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Recent Developments in Instrumentation for Greenhouse Gases and Related Tracer Measurements

The World's Highest Performance and Easiest to Use Analyzers

CO_2 Experts Meeting
7-10 September 2009, Jena, Germany
Aaron Van Pelt
Applications Engineer, Picarro, Inc. avanpelt@picarro.com

2007 Experts Meeting → to Today's…

2007, Finland → 2009, Jena → 2011

2007, Finland

Presented early data (OSU, Penn State, NOAA) showing Picarro analyzers' applicability to global/regional background GHG measurements

2009, Jena

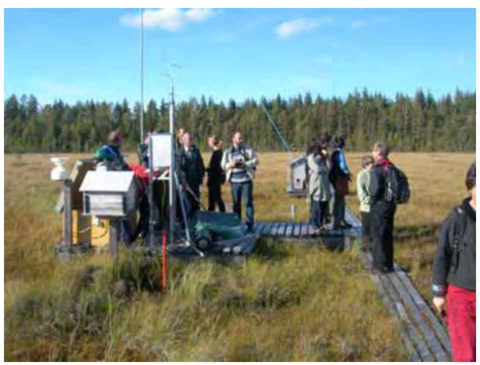
Multiple groups now *using* them for this work…

Discuss new EC flux, tracer, isotope analyzer developments

2011

New field campaigns…

Next developments: Additional species, increased sensitivity…



Collaborations, implementation of community's recommendations for improvements, applicate around core analyzer for specific uses

→

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Picarro Roadmap (GHG & tracers): 2007-2011

2007	2008	2009	2010	2011
CO_2 CH_4 H_2O	CO_2: $\delta^{13}C$ H_2O: $\delta^{18}O$, δD	CO_2 CO COS C_2H_2	N_2O: $\delta^{15}N$, $\delta^{18}O$	What next?

Near-IR platform

Mid-IR platform

Enabling:

- Combinations of multiple species with isotopes
- Higher sensitivity for currently-measured species

High-speed
Flight-ready

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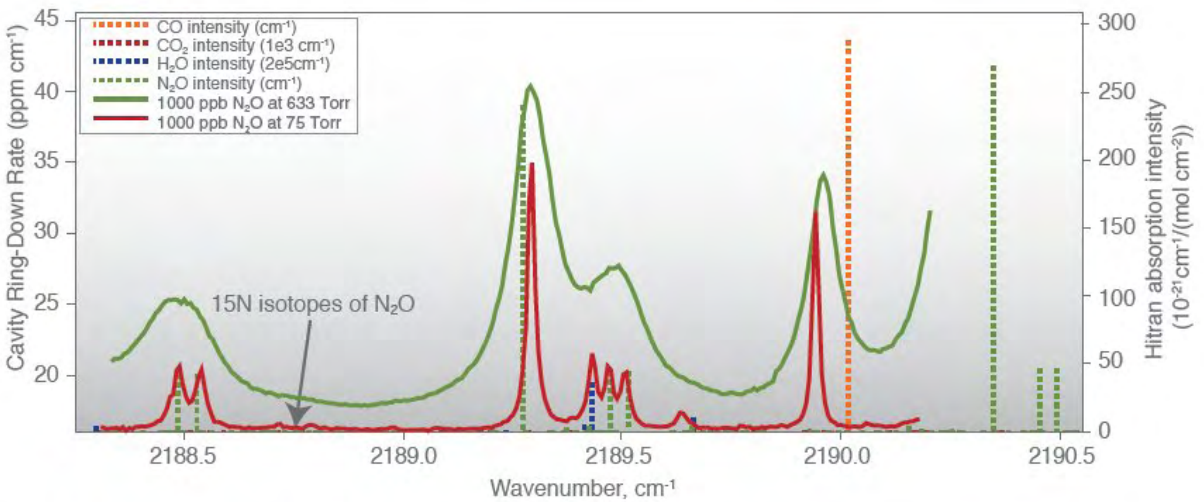
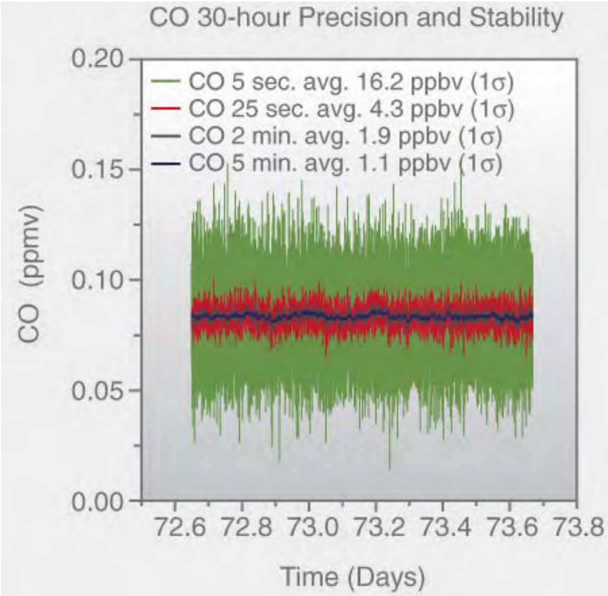
N_2O & CO Analyzers

- $CO/CO_2/H_2O$ Concentration Analyzer (current Near-IR platform)
  - CO_2 precision 1σ (typ.): ~40ppb
  - CO precision 1σ: ~1ppb, 0.5ppb achievable
  - ~6ppb (CO), ~90ppb (CO_2) drift (peak-peak, typ.) in 24 hours (w/o calibration)
- N_2O Concentration and Isotope Analyzer (Mid-IR platform)
  - Concentration precision 1σ: < 0.1ppb
  - <0.2 ppb drift (peak-peak) in 24 hours, < 0.5 ppb in 1 month (w/o calibration)
  - Isotope precision: 1σ: $\delta^{15}N$ and $\delta^{18}O$ <1‰ (5 min.)



High resolution scan showing interfering and Nitrogen isotope lines.

