High Performance Analyzers for Fast, Real-time Measurements

15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques

Max-Planck-Institute for Biogeochemistry (MPI-BGC)
Jena, Germany

Doug Baer, Ph.D.
Los Gatos Research

L G R

Novel Instruments Provide New Opportunities

- *Fast Greenhouse Gas Analyzer:* CH_4, CO_2, H_2O at 10 Hz
- *Fast N_2O/CO Analyzer:* N_2O and CO at 20 Hz
- *Carbon Dioxide Isotope Analyzer:* $\delta^{13}CO_2$ and CO_2 at 2 Hz
- *Fast Methane Analyzer:* CH_4 at 20 Hz
- *Water Vapor Isotope Analyzer:* $\delta^{18}O$, $\delta^{2}H$ and H_2O at 2 Hz
- *Liquid Water Isotope Analyzer:* $\delta^{18}O$, $\delta^{2}H$ at 120 samples/day
- *Fast Ammonia Analyzer:* NH_3 at 10 Hz

Novel Instruments Provide New Opportunities (> 280 instruments on 7 continents)

Christensen, et al, **Nature** 2008;456 (7222):628-30

Novel Instruments Provide New Opportunities (> 280 instruments on 7 continents)

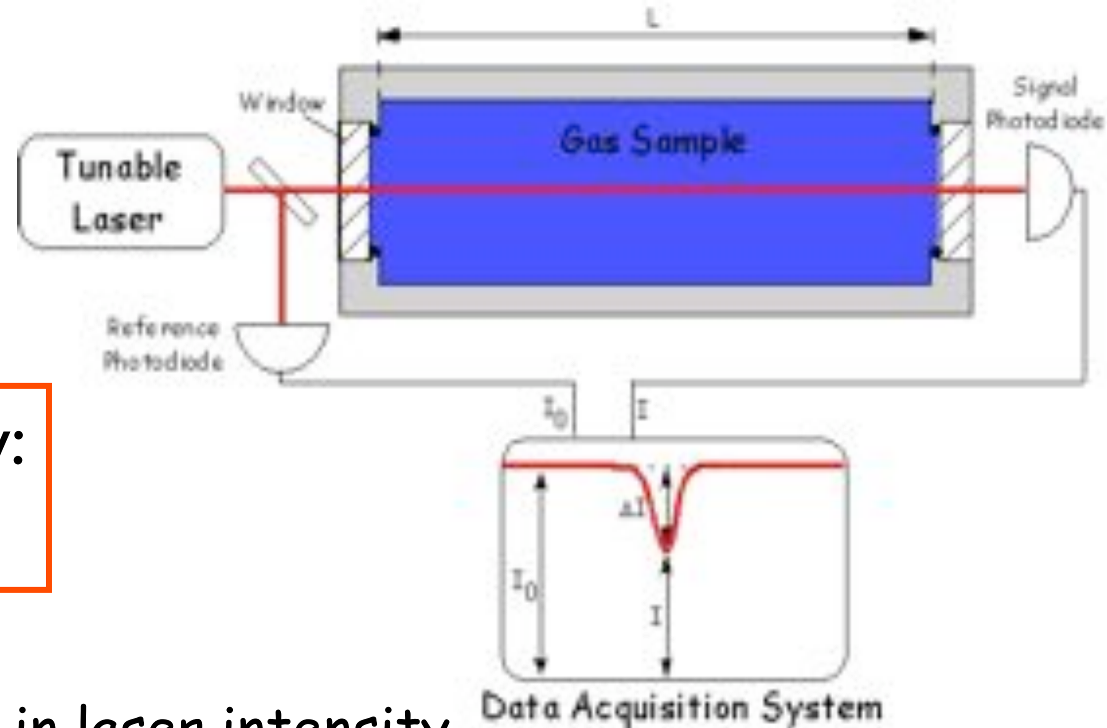
Lake Untersee, Antarctica (NASA)

L G R

Novel Instruments Provide New Opportunities (> 280 instruments on 7 continents)

Measurements on-board UAV (ETH Zurich)

High Resolution Absorption Spectrometry: General Overview



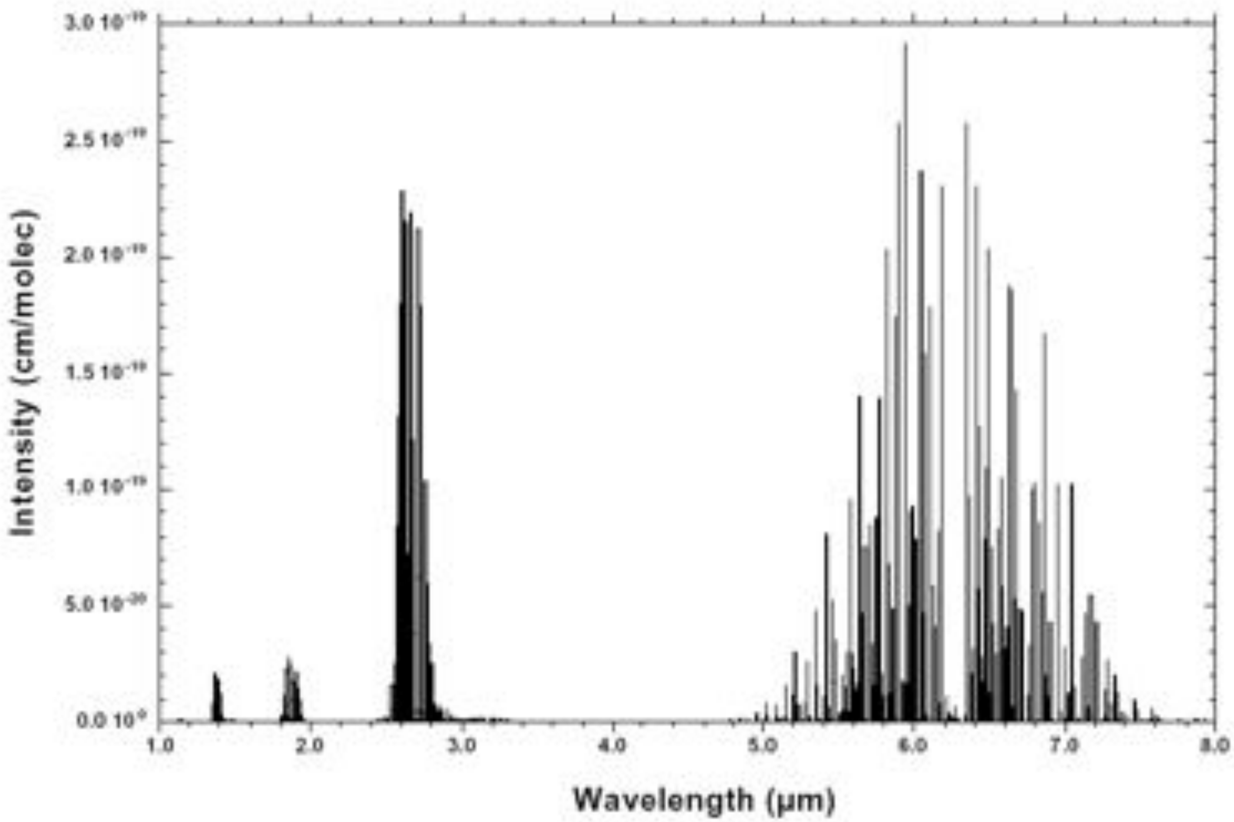
Beer-Lambert-Bouguer Law:

$$\Delta I/I_o = 1\text{-}\exp(-\alpha L_{eff})$$

$\Delta I/I_o$	=	fractional change in laser intensity
S	=	absorption line strength
χ	=	mixing ratio (mole fraction)
P	=	total pressure
L_{eff}	=	effective optical path length
$\alpha(\lambda)$	=	absorption coefficient, $S\, P\, \chi\, \phi(\lambda)$

Absorption Spectrometry

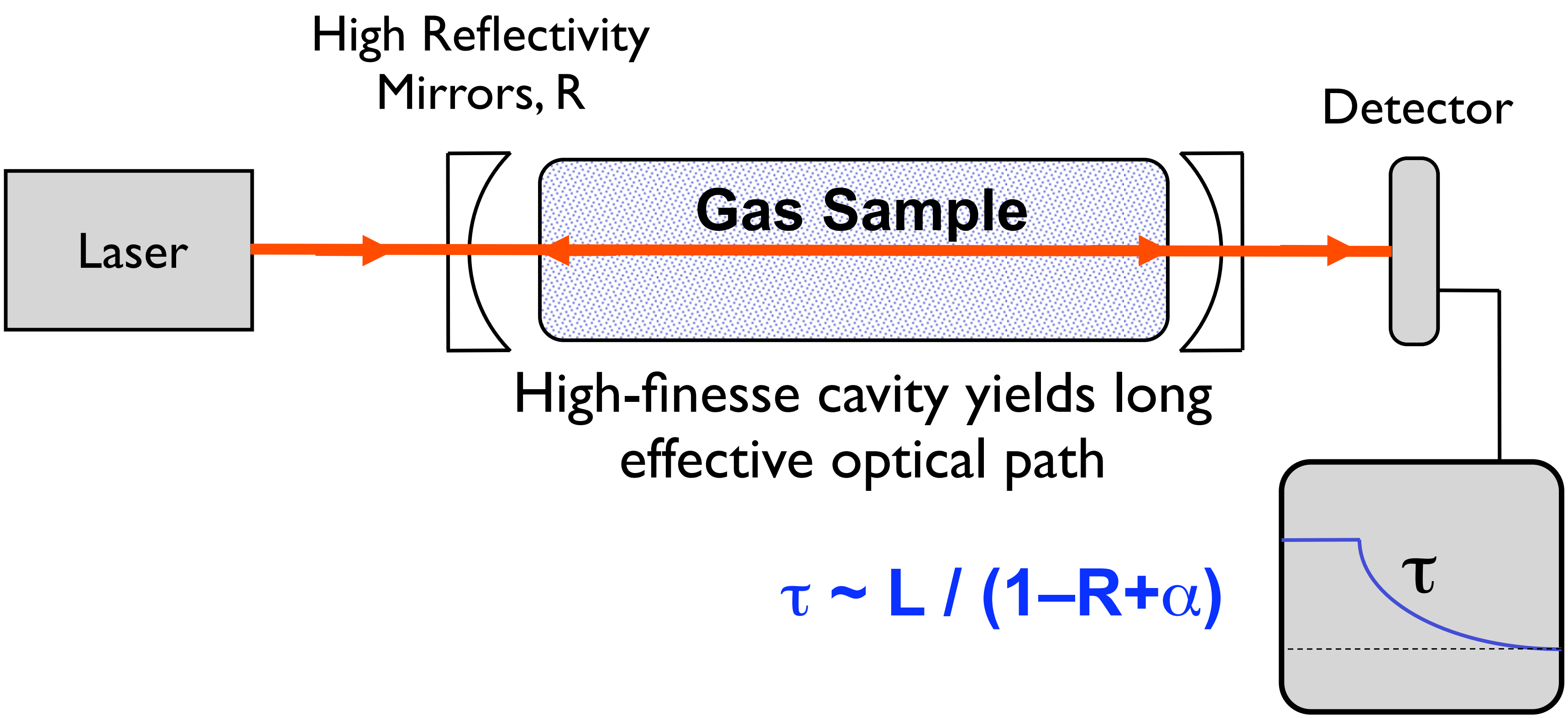
Water Spectrum



- Mid-IR strongly absorbs, but is hardware limited
- Near-IR region is accessible with inexpensive telecom lasers
- Near-IR lasers are robust, reliable, easy to use, inexpensive

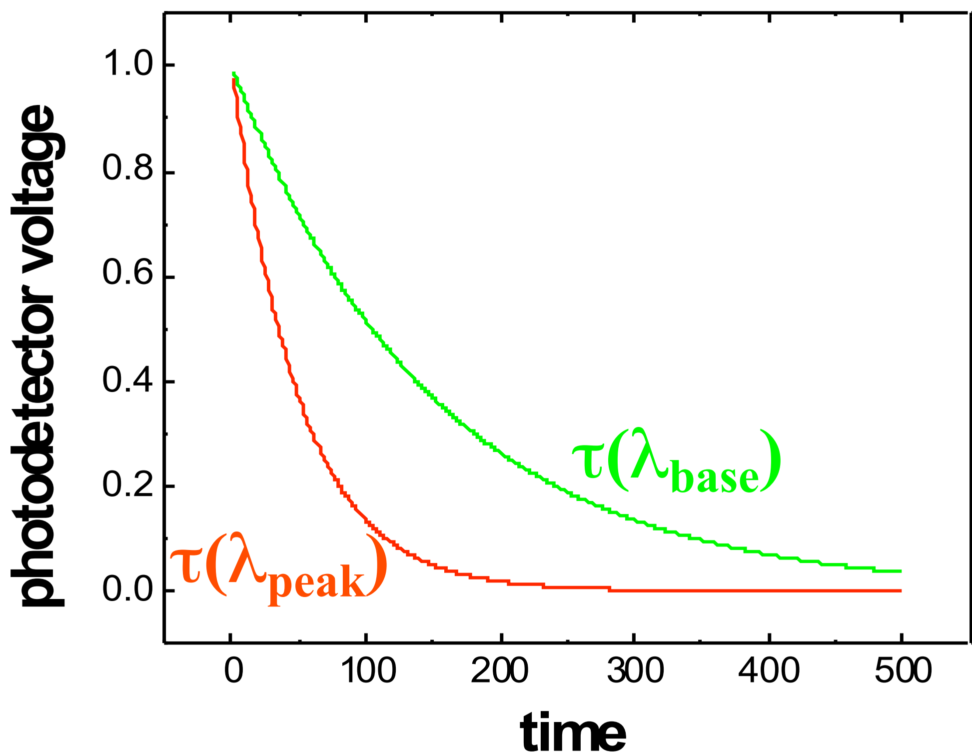
Cavity Ringdown Spectroscopy (CRDS)

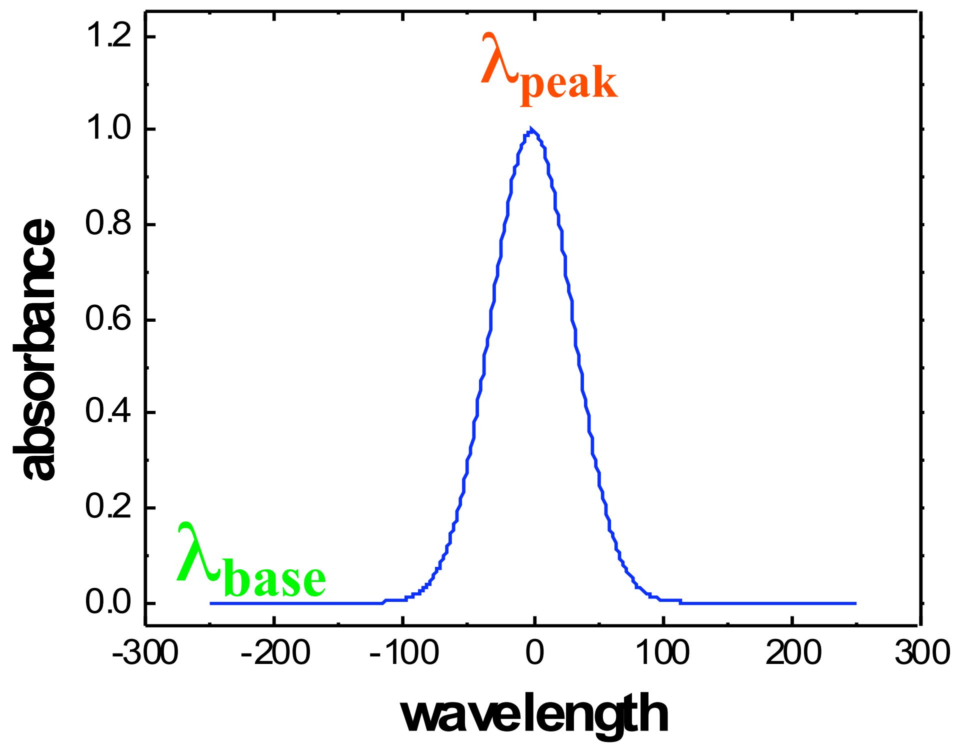
Invented in 1988 by LGR founder (O'Keefe)



- Rate of decay ($1/\tau$) depends on absorption α
- Sensitivity derived from long optical path
- Independent of laser amplitude fluctuations

Absorption determined from $\tau(\lambda)$ vs λ: $\alpha(\lambda) = \frac{1}{c}\left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_o}\right)$

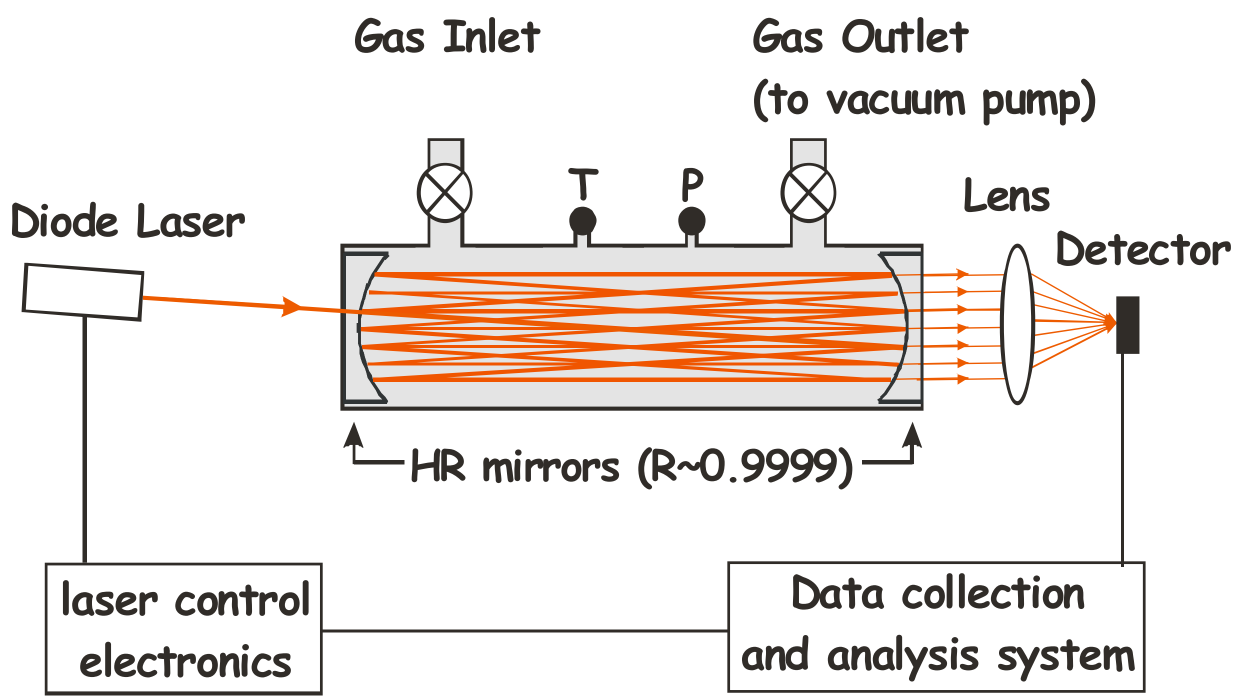




- Measurement of $\tau(\lambda)$ + Beer's Law yields mixing ratio
- Requires good laser spatial-mode quality
- Misalignments decrease sensitivity
- Requires relatively fast electronics

L G R

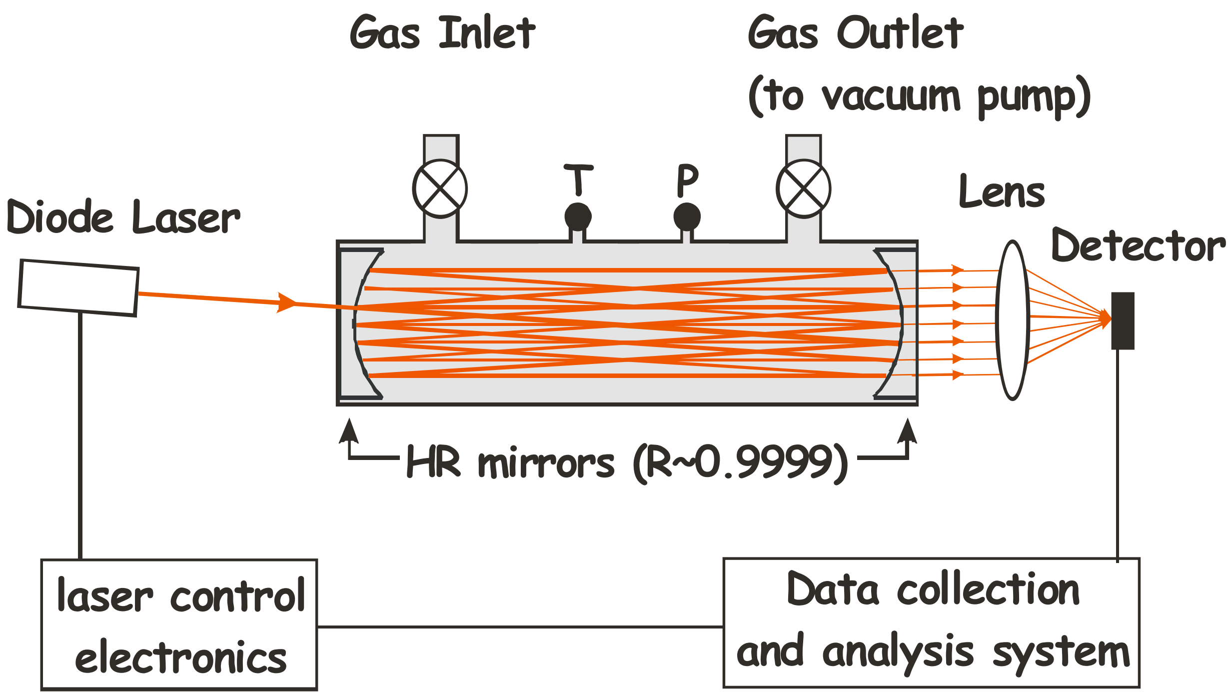
LGR's Off-Axis ICOS: Cavity-Enhanced Absorption Technique



- Optical cavity provides pathlength enhancement: $L_{eff} = L / (1-R) = c\,\tau$
- Typical R = 99.995%, L_{eff} = 3-25 kilometers (or greater)
- Extraordinarily robust - alignment insensitive, telecom-grade components
- Allows for near-IR measurements of overtone and combination bands
- Measurements using mid-IR QC lasers provide extremely high sensitivity

