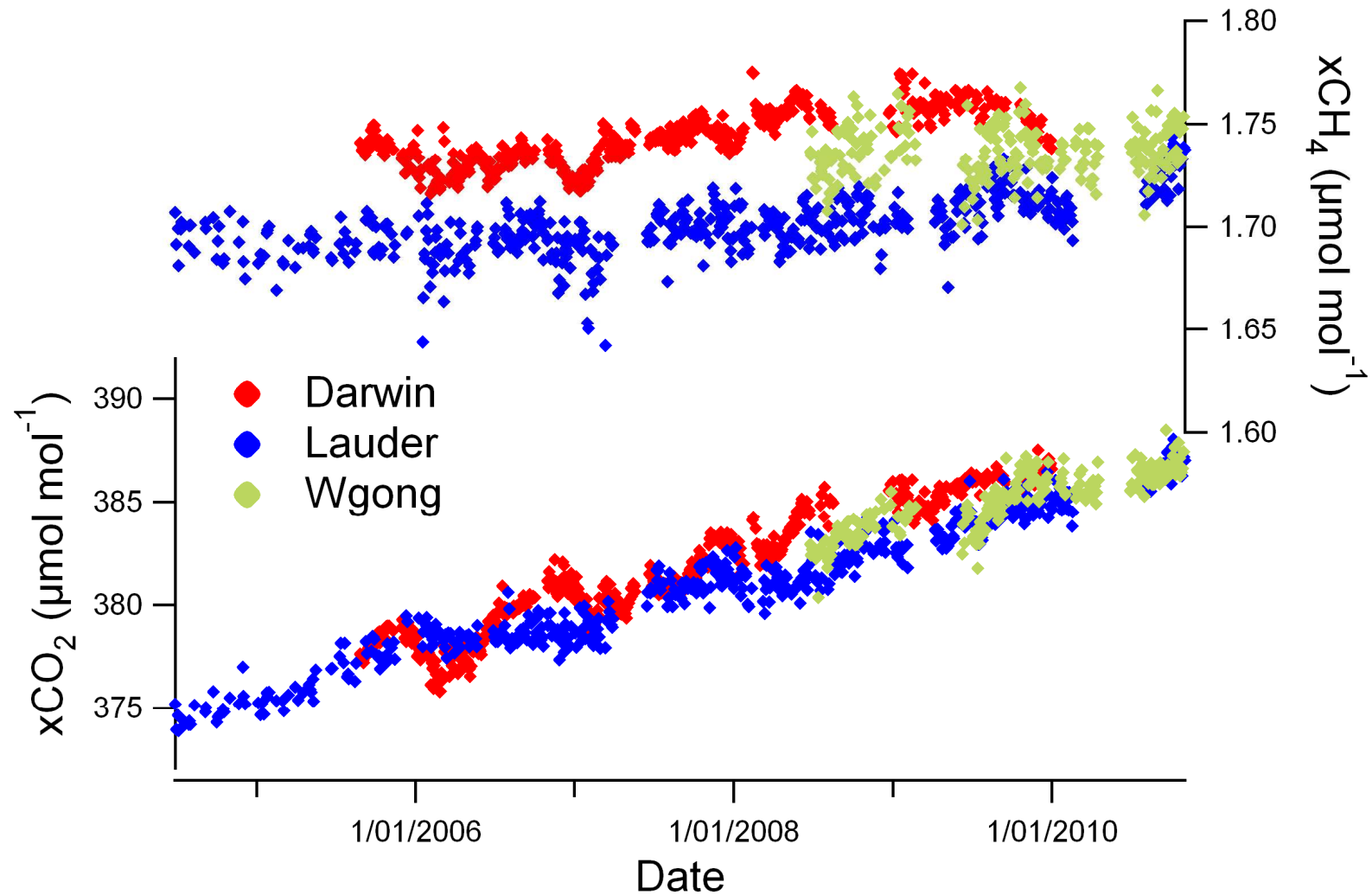
SZA: 73.904 Zobs: .03

# Raw daily column measurements Wollongong, clear sky day



