

# Novel ways to look at N<sub>2</sub>O emissions (using an FTIR analyser)

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1. <sup>15</sup>N labelling in soil chamber experiments
2. Tracer measurements in the nocturnal boundary layer

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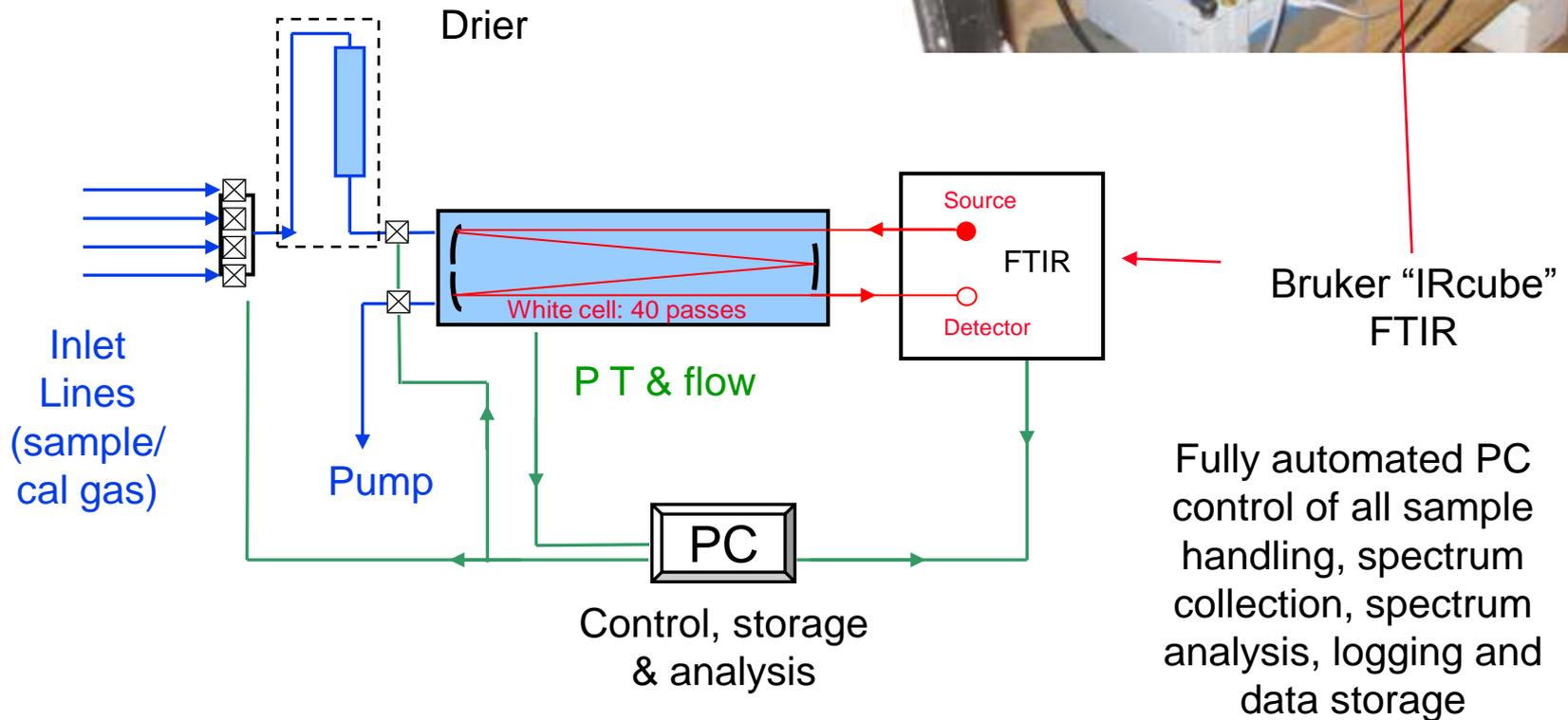
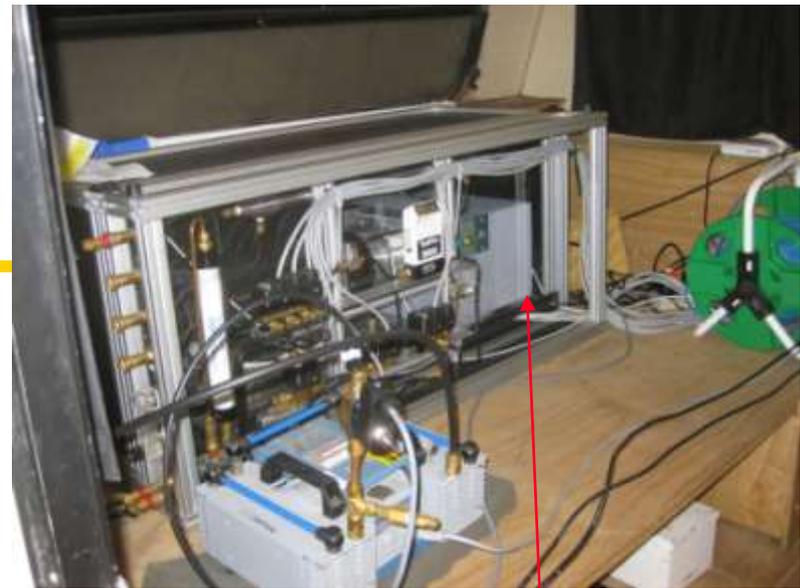
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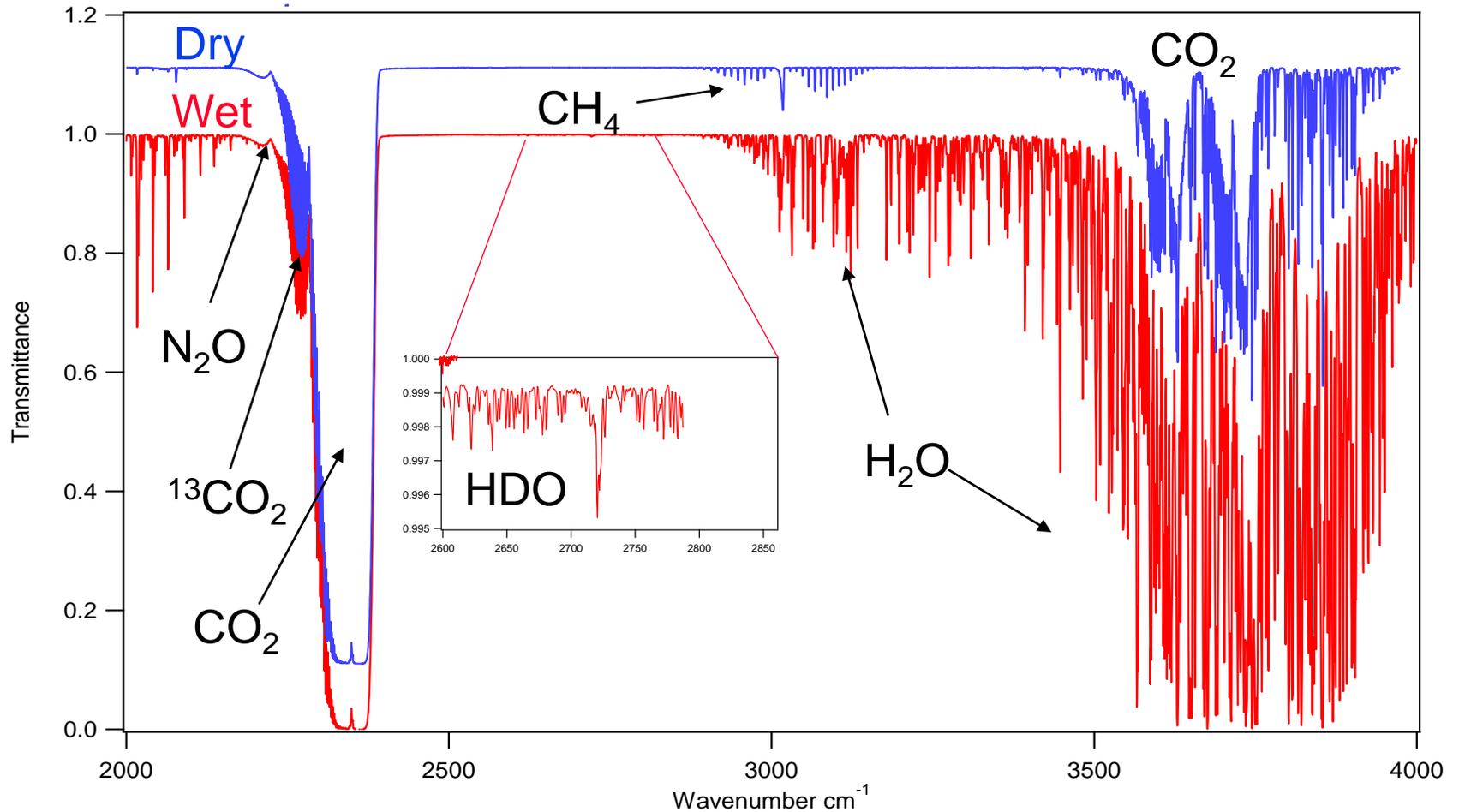