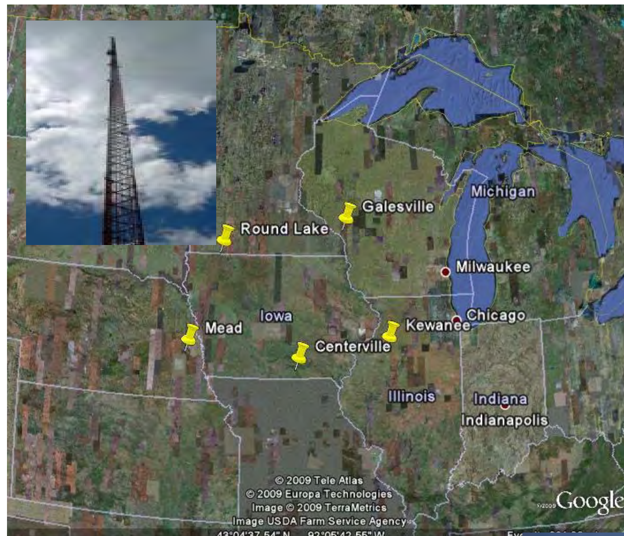


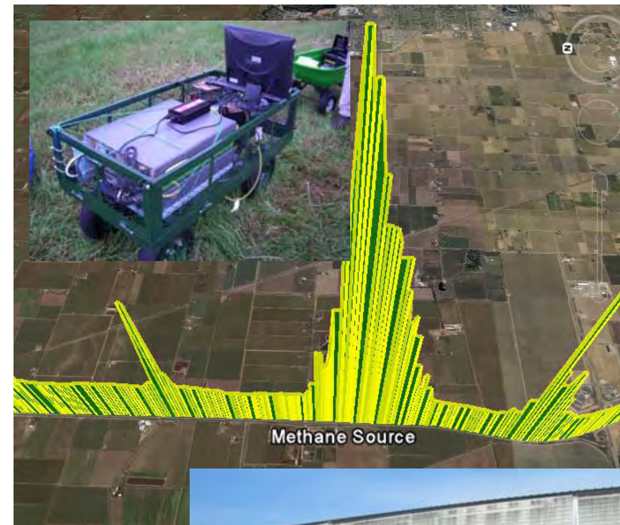
Measuring Green House Gas Emissions

- Global Scale
- Large Nations

- Regional Scale
- States & Small Nations

- Local Scale
- Point Sources & Sinks

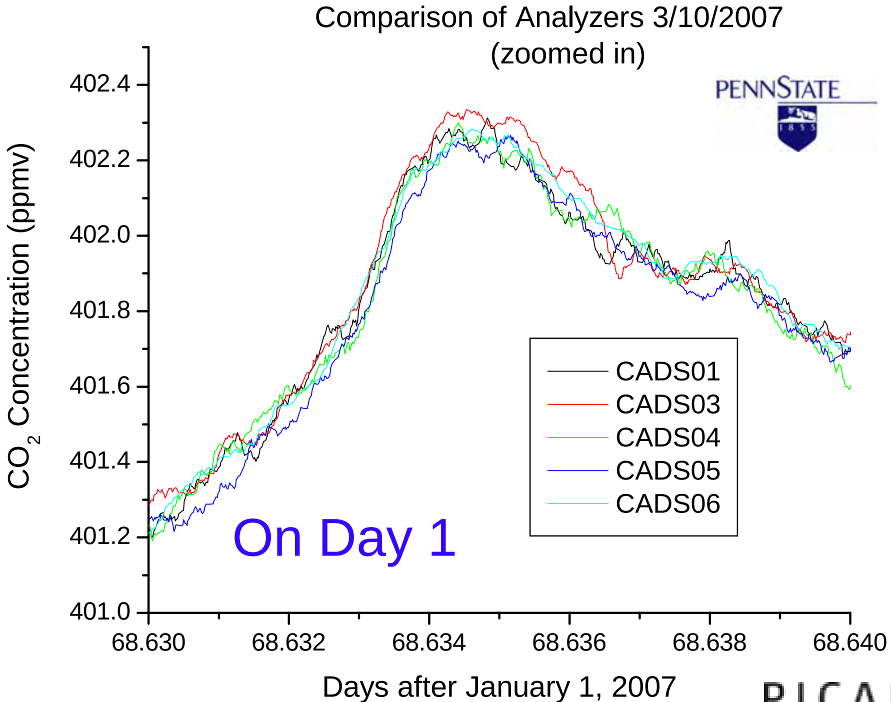


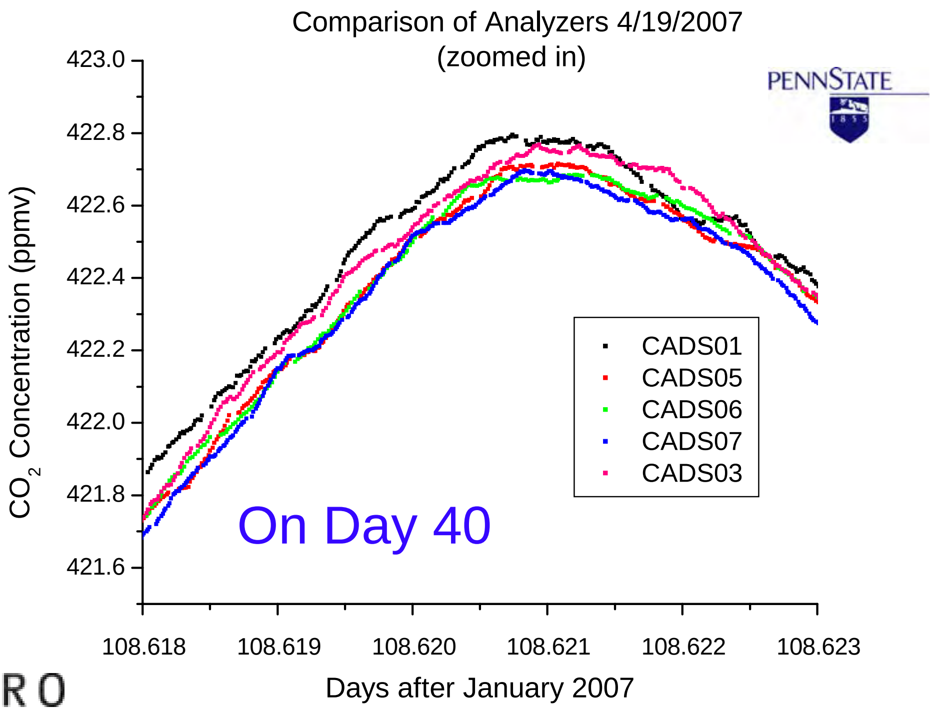


Connecting Measurements on Local←→Regional ←→Global Scales

- Data quality must be equivalent at all scales
- [Inter]comparability required
  - Analyzer-to-analyzer reproducibility critical – common platform?
  - Isotopologues correctly measured/calibrated? – pollution tracers?