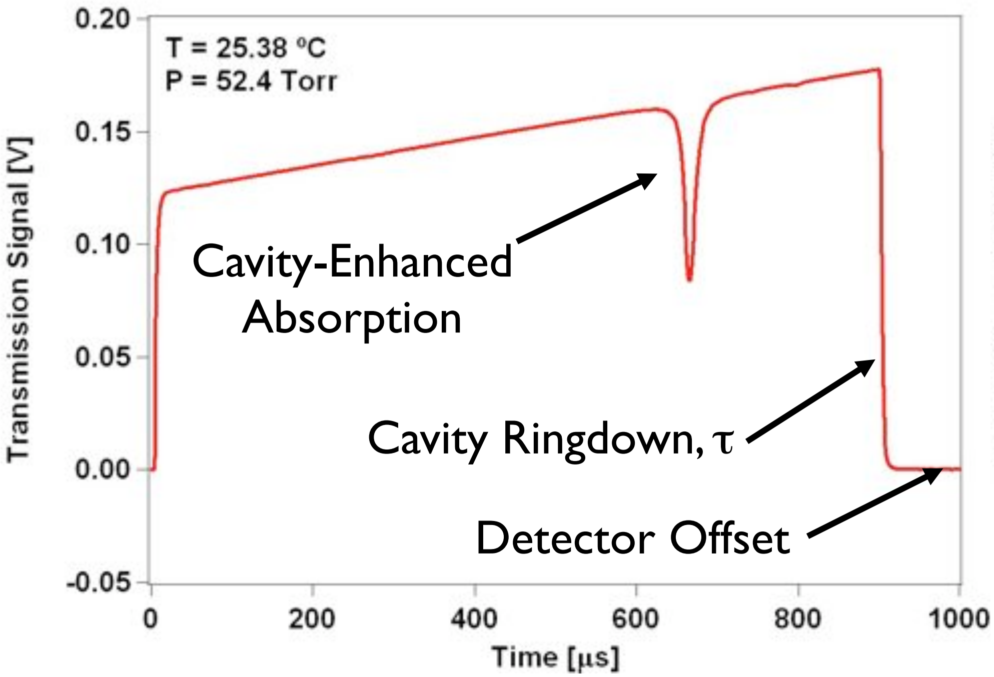
L G R

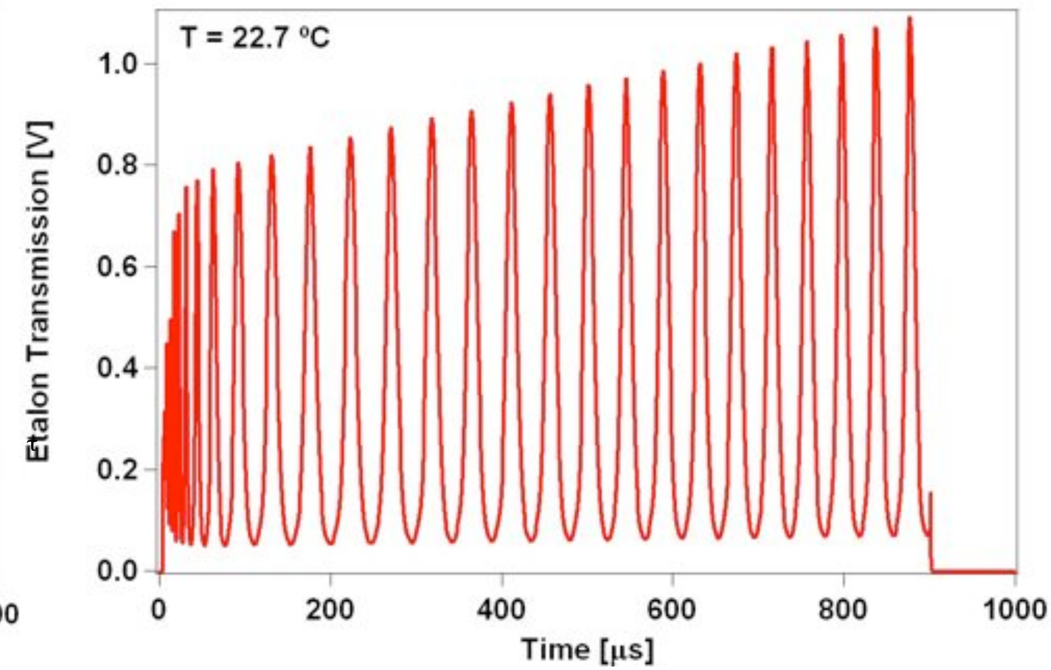
Advantages of Off-Axis ICOS (LGR patent)



- All parameters (absorption, L_{eff}, P, T) determined quickly (300-Hz, typical)
- Robust optical alignment → negligible alignment drift, mechanically stable
- Off-axis alignment spatially separates beam paths through cell
  → lengthens time/distance before beam retraces itself
  → eliminates unwanted resonance interference effects
- Off-axis alignment eliminates optical feedback from cavity to laser source

LGR's Off-Axis ICOS: typical raw data trace





Transmission Spectrum

- Measure absorption, baseline, detector offset
- Measured ringdown yields L_{eff}
- Measure/control gas flow parameters (T, P)
- Sweep laser wavelength at 100 – 500 Hz

Measured Etalon Transmission

- Accurately determines laser tuning rate
- Solid etalon (SiO_2)
- Measure length and temperature
- Converts time to relative laser frequency

Advantages of LGR's instruments

- Sensitive, precise, accurate: long path, absolute measurement
- Selective: high resolution absorption provides specificity
- Fast: absorption spectra recorded directly in milliseconds
- Simple + robust: proven on 7 continents, aircraft, UAV, ocean
- Convenient: low power, open architecture, flexible
- Economical: prices starting at $30k

High accuracy requires minimizing total uncertainty

$$\left(\frac{\Delta\chi}{\chi}\right)^2 = \left(\frac{\Delta(I/I_o)}{I/I_o}\right)^2 + \left(\frac{\Delta\nu_{laser}}{\nu_{laser}}\right)^2 + \left(\frac{\Delta P}{P}\right)^2 + \left(\frac{\Delta S}{S}\right)^2 + \left(\frac{\Delta L_{eff}}{L_{eff}}\right)^2$$

L G R

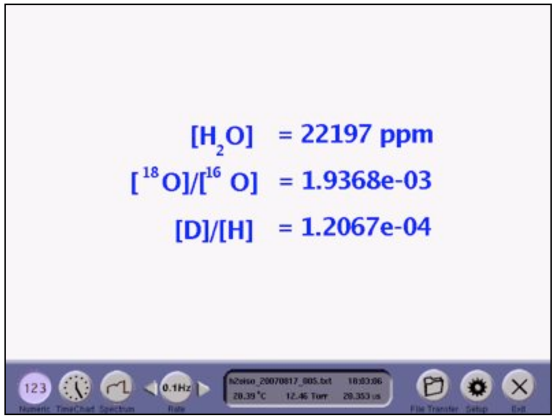
Instrumentation Packaging: Options

rackmount (19” wide, 5U)

benchtop

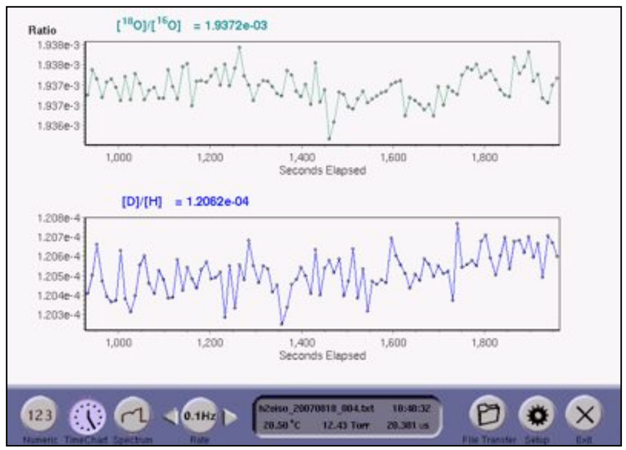
- Portable rugged package allows field operation
- On-board computer provides real-time data analysis & storage
- 90-150 Watts, 27 kg
- No consumables
- Simple user interface; analog, digital (RS232), Ethernet outputs
- Fully autonomous operation

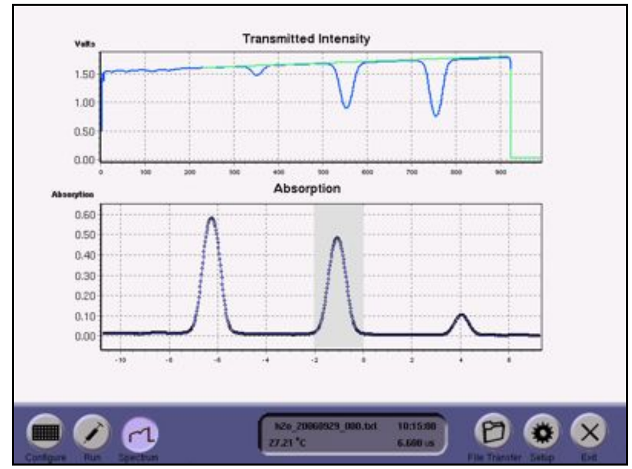
User Interface: Multiple Real-Time Displays



numeric

time chart





raw data / spectra

- Multiple display options: numeric, time chart, raw data/spectra
- Measurements of mixing ratio, gas temperature, pressure
- User-selectable data rate (0.01-20 Hz)

L G R

Gas Analyzer Options

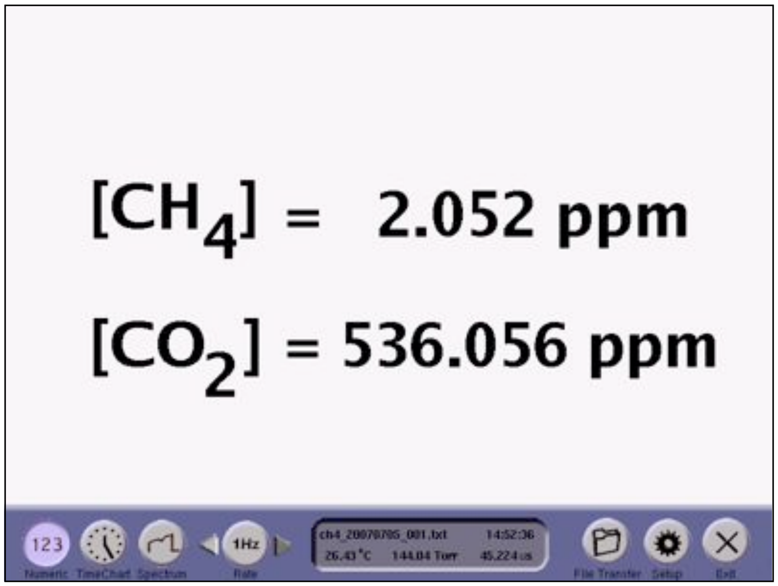
- Multiport Injection Unit: automatic sampling from 16 locations

- Manual injection of discrete samples

- Remote monitoring/control
- Dynamic dilution system (quantification of high concentrations)

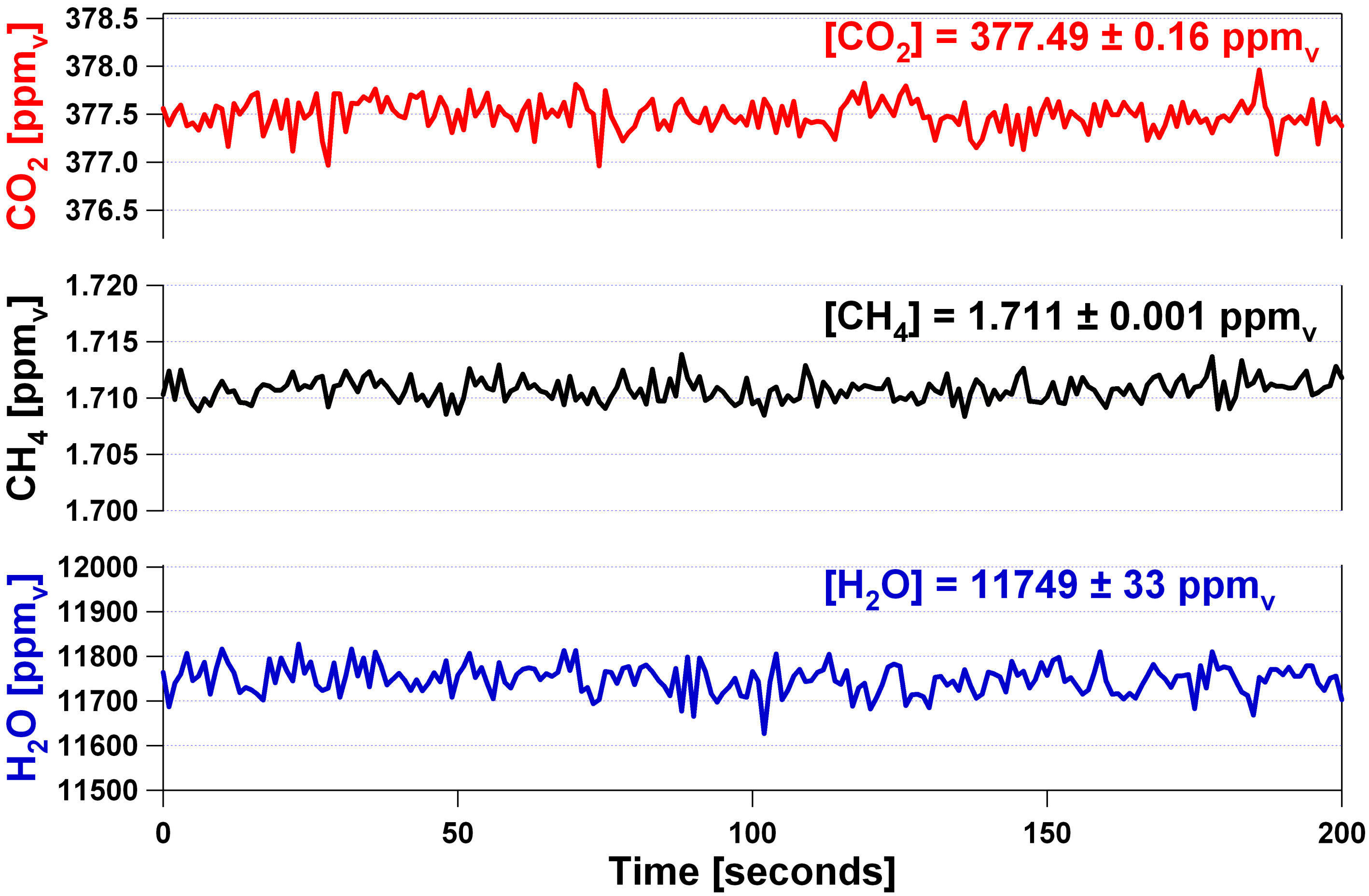
Fast Greenhouse Gas Analyzer (CH_4, CO_2, H_2O)

Applications include atmospheric monitoring, chamber flux



- CH_4, CO_2 H_2O reported in ppm → mixing ratio
- Measurement cell pressure → Torr
- Mirror ringdown time (τ) → microseconds
- Cell temperature → Celsius
- Current data file name, time

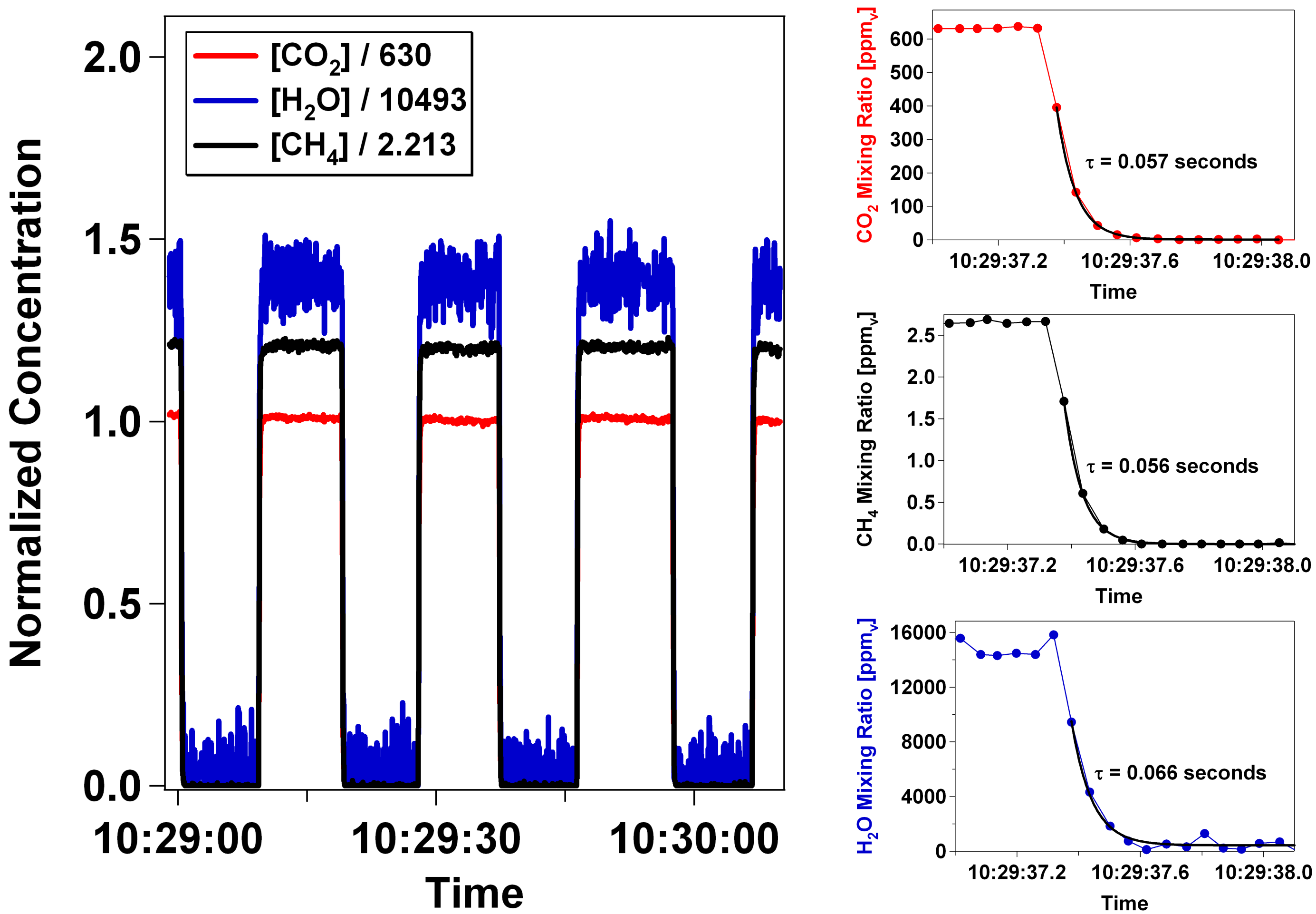
Fast Greenhouse Gas Analyzer: 1-Hz raw data



Precision (1 Hz):

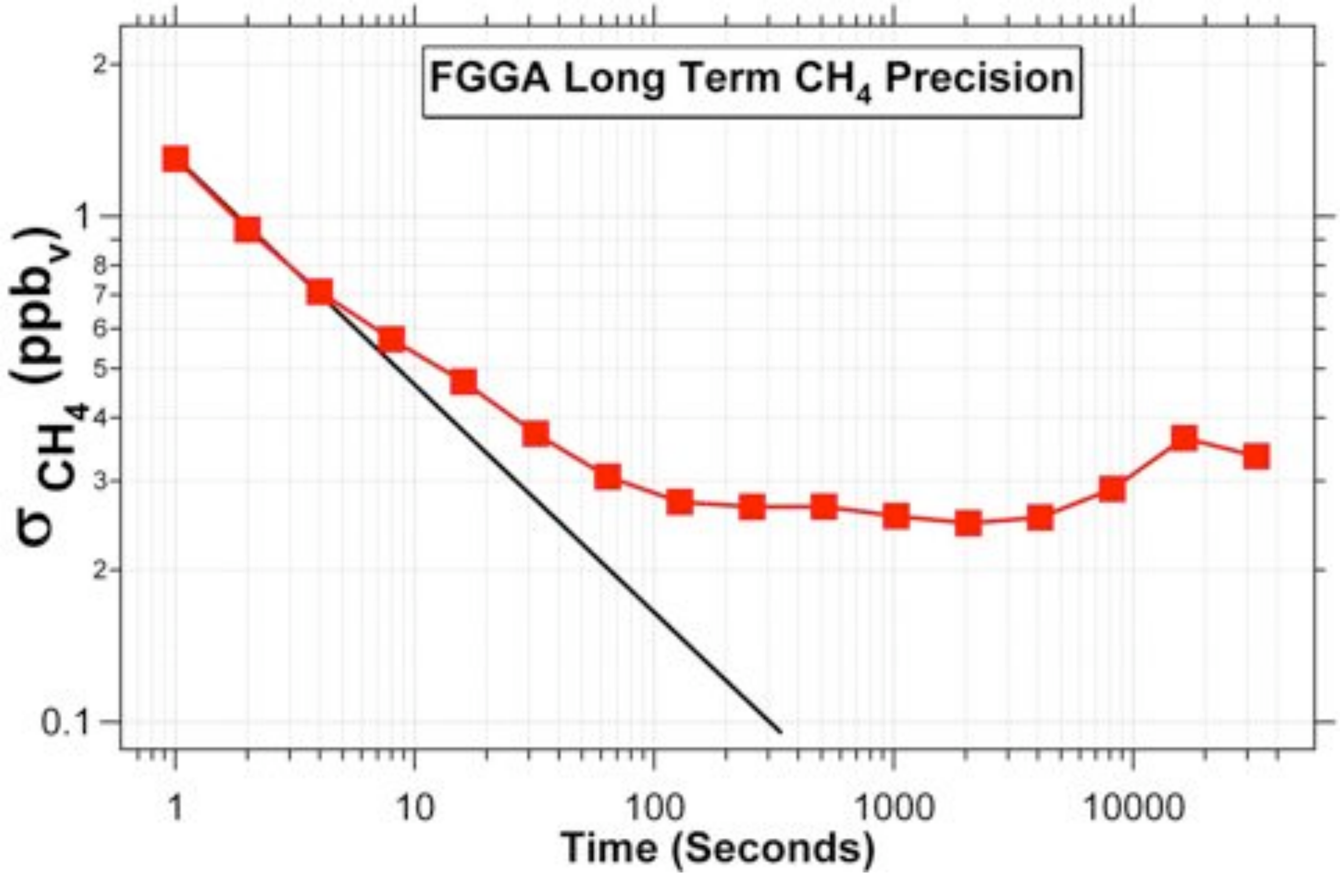
- CH_4: 1 ppbv
- CO_2: 0.16 ppmv
- H_2O: 33 ppmv