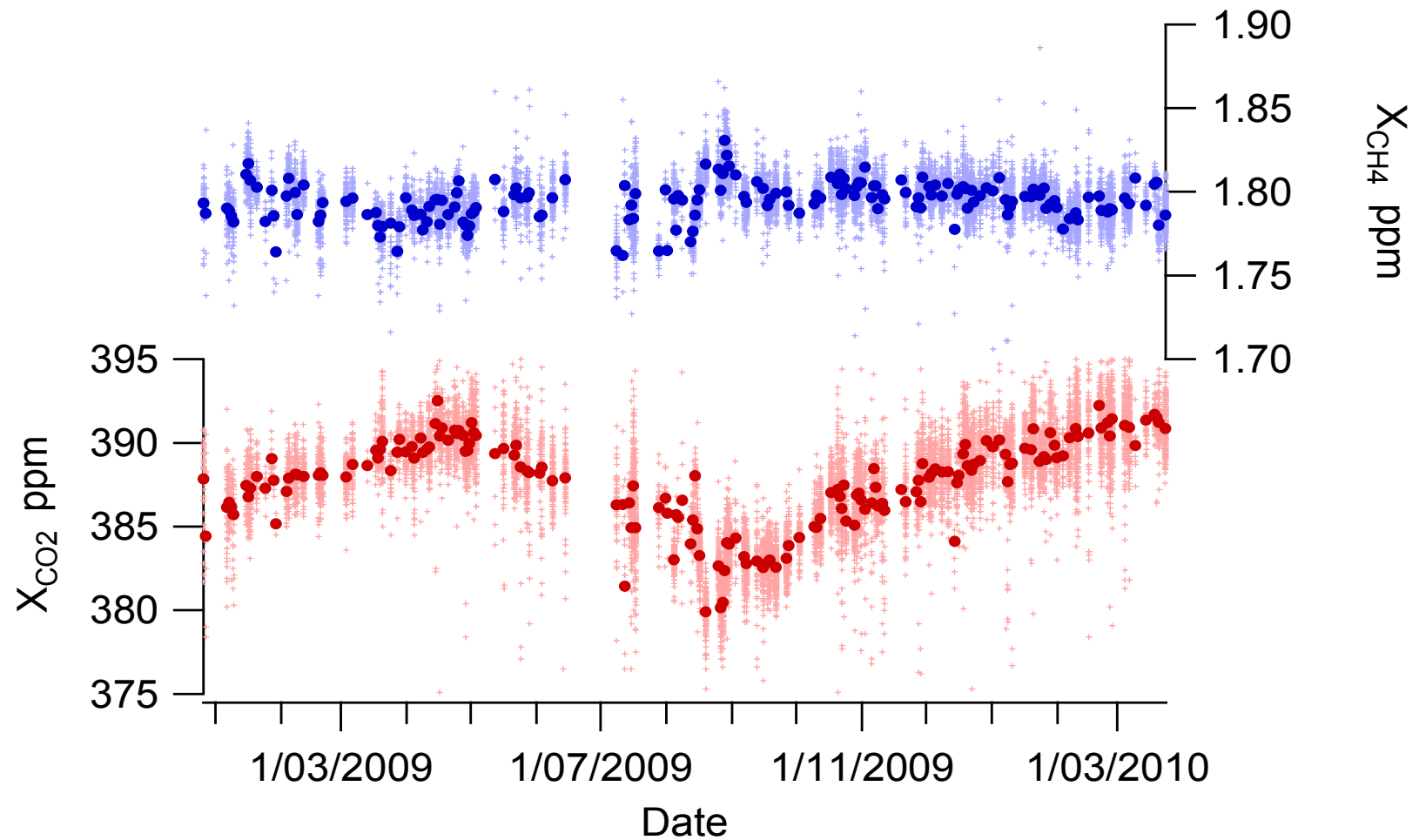


# The TCCON SH data set





# TCCON data - Tsukuba



# TCCON precision, accuracy