Comparison of five CO_2 analyzers one day and 40 days after calibration





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EC Flux Measurements

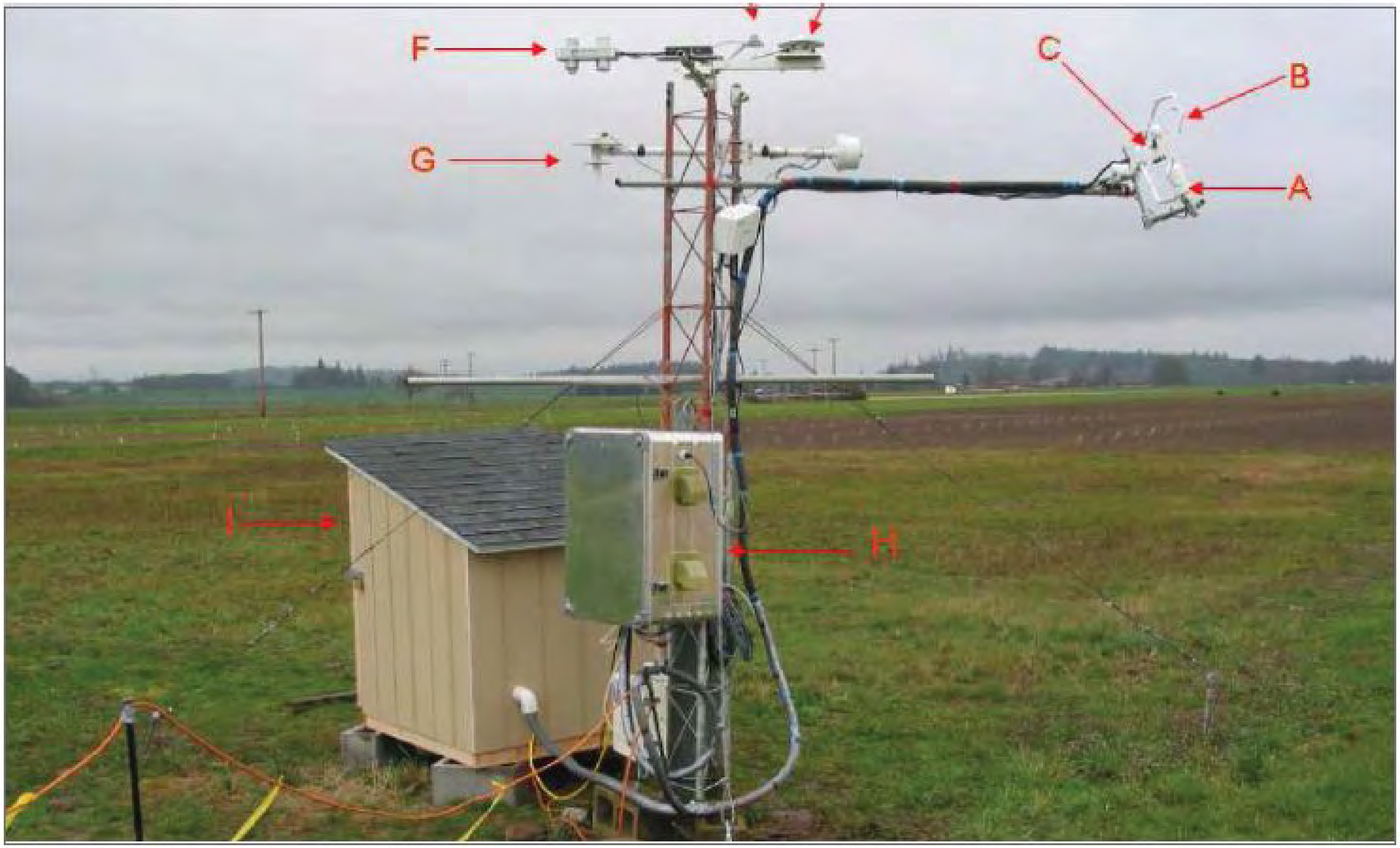
High-speed (10Hz) Analyzer for

Eddy Covariance Flux Measurements

Christoph Thomas
Oregon State University, College of Oceanic and Atmospheric Sciences, Corvallis, OR, USA

Beverly Law
Oregon State University, Dept. of Forest Science, Corvallis, OR, USA

OSU Flux setup for field campaign with Picarro flux analyzer compared to incumbent flux analyzers