Fast Greenhouse Gas Analyzer: Time Response



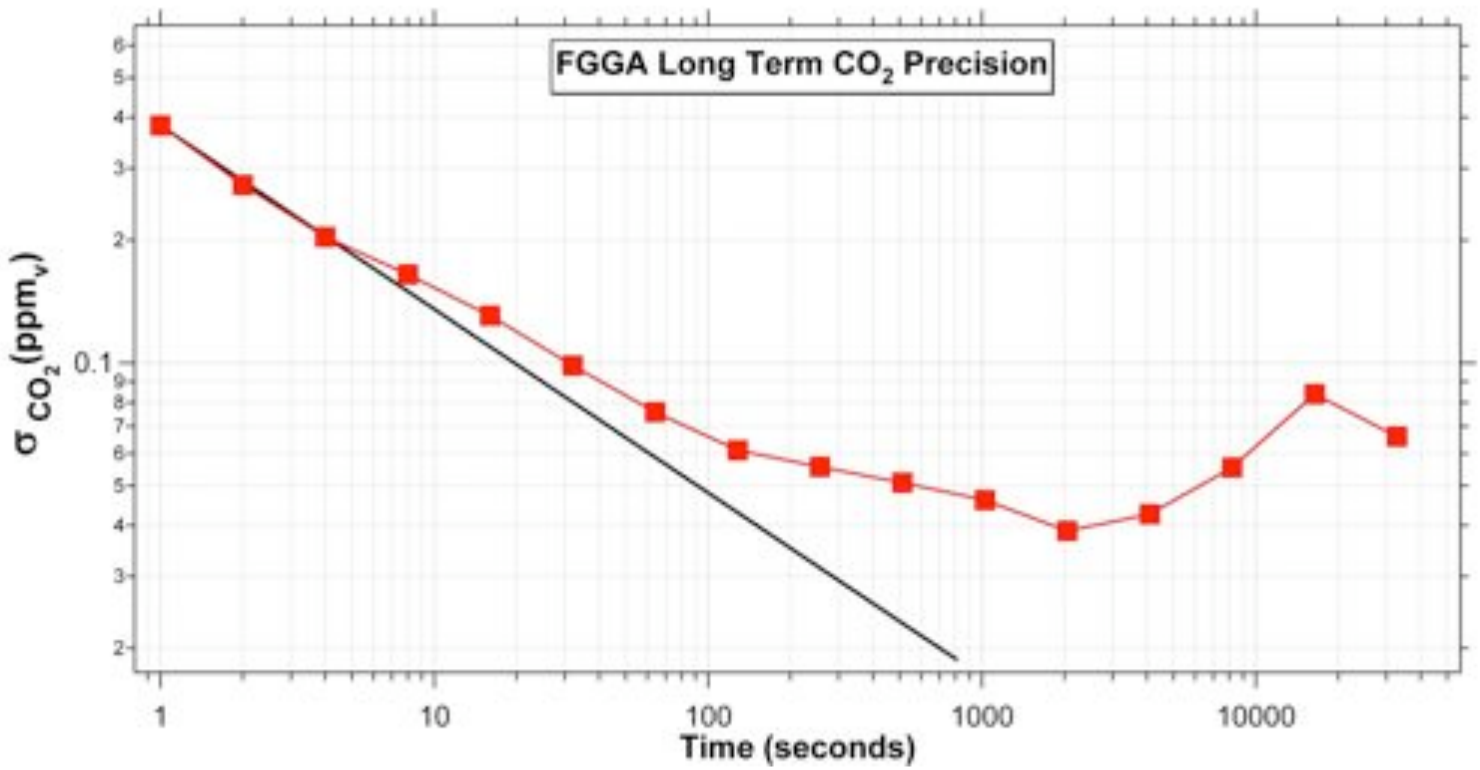
- Inlet switched from air to "zero air" to determine flow response
- Concentration decays yield time constants sufficient for eddy flux

Fast Greenhouse Gas Analyzer: Stability



- CH_4 and CO_2 in air measured at a 1-Hz sampling rate (10-Hz possible)
- Data and associated Allan plots show stable operation and ability to reliably average over long times to improve precision

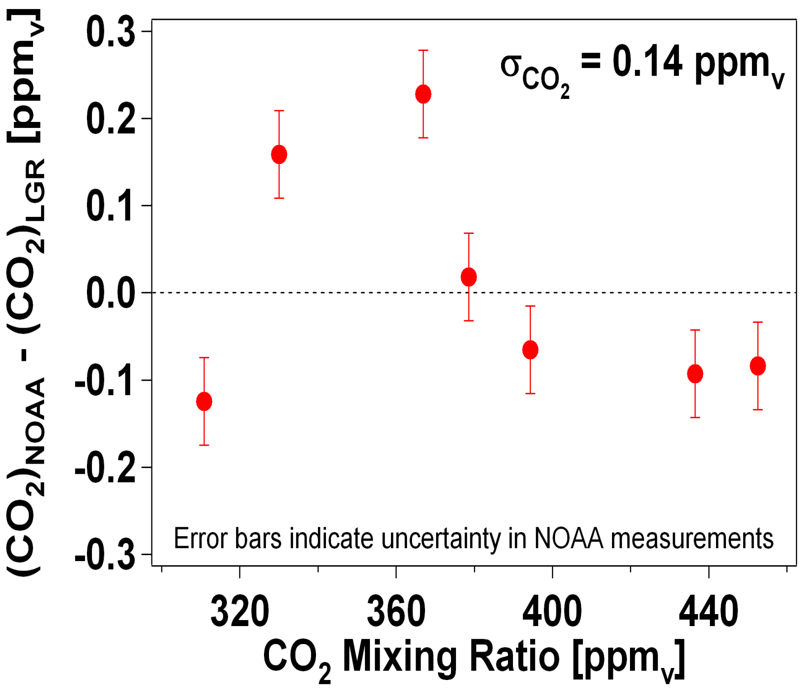
Fast Greenhouse Gas Analyzer: Stability

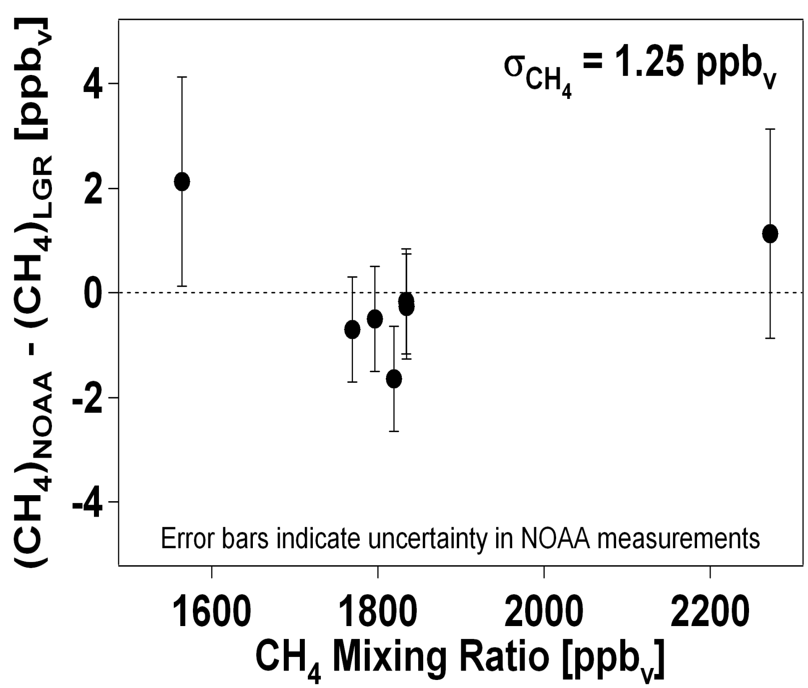


- CH_4 and CO_2 in air measured at a 1-Hz sampling rate (10-Hz possible)
- Data and associated Allan plots show stable operation and ability to reliably average over long times to improve precision.

Fast Greenhouse Gas Analyzer: Accuracy

Comparison between NOAA and LGR measurements for CO_2 and CH_4.

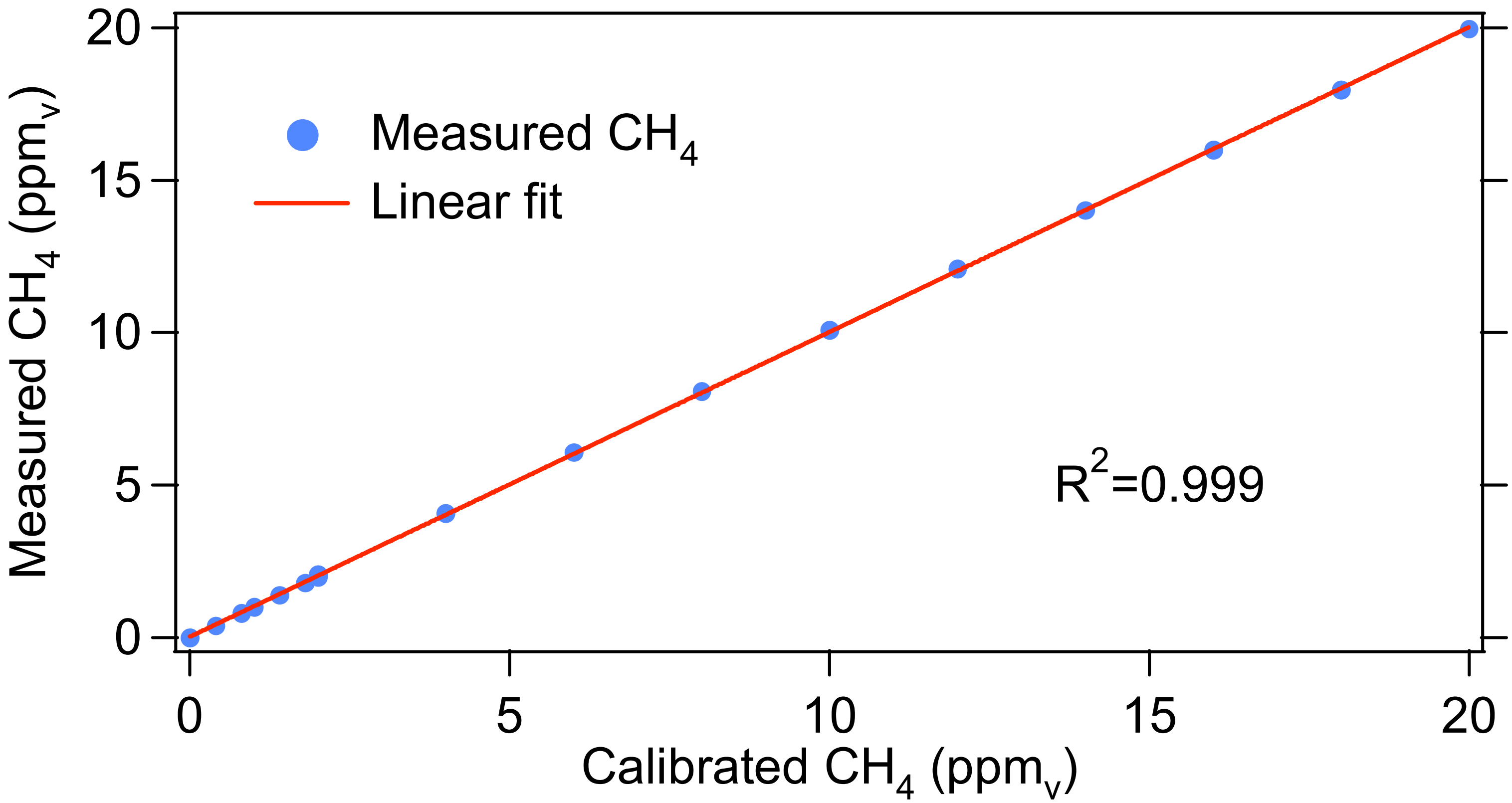




- CO_2 (left) and CH_4 (right) were calibrated on a single-point
- CO_2 error bars indicate NOAA's anticipated uncertainty of ±0.05 ppm
- CH_4 error bars indicate NOAA's anticipated uncertainty of ±1 ppb for concentrations near 1.8 ppm and ±2 ppb for values outside this range
- Analyzer accurate to ±0.14 ppm for CO_2 and ±1.25 ppb for CH_4

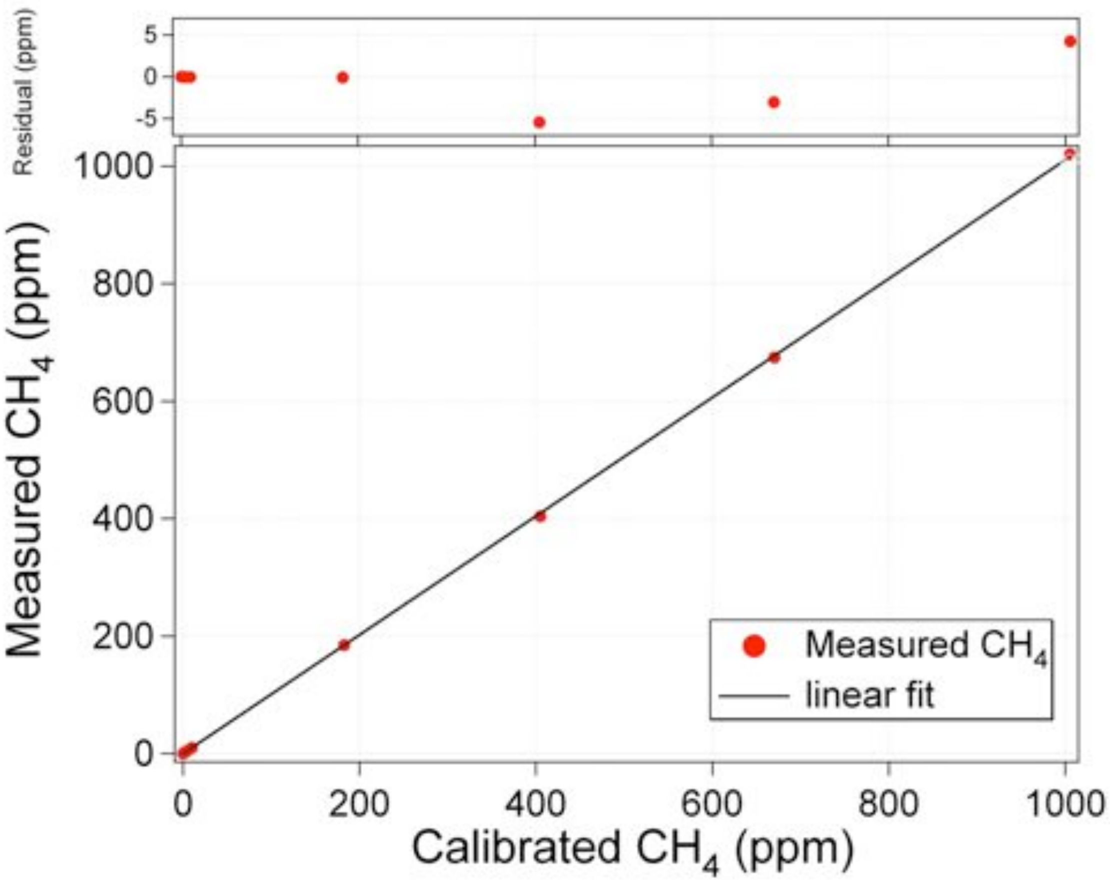
L G R

CH_4 measurements vs ref values



- Measurements agree with ref values to < 0.5% (0.1-25 ppmv)

Accurate CH_4 from ambient to 1000 ppmv

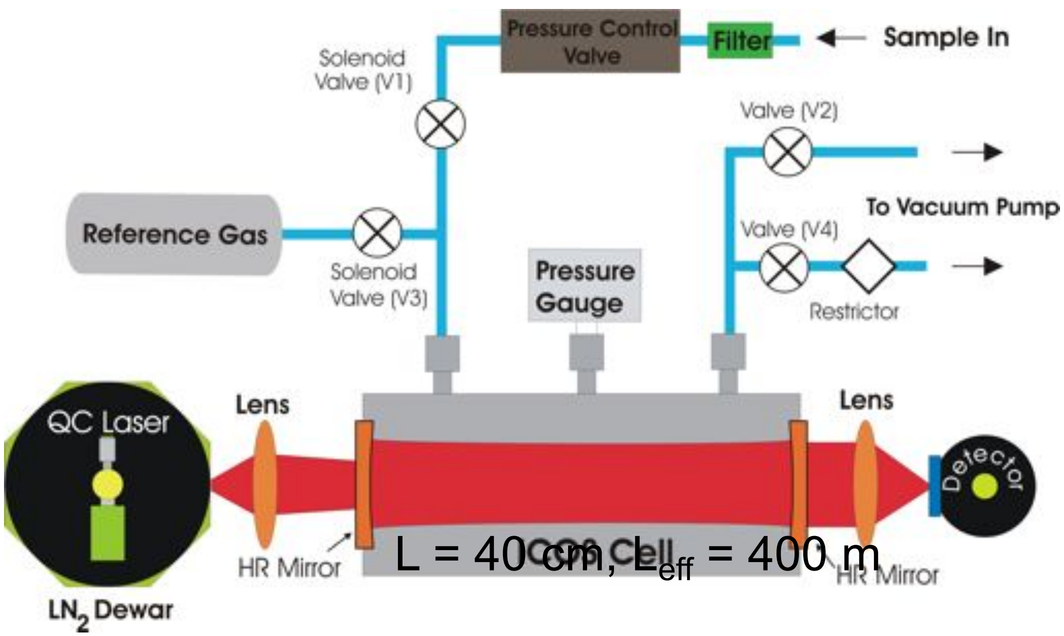


- Measurements agree with ref values to better than 1% (up to 1000 ppmv)
- High CH_4 levels demonstrated in field (rice, peat, landfills) by many users
- Off-Axis ICOS reports mixing ratios with extremely high optical depth

Fast N_2O/CO Analyzer for Flux

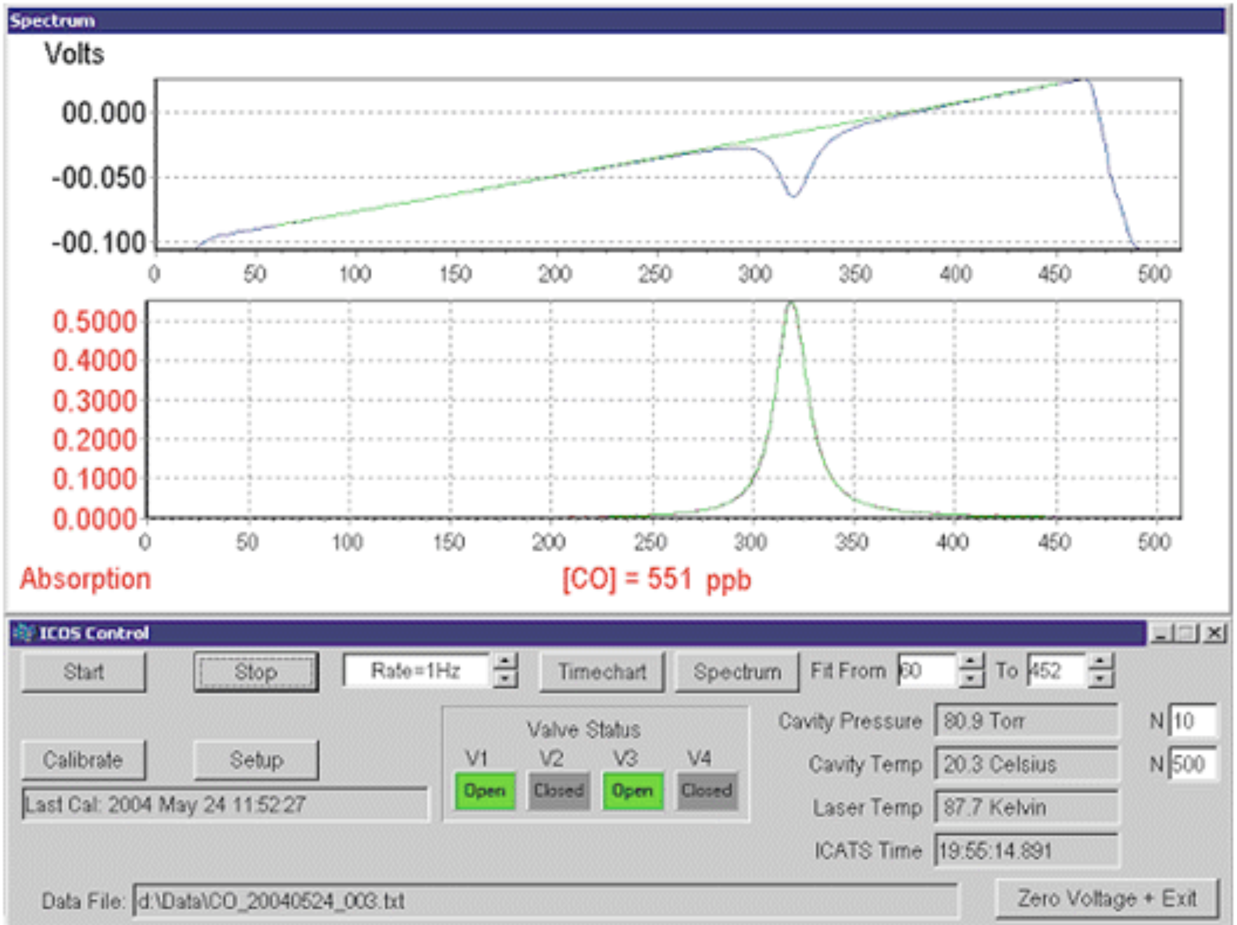
- Real-time continuous measurements in air
- Extremely wide dynamic range
- Fast (20 Hz) allows eddy covariance flux
- Low power (150 watts) facilitates field operation
- No sample prep - direct measurements in air

CO Analyzer (previous version; LN_2)
On-board measurements in troposphere/stratosphere



