

An FTIR analyser for simultaneous high  
precision measurements of  
 $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  and  $\delta^{13}\text{C}$  in  $\text{CO}_2$

Comparison with LoFlo and AGAGE  
measurements at Cape Grim

... and (if there's time) other applications

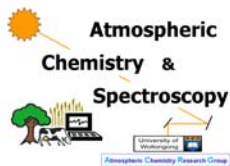
---

**David Griffith, Nicholas Deutscher,**

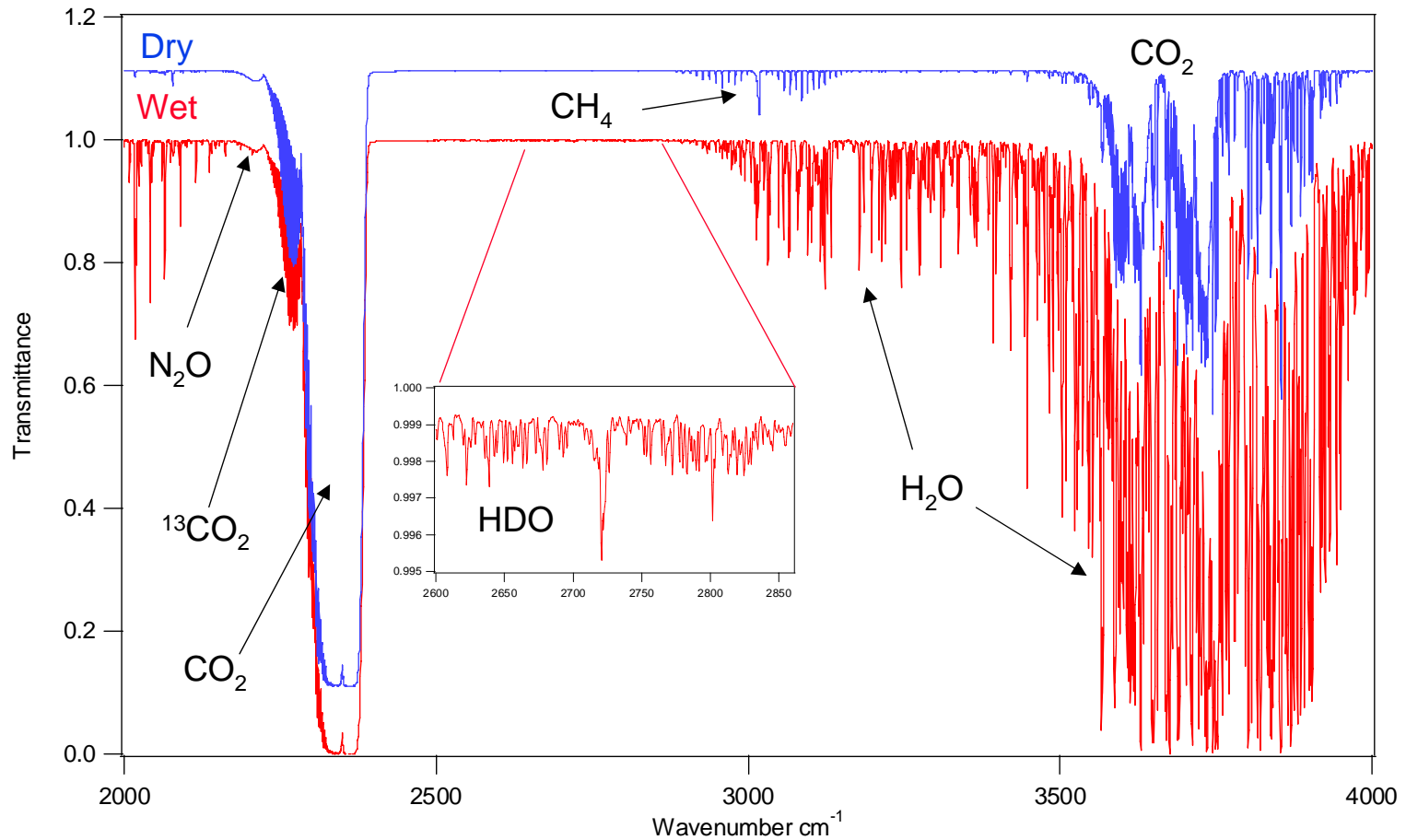
University of Wollongong, Australia

**Paul Fraser, Paul Krummel, Paul Steele**

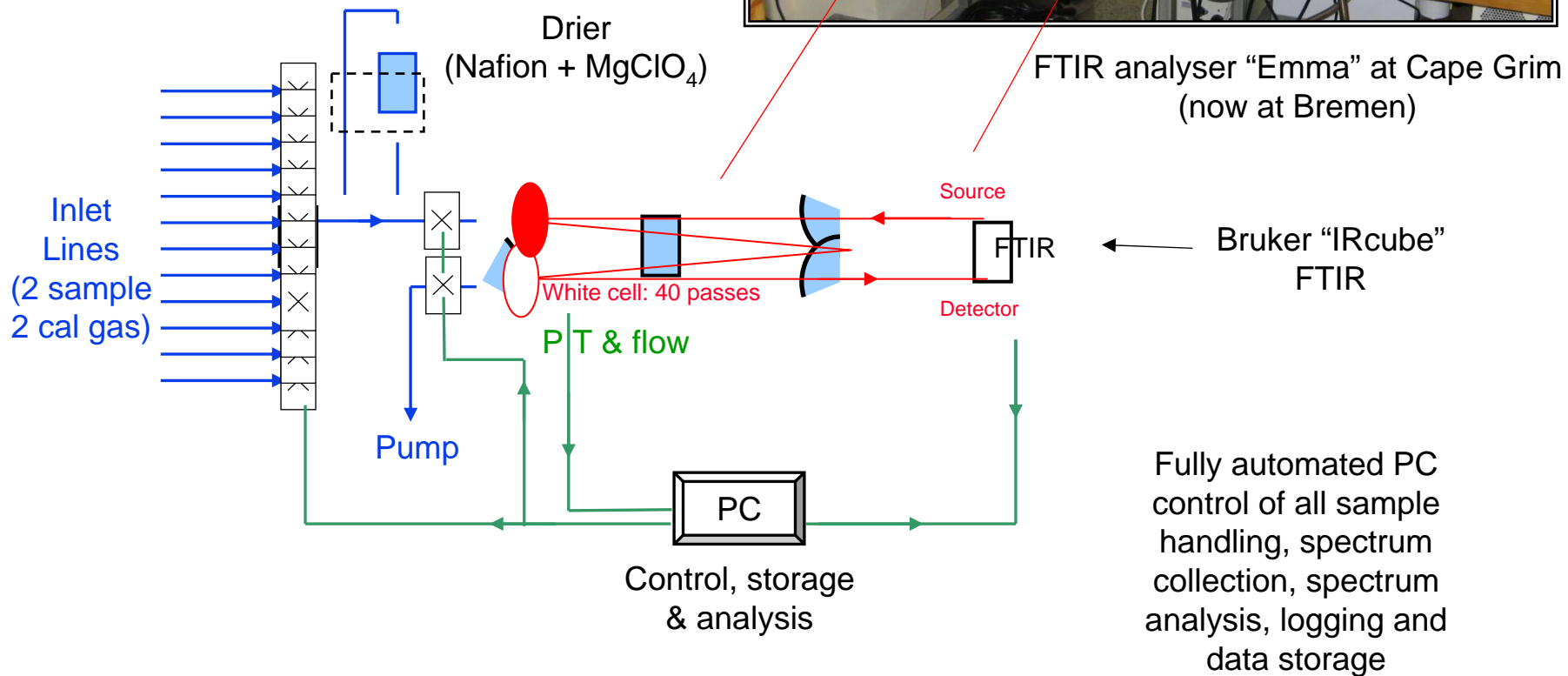
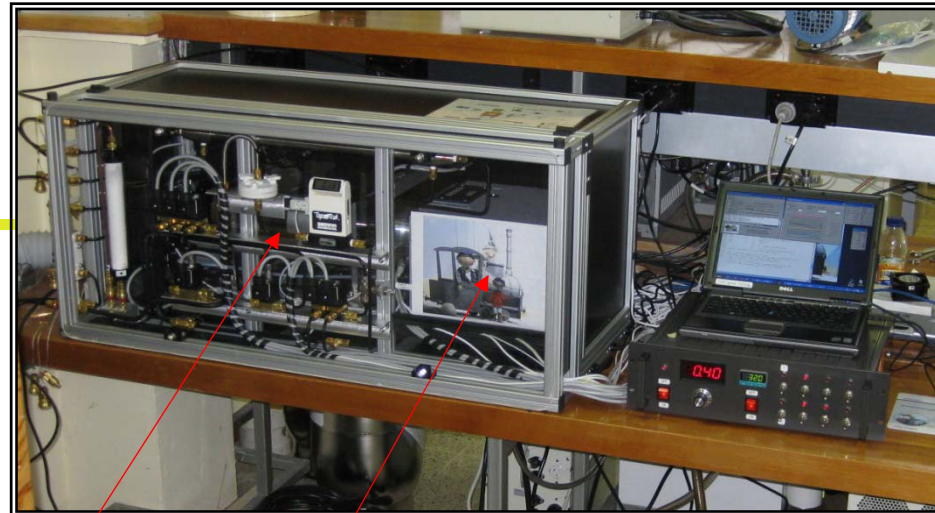
CSIRO Marine and Atmospheric Research, Australia