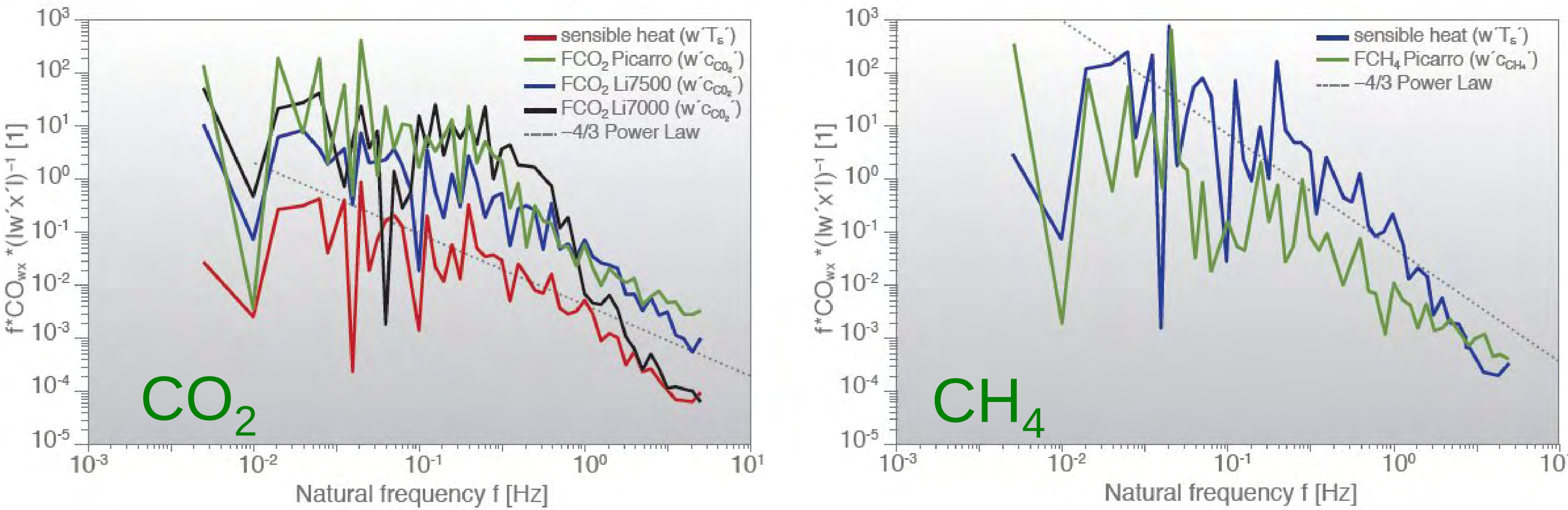
OSU
Oregon State
UNIVERSITY

Field testing courtesy Christoph Thomas & Beverly Law, OSU

The field-site setup of the AmeriFlux portable system (PS) and the Picarro prototype analyzer at the Hyslop Crop Science Field Research Laboratory at Oregon State University. The Picarro analyzer was housed in the weatherproofed box in the background (I), whereas the electronics and the closed-path infrared gas analyzer (Li7000) of the PS were located in the aluminum box in the foreground. Other instrumentation: anemometer (B), open-path Li7500 (A), closed-path Li7000 (C), radiometer (F), pyranometer (D), radiation sensor (E), temperature sensor (G), pressure transducer (H).

Cospectra of sensible heat, Picarro & LiCOR fluxes compared

OSU, Hyslop trial, mean cospectra, N= 14



Cospectra follow expected -4/3 power law

Mean, bin-averaged cospectra of turbulent fluxes of sensible heat and carbon dioxide (CO2) using the signals from different gas analyzers. Spectral densities were normalized by their covariance. The dashed line indicated the expected -4/3 power law of cospectral decay.

Measured instrument precision at 10Hz:

- 230 ppbv CO_2
- 1.2 ppbv CH_4

Analysis courtesy Christoph Thomas, OSU

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An Acetylene Tracer-Based Approach to Measuring Fugitive from Emissions from Large-Area Sources

Sze M. Tan, Eric R. Crosson and Bruce A. Richman

Picarro Inc.

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Landfill Methane Measurements

- Landfills contribute to ~25% of total man-made methane in U.S. (>10% worldwide). Need to monitor emissions for inventory and to verify effectiveness of remediation methods.

- Concentration field is spatially inhomogeneous and temporally variable, depending on bacterial activity and atmospheric conditions.

- Total emission rate from extended area is often of interest.

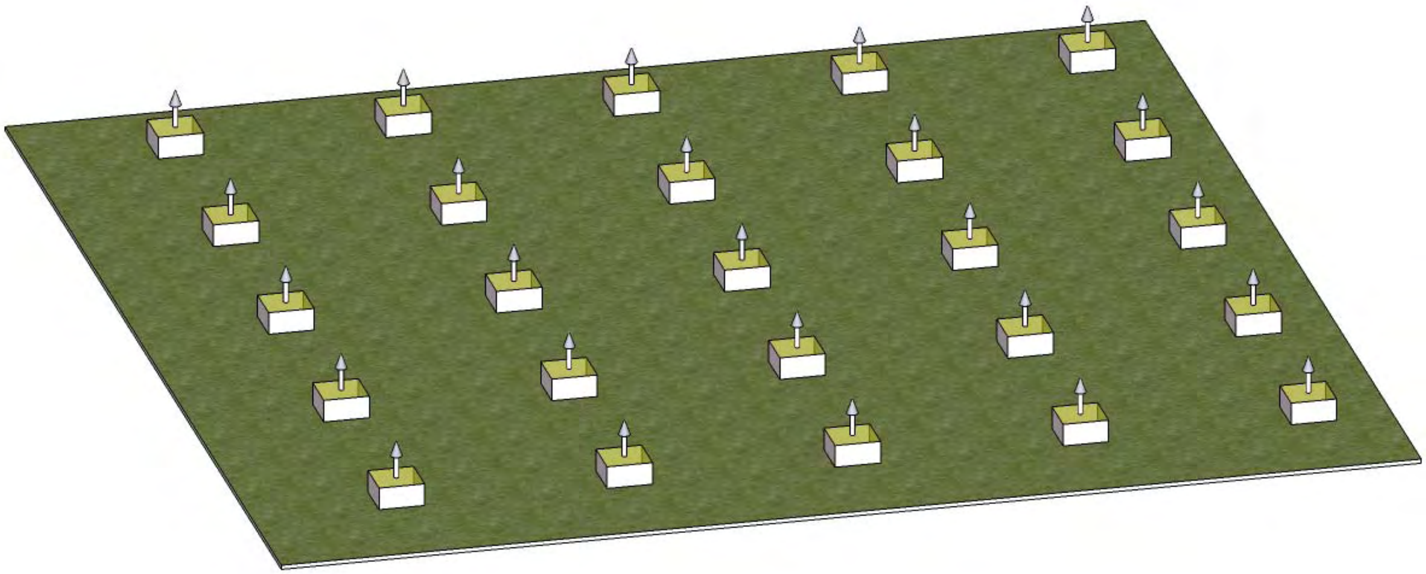
Measurement Methods

- Direct / total measurements:
  - Flux chambers
  - Eddy covariance
  - Plume mapping