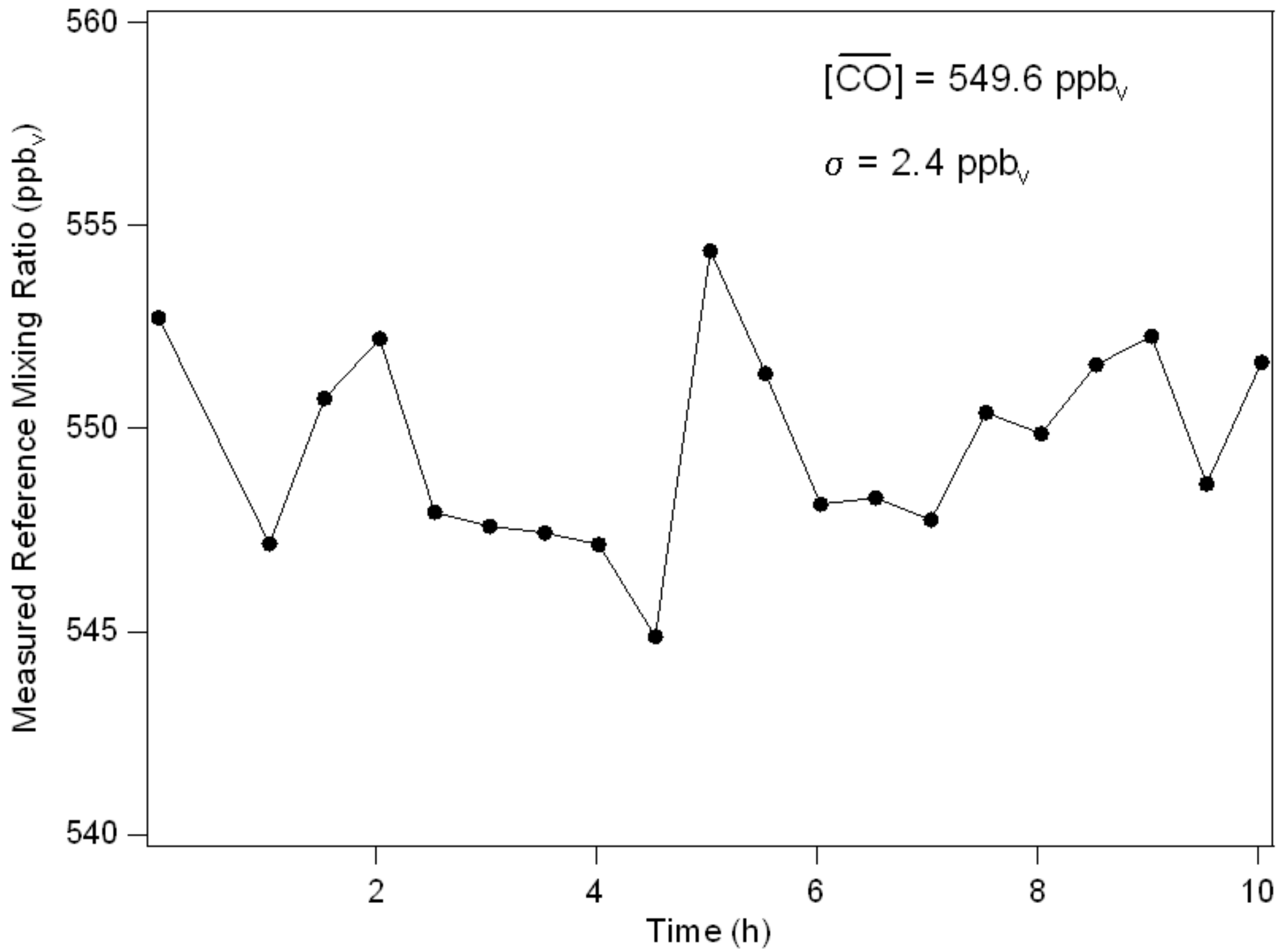
- Autonomous measurements of CO at 1 Hz on NASA DC8
- Reference gas cylinder used to verify mirror health

CO measurements in stratosphere (NASA DC-8)



- QC laser probes R(7) transition (v band) at 4602 nm (2173 cm^{-1})
- Cavity enhanced transmission (top) and absorption (bottom)

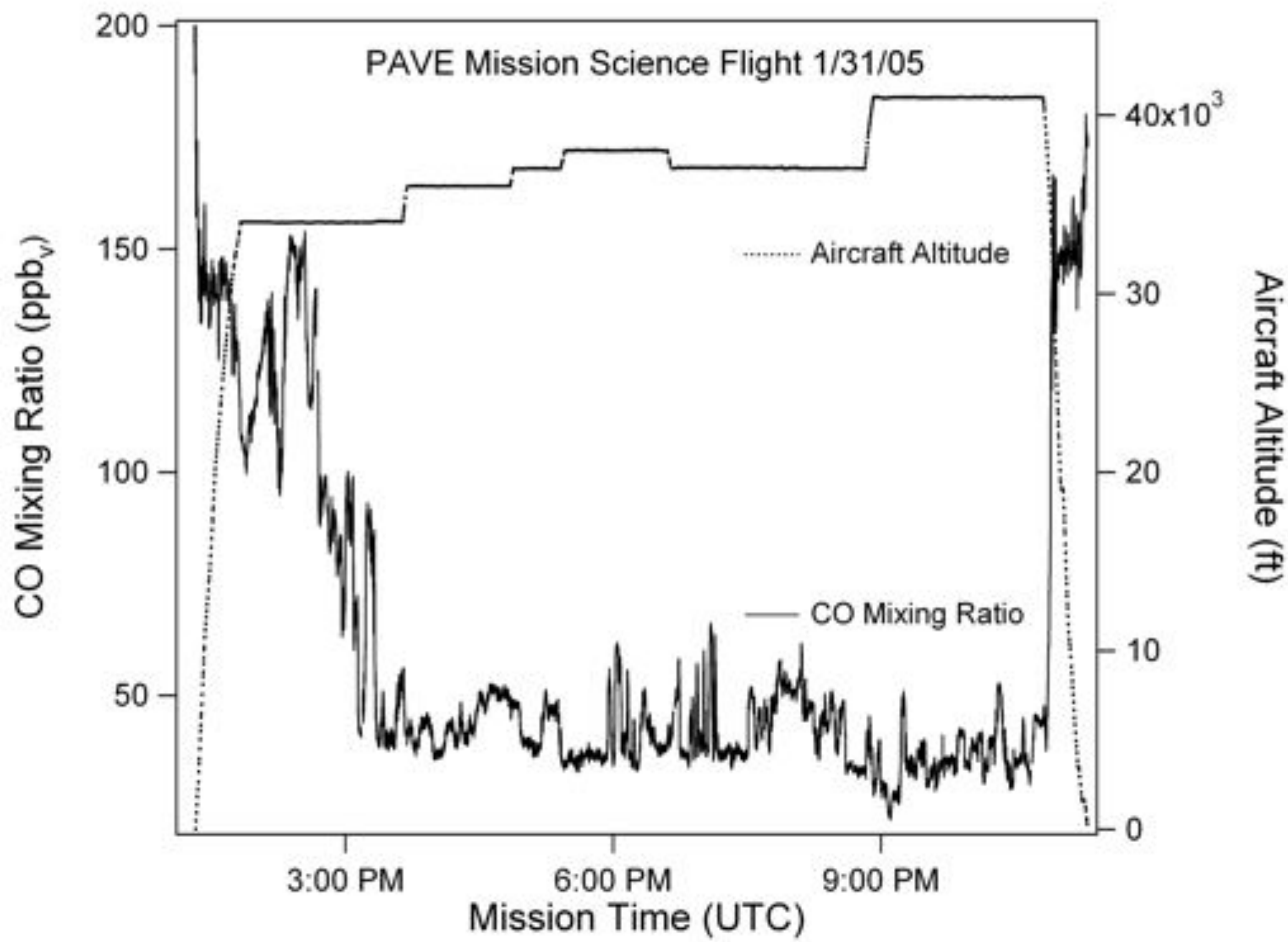
Measured CO in ref cylinder during Polar Aura Validation Experiment flight



- CO reference measurements stable (< 0.5%) over 10 hours
- Reproducibility demonstrated w/o regular calibration

L G R

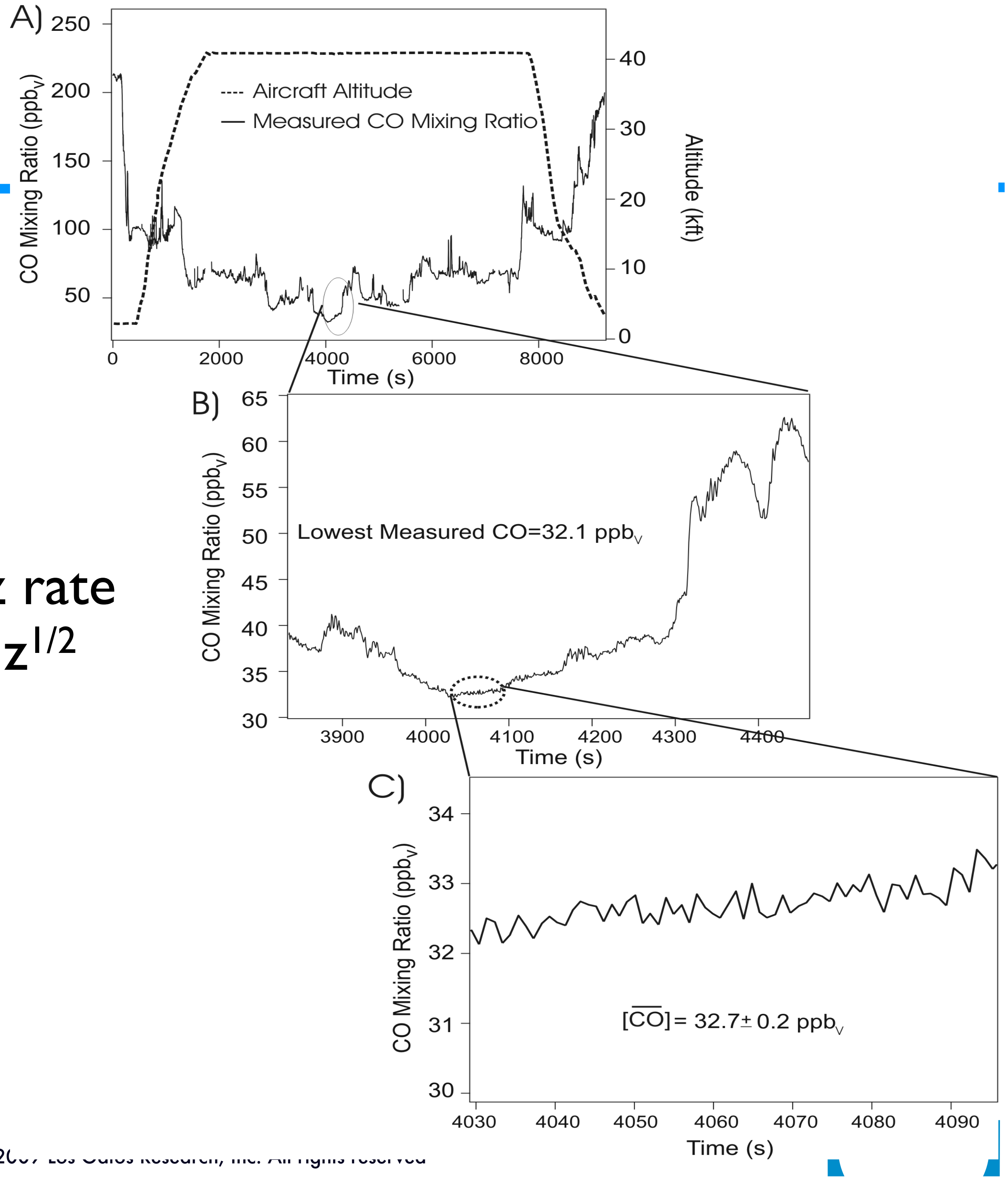
Measured CO during a 10-hour flight



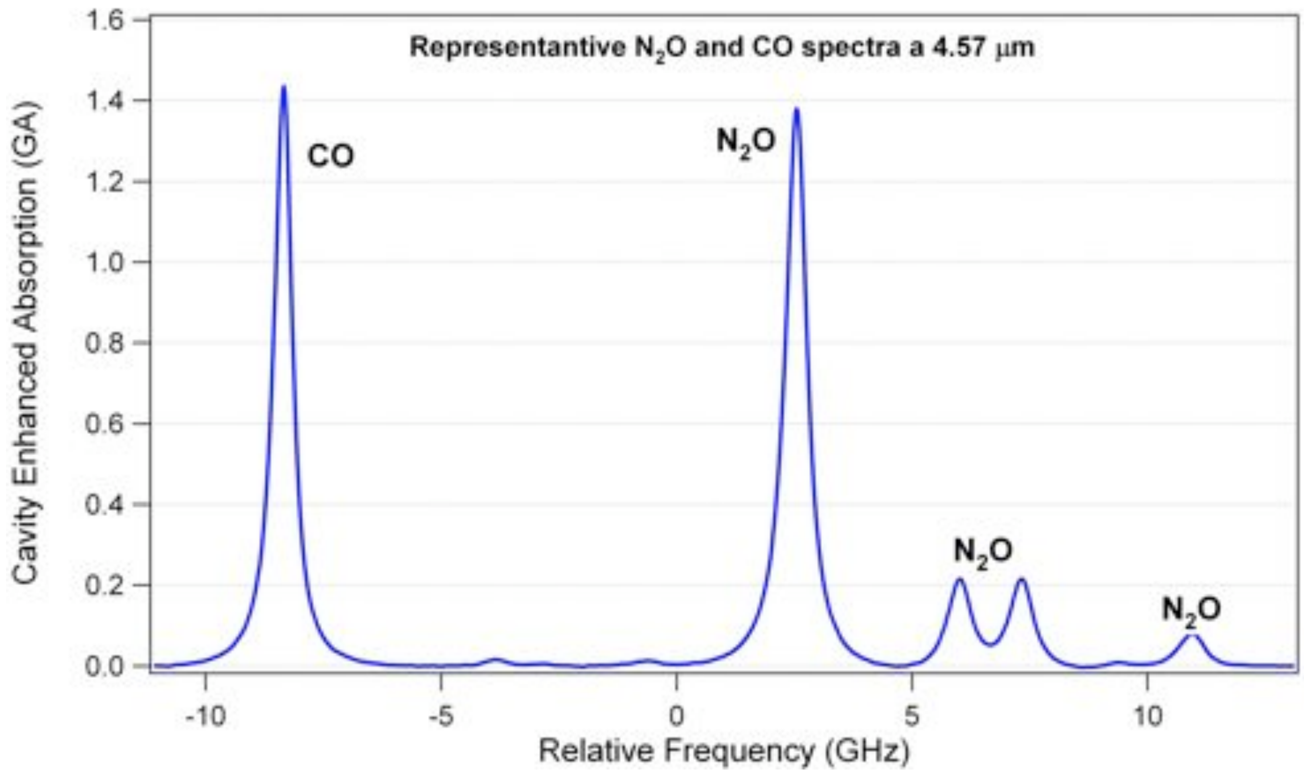
- [CO] reached 24 ppbv (13 km, 41,000 ft)

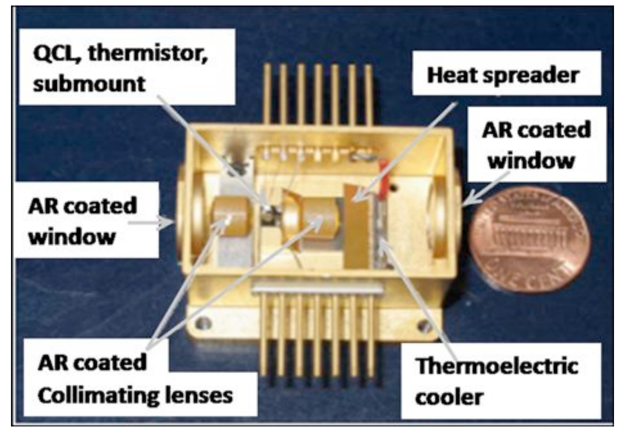
CO in ambient air during NASA DC8 flight

- Data reported at 1-Hz rate
- Precision: <0.5 ppbv/Hz$^{1/2}$



CO + N_2O Analyzer: No cryogenic requirements

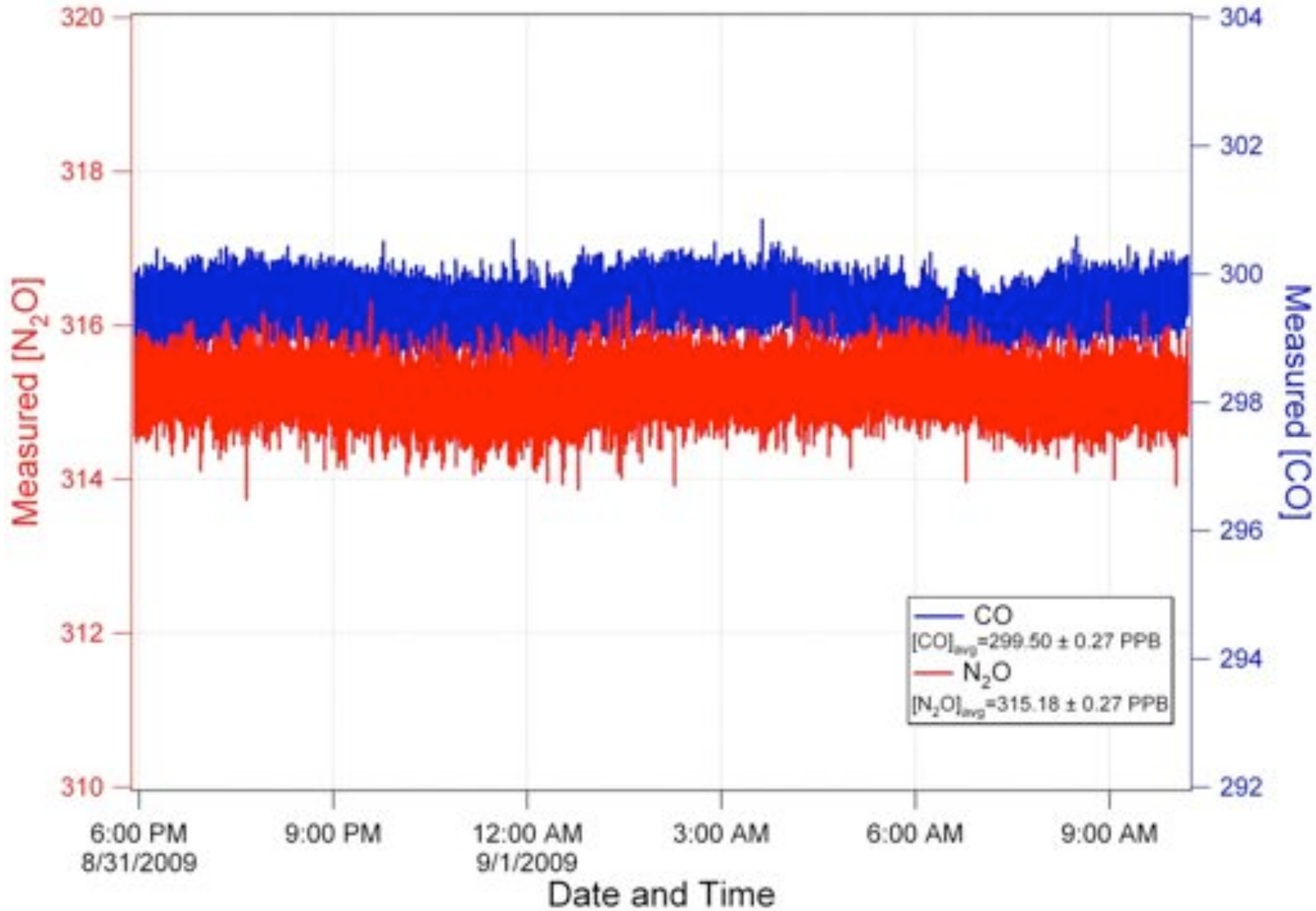




- Simultaneous, rapid, accurate measurements of CO and N_2O
- Sub-ppb precision in < 1 second

L G R

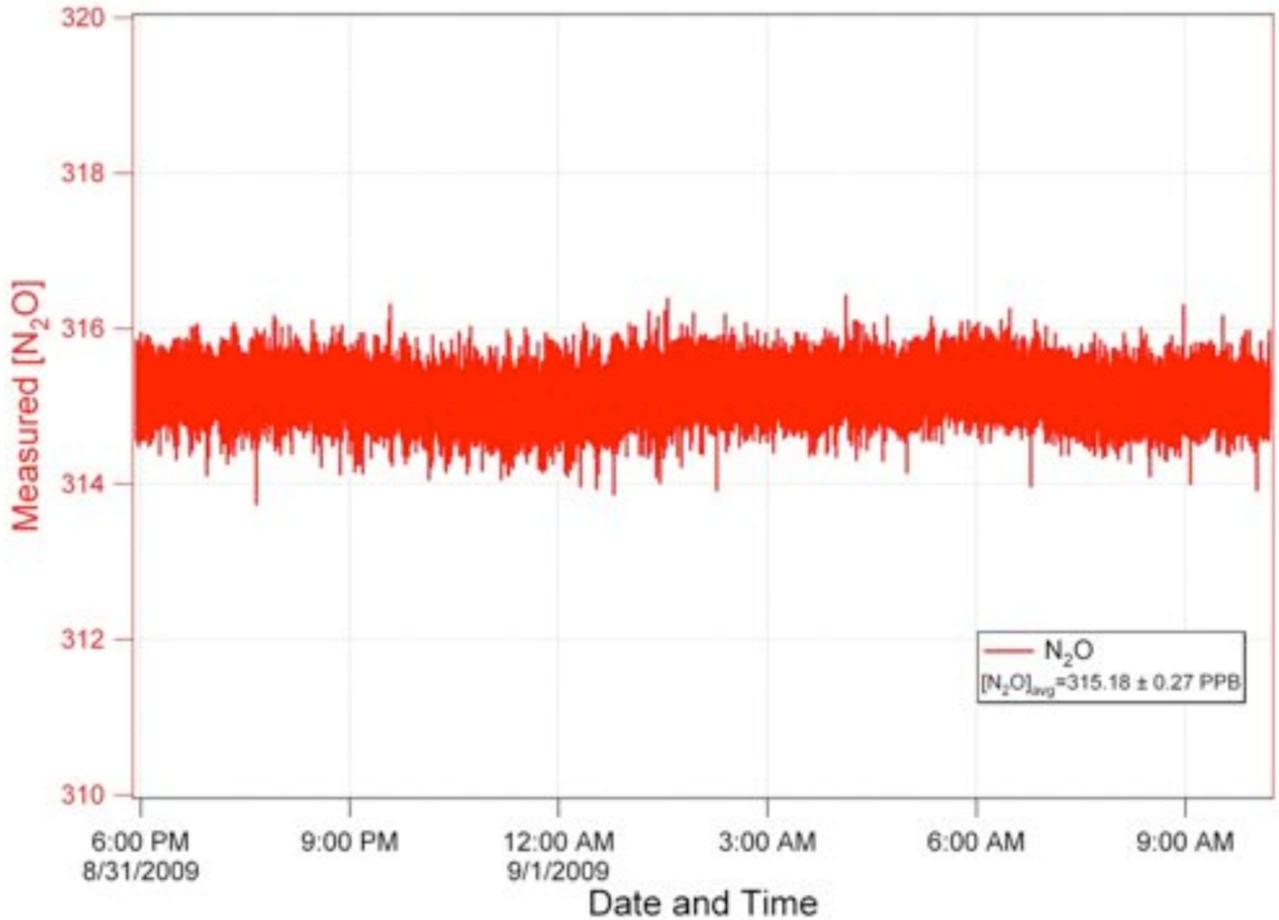
Fast CO + N_2O Analyzer: compressed air



- Simultaneous measurements of CO and N_2O
- CO precision: < 0.3 ppbv in 1 second
- N_2O precision: < 0.3 ppbv in 1 second