# Infrared spectrum of clean air



# FTIR trace gas analyser



# Precision - repeatability

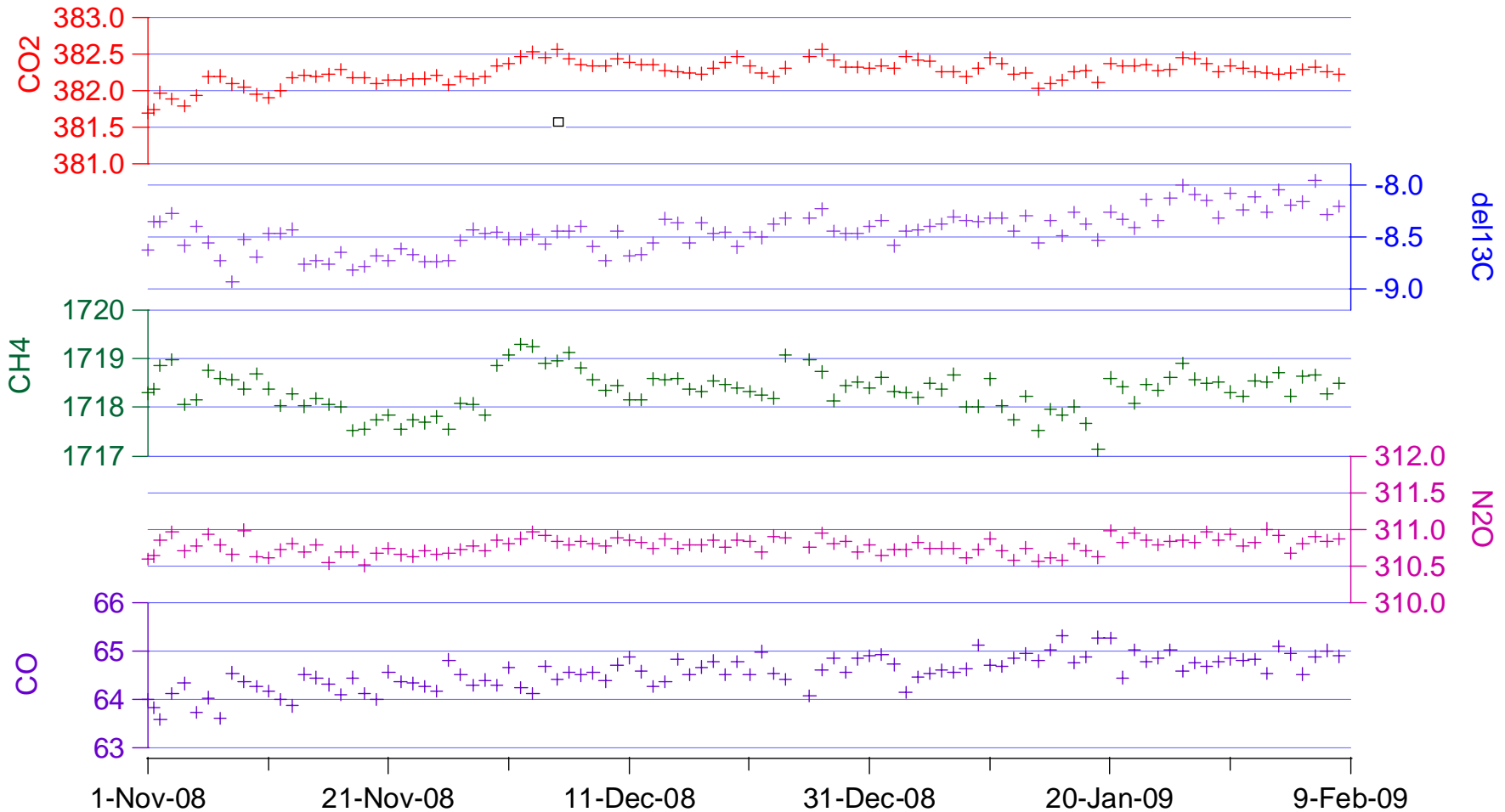
---

- Determined from Allan Variance measurements
- Confirmed in Cape Grim study
- $1\sigma$  repeatability for 10 minute averages:

• $\text{CO}_2$	0.05	$\mu\text{mol mol}^{-1}$
• $\text{CH}_4$	0.2	$\text{nmol mol}^{-1}$
• $\text{CO}$	0.2	$\text{nmol mol}^{-1}$
• $\text{N}_2\text{O}$	0.06	$\text{nmol mol}^{-1}$
• $\delta^{13}\text{C}$ in $\text{CO}_2$	0.08	‰
- Accuracy depends on gas standard(s) used

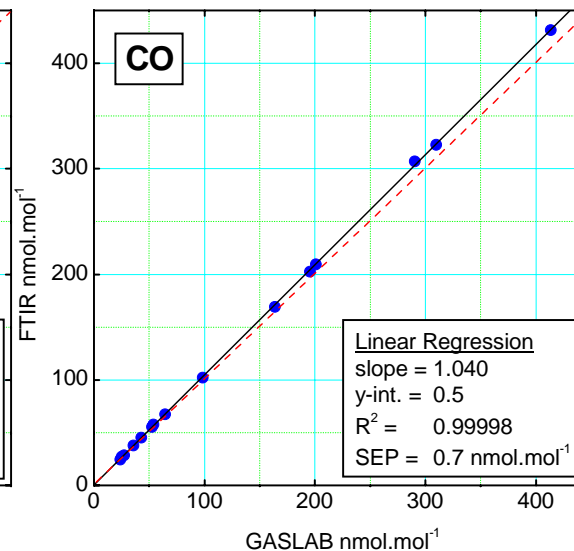
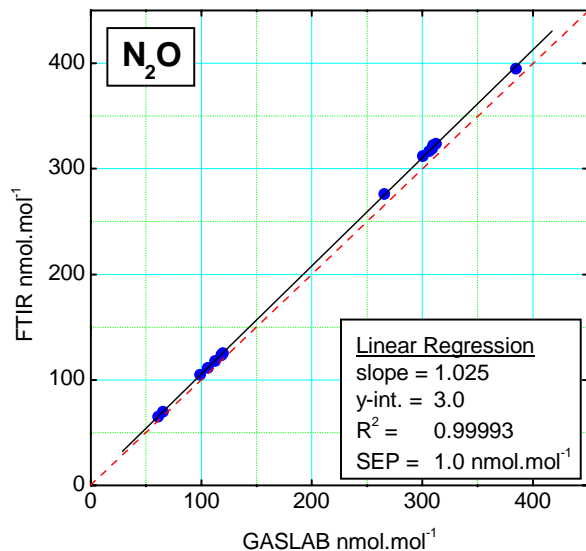
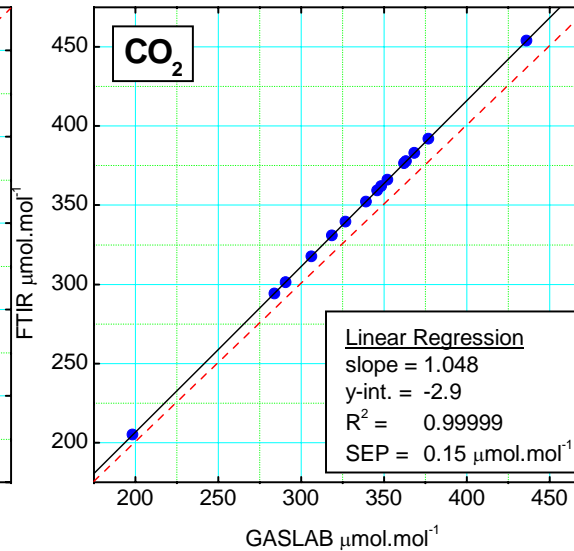
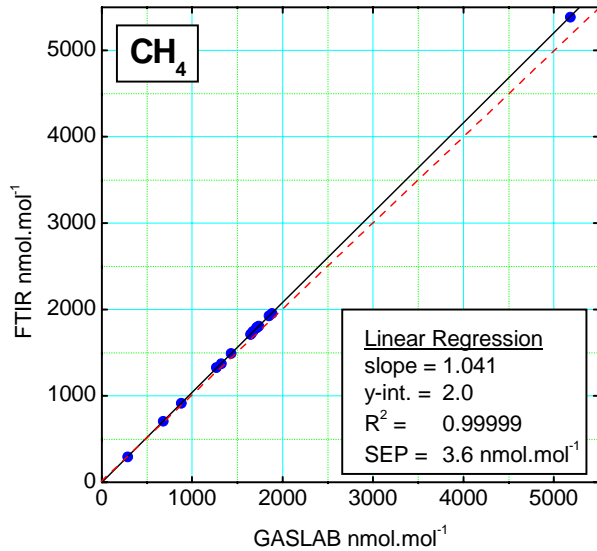
# Calibration: stability