- Indirect / partial measurements:
  - Inverse dispersion methods
  - Tracers

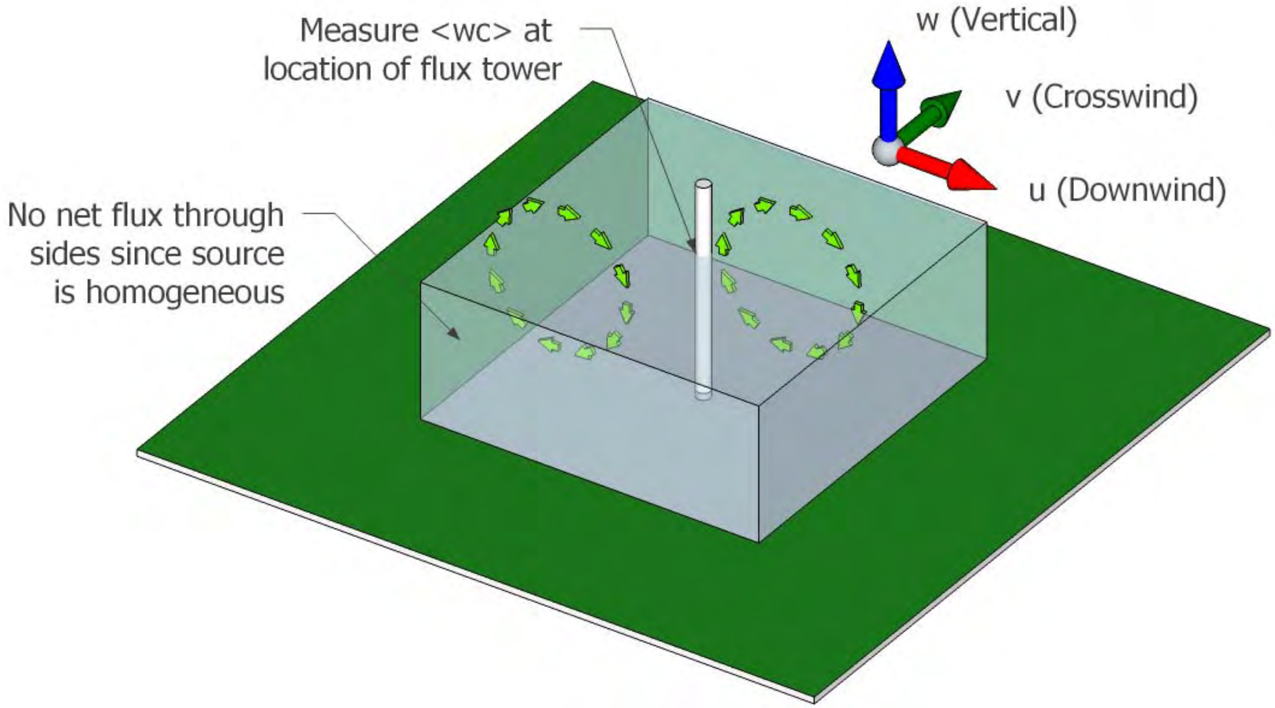
Flux Chambers

- Large number needed for a representative sample of inhomogeneous field.
- Individual measurements are inexpensive, but finding total is slow and labor intensive.



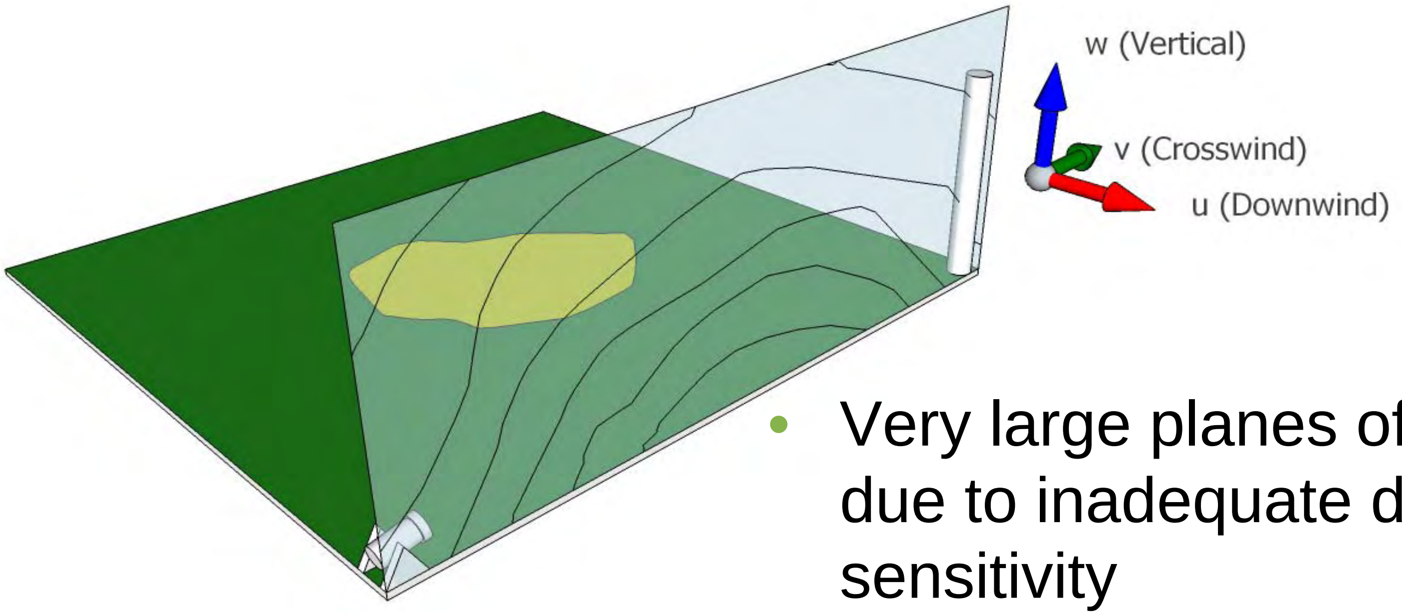
Eddy covariance

- Measures vertical flux within homogeneous source.
- For inhomogeneous flux, need size of fetch (collection footprint) which depends on meteorology.
- Multiple towers needed for coverage, each with high-speed analyzer and 3-d anemometer.



Plume Mapping

- Determine integral of concentration over a plane, and combine with wind speed to give flux through plane.
- Several technologies, e.g. Differential LIDAR, Path Integrated Optical Remote Sensing (+ Radial Plume Mapping).
- Most effective when all emission goes through plane.