# The UoW FTIR trace gas analyser\*



\*Now commercially available as Spectronus, Ecotech P/L

# Mid-infrared spectrum of clean air



# 1. $^{15}\text{N}$ labelling in soil chamber experiments

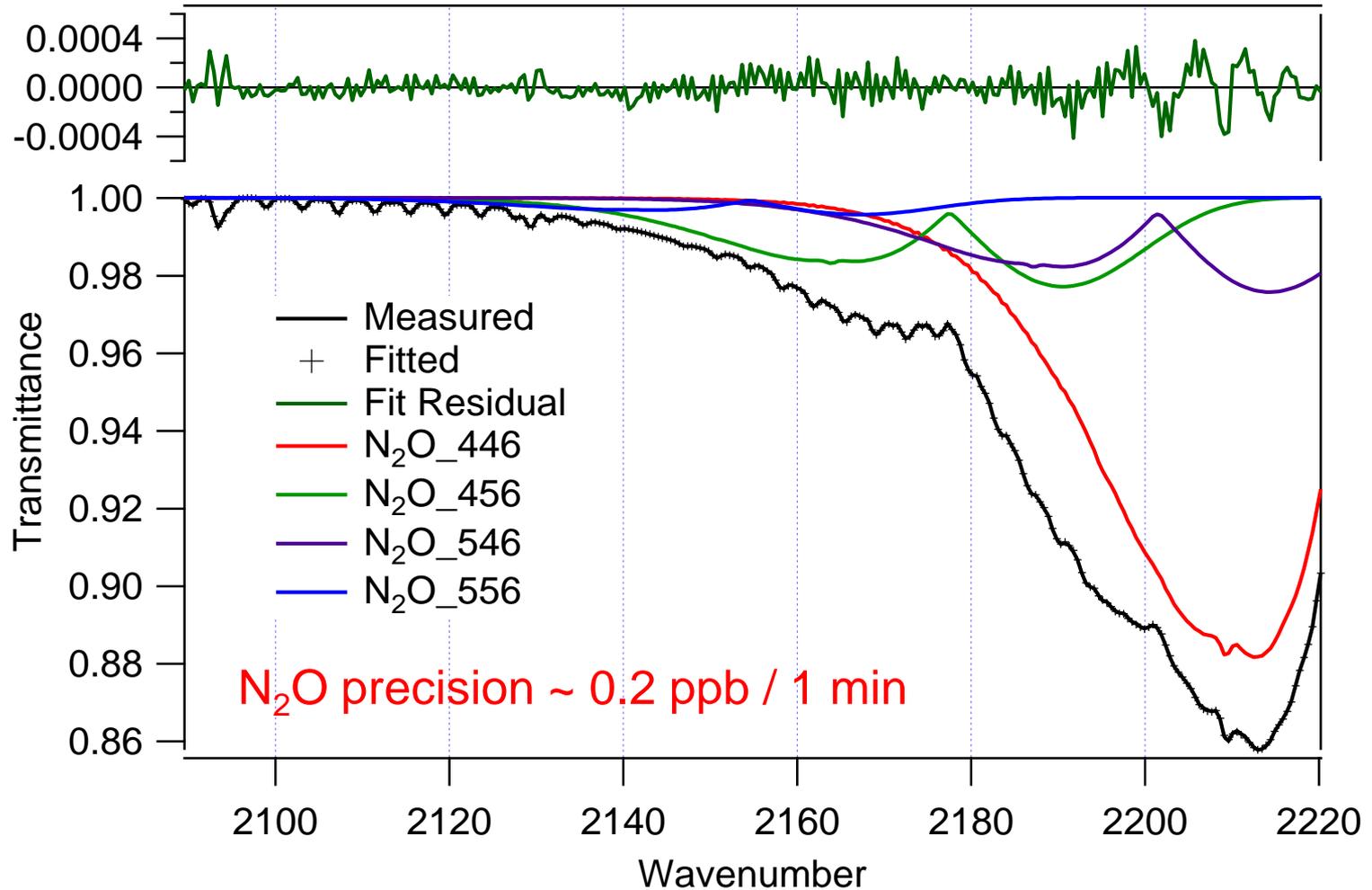
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## Outline

- ◆ Combine the FTIR analyser with automated chambers
  - Continuous measurements of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , all  $^{15}\text{N}$ - $\text{N}_2\text{O}$  isotopologues,  $\text{CH}_4$ ,  $\text{CO}$
- ◆ Add  $^{15}\text{N}$  as nitrate or urea to soil
  - Partition emitted  $^{15}\text{N}_2\text{O}$  into soil N pool and added  $^{15}\text{N}$
- ◆ Use FTIR to measure emissions of
  - $^{14}\text{N}^{14}\text{NO}$  - 446
  - $^{14}\text{N}^{15}\text{NO}$  - 456
  - $^{15}\text{N}^{14}\text{NO}$  - 546
  - $^{15}\text{N}^{15}\text{NO}$  - 556
- ◆ Measure  $^{15}\text{N}$  in soil/root/shoot/microbial components (IRMS)
- ◆ Attempt a N mass balance for the added  $^{15}\text{N}$