## 110 daily cal.tank measurements at Cape Grim



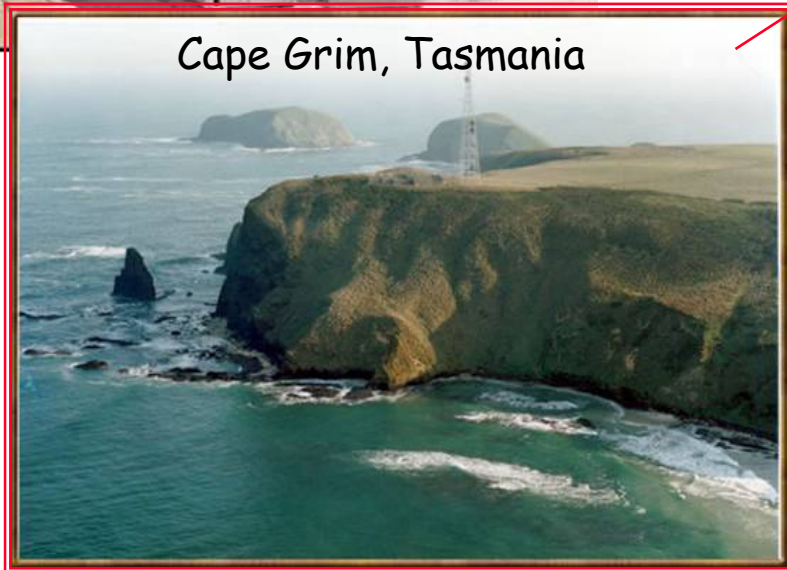
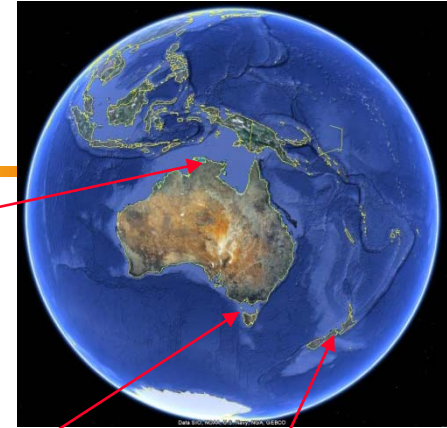
# Calibration: linearity

## FTIR vs GasLab calibration values (2002), 14 tanks



# Cape Grim trial, Oct 2008 - Feb 2009

## Continuous air measurements



# Cape Grim intercomparison

## FTIR vs LoFlo ( $\text{CO}_2$ ) and AGAGE-GC ( $\text{CH}_4$ , $\text{CO}$ , $\text{N}_2\text{O}$ )

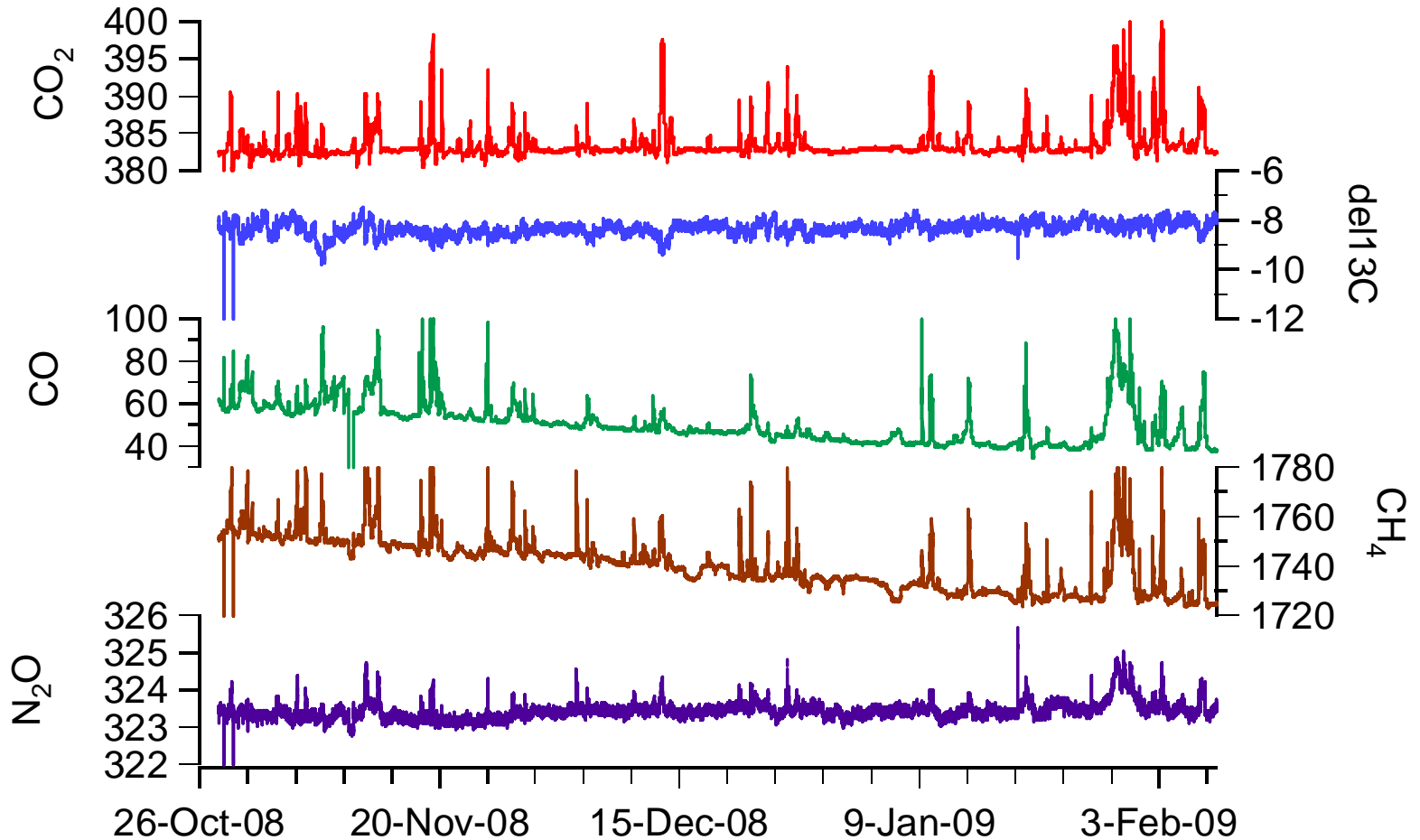
---

- Oct 2008 - Feb 2009, 110 days
- Air drawn continuously at  $0.5 \text{ L min}^{-1}$  from 70 m tower inlet
  - Parallel to LoFlo and AGAGE inlets
- Continuous real time analysis
  - FTIR measurements are 10 min averages
  - Precision improves with further averaging
  - Comparison values timed/averaged to coincide in time with LoFlo/AGAGE
- Calibration once per day
  - single clean air tank, flask subsamples analysed at GasLAB (awaiting reanalysis)
- Managed over internet to host PC (Windows Remote Desktop)
- Low maintenance, minimal consumables
  - Purge  $\text{N}_2$   $0.2 \text{ L min}^{-1}$ ,  $\text{MgClO}_4$ , calibration gas
  - No  $\text{LN}_2$ , use dried sample air + vacuum for Nafion backflush