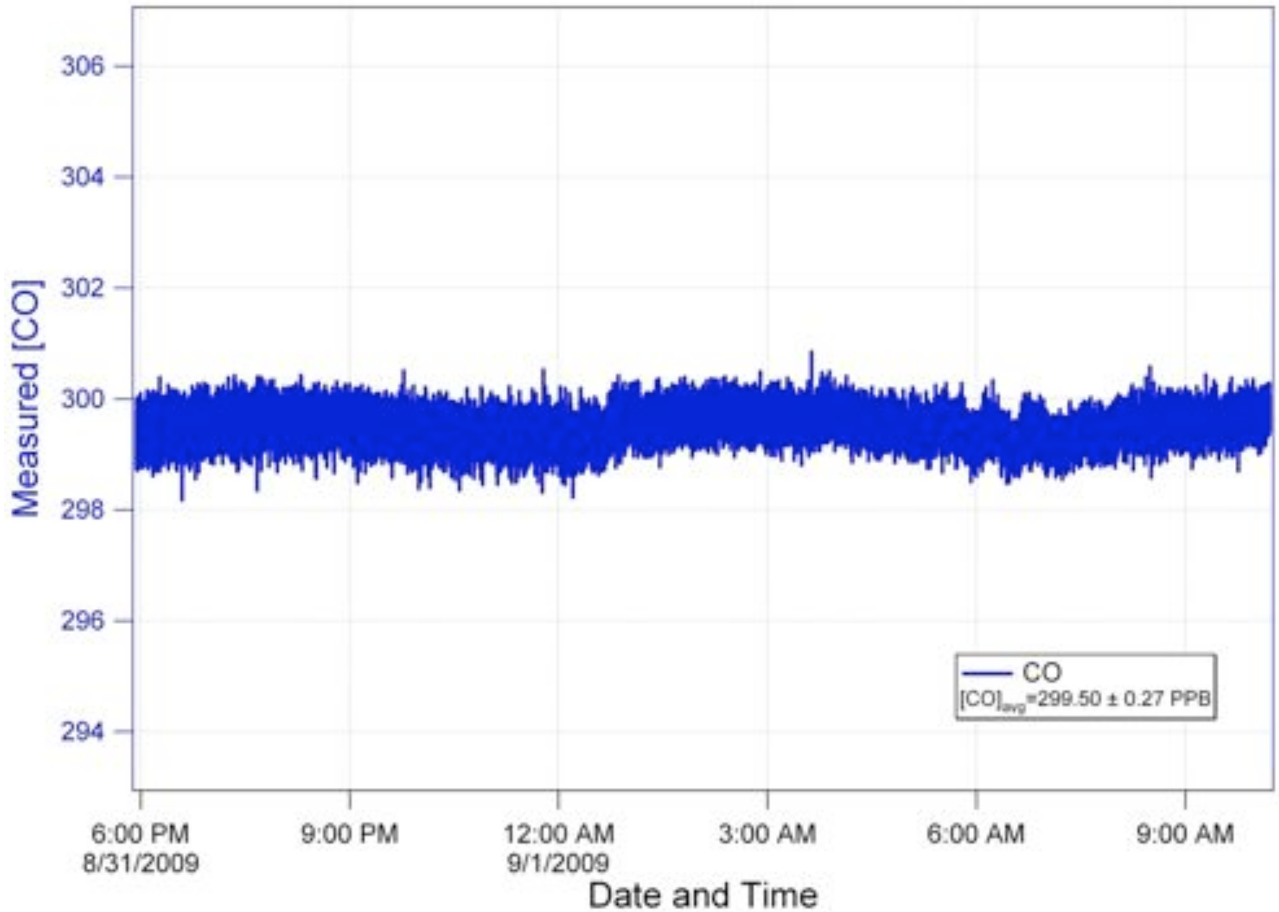
[L G R]

Fast CO + N_2O Analyzer: N_2O measurements



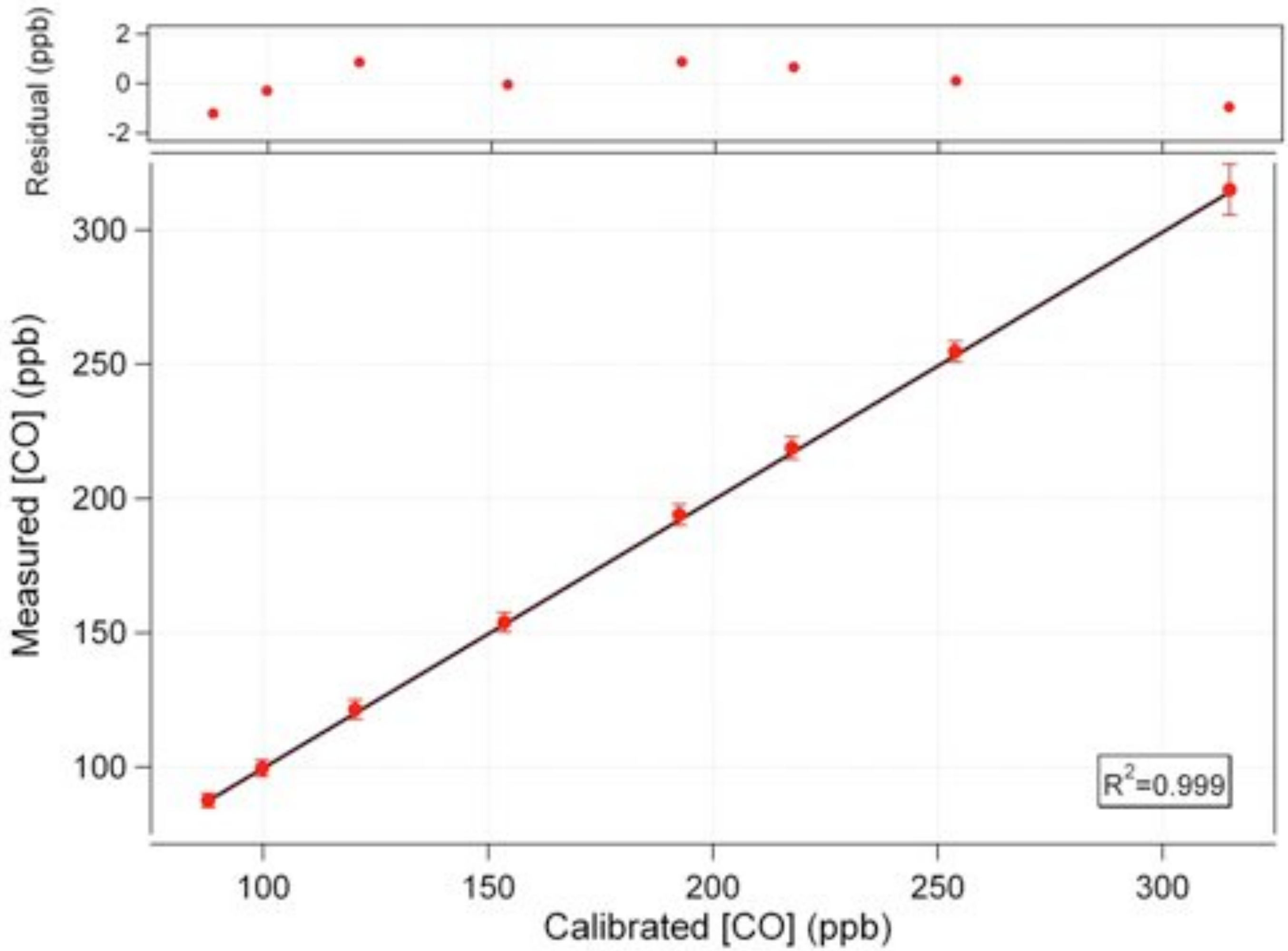
- Simultaneous measurements of CO and N_2O
- CO precision: < 0.3 ppbv in 1 second
- N_2O precision: < 0.3 ppbv in 1 second

Fast CO + N_2O Analyzer: CO measurements



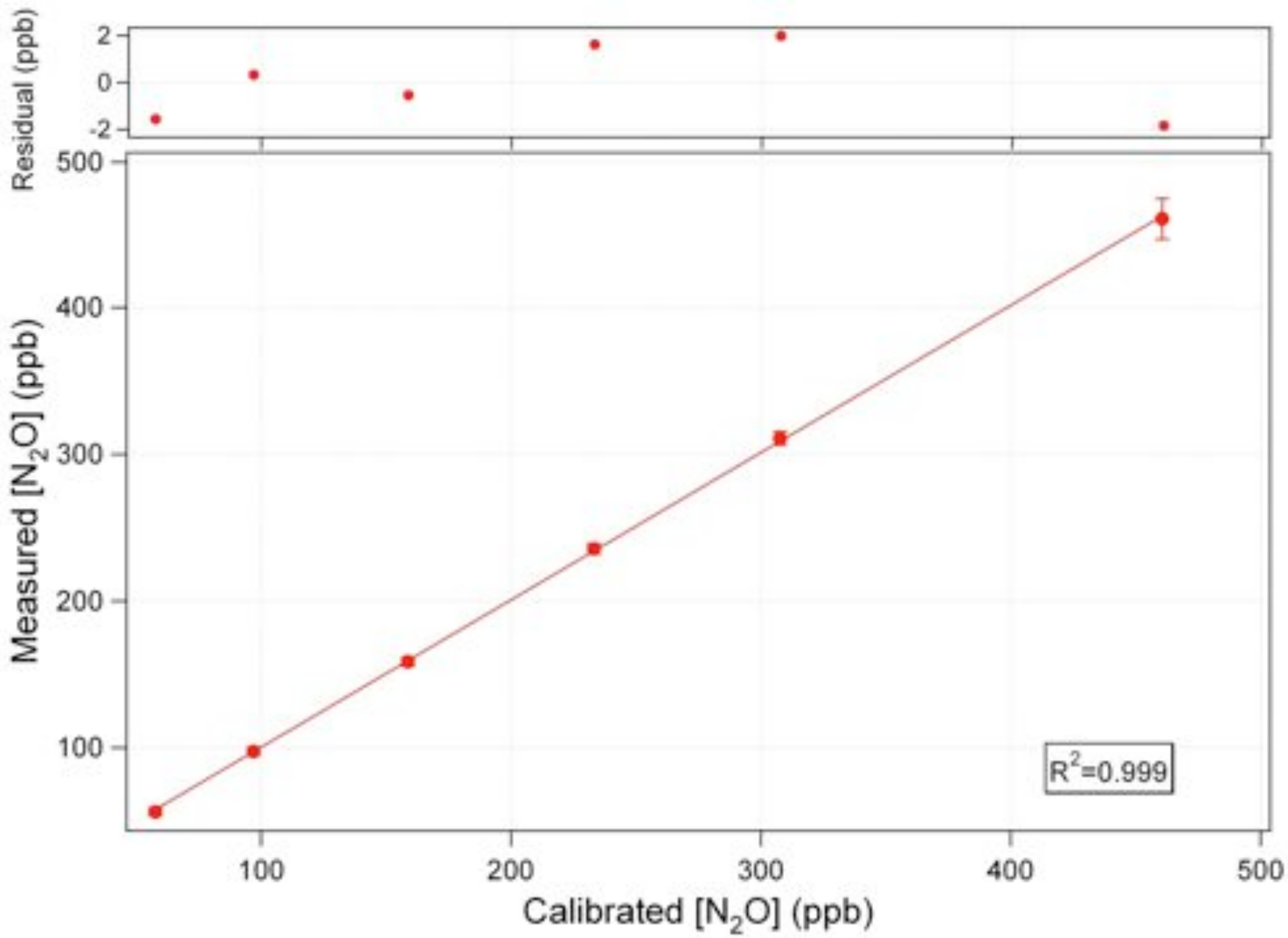
- Simultaneous measurements of CO and N_2O
- CO precision: < 0.3 ppbv in 1 second
- N_2O precision: < 0.3 ppbv in 1 second

Fast CO + N_2O Analyzer: CO Accuracy



- Linear measurements over wide range
- Agree with mixture values (to within uncertainty)

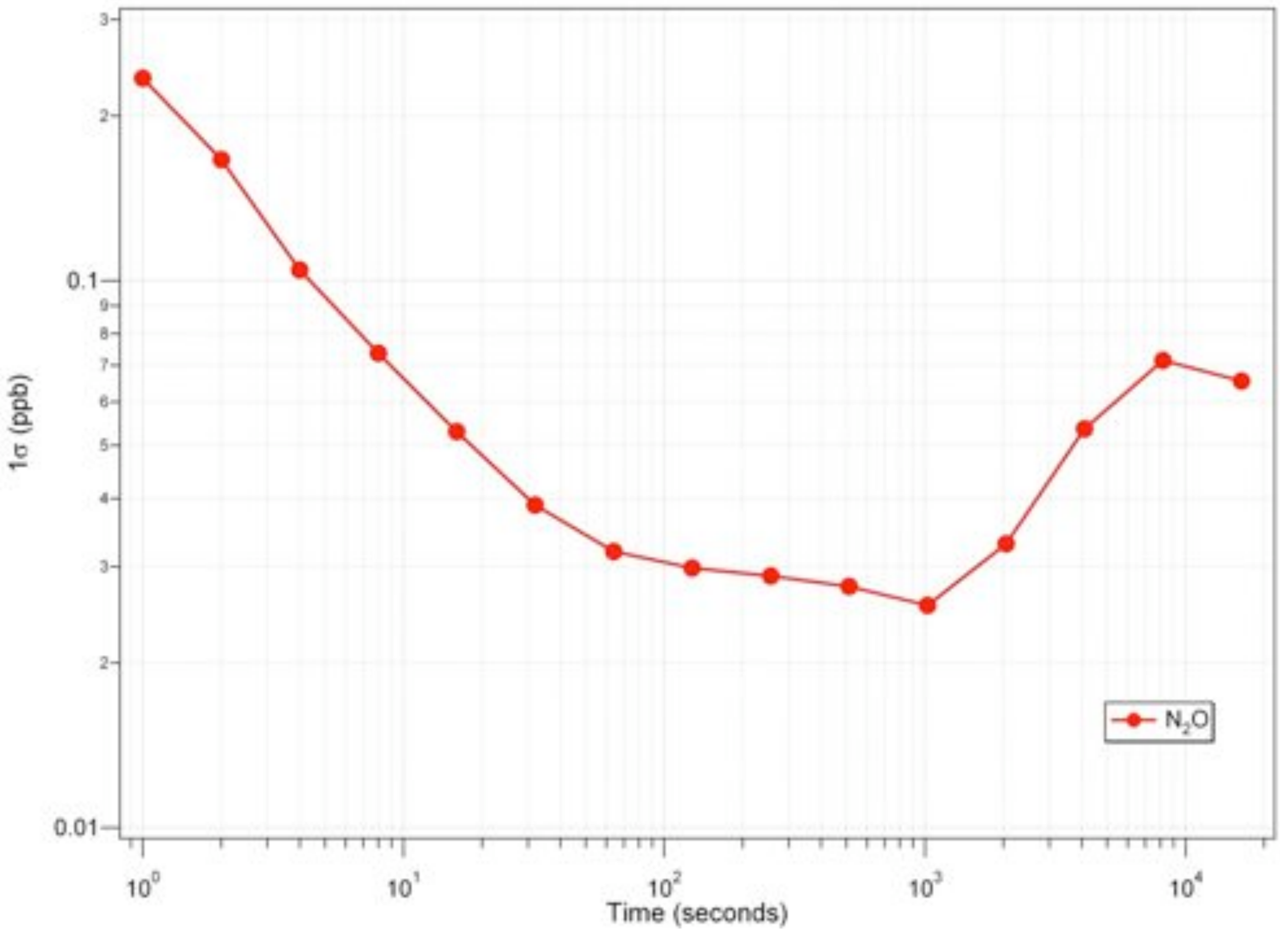
Fast CO + N_2O Analyzer: N_2O Accuracy



- Linear measurements over wide range
- Agree with mixture values (to within uncertainty)

L G R

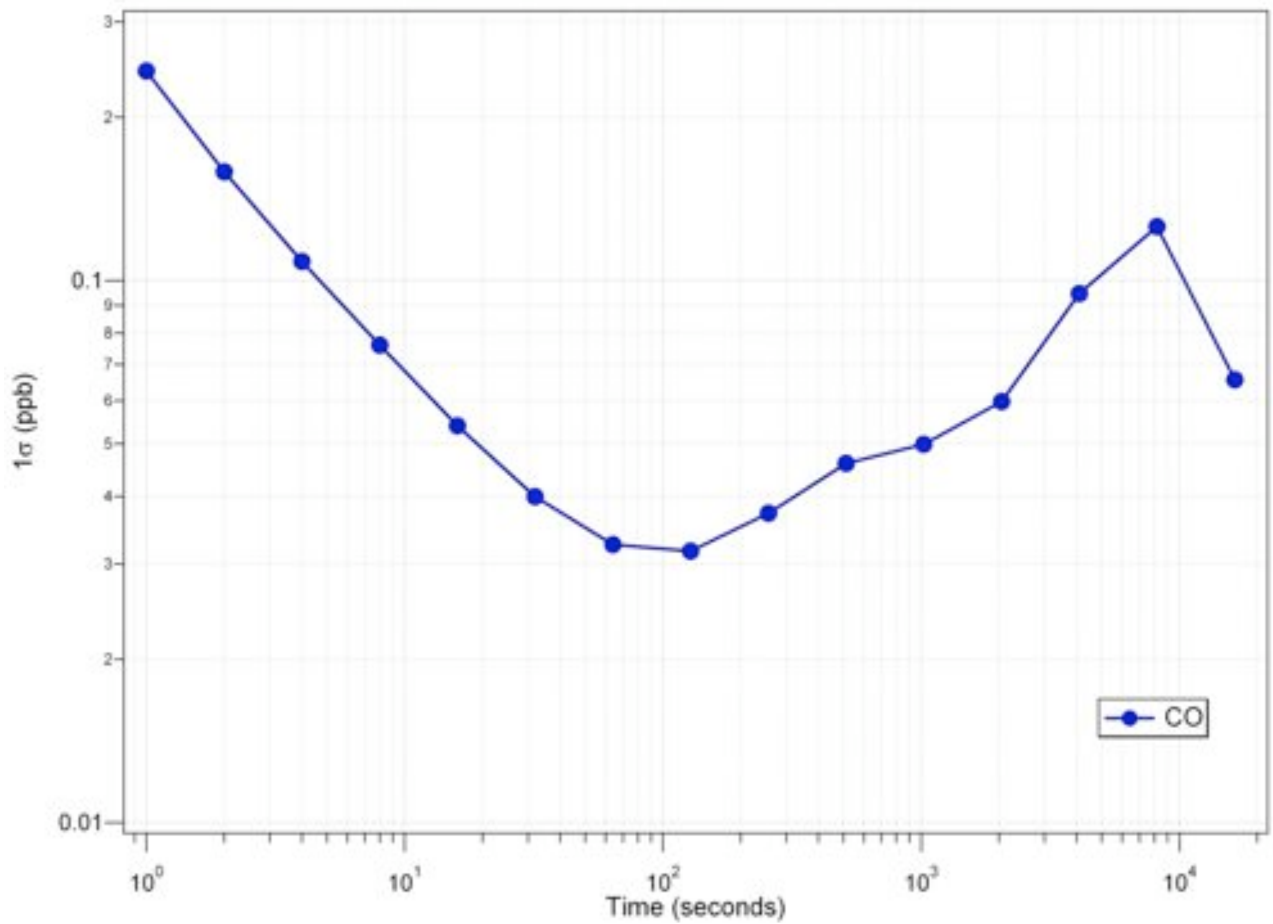
Fast CO + N_2O Analyzer: σ_{N2O} vs. t



- Simultaneous CO and N_2O measurements
- CO precision: 30 pptv in 100 seconds
- N_2O precision: 30 pptv in 100 seconds

LGR

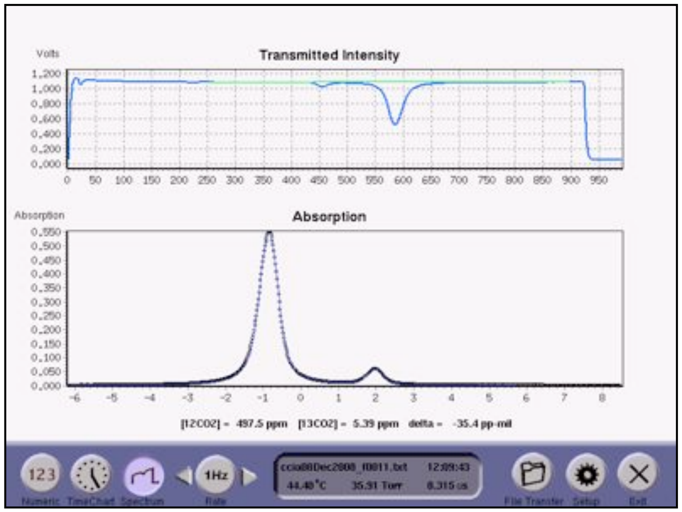
Fast CO + N_2O Analyzer: σ_{CO} vs. t

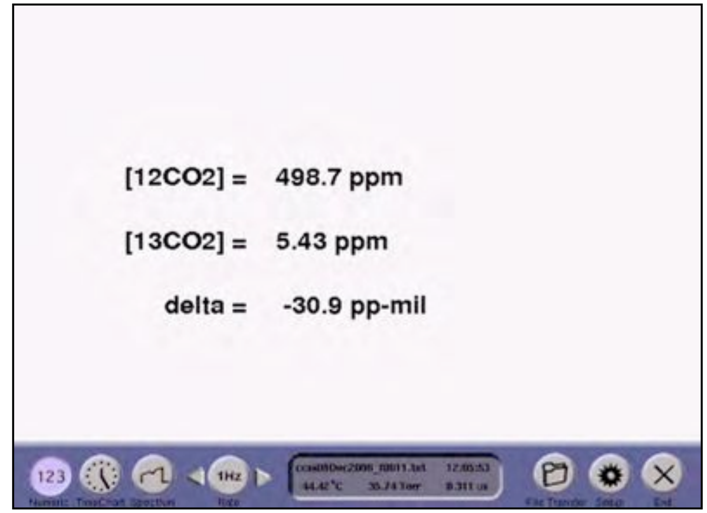


- Simultaneous CO and N_2O measurements
- CO precision: 30 pptv in 100 seconds
- N_2O precision: 30 pptv in 100 seconds

L G R

Carbon Dioxide Isotope Flux: $\delta^{13}C$ and CO_2





- Continuous measurements of ($^{13}CO_2/^{12}CO_2$) $\delta^{13}CO_2$ and CO_2
- Fast (2 Hz) allows eddy covariance flux
- Low power (150 watts) facilitates field operation
- No sample prep - direct measurements in air
- Precise: $\delta^{13}CO_2$ < 0.2 per mil (30 seconds)

LGR

Deployment: CCIA at ZERT (Carbon Sequestration)

Zero Emissions Research and Technology (ZERT) test site
Bozeman, Montana (July 2009)

Month-long release of CO_2 (buried pipe) for testing various schemes of leak detection in carbon sequestering

- Quantify $\delta^{13}C$ signature of CO_2 release
- Measure $\delta^{13}C$ from ambient sources (plant respiration)
- Record spatial profile transverse to pipe
- Record temporal variations at several locations
- Compare co-located measurements with other groups