# Fitted IR spectrum

## N<sub>2</sub>O isotopologues ~ 2200 cm<sup>-1</sup>



# Site: Nowra, SE NSW

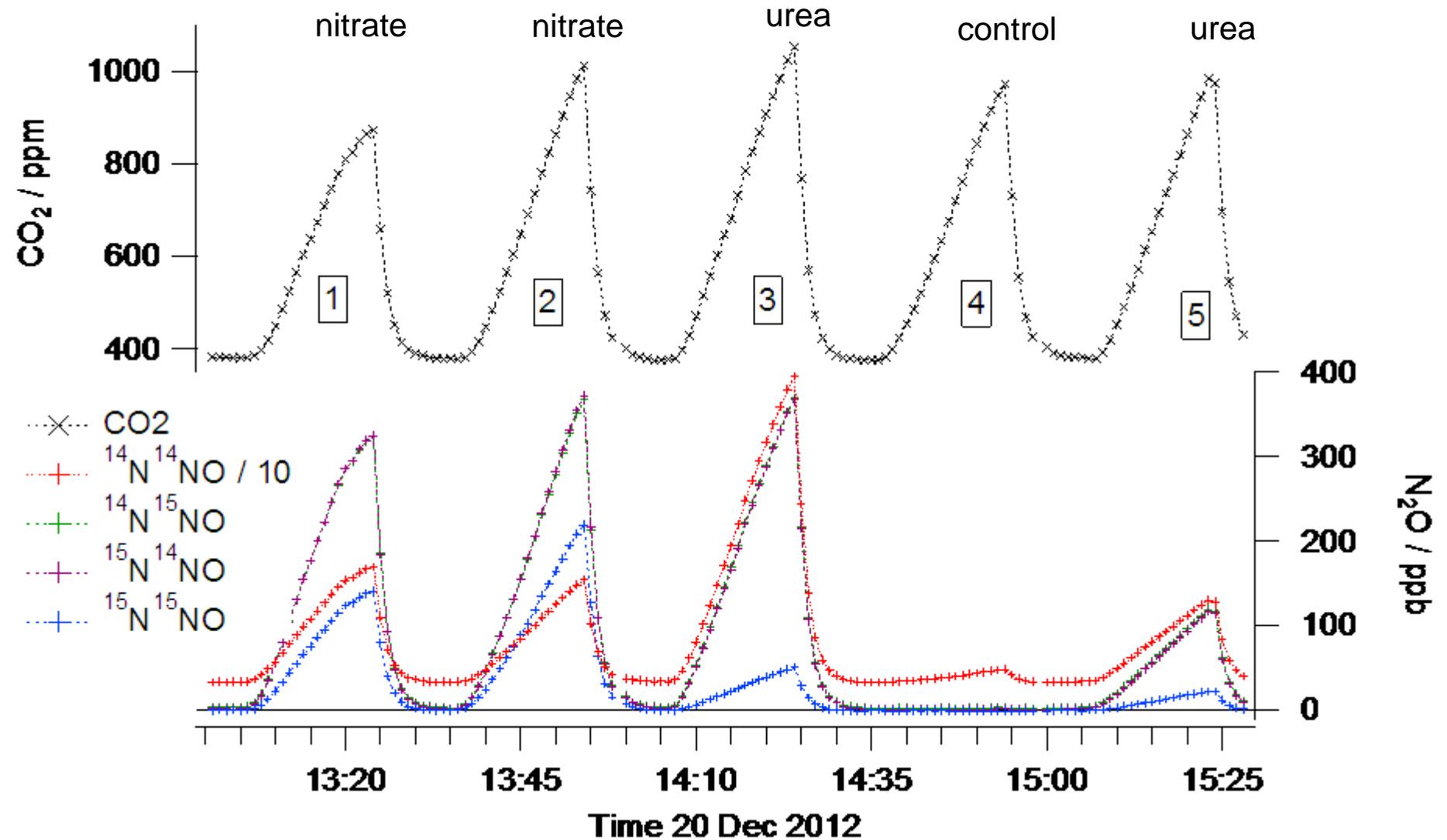


# Measurement Protocol

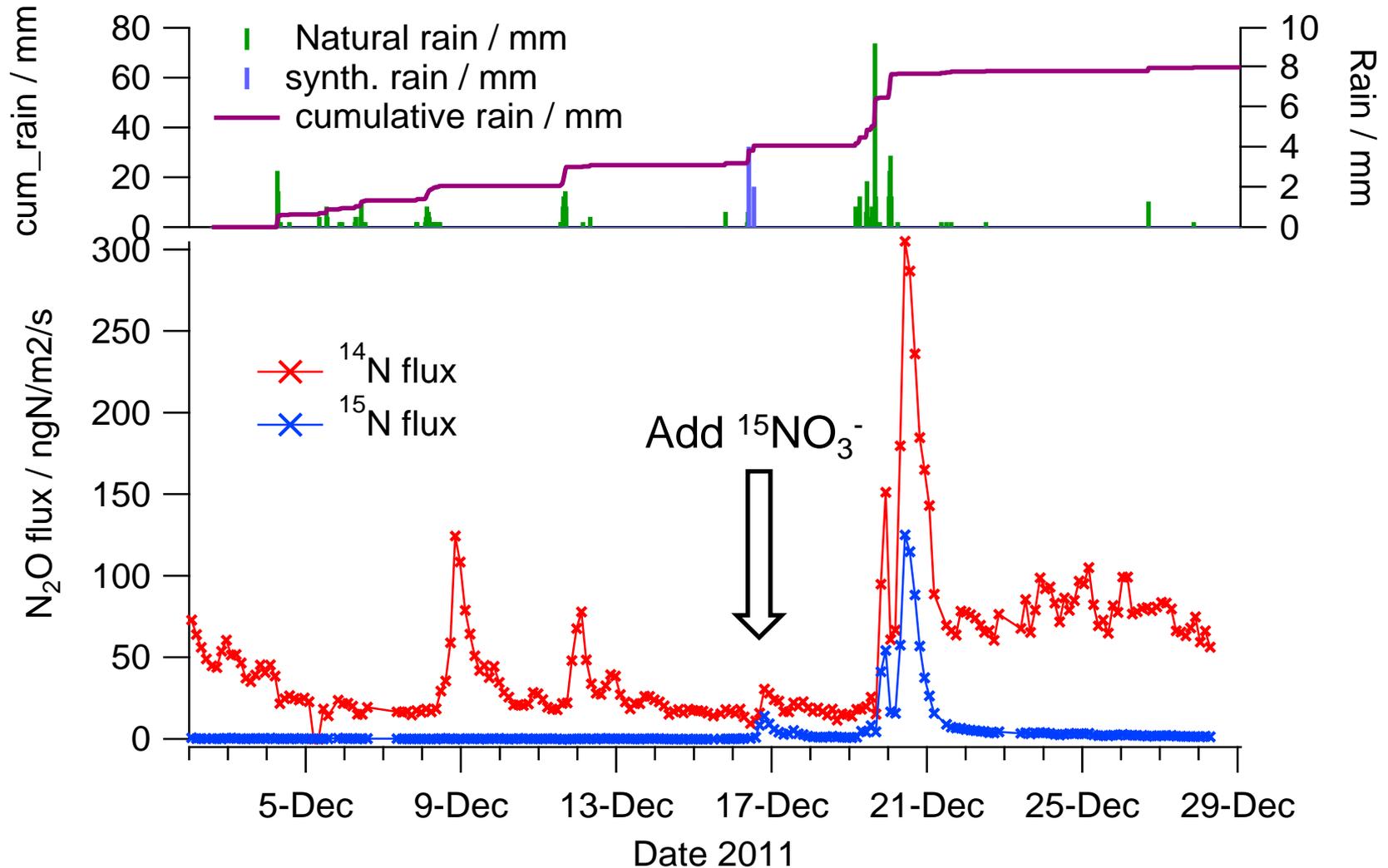
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- ◆ Two 4-week trials
  - 2-28 Dec 2011
  - 2-30 Jan 2012
- ◆ 5 chambers: for each trial
  - 2 dosed with  $\text{K}^{15}\text{NO}_3$  at  $\sim 800$  or  $400 \text{ mg}^{15}\text{N m}^{-2}$
  - 2 dosed with  $^{15}\text{urea}$  at  $\sim 400 \text{ mg}^{15}\text{N m}^{-2}$ 
    - $4\text{-}8 \text{ kg ha}^{-1}$ ,  $\sim 10\%$  of soil N pool
  - 1 control
  - Chambers moved between trials
- ◆ Each chamber sampled every 3 hours
  - 30 min per chamber
  - 6 min open, 18 min closed, 6 min open
  - 1 min per FTIR measurement of  $\text{N}_2\text{O}$ , isotopologues,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$
  - Gradient measurement on mast in 6th half hour period
  - Continuous over each 4 week period

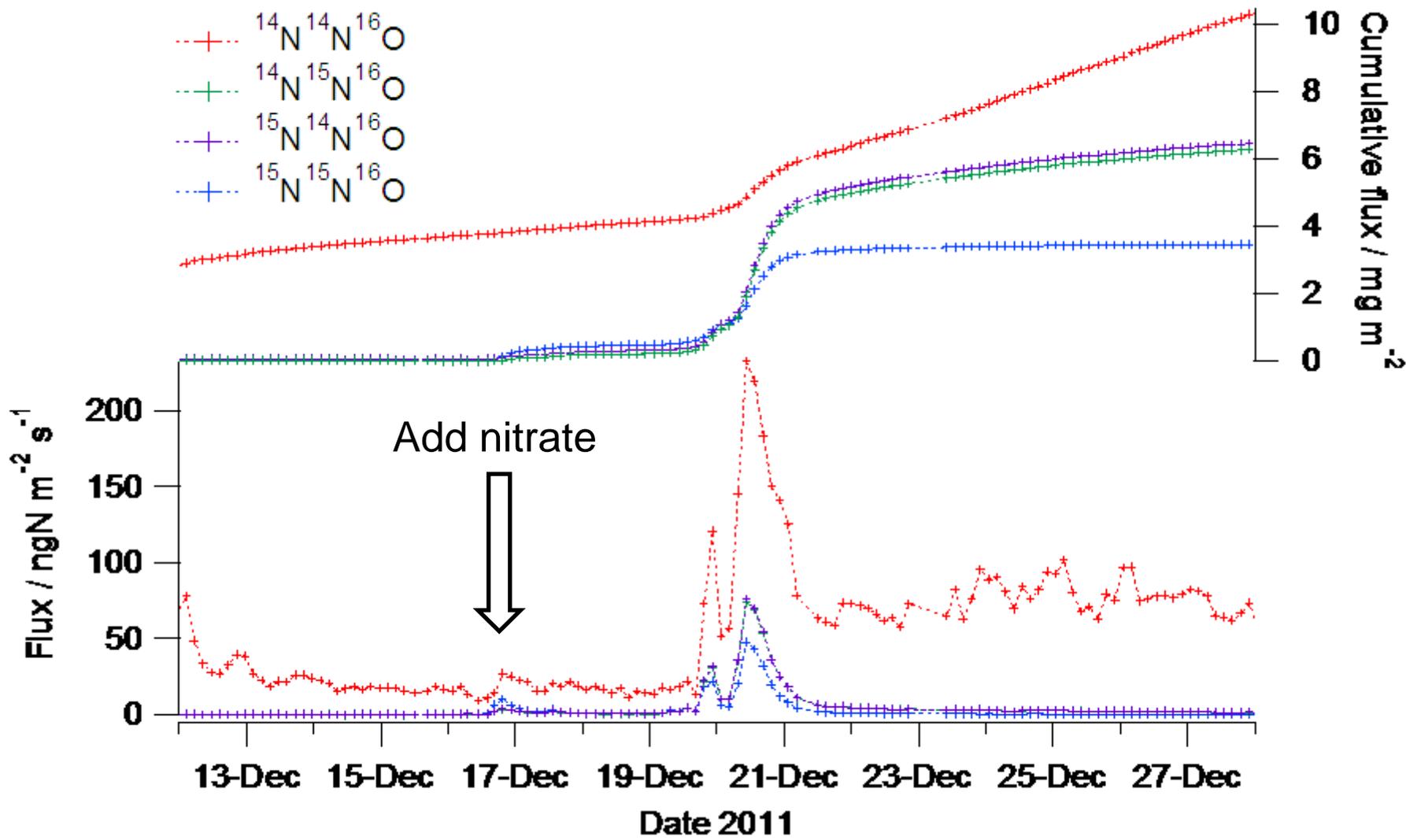
# Time series (1 cycle, 5 chambers)