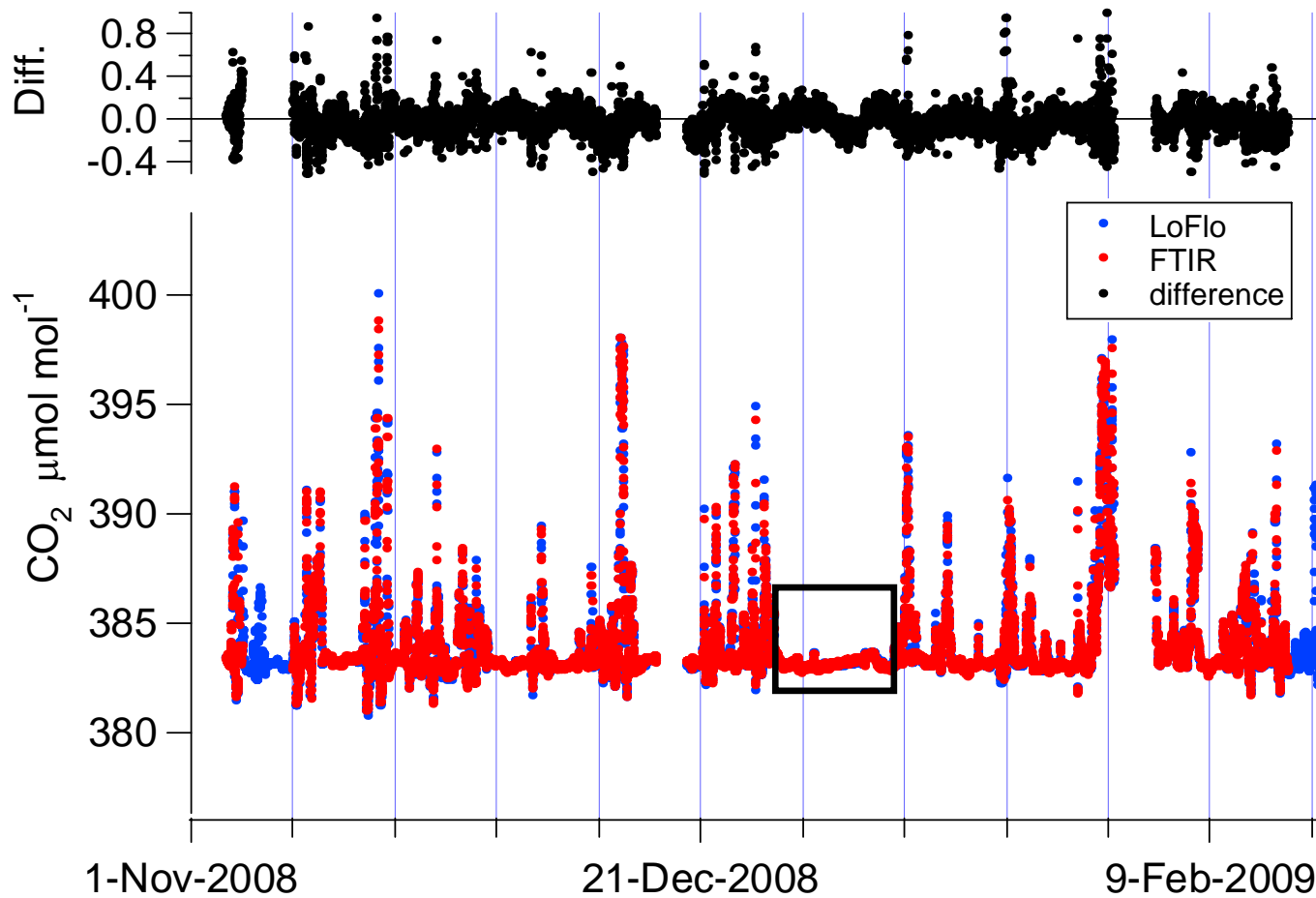


# FTIR at Cape Grim - overview

---

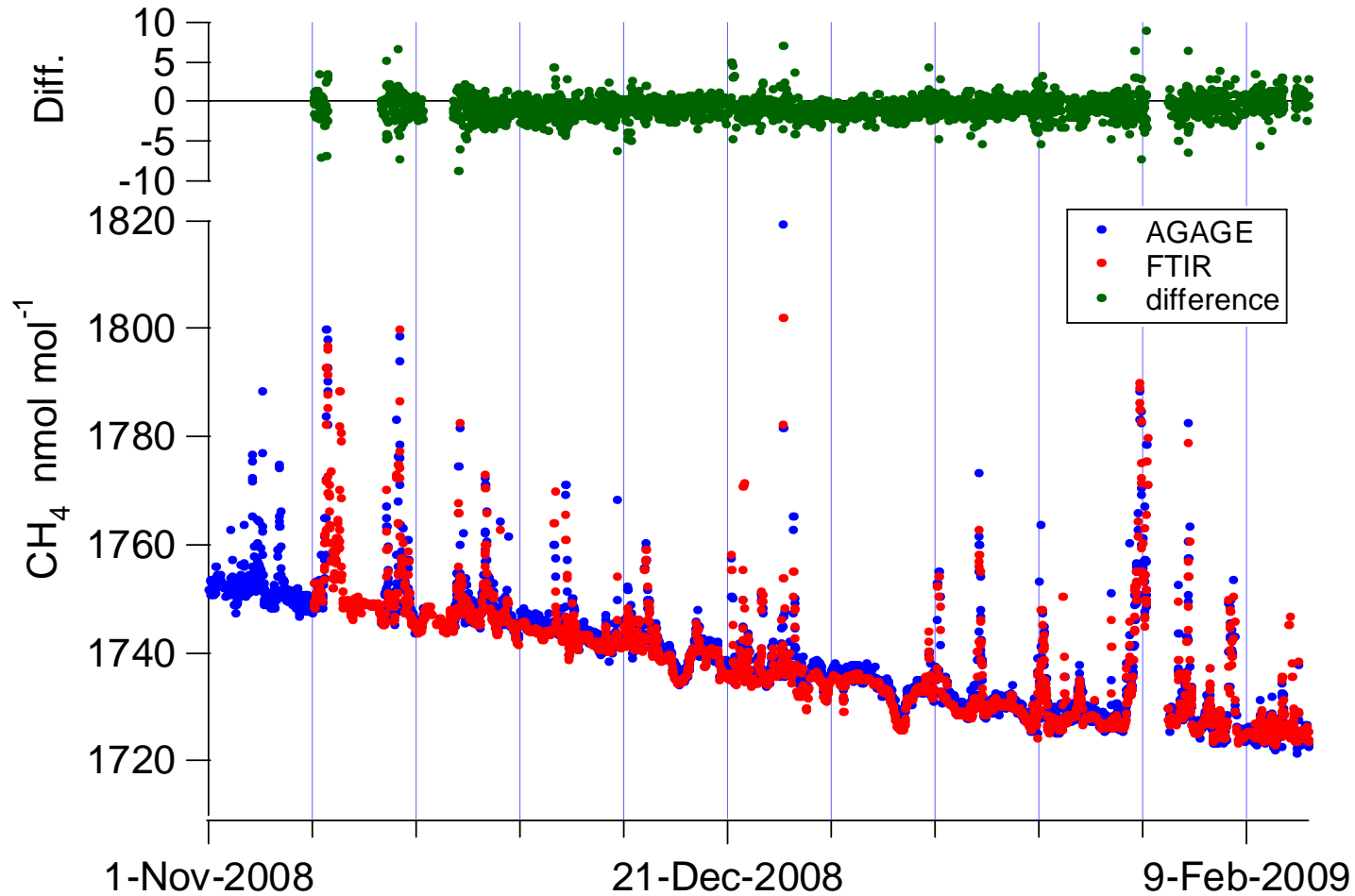


# CO<sub>2</sub> : FTIR vs LoFlo

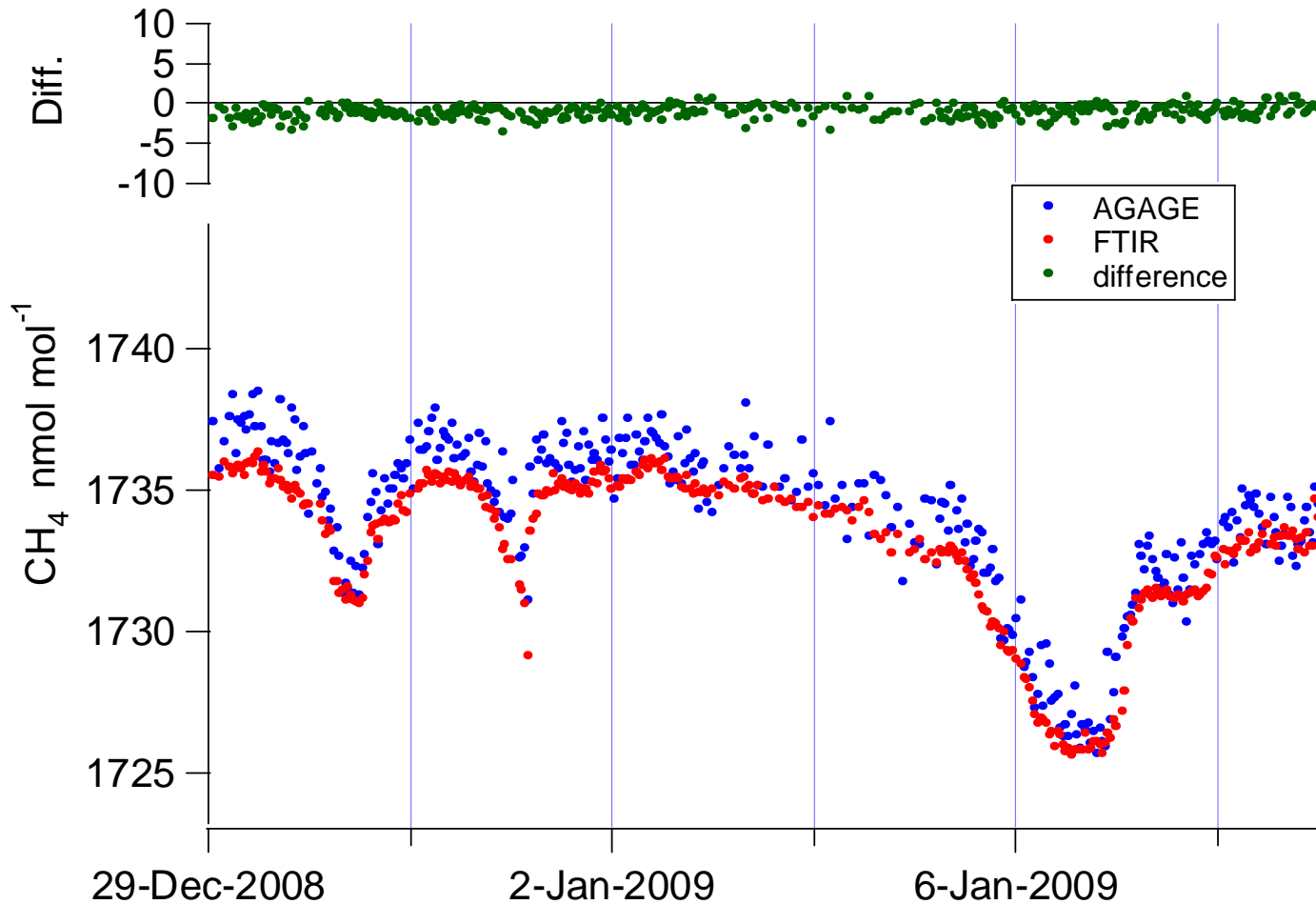