LGR

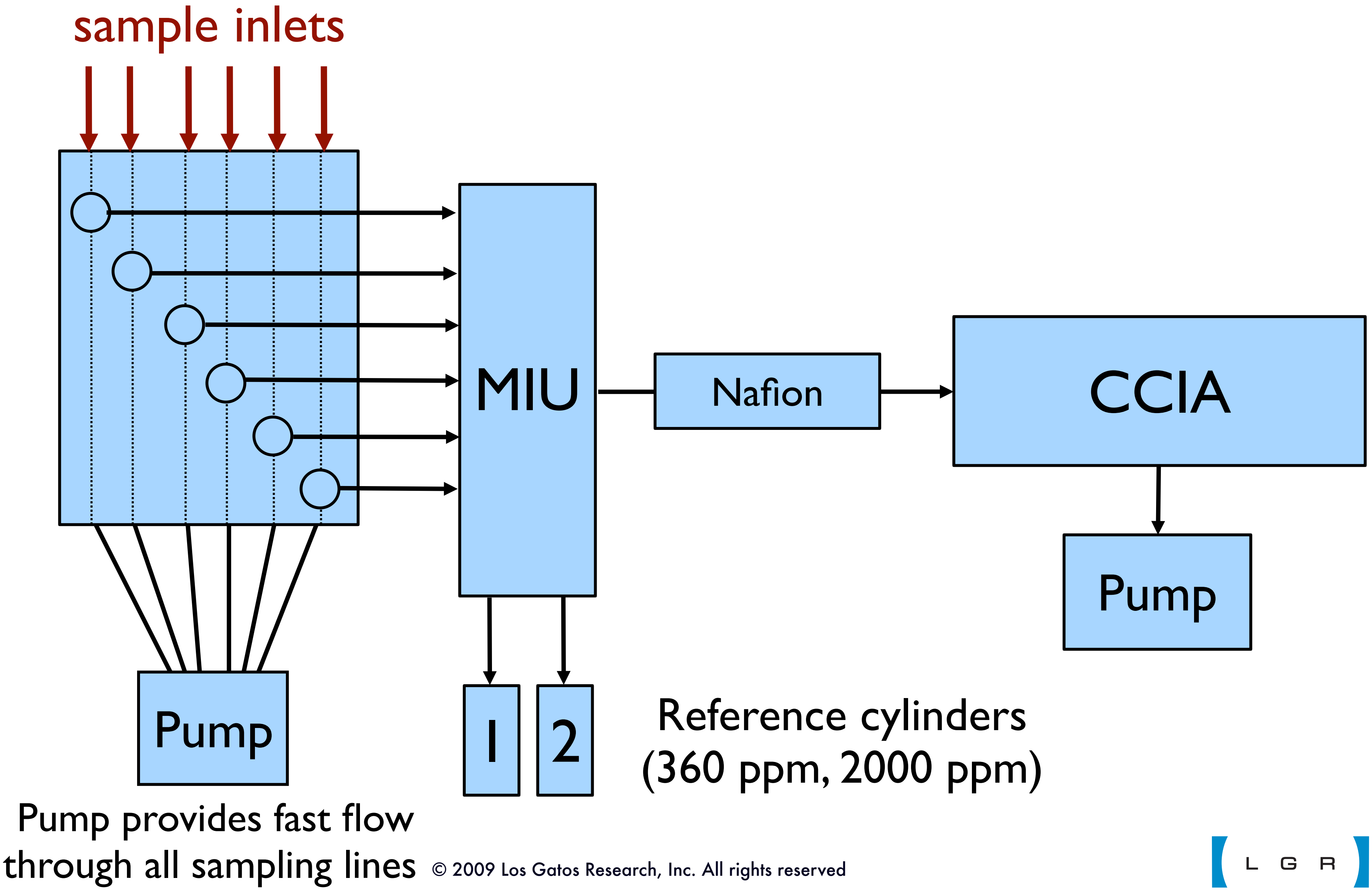
Arriving to ZERT site in Van

ZERT: 0.2 tons/day release of CO_2

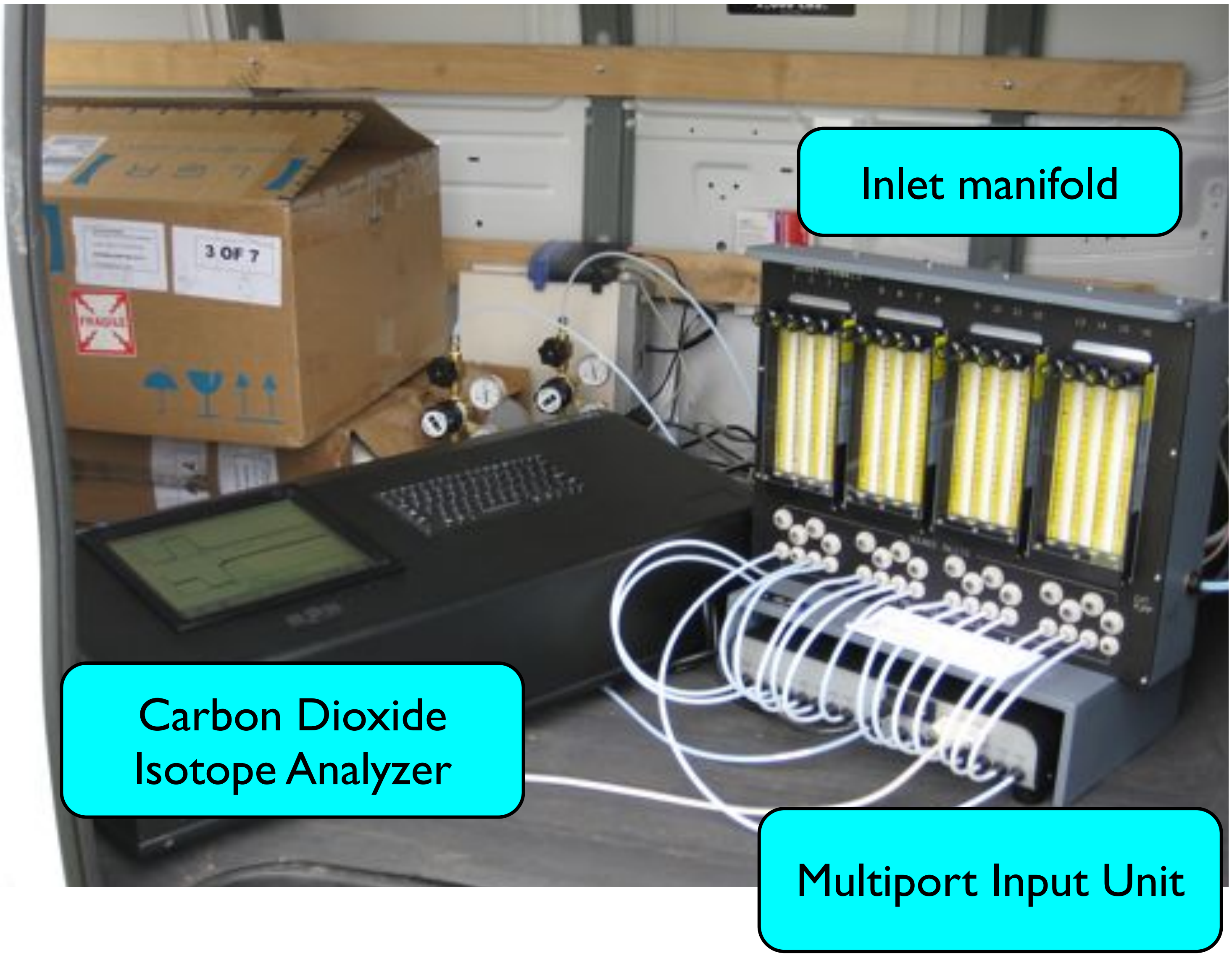
Month-long release of CO_2 (buried pipe) for testing various schemes of leak detection in carbon sequestering

L G R

Multi-location continuous $\delta^{13}CO_2$ and CO_2 (w/ LLNL)



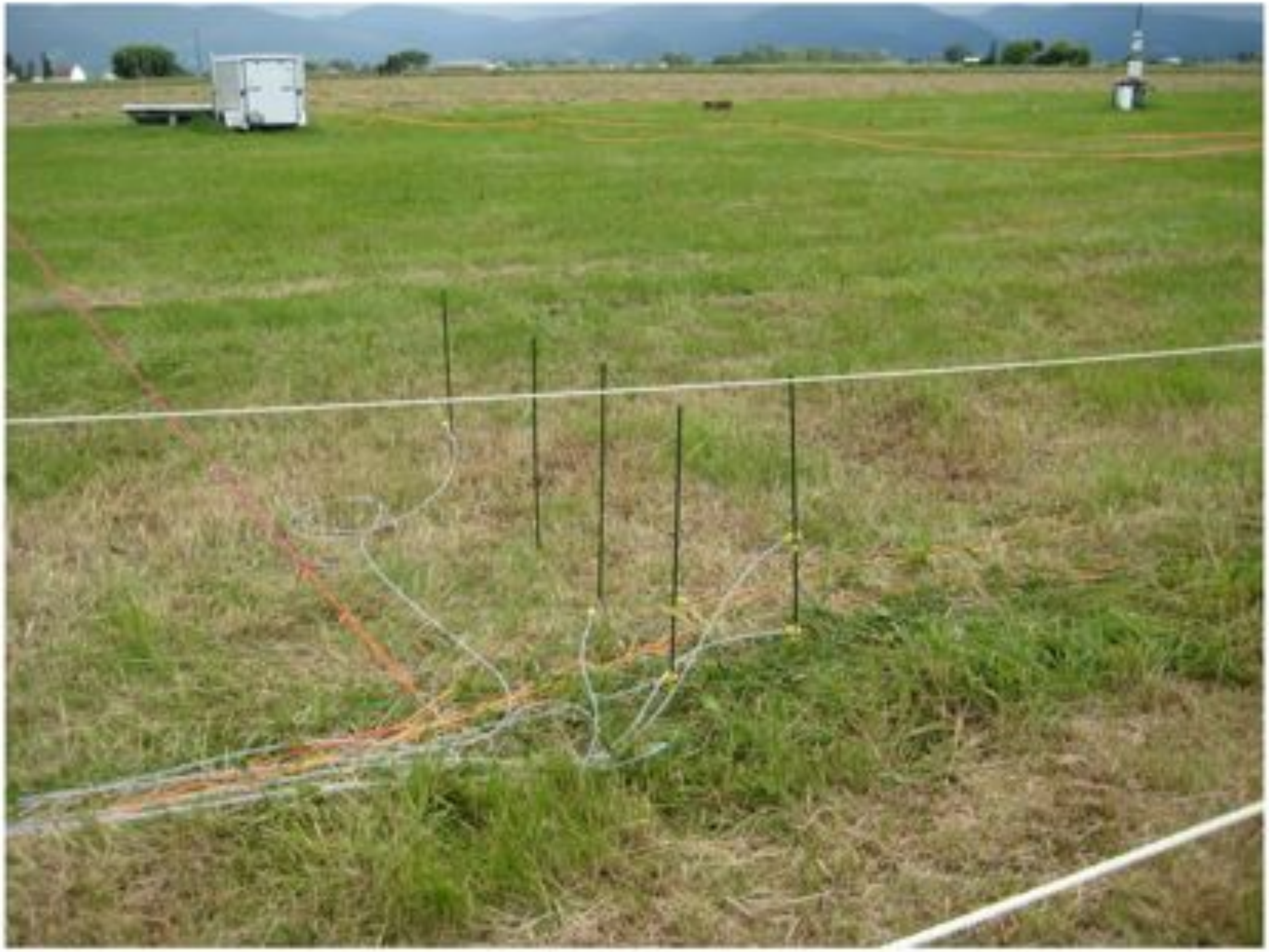
Carbon Dioxide Isotope Analyzer w/ Multiport Input Unit



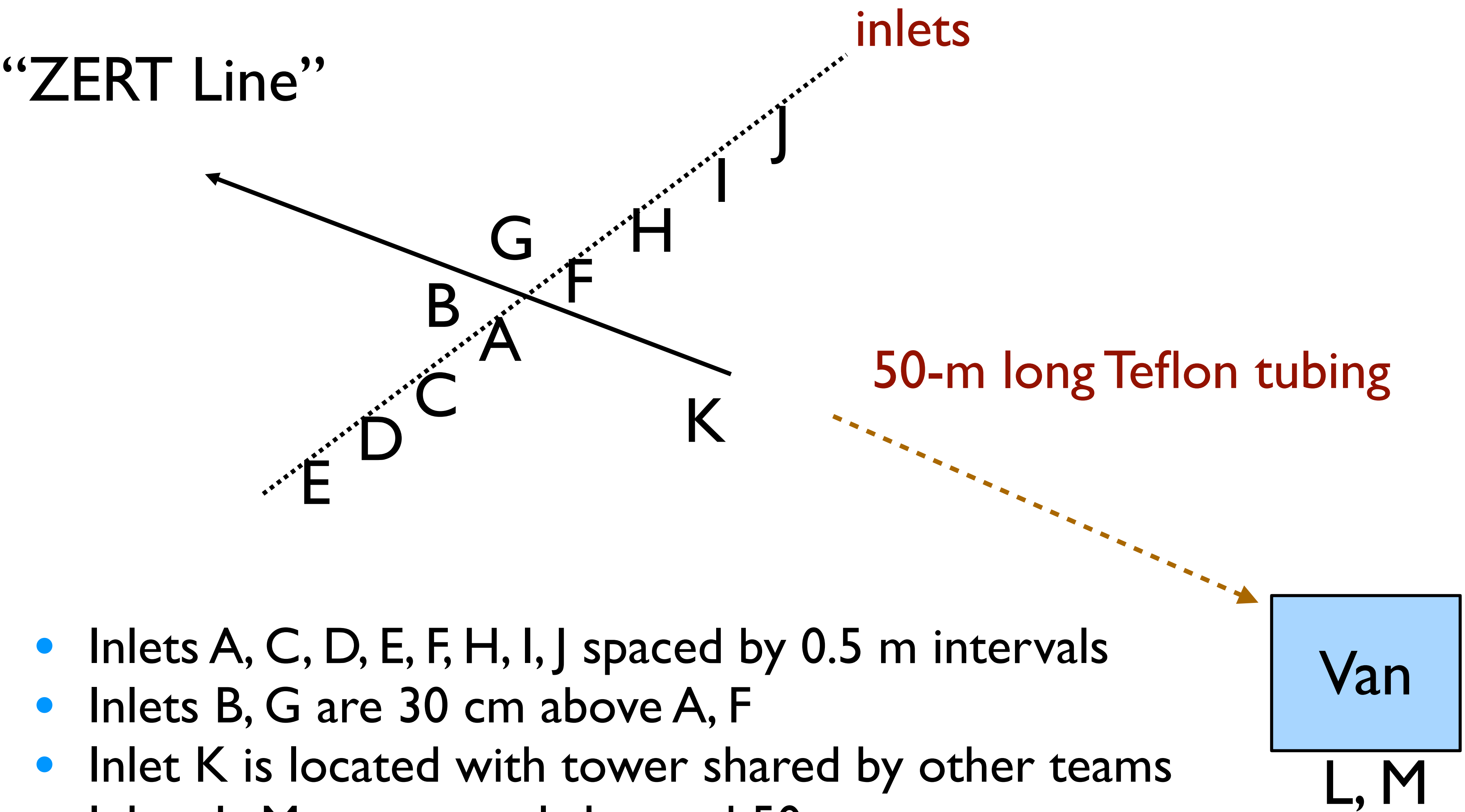
L G R

L G R

Setting Up Inlets

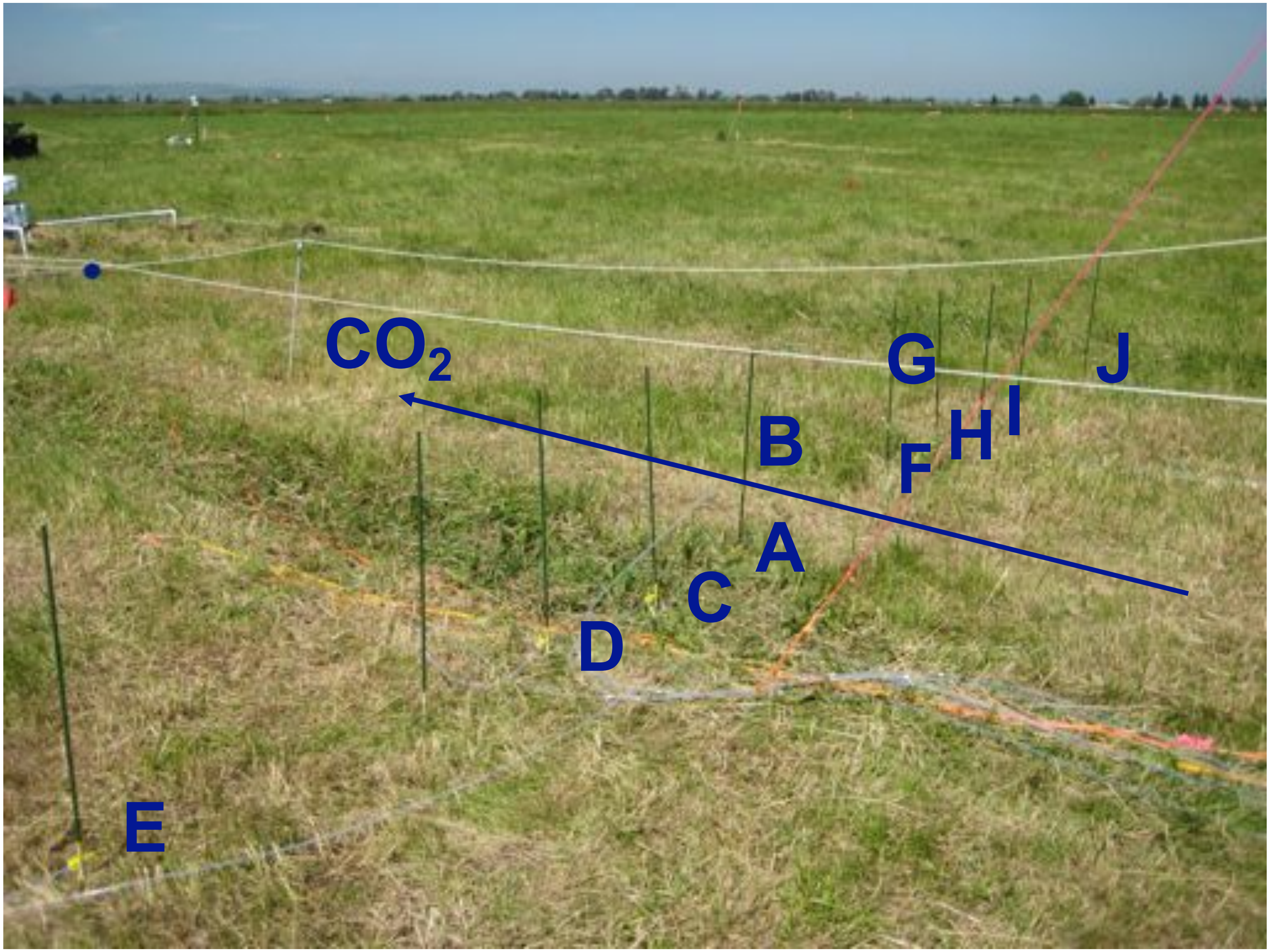


Layout of Sample Inlets: Grid, Tower, Controls

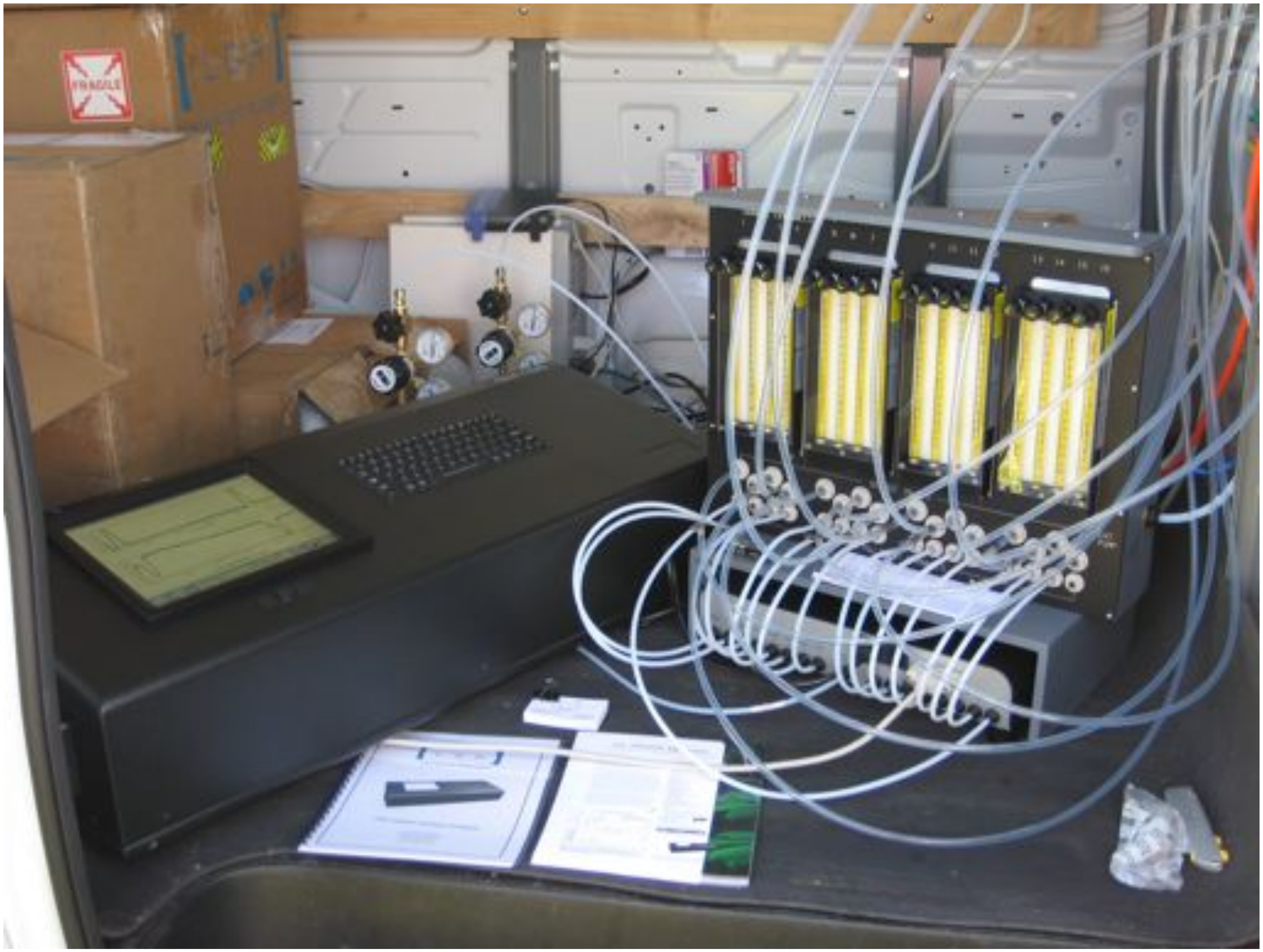


- Inlets A, C, D, E, F, H, I, J spaced by 0.5 m intervals
- Inlets B, G are 30 cm above A, F
- Inlet K is located with tower shared by other teams
- Inlets L, M are controls located 50 m away