and calibration

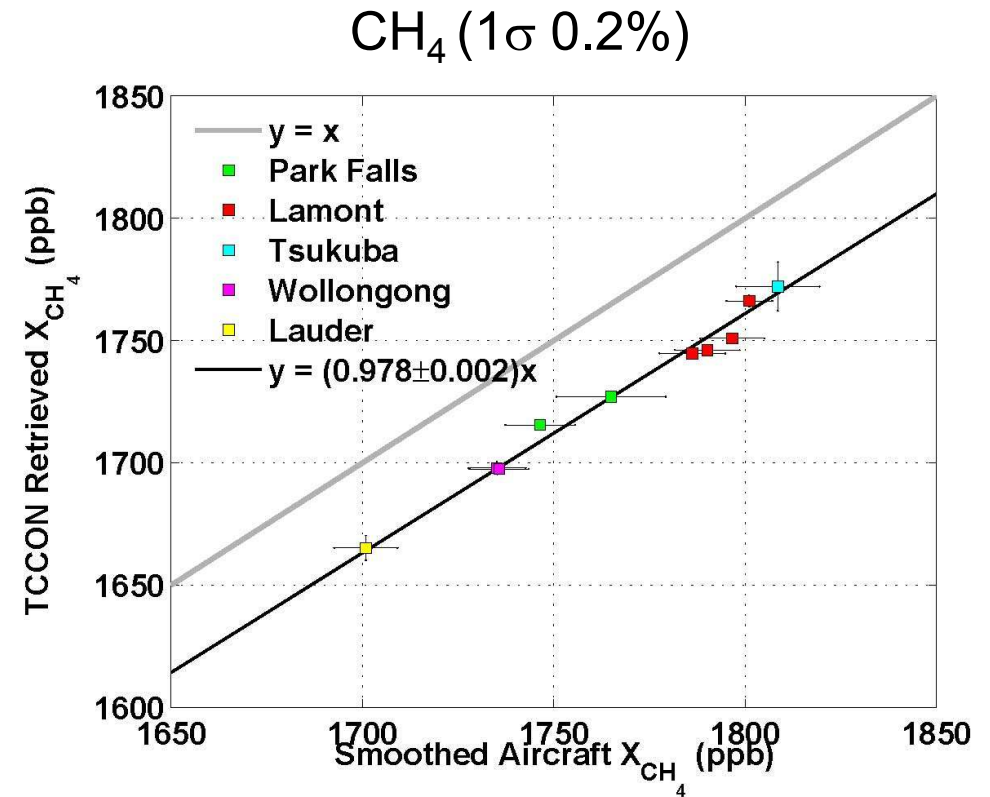
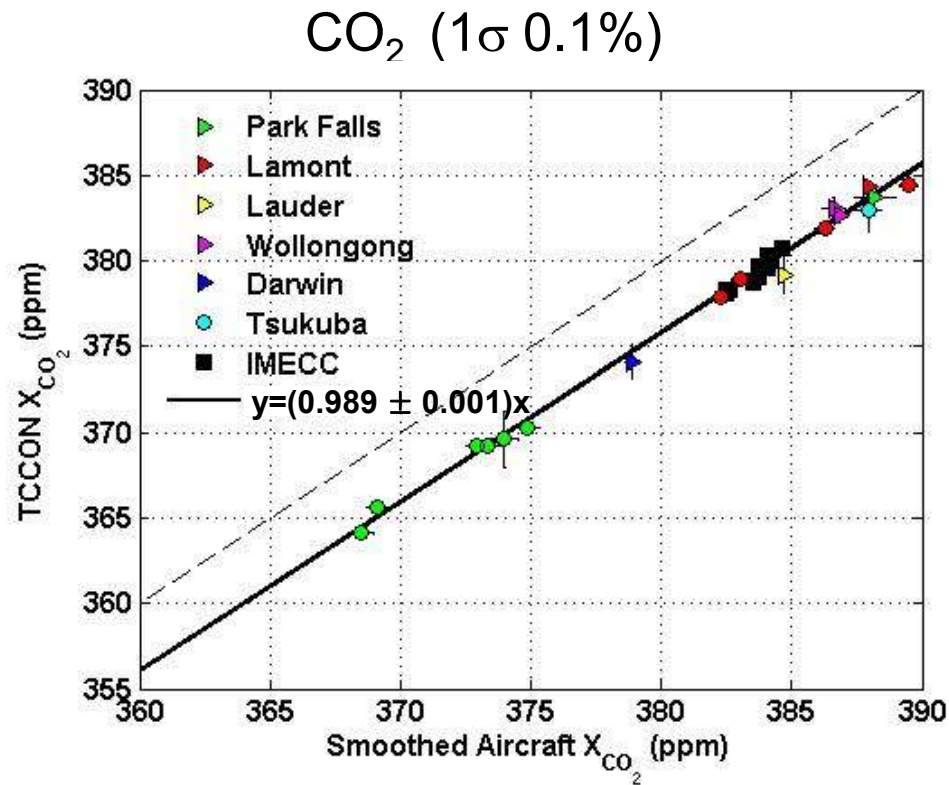
## CO<sub>2</sub>