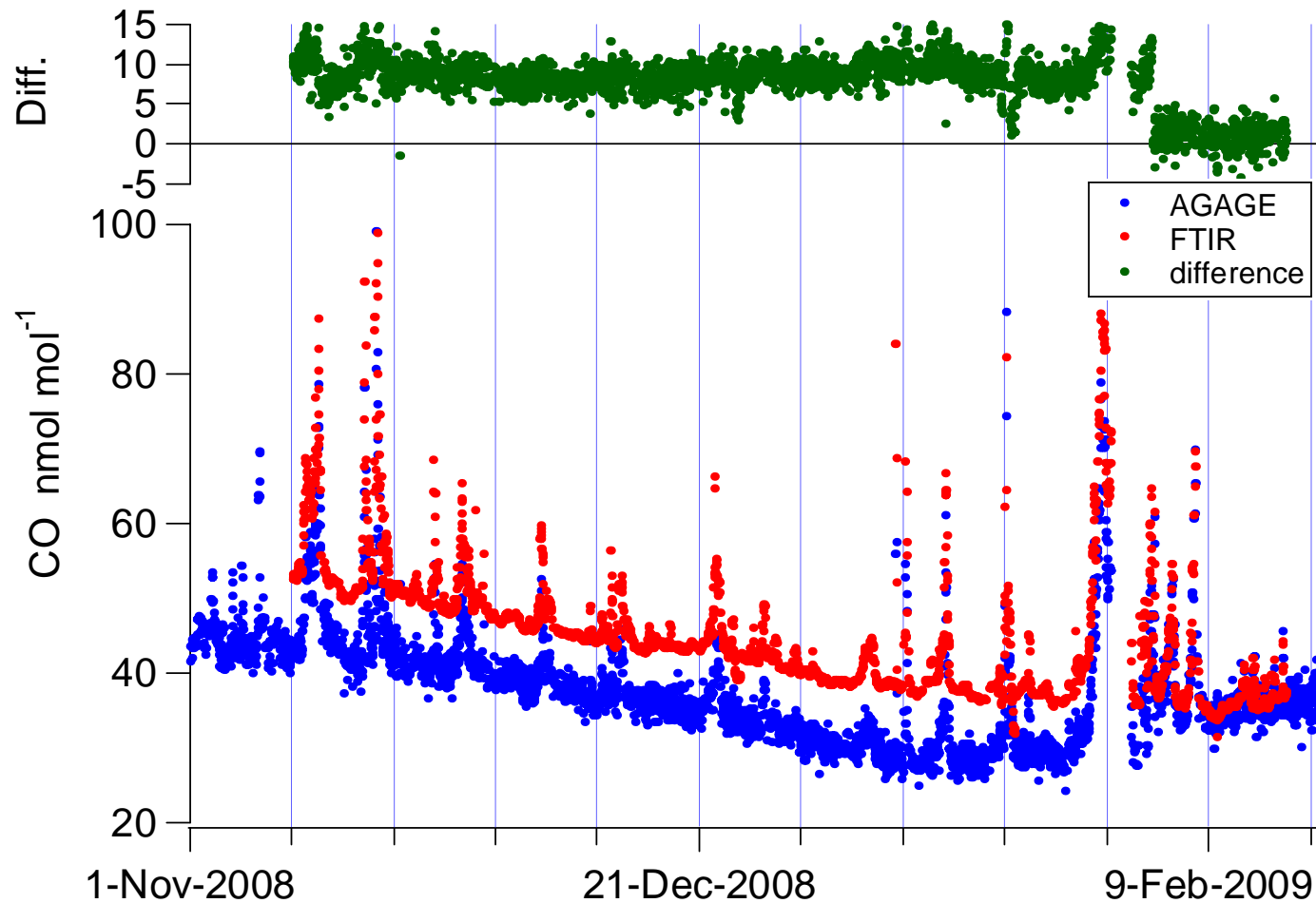
# CH<sub>4</sub>: FTIR vs AGAGE (GC)



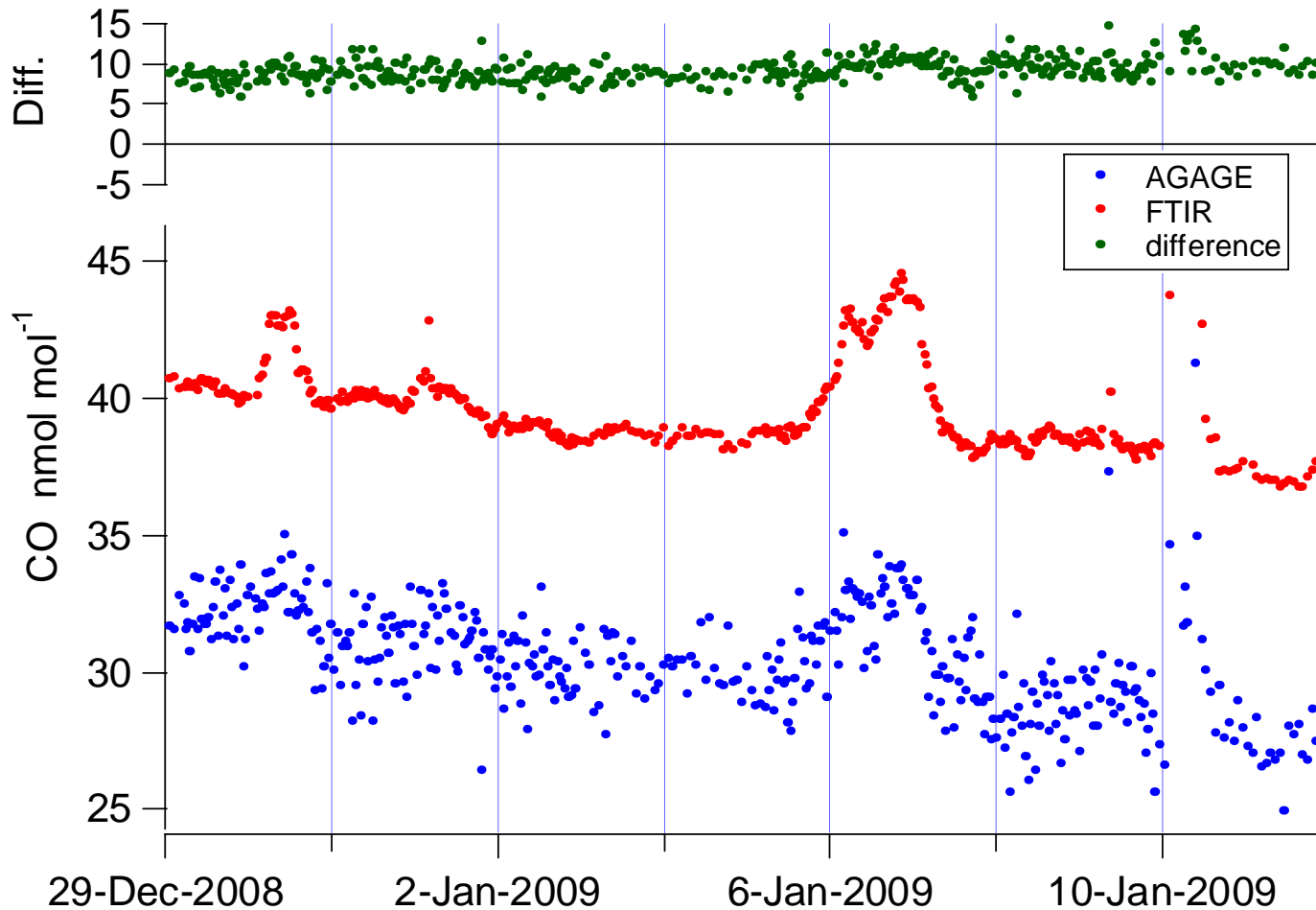
# CH<sub>4</sub>: FTIR vs AGAGE (GC)