Transverse Grid

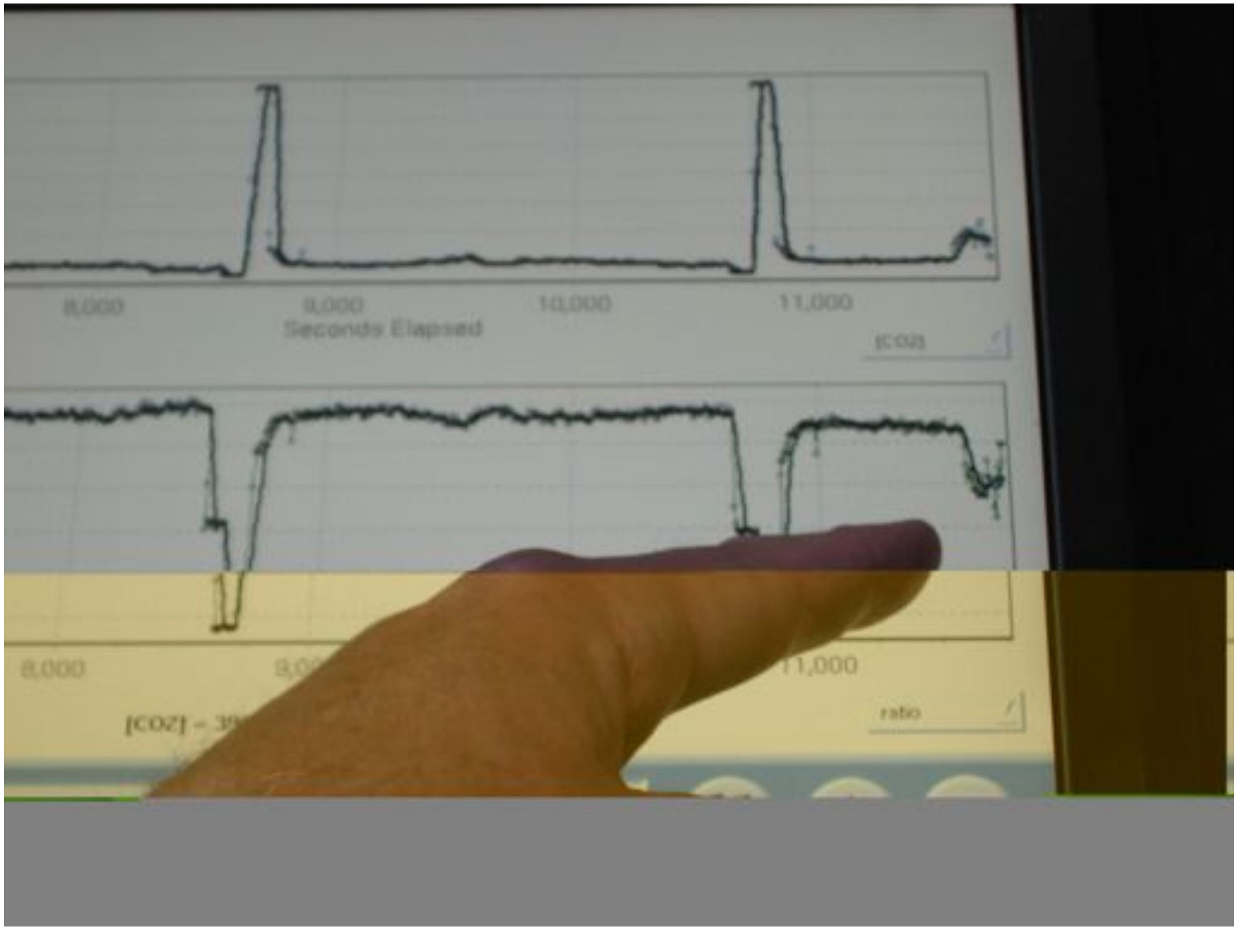


Ready to Go



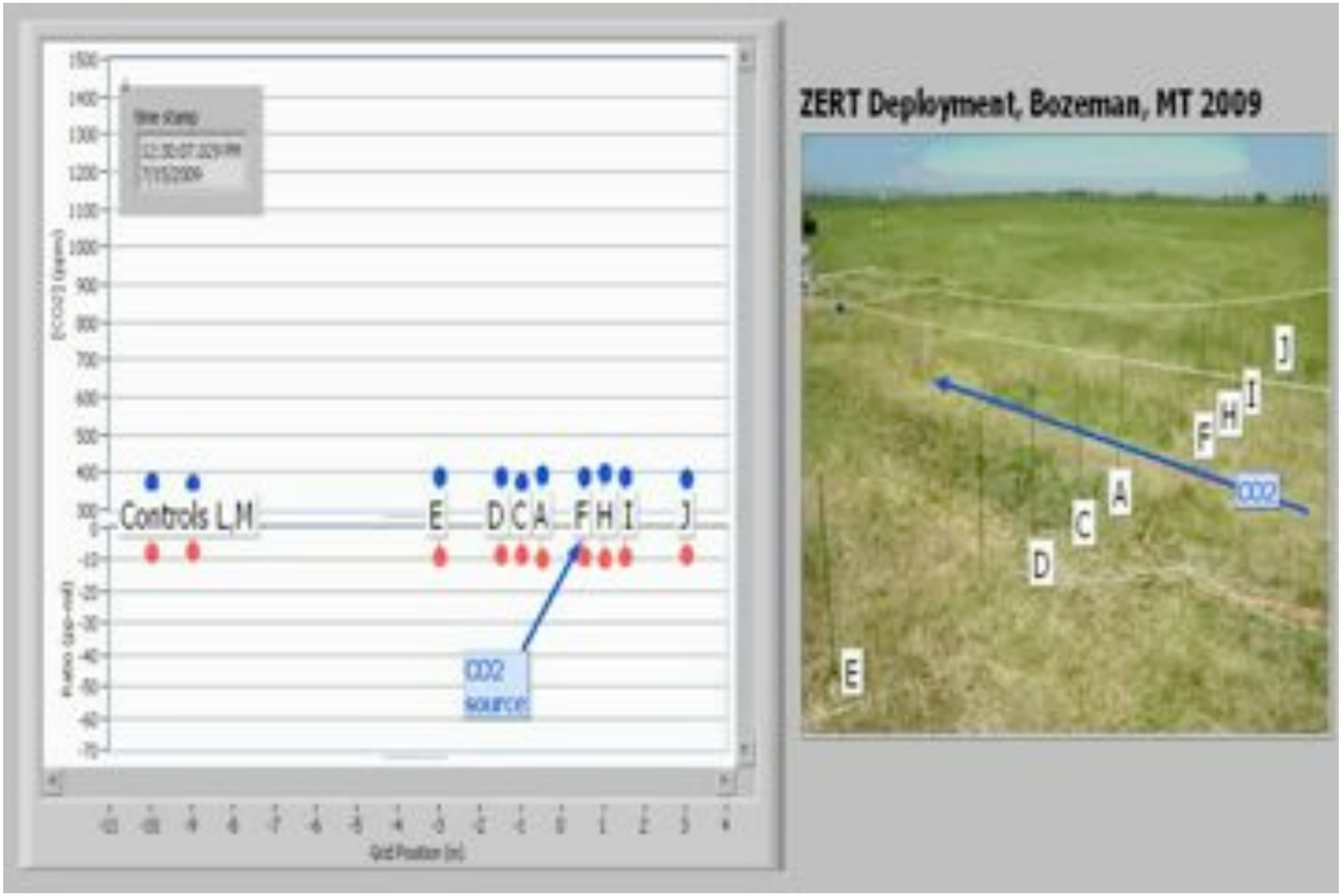
L G R

Release Starts 7/15/09 at noon

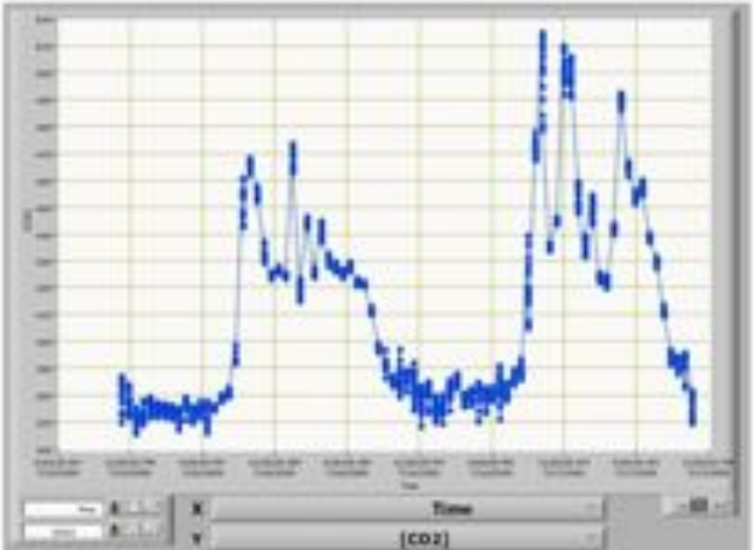


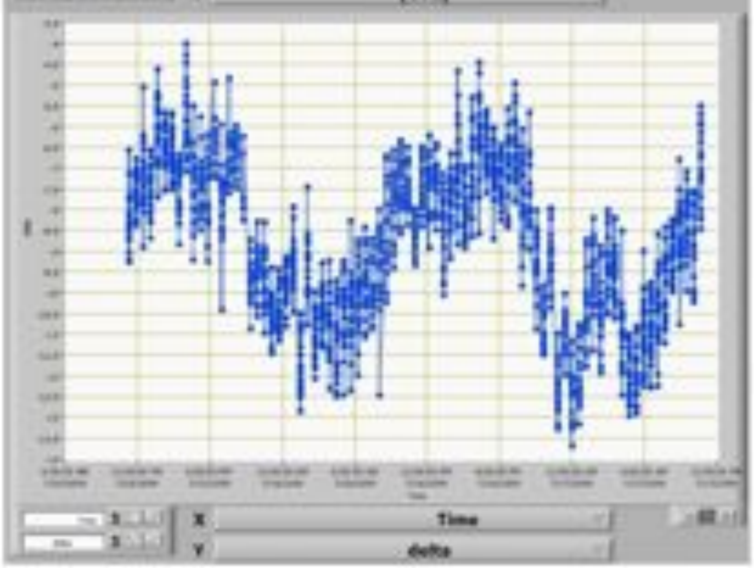
First signal seen at Port F less than an hour after release!

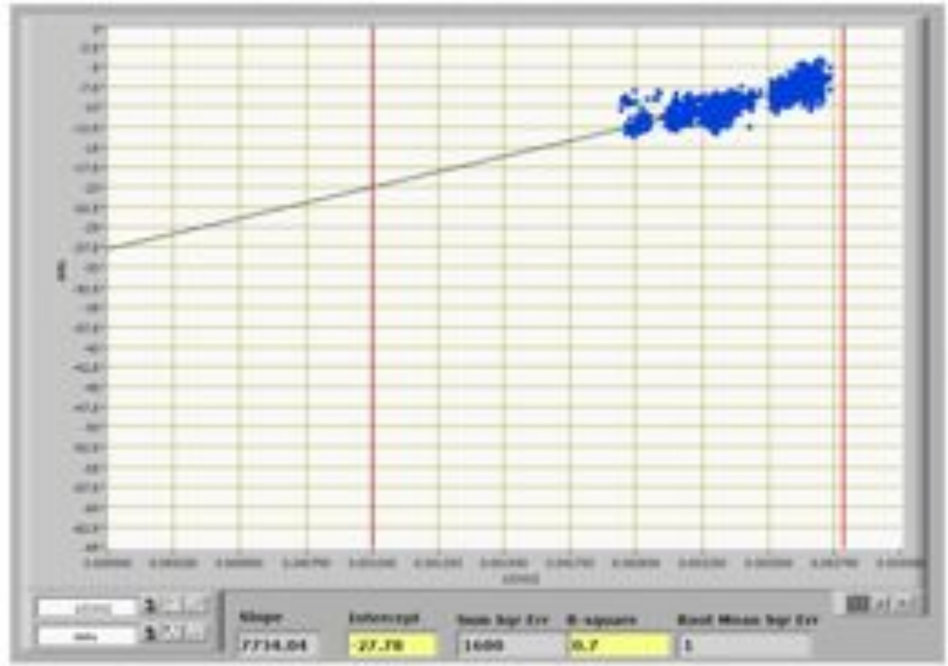
Time Record of Grid 7/15 to 7/17



Inlet L (control): observation of plant respiration

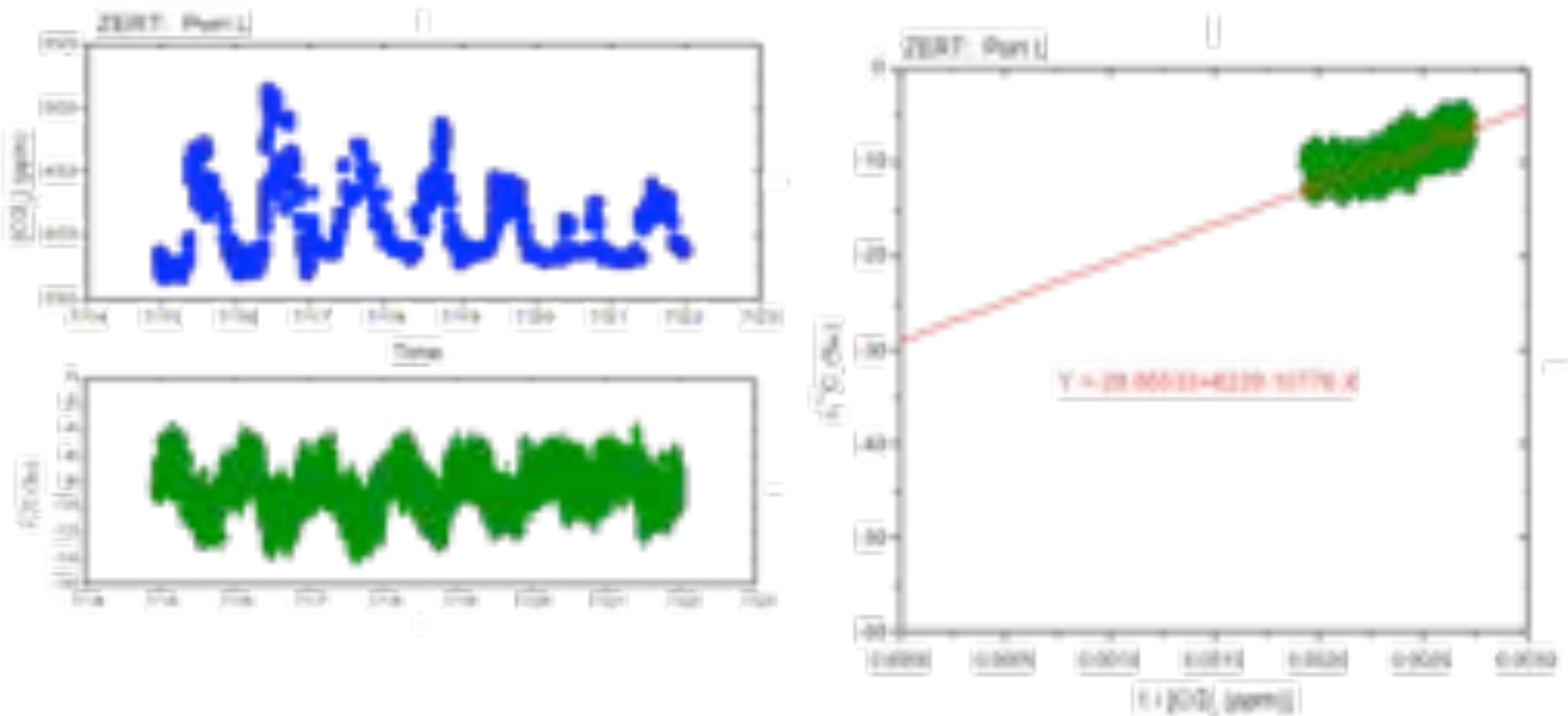






$\delta^{13}C$= -27 ‰ plant signature
(Keeling plot for one day)

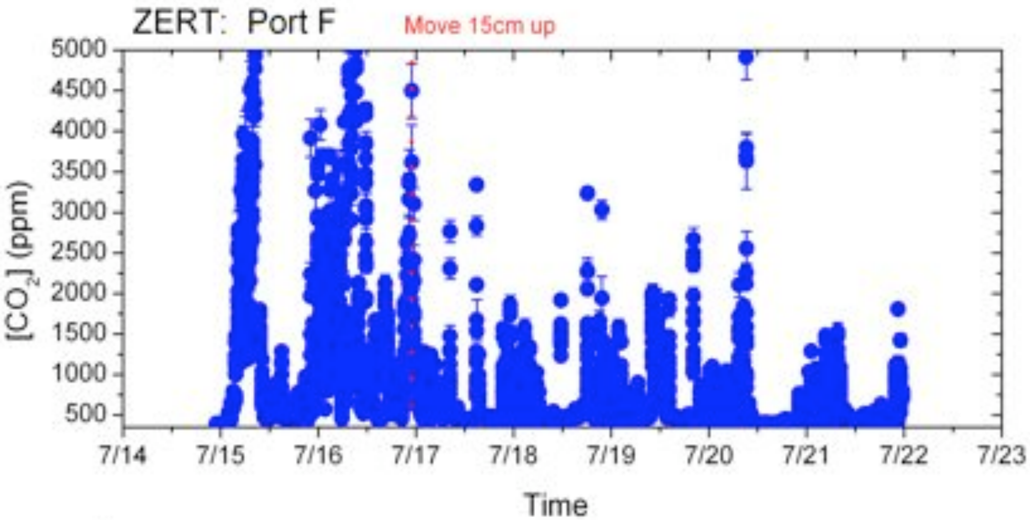
Inlet L (control): observation of plant respiration

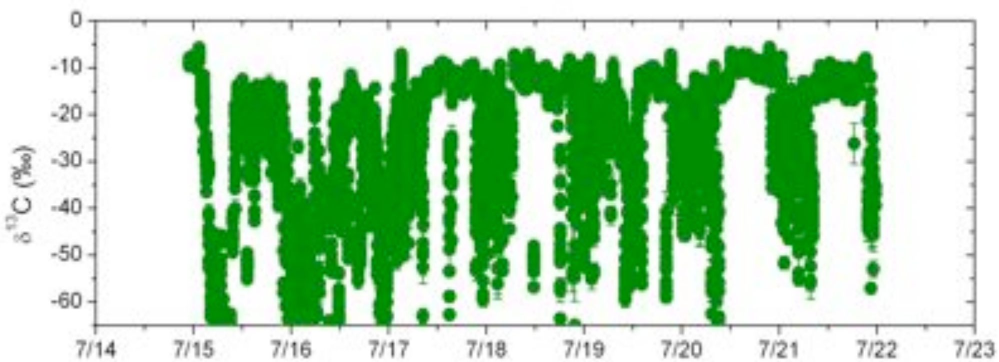


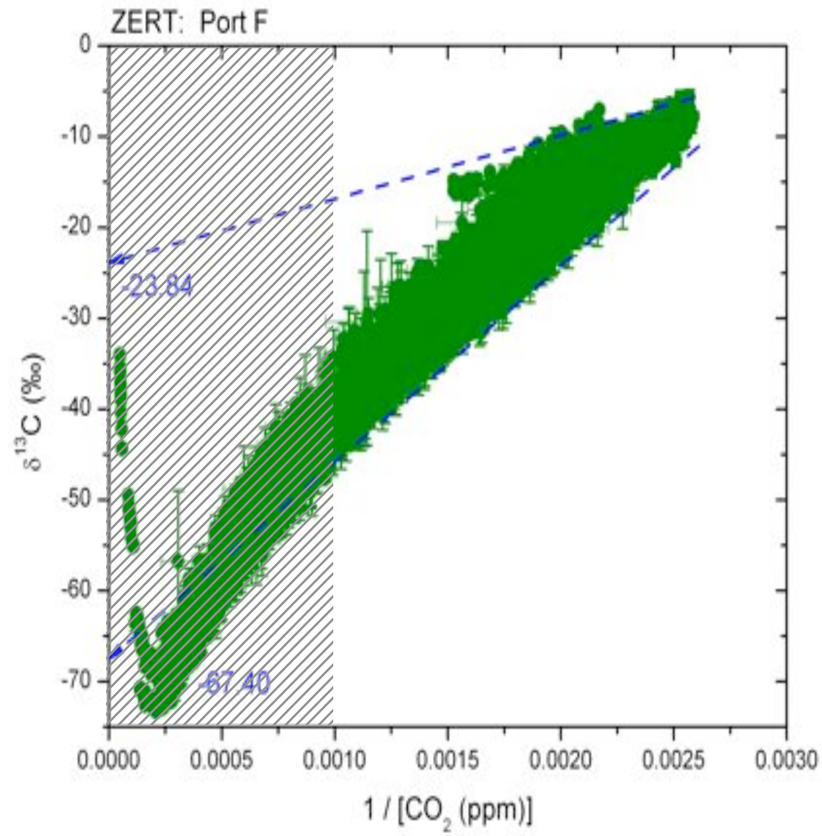
$\delta^{13}C$ = -29 ‰ plant signature

(Keeling plot over 7 continuous days)