# Trial 1: total $^{14}\text{N}$ and $^{15}\text{N}$ fluxes relationship to rain



# Cumulative fluxes, trial 1 nitrate addition



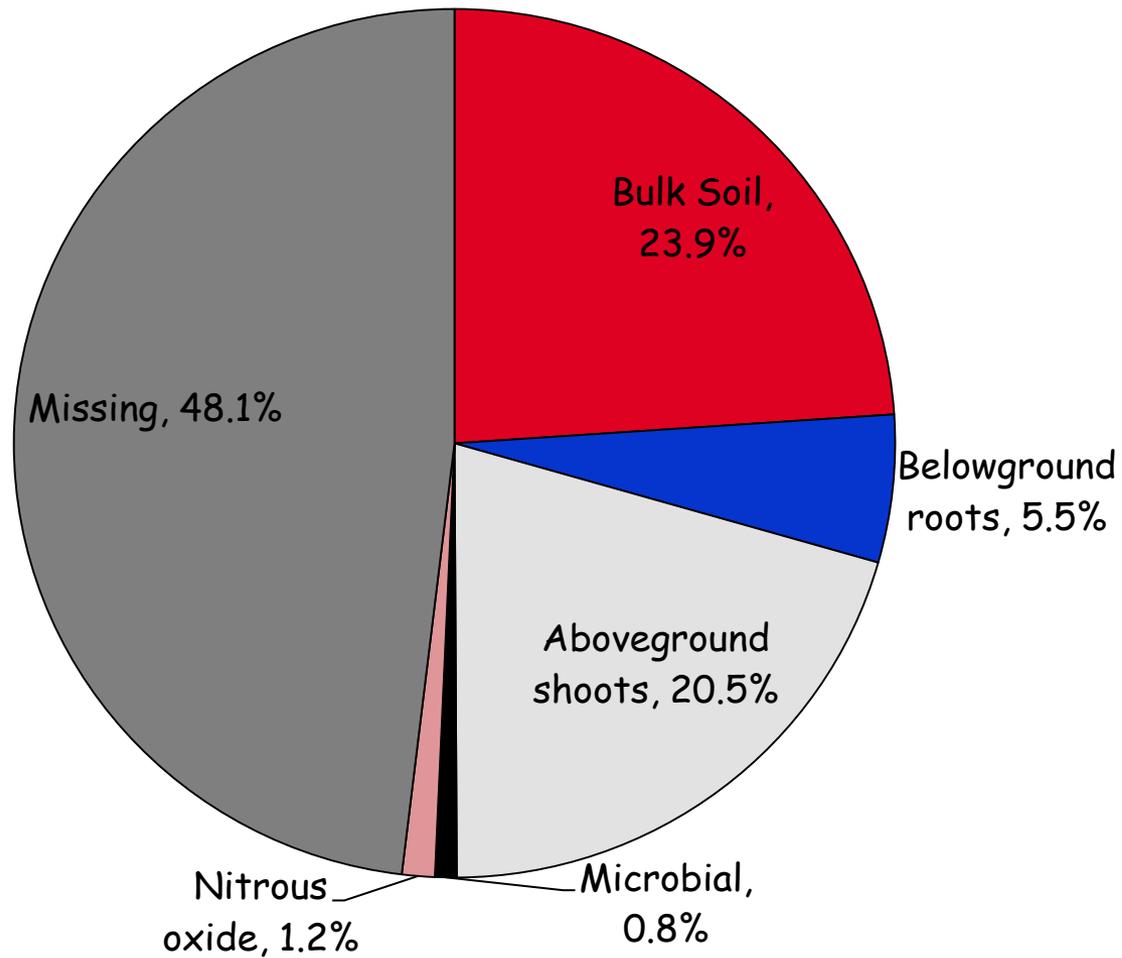
# <sup>15</sup>N recovery, all measurements

Chamber	Added <sup>15</sup> N mg/m <sup>2</sup>	Bulk Soil mg/m <sup>2</sup>	Belowground roots mg/m <sup>2</sup>	Aboveground shoots mg/m <sup>2</sup>	Microbial mg/m <sup>2</sup>	Nitrous oxide mg/m <sup>2</sup>	Total <sup>15</sup> N recovery mg/m <sup>2</sup>	Total <sup>15</sup> N recovery %	Recovery as N <sub>2</sub> O %
1	858	205.4	47.1	175.8	6.8	10.3	445.4	51.9%	1.2%
2	858	139.7	25	121	9.2	10	304.9	35.5%	1.2%
3	503	202.5	13.1	83.6	14	9.55	322.8	64.2%	1.9%
5	503	208.5	39.9	68.8	30.3	3.95	351.5	69.9%	0.8%
4	0					-0.02			
1	419	134.6	40.4	71	16.7	3.04	265.7	63.4%	0.7%
2	419	236.7	25.7	35.8	8.6	4.19	311.0	74.2%	1.0%
3	415	177	32.2	36.3	13	3.75	262.3	63.2%	0.9%
4	415	340.3	25.6	28.2	14.4	1.55	410.1	98.8%	0.4%
5	0					-0.02			

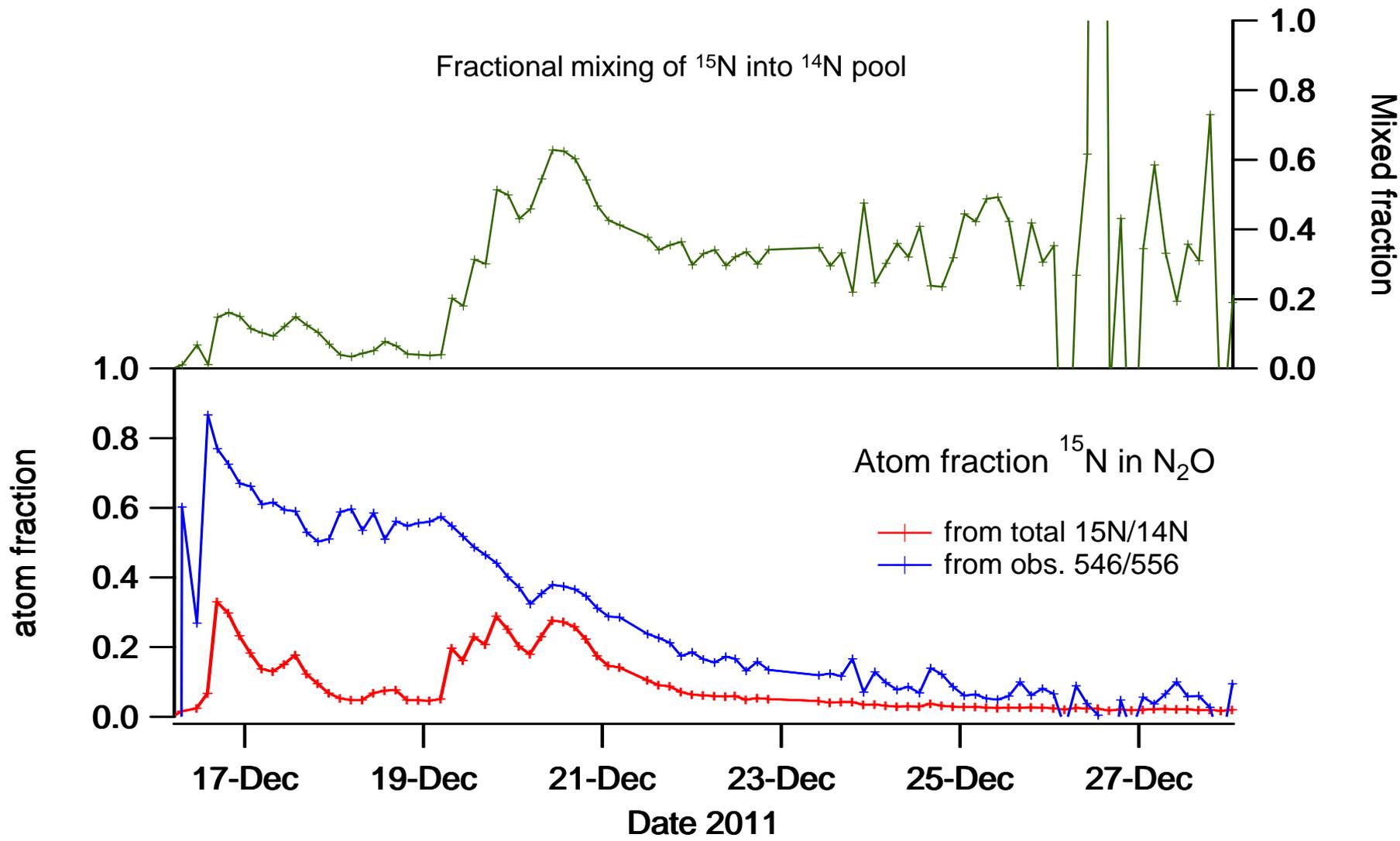
# $^{15}\text{N}$ mass balance

## Trial 1, chamber 2 (nitrate)

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# $^{15}\text{N}$ mixing into the $^{14}\text{N}$ pool