- Very large planes often infeasible due to inadequate detection sensitivity

Inverse Dispersion Methods

- Inverse Dispersion methods:
  - Assumes steady-state relationship between source fluxes and measured concentrations

$$C_i\left(x,y,z\right)-C_{i,b}=\int_A D_i\left(x,y,z\,|\,\xi,\eta\right)F_i\left(\xi,\eta\right)\mathrm{d}\xi\,\mathrm{d}\eta$$

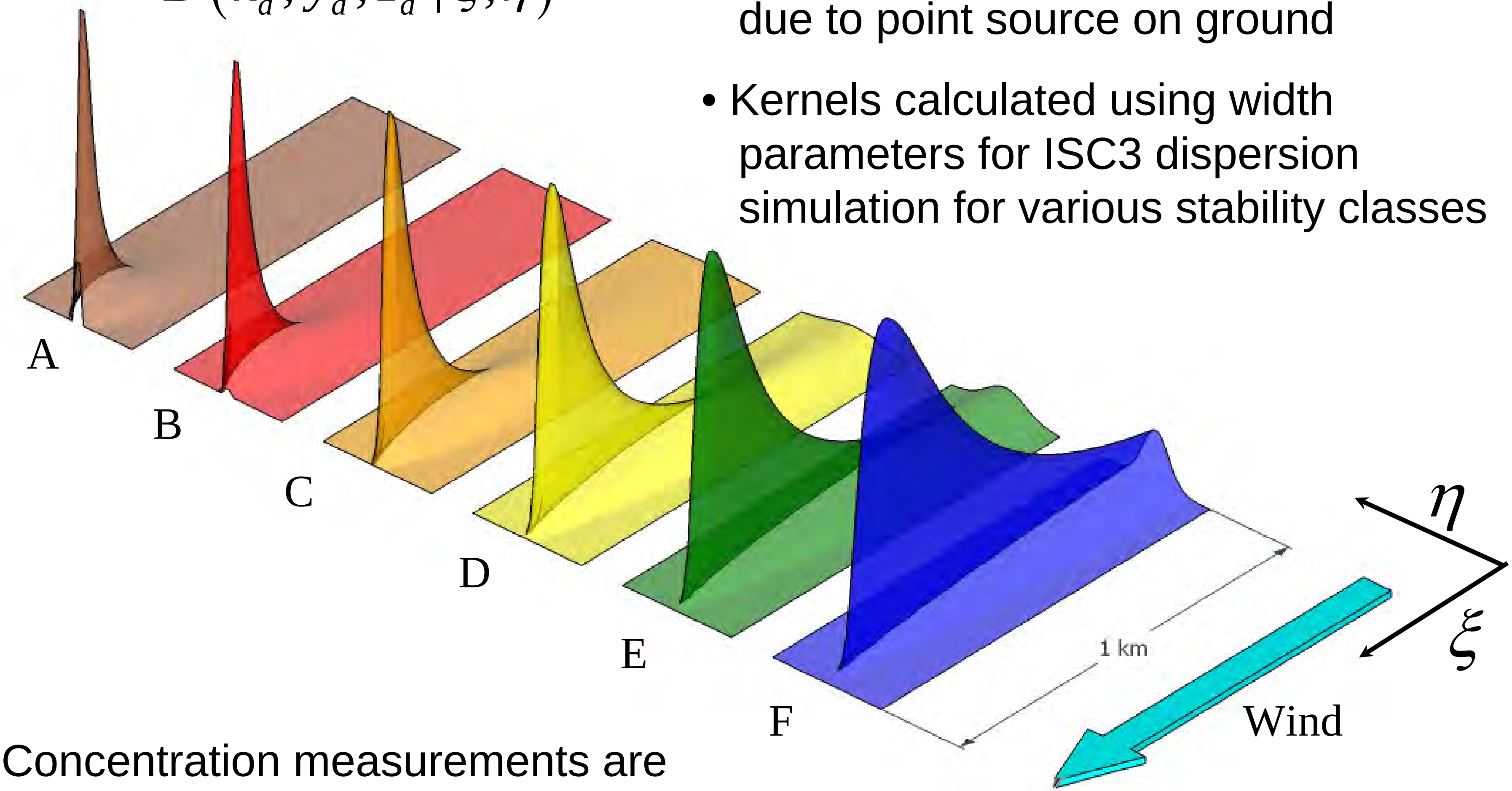
Concentration | Background | Dispersion kernel | Source flux

  - D_i depends strongly on meteorological conditions, can vary by several orders of magnitude
  - Method relies on measuring conditions with enough accuracy and detail to determine D_i and infer source properties from concentration measurements
  - Point concentrations or path-integrated concentrations may be measured

Gaussian Dispersion Kernels

$$D\left(x_d, y_d, z_d \mid \xi, \eta\right)$$

- Concentration at 5m high detector due to point source on ground
- Kernels calculated using width parameters for ISC3 dispersion simulation for various stability classes