---

- ◆ *Precision* (1- $\sigma$  repeatability) achieved: <0.2 ppm
- ◆ *"Absolute" calibration* by comparison of TCCON total columns with integrated aircraft in situ profiles using WMO-calibrated instruments
  - eg. HIPPO, TWP-ICE, IMECC
  - Extrapolated to top and bottom of the atmosphere
- ◆ *Accuracy* achieved: ~ 0.4 ppm (1- $\sigma$ ) across the network
  - This accuracy (0.1%) is unprecedented in remote sensing
  - Measurements and analysis standardised to avoid bias
  - Ongoing work to improve:
    - Instrumentation, software, spectroscopy



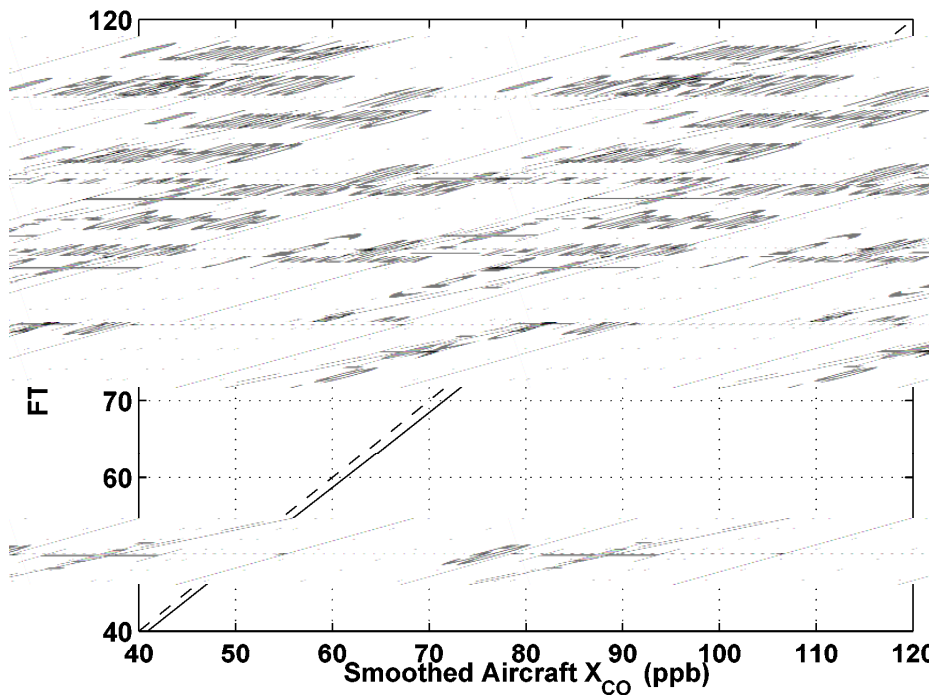
# TCCON calibration against aircraft profiles $\text{CO}_2$ and $\text{CH}_4$