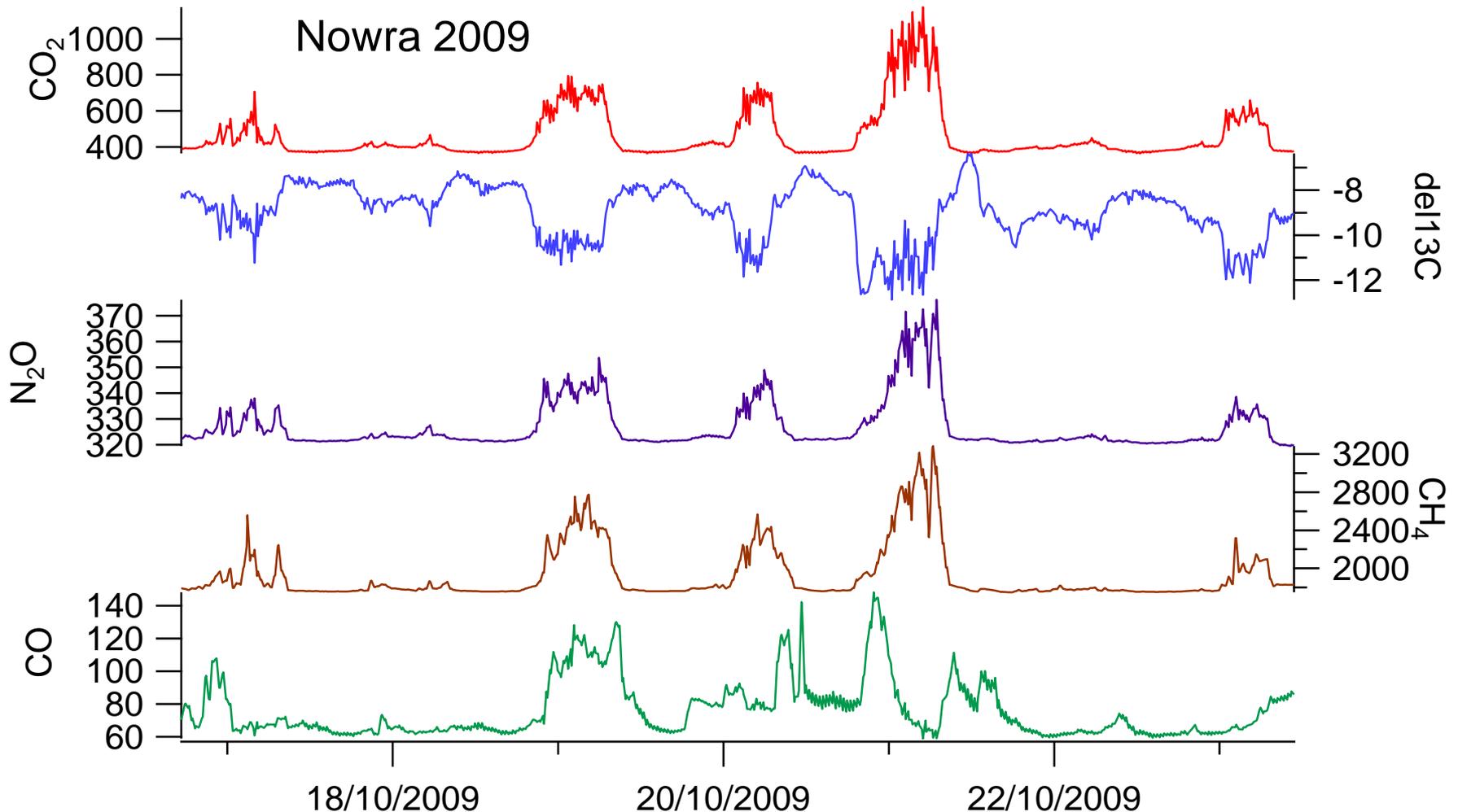


# Summary - $^{15}\text{N}$ chambers

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- ◆ Partition  $\text{N}_2\text{O}$  emissions from added  $^{15}\text{N}$  and existing soil  $^{14}\text{N}$  pool
  - Direct measurement of  $\Delta\text{N}_2\text{O}/\Delta\text{fertiliser}$
- ◆ Recover ~ 50-60% of added  $^{15}\text{N}$ 
  - $\text{N}_2\text{O}$
  - Soil
  - Roots
  - Shoots
  - Microbial
- ◆ ~1% of added N emitted as  $\text{N}_2\text{O}$ 
  - Consistent with IPCC tier 1 guideline
- ◆ Added  $^{15}\text{N}$  mixes with only 40% of soil pool

## 2. N<sub>2</sub>O fluxes from tracer measurements in the NBL



# An earlier FTIR study (open path)

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Agricultural and Forest Meteorology 111 (2002) 29–38

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## Measuring nitrous oxide emission rate from grazed pasture using Fourier-transform infrared spectroscopy in the nocturnal boundary layer

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Michael J. Harvey<sup>b</sup>, Sally J. Price<sup>c</sup>, Robert R. Sherlock<sup>c</sup>

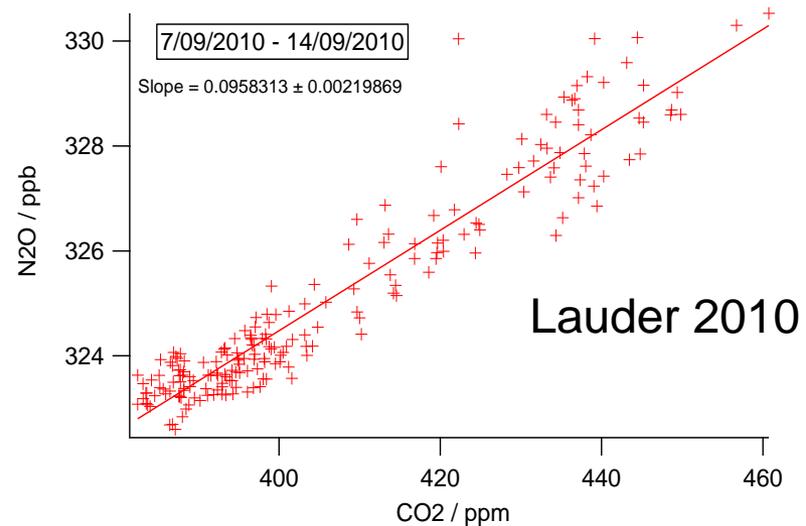
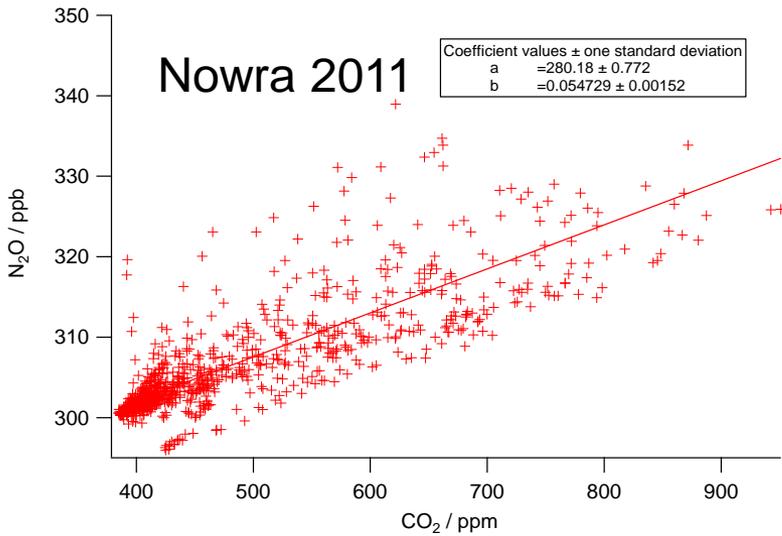
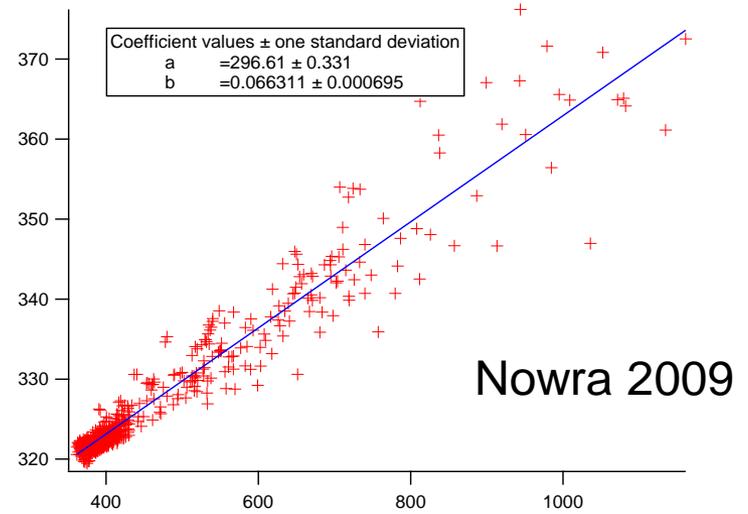
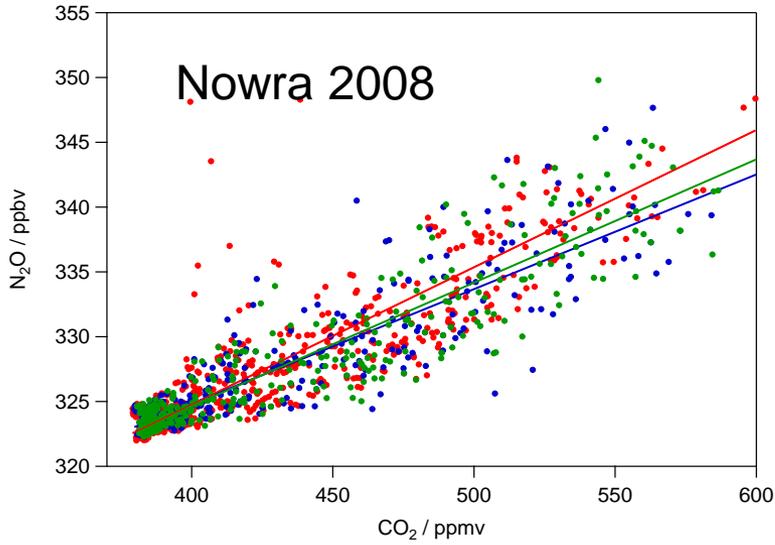
<sup>a</sup> *Manaaki Whenua—Landcare Research, P.O. Box 69, Lincoln, New Zealand*

<sup>b</sup> *National Institute of Water and Atmospheric Research, P.O. Box 14901, Wellington, New Zealand*