- Concentration measurements are very sensitive to nearby emission

Tracer Methods

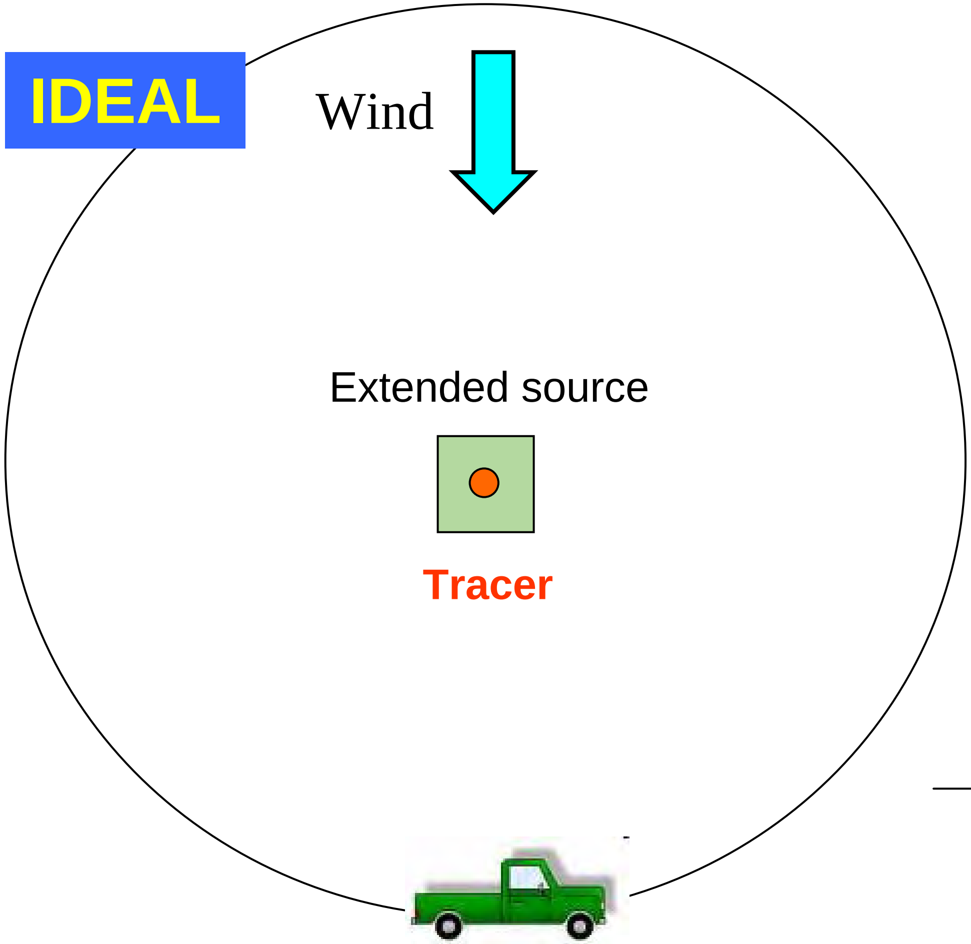
- Use a tracer gas with same dispersion as target gas, released at a known rate
- For perfectly coincident tracer and target sources…

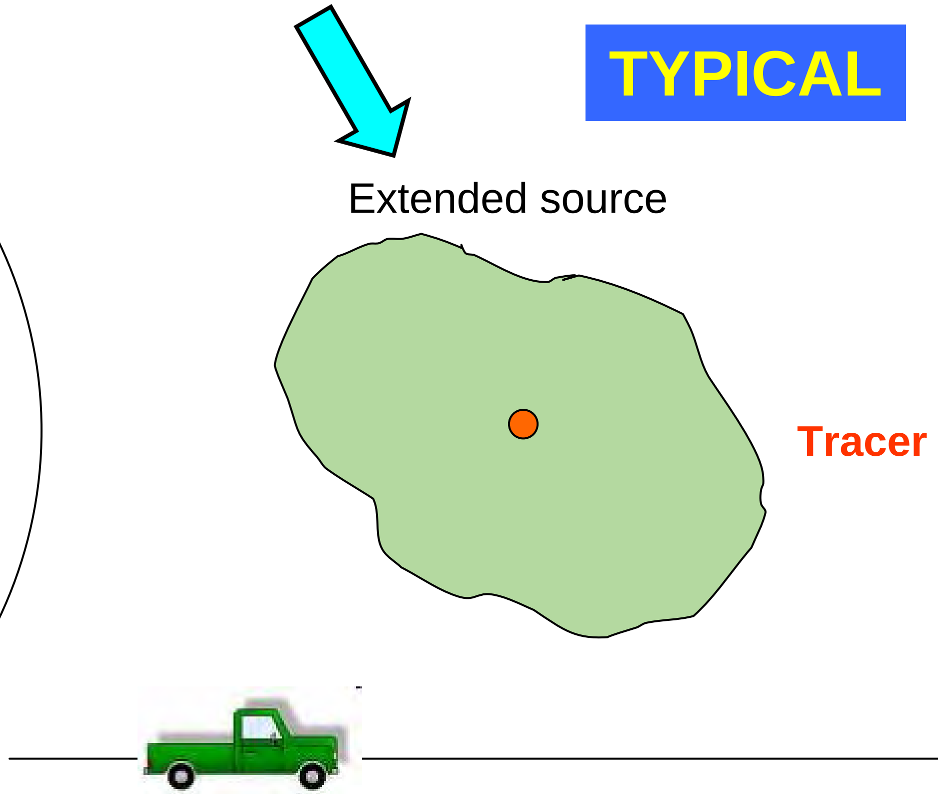
$$\frac{Q_{\text{target}}}{Q_{\text{tracer}}} = \frac{C_{\text{target}} - C_{\text{target, bckgnd}}}{C_{\text{tracer}} - C_{\text{tracer, bckgnd}}}$$

…concentration measurements of tracer and target at a single location suffice, independent of dispersion.

- Choose location to exploit averaging properties of dispersion kernel to measure total flux – go to far-field where kernels are smooth and slowly-varying
- Need to be able to find the plumes downwind of source:
  - Static Plume Method: Fixed detector, wait for favorable wind direction
  - Mobile Plume Method: Move detector through plumes