Port F: Hot Spot of ZERT Release

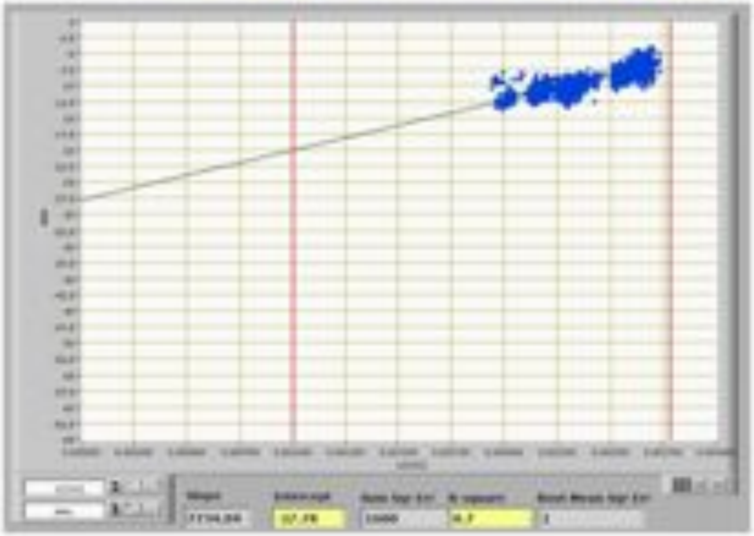






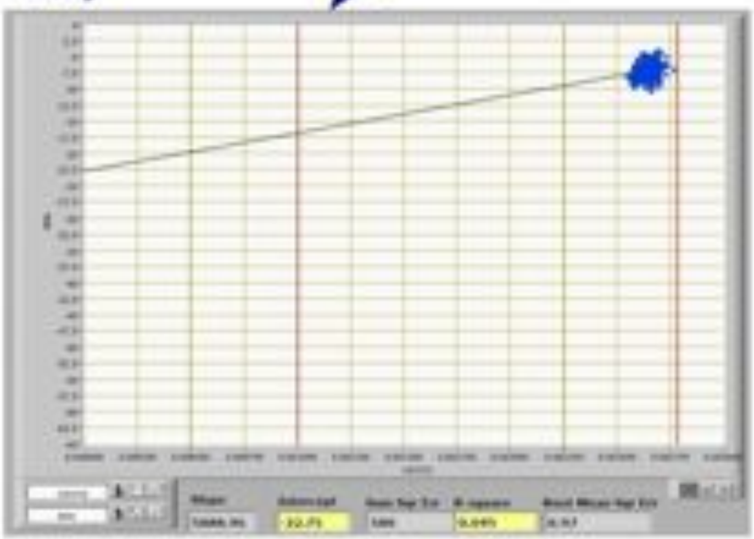
- Some CO_2 bursts exceed 2000 ppmv
- Data within instrument range: $\delta^{13}C$ = -58 ‰ (ZERT source)

Control L: Filter Day/Night

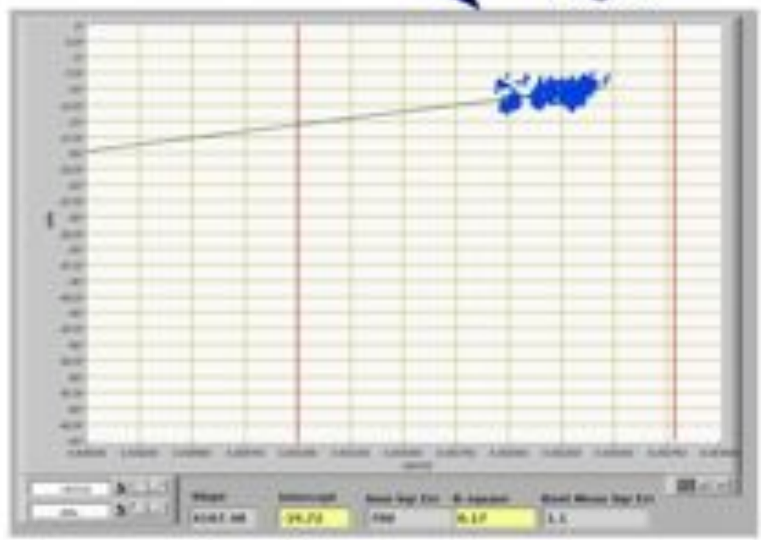


Respiration seen at night

Day

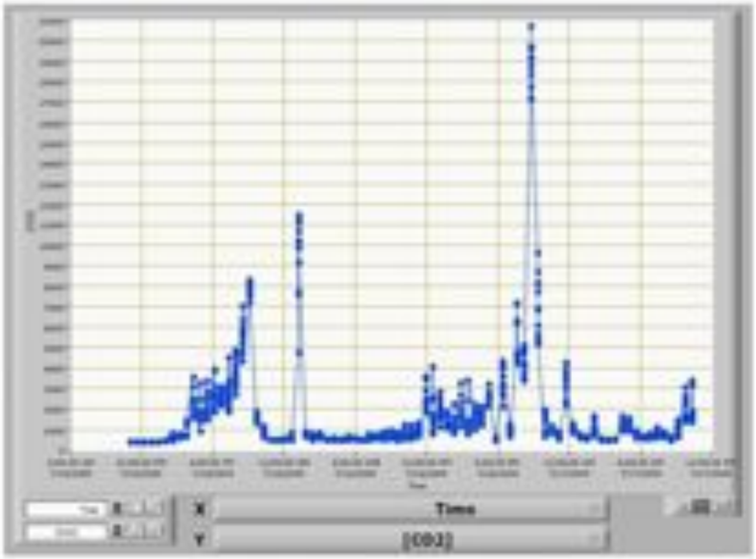


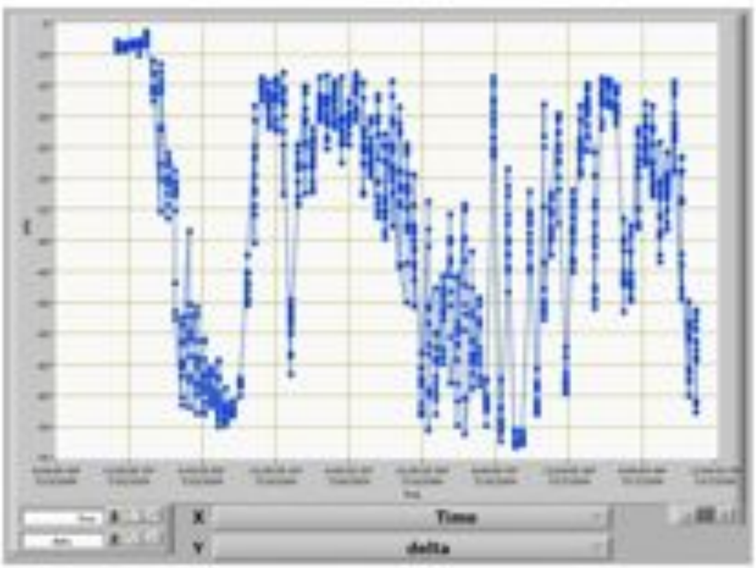
Night

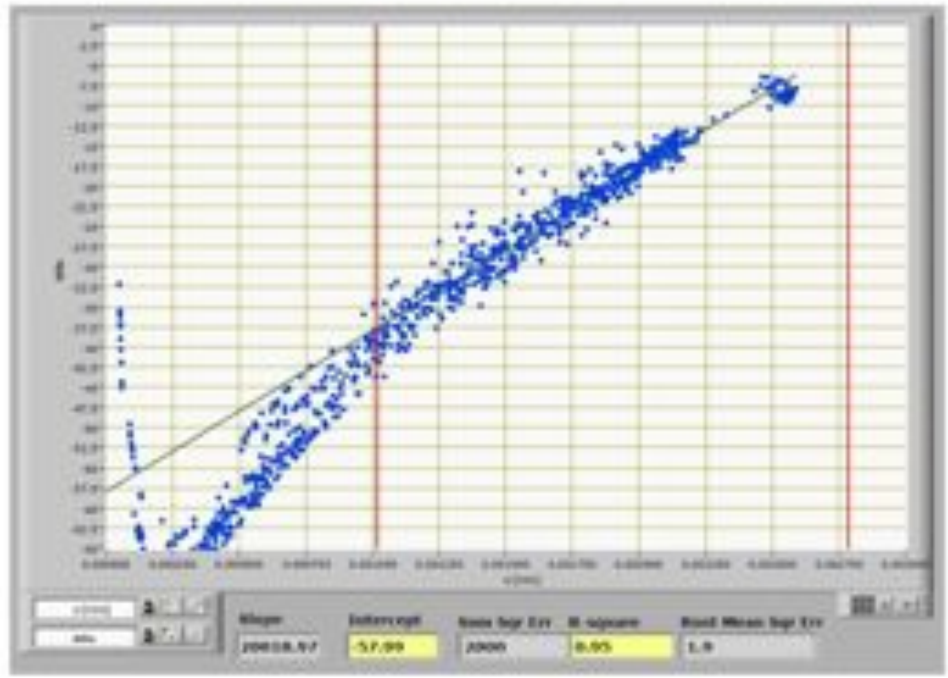


LGR

Port F: Hot Spot of ZERT Release

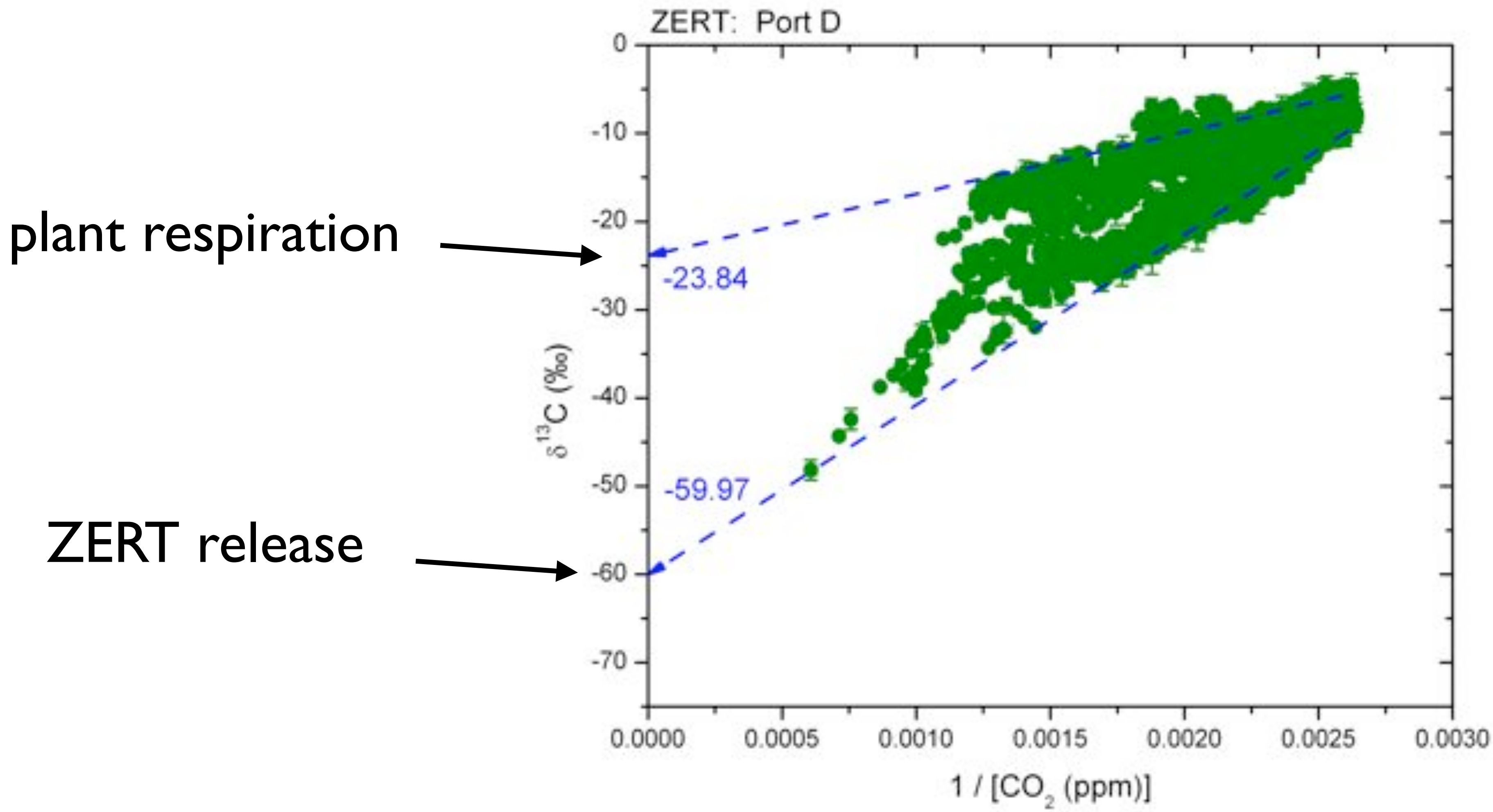






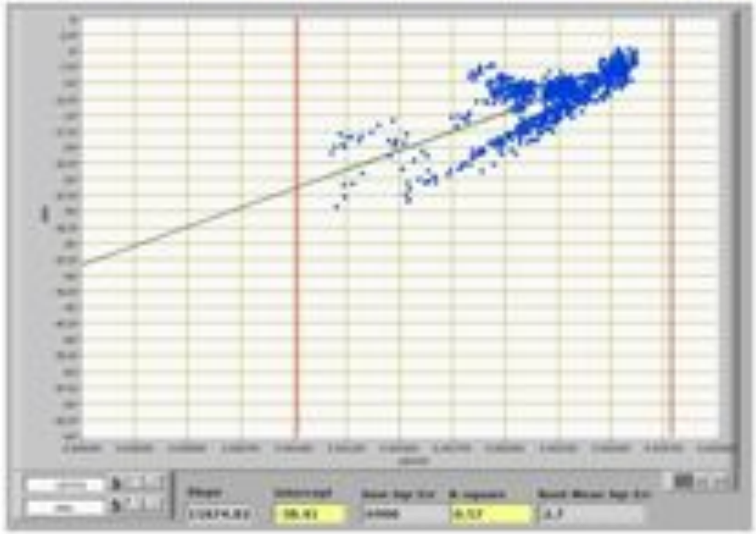
High CO_2 bursts observed
$\delta^{13}C$ = -58‰ corresponds to source release

Port D: Mixing of Plant and ZERT Leak



Keeling analysis suggests 2 sources

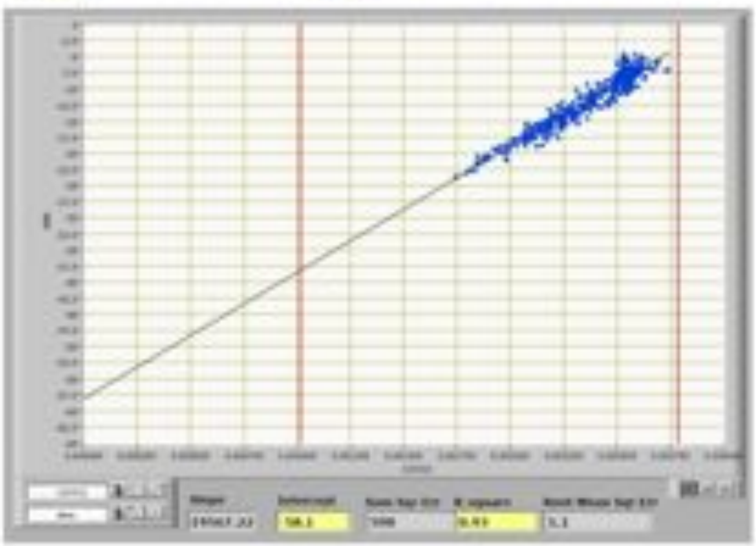
Port D: Filter Day/Night



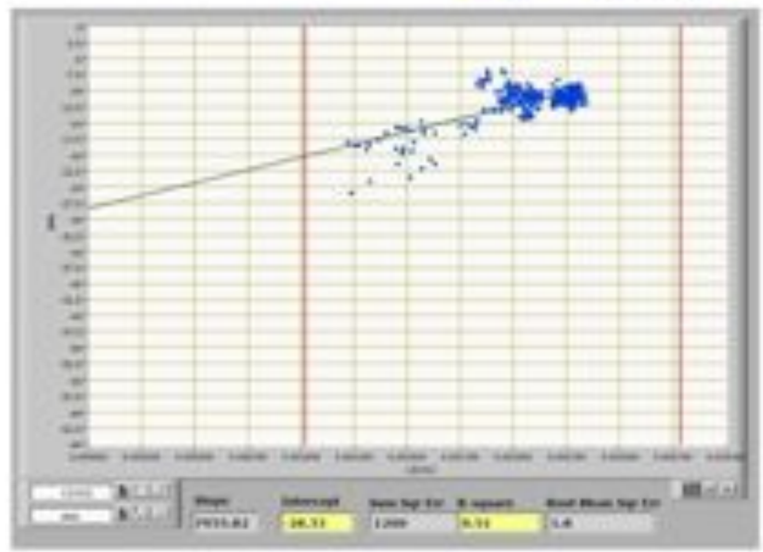
Respiration of plants is minimally seen during day; good signature of release

Little of plume seen, perhaps wind is calm at night.

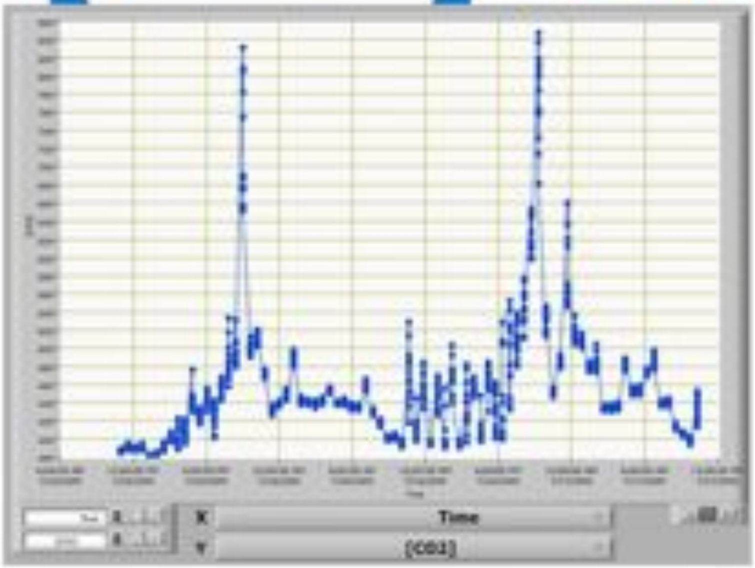
Day

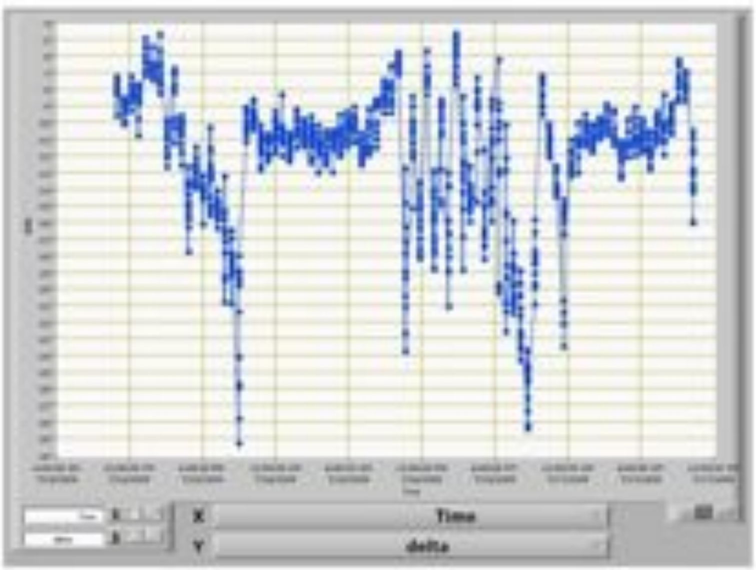


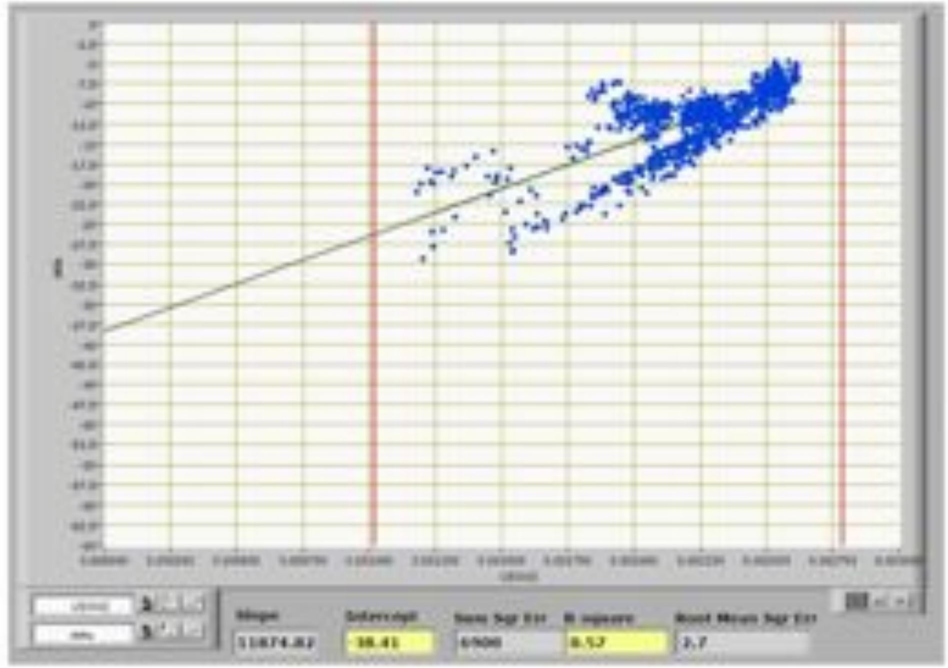
Night



Port D: Mixing of Plant and Leak







Evidence of both sources seen in Keeling analysis. Clear signatures of both plant respiration and ZERT release.

Deployment of CCIA for Carbon Sequestration

Real-time spatial, temporal measurements of $\delta^{13}C$ and CO_2 at ZERT test site

- Ability to record distinct $\delta^{13}C$ signature of CO_2 release
- Measures $\delta^{13}C$ from ambient sources (plant respiration)
- Records physical map of release transverse to pipe
- Records temporal variations of release at several locations
- Multi-port system provides real-time spatial and temporal measurements of $\delta^{13}C$ and CO_2

L G R

Summary: Novel Instruments Provide New Opportunities

- Fast, accurate, continuous real-time data in the field
- Measurements up to 20 Hz (fluxes)
- Precise, accurate over wide concentration ranges
- Measurements of discrete samples (via syringe)
- Measurements of $\delta^{13}C$, $\delta^{2}H$, $\delta^{18}O$ at 2 Hz
- Low power requirements
- Prices starting at $30k

[L G R]

Summary: Novel Instruments Provide New Opportunities

- *Fast Methane Analyzer:* CH_4 at 20 Hz
- *Fast Greenhouse Gas Analyzer:* CH_4, CO_2, H_2O at 10 Hz
- *Carbon Dioxide Isotope Analyzer:* $\delta^{13}CO_2$ and CO_2 at 1 Hz
- *Fast N_2O Analyzer:* N_2O at 20 Hz
- *Methane Isotope Analyzer:* $\delta^{13}CH_4$ and CH_4 in real time
- *Water Vapor Isotope Analyzer:* $\delta^{18}O$, $\delta^{2}H$ and H_2O at 2 Hz
- *Liquid Water Isotope Analyzer:* $\delta^{18}O$, $\delta^{2}H$ at 120 samples/day
- *Fast Ammonia Analyzer:* NH_3 at 10 Hz

L G R

Summary

- Fast, real-time field data w/o frequent calibration
- Measurements up to 20 Hz (eddy fluxes)
- Ultra-precise, accurate over wide concentration ranges
- Measurements of discrete samples (syringe injection)
- Measurements of $\delta^{13}C$, $\delta^{2}H$, $\delta^{18}O$ at 1 Hz

L G R