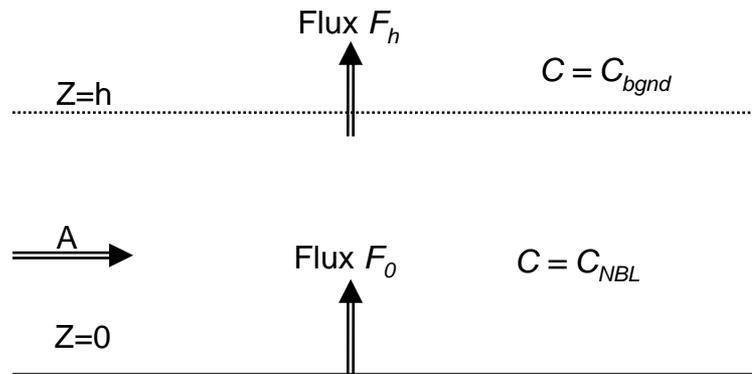
<sup>c</sup> *Lincoln University, P.O. Box 84, Lincoln, New Zealand*

Received 10 July 2001; received in revised form 17 January 2002; accepted 19 January 2002

# FTIR measurements of N<sub>2</sub>O vs CO<sub>2</sub>



# NBL tracer model

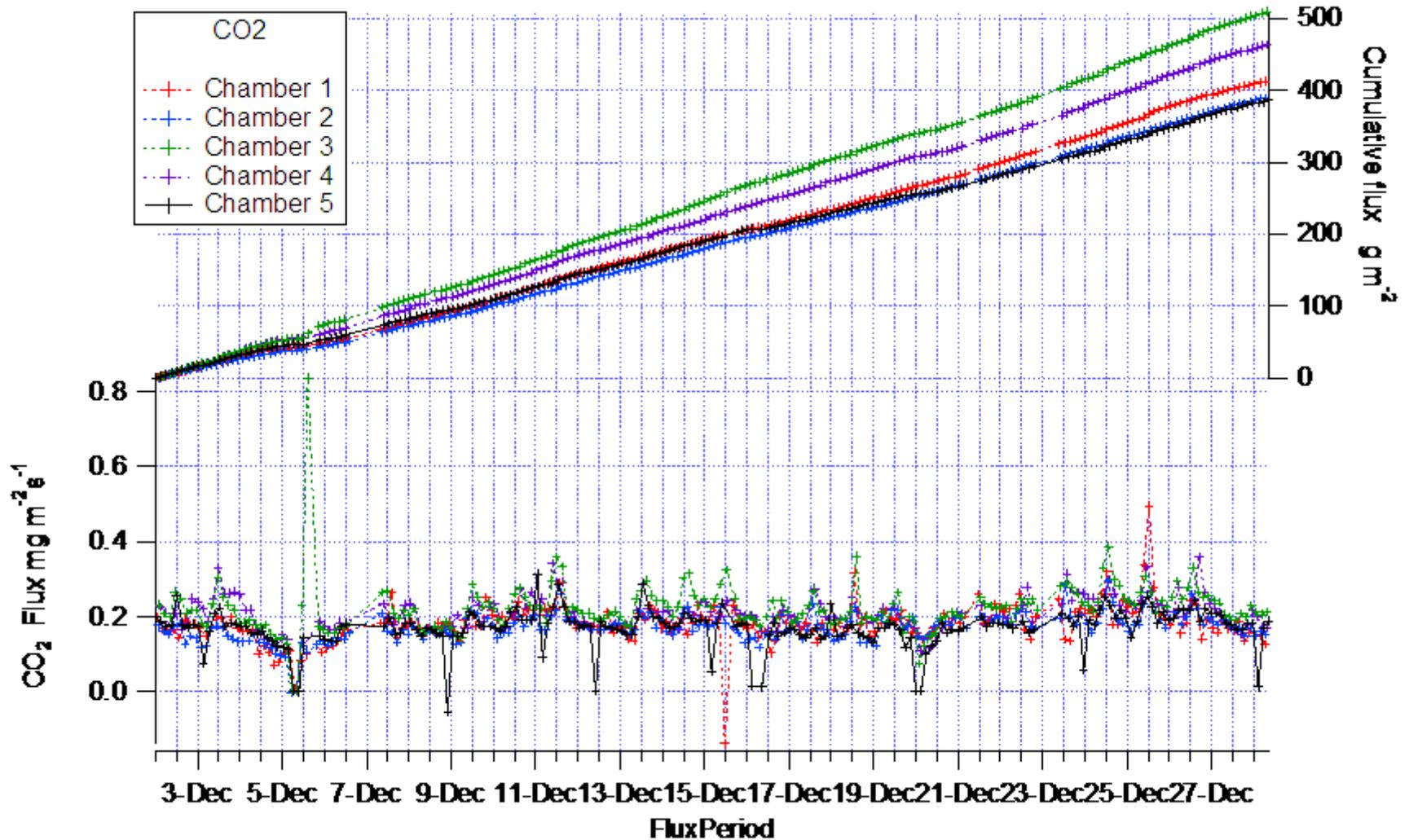


$$F_{0,N_2O} = F_{0,CO_2} \cdot \frac{dC_{NBL,N_2O}}{dC_{NBL,CO_2}}$$

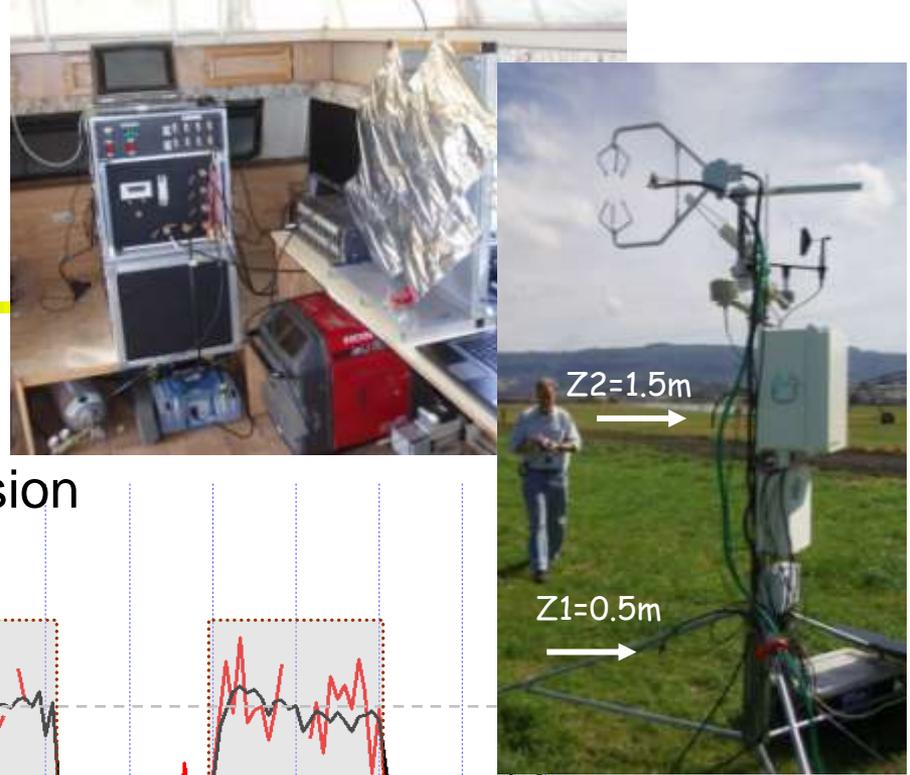
## ◆ Assumptions / limitations

- $A=0$ : no advection (infinite horizontal extent)
- $N_2O$  and  $CO_2$  releases have same footprint (surface)
- $F_h \propto^{nl} C_{NBL} - C_{bgnd}$  entrainment flux depends on gradient at  $h$
- Point measurements of  $C$  are  $\propto^{nl}$  to  $C_{NBL}$
- $C_{NBL} \sim C_{BGND}$  at  $t=0$  (start of the night)