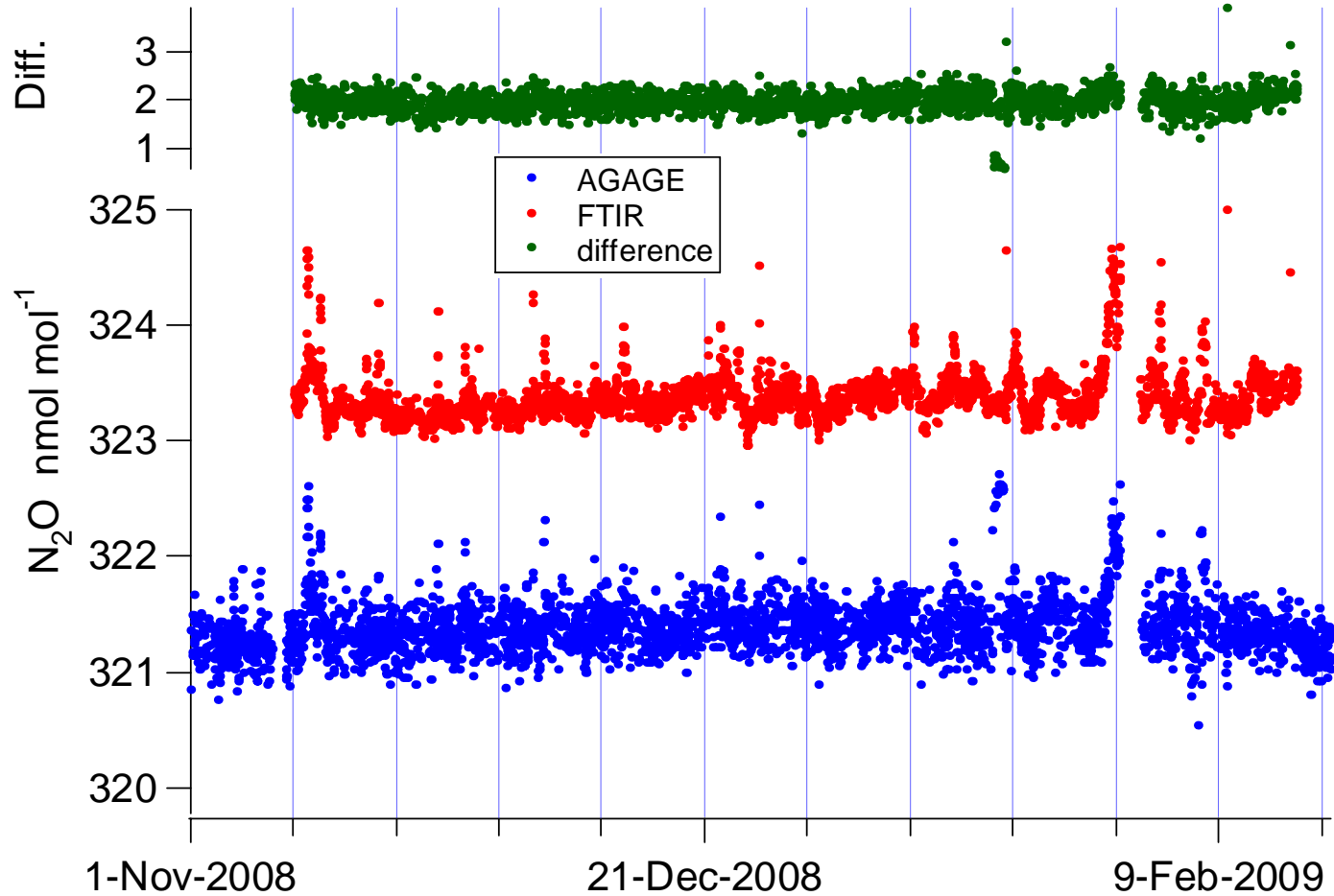
# CO: FTIR vs AGAGE (GC)



# CO: FTIR vs AGAGE (GC)



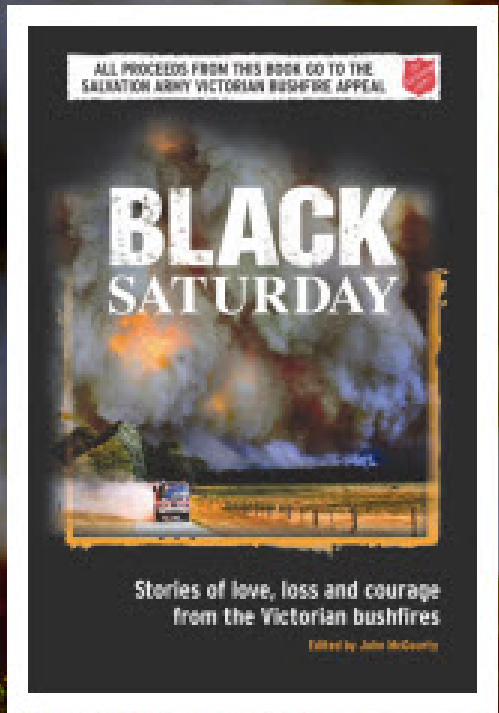
# N<sub>2</sub>O: FTIR vs AGAGE (GC)





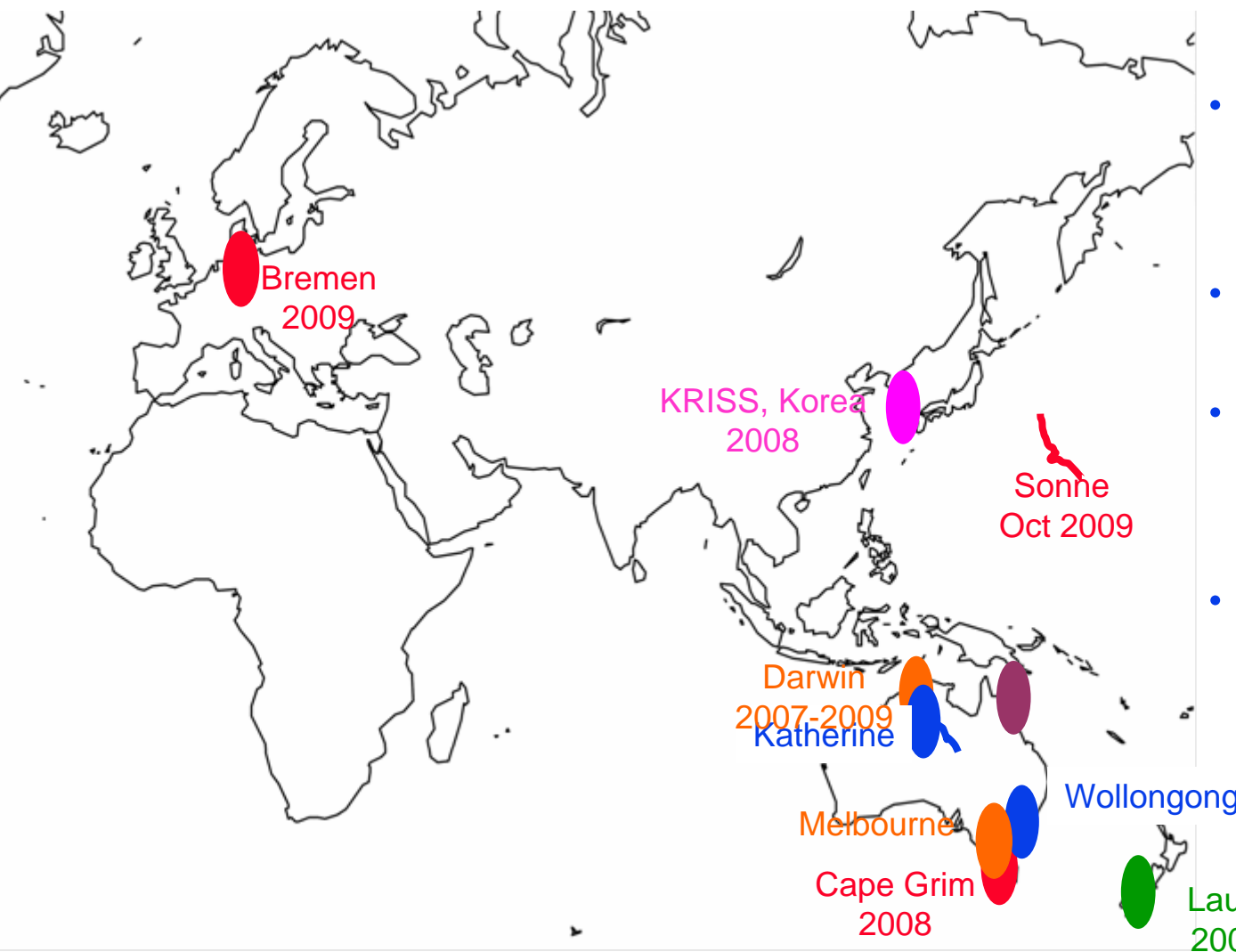
# Black Saturday fires, 7 Feb 2009

NOAA HYSPPLIT MODEL  
Backward trajectories ending at 0900 UTC 07 Feb 09  
GDAS Meteorological Data