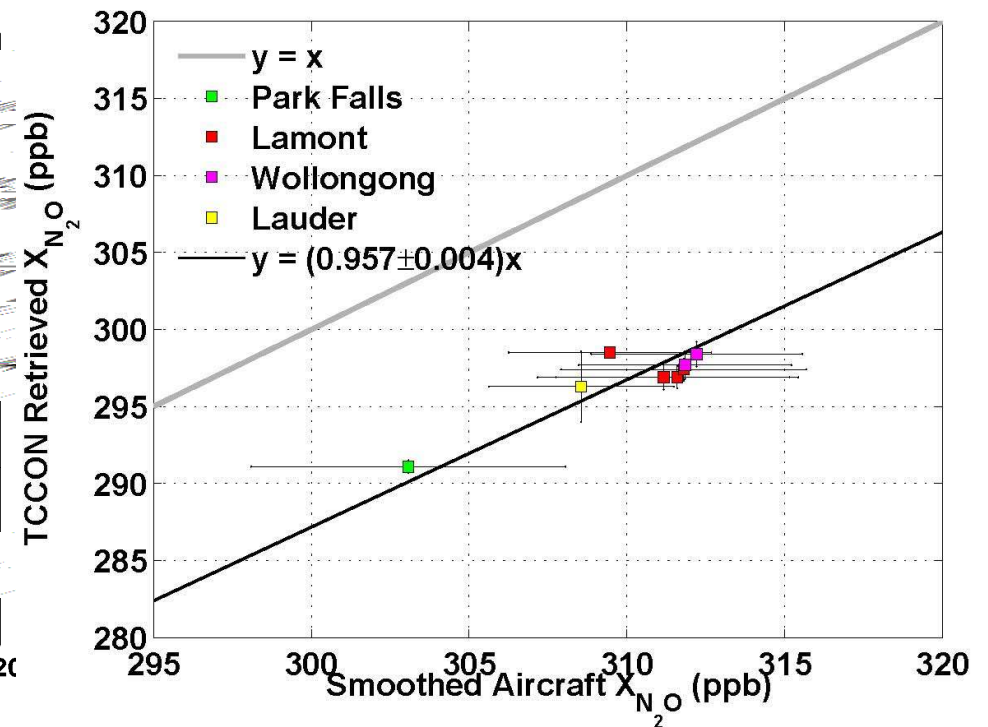
- ◆ Further detail:  
Wunch, D., et al. (2010), Calibration of the Total Carbon Column Observing Network using Aircraft Profile Data, *Atmos. Meas. Techn.*, 3, 1351-1362.

# TCCON calibration against aircraft profiles CO and N<sub>2</sub>O

CO (1 $\sigma$  2%)



N<sub>2</sub>O (1 $\sigma$  0.4%)



- ◆ Further detail:  
Wunch, D., et al. (2010), Calibration of the Total Carbon Column Observing Network using Aircraft Profile Data, *Atmos. Meas. Techn.*, 3, 1351-1362.