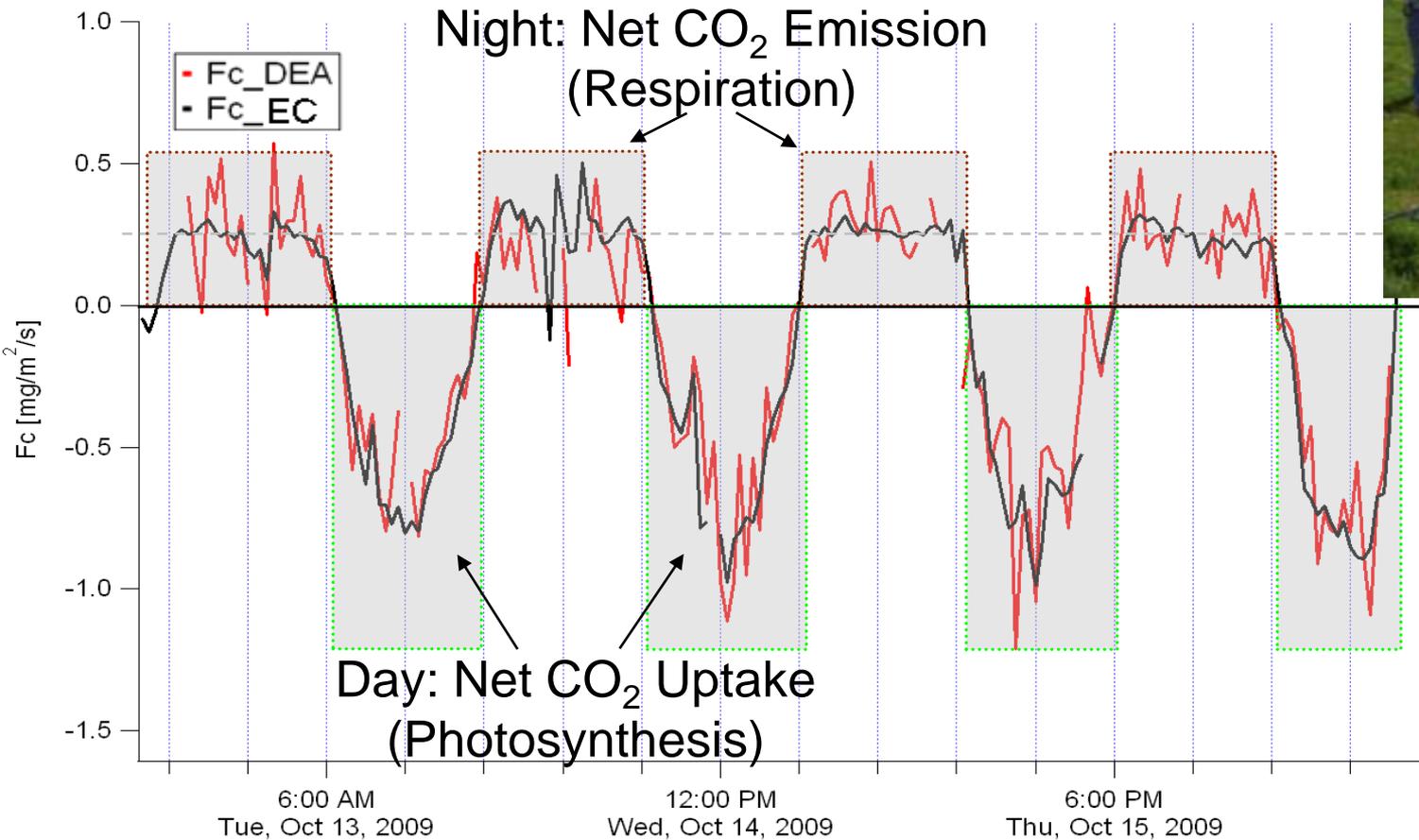
# CO<sub>2</sub> flux, chambers, trial 1



# Fluxes: flux gradient and eddy accumulation methods



Here: Disjunct Eddy Accumulation



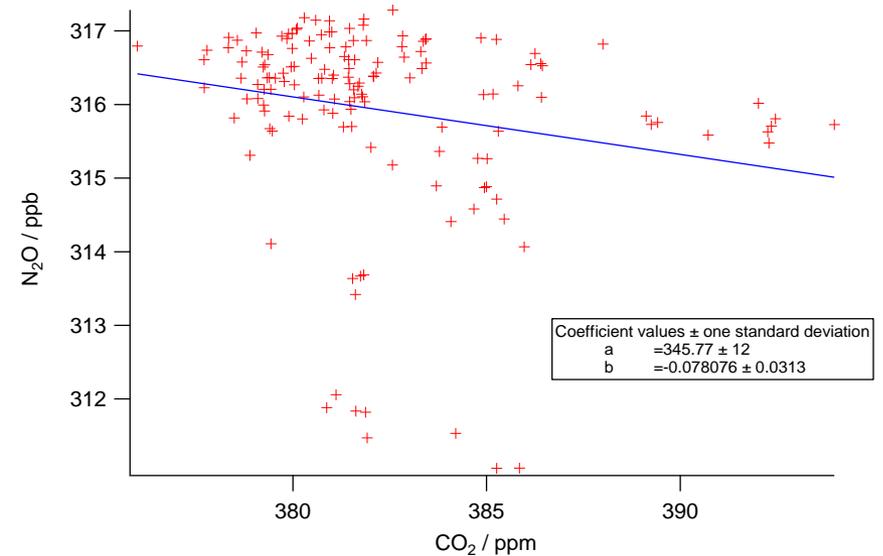
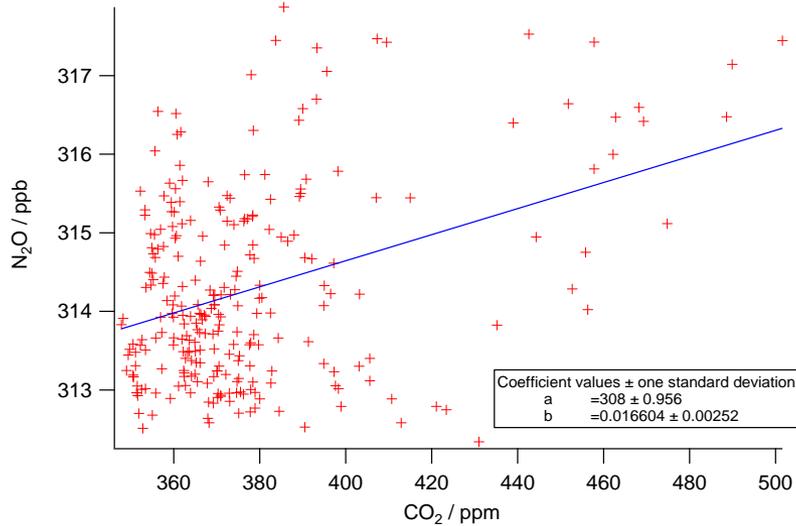
# Regional N<sub>2</sub>O emissions estimates

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Location	Slope ppb/ppm	F <sub>CO2</sub> mgCO <sub>2</sub> m <sup>-2</sup> s <sup>-1</sup>	F <sub>N2O</sub> ngN m <sup>-2</sup> s <sup>-1</sup>
Nowra Aug 2008	0.092	0.1	5.8
Nowra Oct 2009	0.066	0.25	10.5
Nowra Dec 2011	0.056	0.2	7.1
Lauder Sept 2010	0.095	0.1*	6.0

\* *guesstimate*

# It doesn't always work!

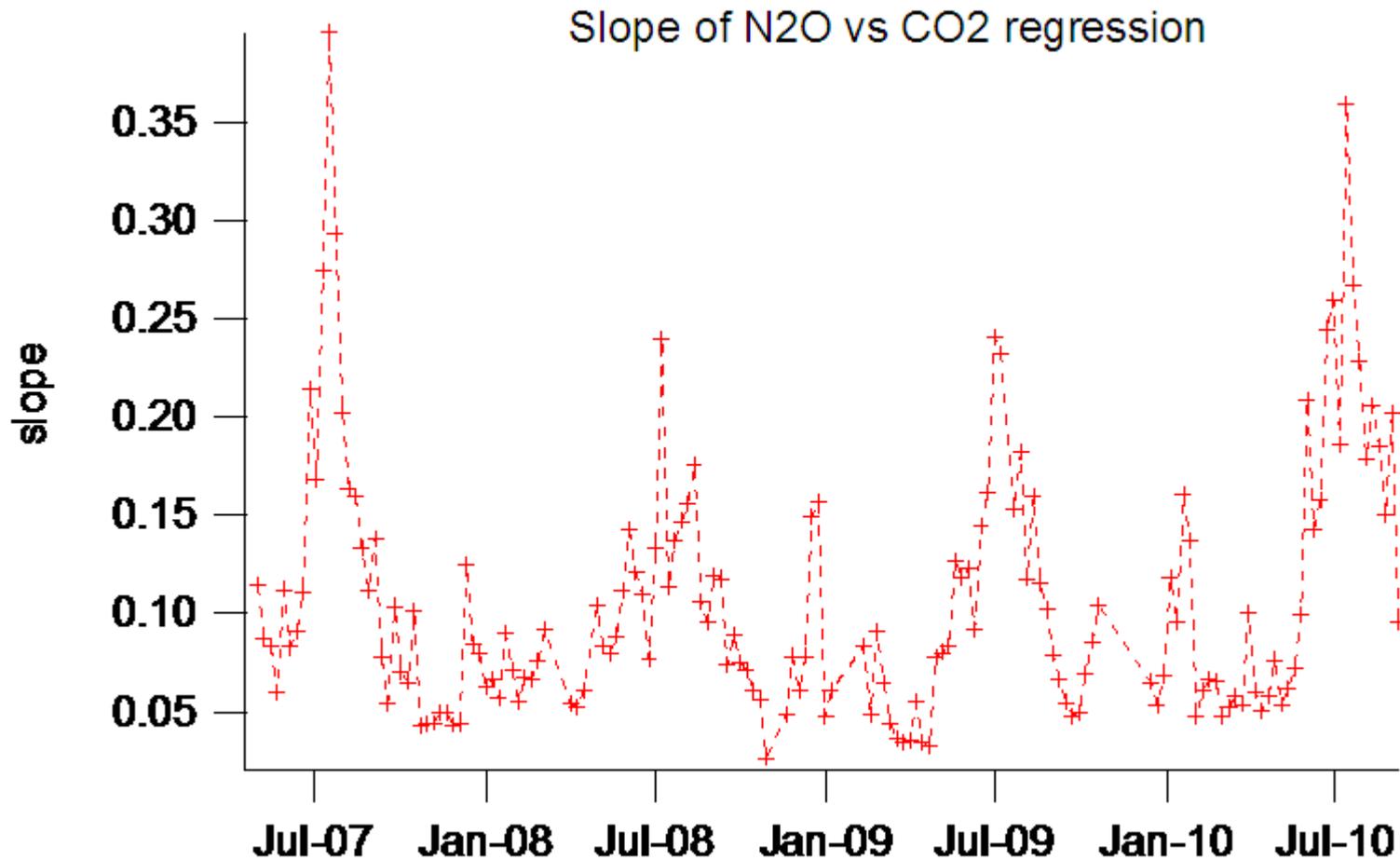


- ◆ OASIS - Wagga Wagga
- ◆ October 1995
- ◆ 22m tower, mixed agriculture
- ◆ Spring lucerne pasture

- ◆ Ozflux tower, Tumbarumba
- ◆ Nov 2006
- ◆ 70 m tower, eucalypt forest
- ◆ Weak N<sub>2</sub>O uptake?