# Some applications

- around (some of) the world



- Fixed stations
  - GAW, ICOS?
  - Characterise new sites
  - towers
- mobile platforms
  - train
  - ship
- Campaigns
  - Tower measurements
  - Micrometeorology - Flux measurements
  - Caves
- Calibration propagation
  - Multi species correlations

# Mobile measurements

## Transects of the Australian continent

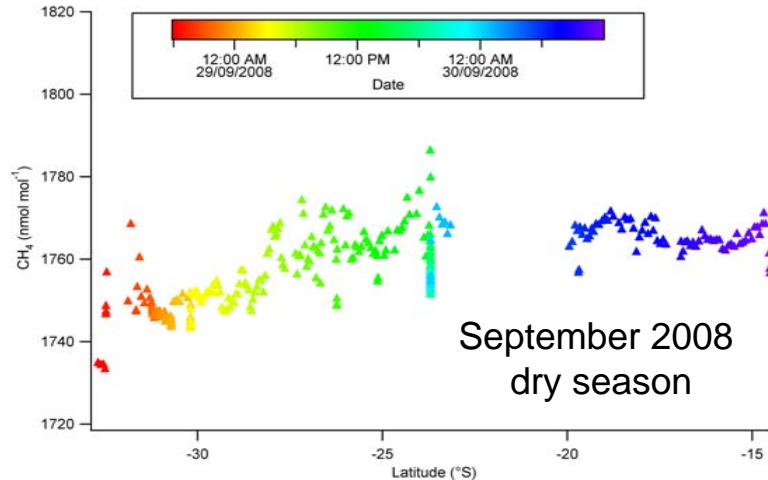
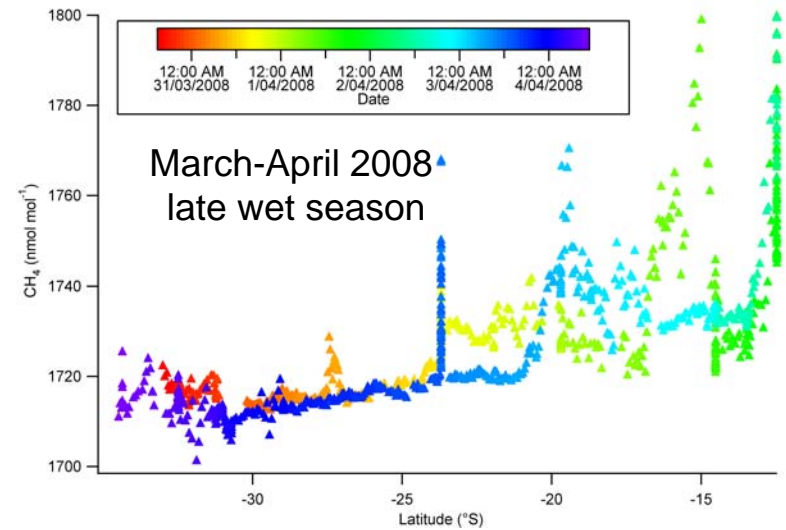
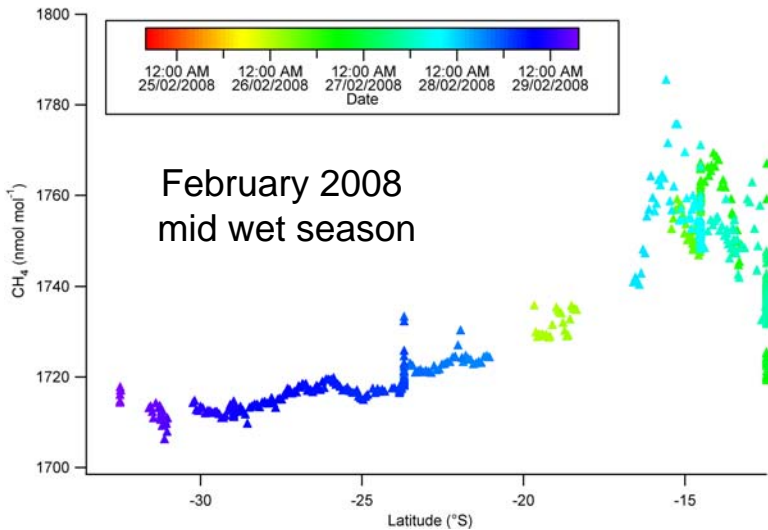


The Ghan



FTIR analyser in luggage van

# CH<sub>4</sub> increases in tropical wet season

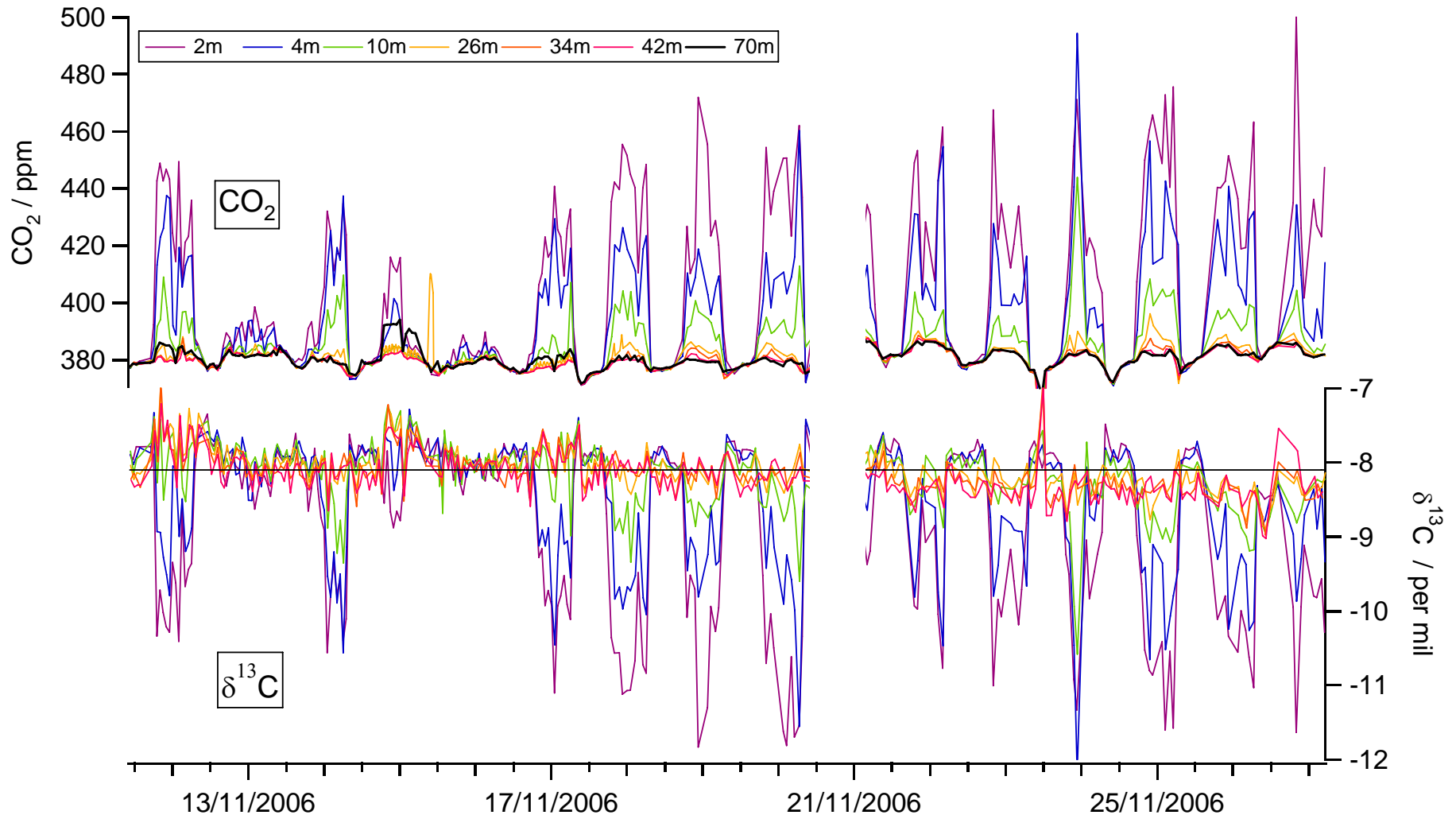


- 40-50 nmol mol<sup>-1</sup> increase in CH<sub>4</sub> toward equator in wet season
- Due to ephemeral wetlands, + latitudinal gradient
- Ephemeral and permanent wetlands approx. equal annual source strength (~0.4 Tg y<sup>-1</sup>)
- Deutscher et al., JGR submitted 8 Sept 2009