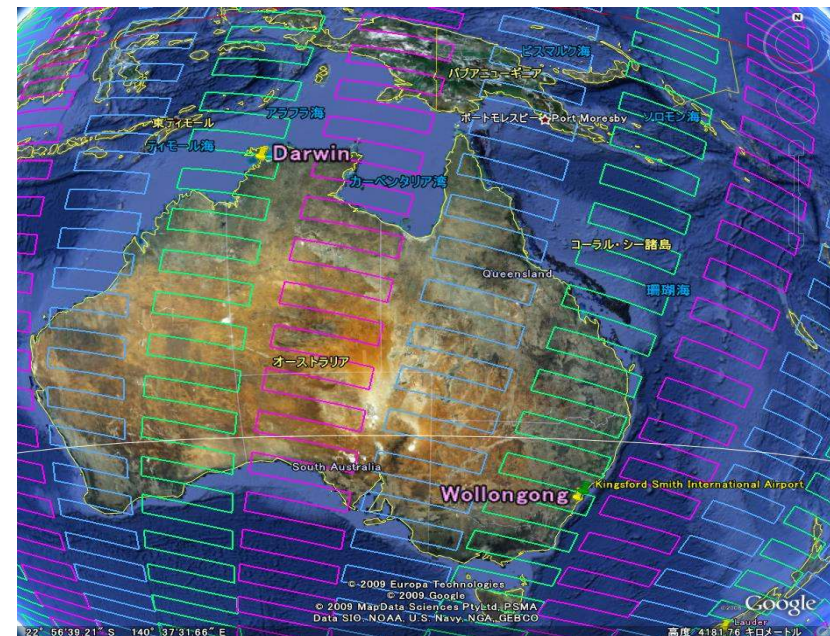
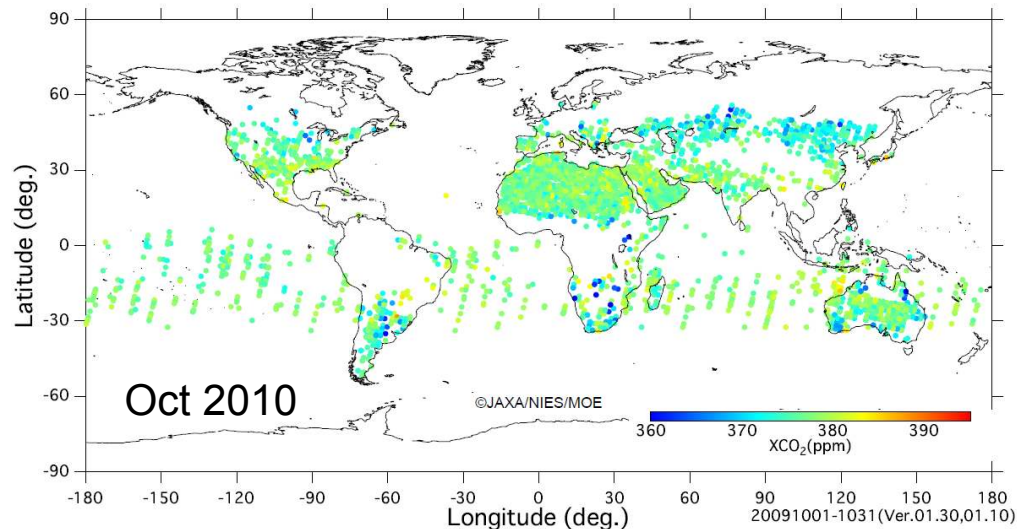
# GOSAT

## Greenhouse gas Observing SATellite

- ◆ FTIR spectrometer, backscattered solar NIR
- ◆ CO<sub>2</sub>, CH<sub>4</sub> analysis
- ◆ Launched Jan 2009 by JAXA, Japan
- ◆ 3 day repeat orbit
- ◆ Validation by TCCON overpasses