# Lauder time series $dN_2O/dCO_2$

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# Summary - NBL regional estimates

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- ◆ Require 2 measurements:

- $dN_2O/d(\text{tracer})$
- an independent estimate of  $F_{\text{tracer}}$ 
  - Here tracer is  $CO_2$

$$F_{0,N_2O} = F_{0,CO_2} \cdot \frac{dC_{NBL,N_2O}}{dC_{NBL,CO_2}}$$

- ◆ If

- $N_2O$  and tracer ( $CO_2$ ) emissions are co-located
- Uniform emissions landscape

- ◆ Then

- Regional emissions estimates to  $< 2 \text{ ngN m}^{-2} \text{ s}^{-1}$ 
  - $2 \text{ ngN m}^{-2} \text{ s}^{-1} \Rightarrow \text{vertical gradient of } \sim 0.02 \text{ ppb m}^{-1}$

- ◆ Suitable for background emissions over large uniform areas

- Eg cropping & pasture
- Ozflux sites
- Canterbury Plains - Landcare's FTIR
- $CH_4$  too?

# Thank you



Feike  
Dijkstra

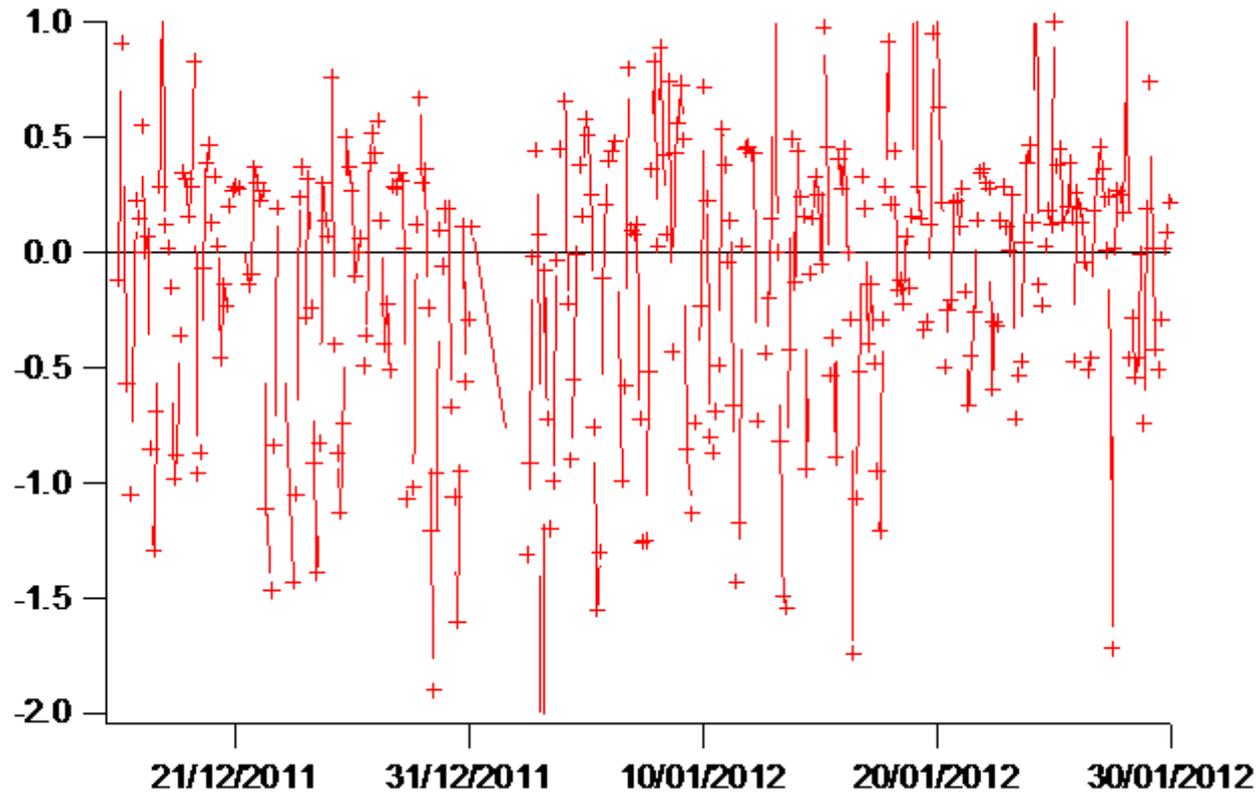
Beckie  
Phillips



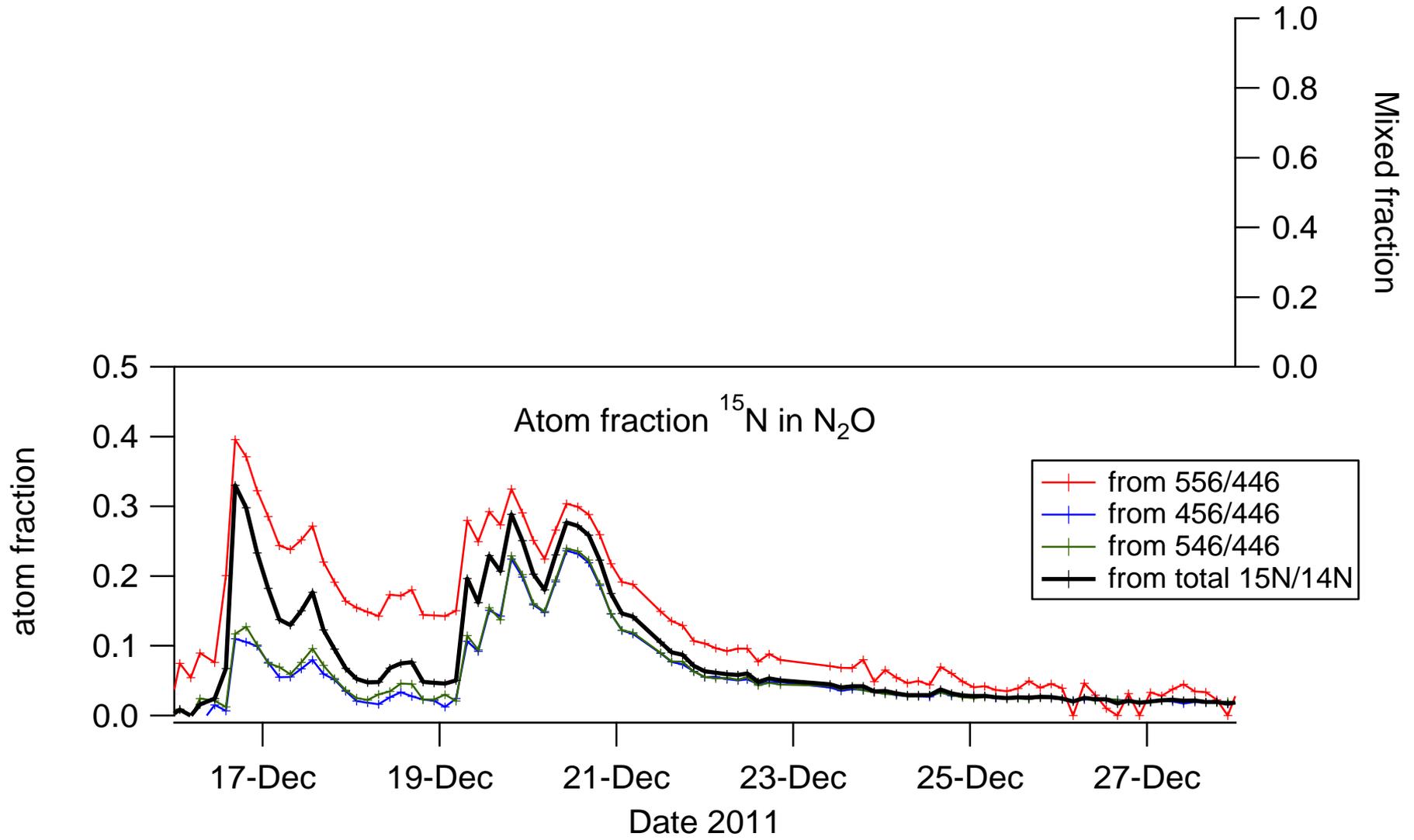
- ◆ UoW:  
Chris Caldw, Graham Kettlewell, Travis Naylor, Martin Riggerbach
- ◆ Manildra site:  
Glenys Lugg, Roy Lawrie
- ◆ CSIRO:  
Ray Leuning, Tom Denmead
- ◆ Uni Bremen:  
Katinka Petersen, Thorsten Warneke

# CO<sub>2</sub> flux - eddy covariance

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# $^{15}\text{N}$ mixing



# $^{15}\text{N}$ mixing