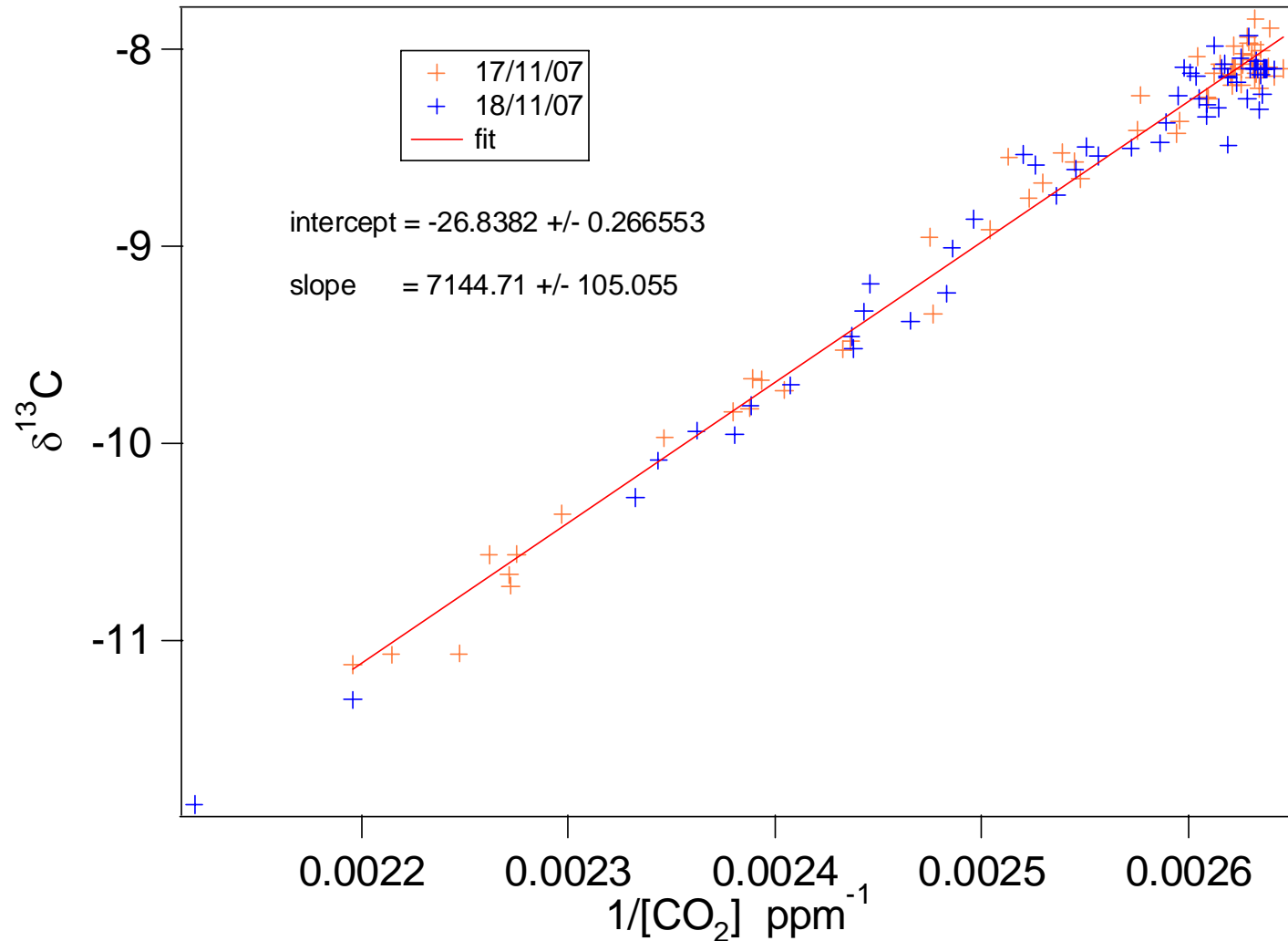
# Forest tower profiles: using trace gas and isotopic fractionation profiles to partition C and H<sub>2</sub>O exchange



# CO<sub>2</sub> and $\delta^{13}\text{C}$ - tower profiles 7 heights vs time

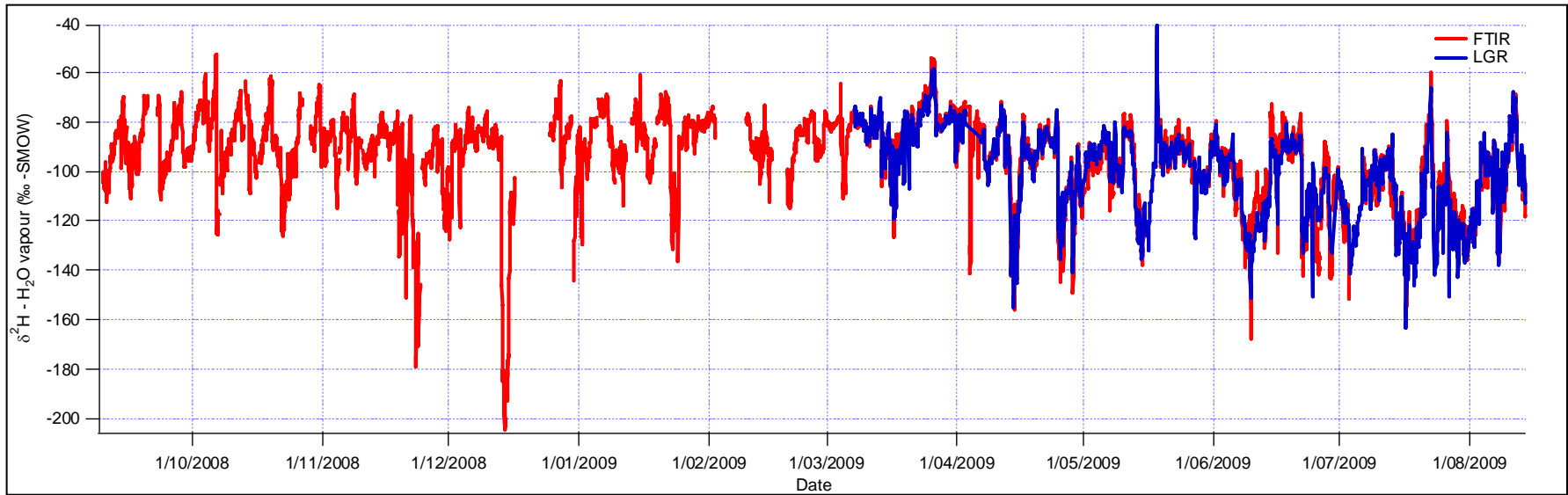


# CO<sub>2</sub> and $\delta^{13}\text{C}$ - night time Keeling plots



# Water vapour isotopes

- FTIR vs Los Gatos (Stephen Parkes, ANSTO)







- FTIR calibration against IRMS water standards (undried air)
  - $\delta^2\text{H}$  in  $\text{H}_2\text{O}$             1            ‰
  - $\delta^{18}\text{O}$  in  $\text{H}_2\text{O}$             0.4        ‰







# FTIR vs laser

---

## FTIR

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

## Laser

- Narrowband, single lines 
  - Single species or pair (per laser)
- Laser source 
  - High brightness
  - => high SNR, fast meas.
- Near IR, low pressure (!QCL) 
  - Weak absorption
- Narrow band fit 
  - less spectral information
  - Drift, more freq. calib.

Net result: similar precision 

- Portable 

- More portable 

# Summary

---

- Cost effective 5-in-1 analyser for  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  and  $\delta^{13}\text{C}-\text{CO}_2$
- Simultaneous and continuous analysis
- High precision
  - Accuracy determined by calibration gases
- Good calibration stability & linearity
  - 1 calibration per day, air standard
- Low maintenance and consumables (no  $\text{LN}_2$ )
- Low "cost of ownership"
- Manage remotely (internet)
- Applications include:
  - Fixed sites (GAW, ICOS?)
  - Mobile platforms - train, ship
  - Tower profiling
  - Micrometeorology and flux measurements
  - Calibration propagation for air standards

## Acknowledgements

- Graham Kettlewell - software
- Martin Riggbach - construction
- Cape Grim station and staff (John Chris, Jeremy)
- CSIRO/GasLab staff (Marcel Vandershoot, Darren Spencer)
- University of Bremen (the instrument)

Nick



- For funding:
- University of Wollongong, Aust. Research Council