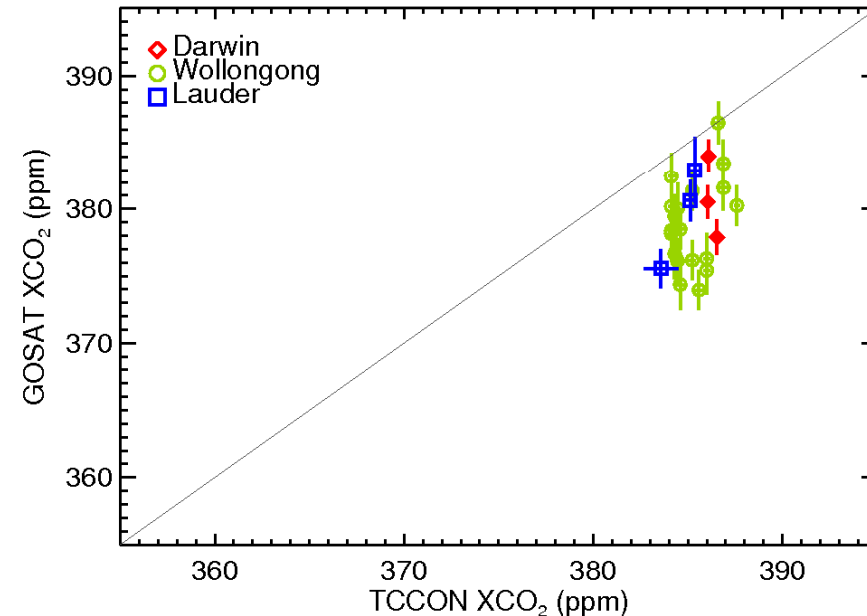
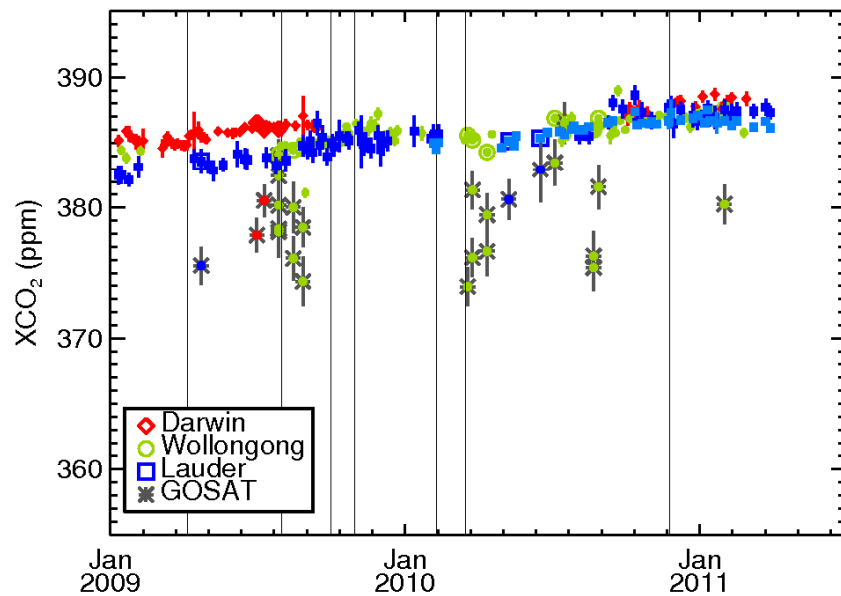


GOSAT (Japan)  
Launched Jan 2009



# GOSAT-TCCON SH validation $\text{CO}_2$

- ◆ TCCON : 1-2 hour average around GOSAT overpasses
- ◆ GOSAT:  $2 \times 2^\circ$  region around TCCON sites



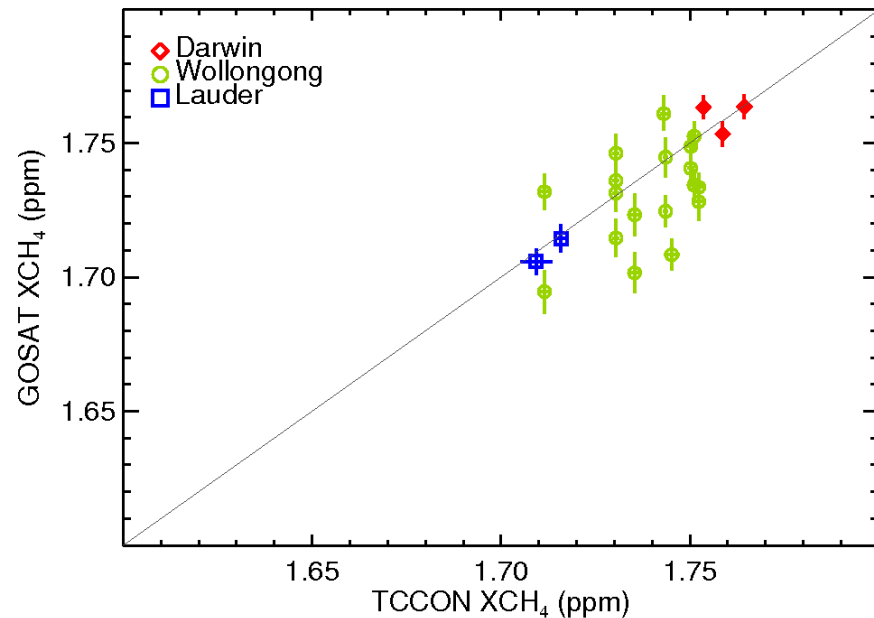
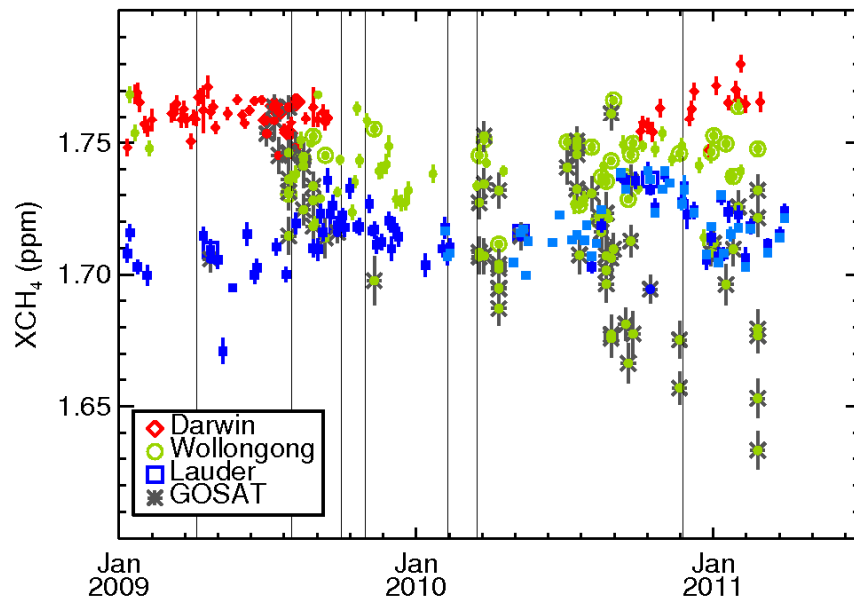
Also GOSAT retrievals from ACOS, SRON

- lower bias
- AOD and scattering corrections

# GOSAT-TCCON SH validation

## CH<sub>4</sub>

- ◆ TCCON : 1-2 hour average around GOSAT overpasses
- ◆ GOSAT: 2 x 2° region around TCCON sites





# Thank you



## FTIR Analyser

UoW: Nick Deutscher, Chris Caldow, Graham Kettlewell, Martin Riggenbach

CSIRO: Paul Fraser, Paul Krummel, Marcel Vanderschoot, Zoe Loh

U. Heidelberg: Sam Hammer, Ingeborg Levin

## TCCON

UoW: Nick Deutscher, Ronald Macatangay

NIWA, NZ: Vanessa Sherlock

Cal Tech: Debra Wunch, Paul Wennberg