Mobile Plume Tracer Method



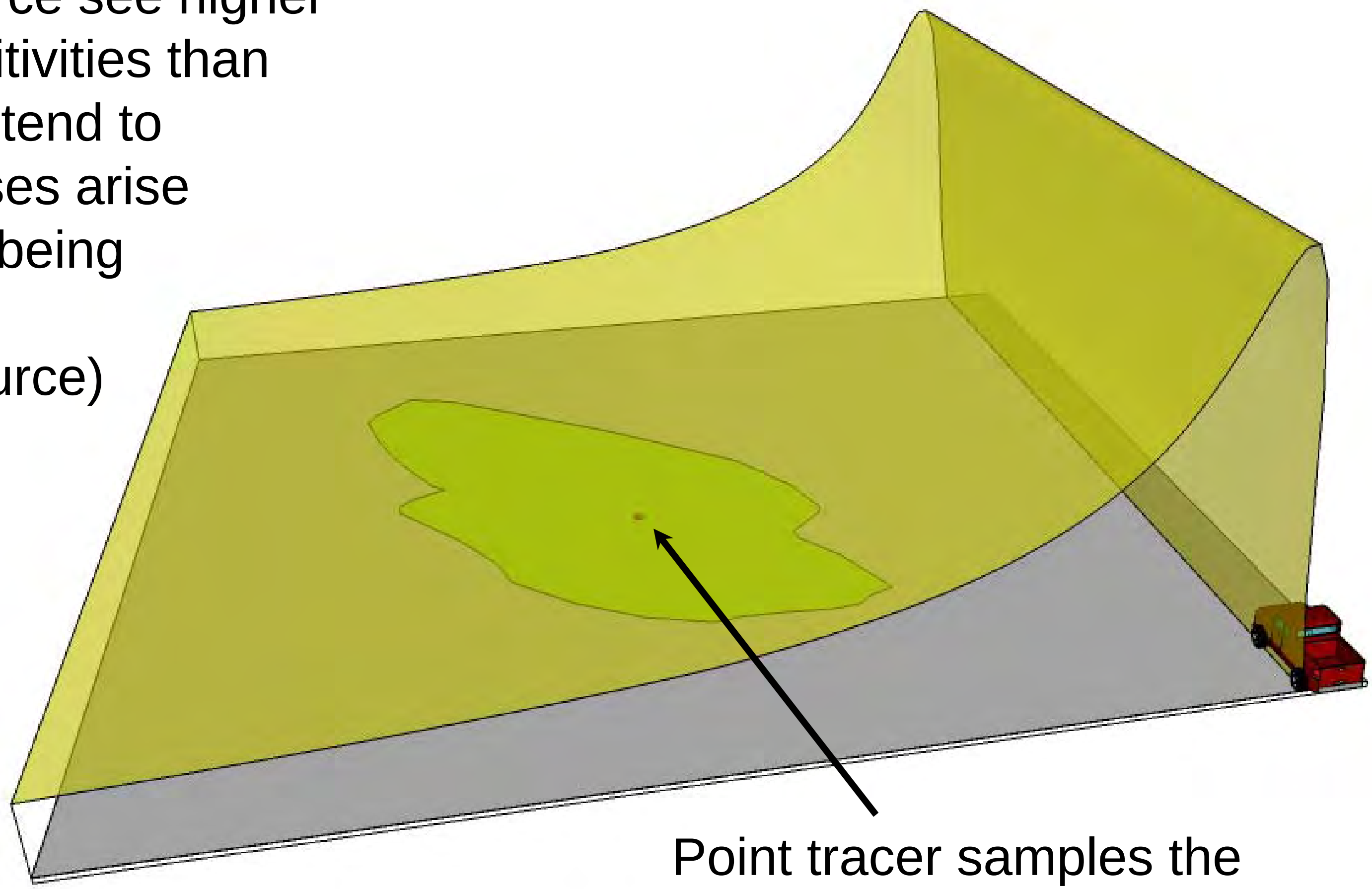


Drive concentration sensor on path in far-field
Use ratio of path-integrated concentrations (PIC)

What are effects of:
- Large extended source with point tracer?
- Non-normal wind direction?

What is being measured?

- Calculating path integrated concentration (PIC) smears out dispersion kernel along path.
- Portions of source see higher and lower sensitivities than tracer – effects tend to cancel (i.e. biases arise from tracer not being in exact center of extended source)



Point tracer samples the surface at single location

Acetylene as a Tracer

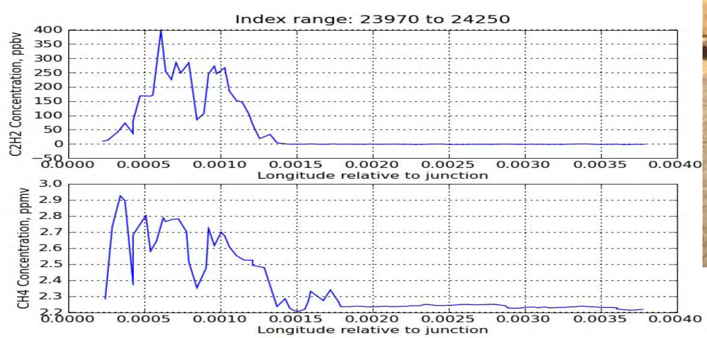
- Previous tracer studies have used SF_6 & N_2O because of the detection technologies used
- Acetylene tracer recently used to validate extended source emission measurements
  - Molecular mass 26 – close to air
  - Naturally-occurring concentrations low (~1 ppbv)
  - Decomposes in atmosphere: half-life ~13 days
  - Readily available and inexpensive
  - Strong absorption bands in Near-IR
  - Flammable, but outdoors, dilutes rapidly to <2.5% (flammability limit)
  - Can release up to ~30 Lpm safely from one bottle

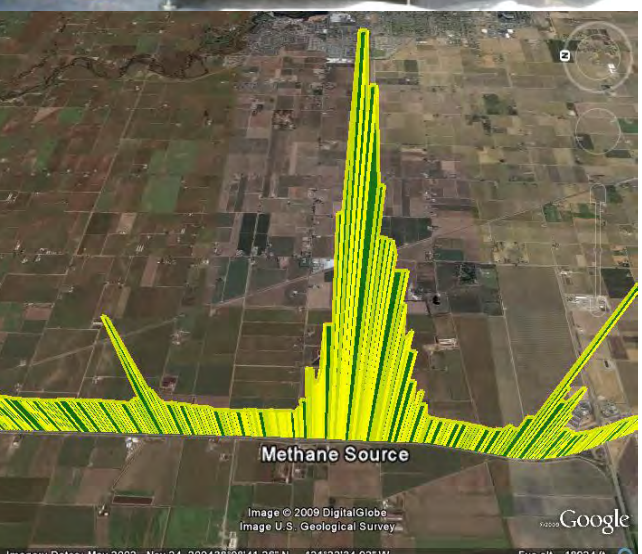
Methane & Acetylene Analyzer Performance

- Simultaneous CH_4 & C_2H_2 measurement in <2sec
- Measurement precision (1-sigma):
  - 0.35 ppb for acetylene
  - 1 ppb for methane
- Analyzer cavity: pressure 70Torr, volume 25 ml, flow rate 230 sccm
  - Gas exchange time ~1s
- Gas sampled at ~5m height, brought to analyzer with auxiliary pump: 20 Lpm for turbulent flow in tube
- Powered from vehicle battery using inverter ~350W
- GPS for position data at 1s intervals, incorporated with concentration data

10 Hz CH_4 Measurements at Landfills

Methane emission rates using tracer methodology



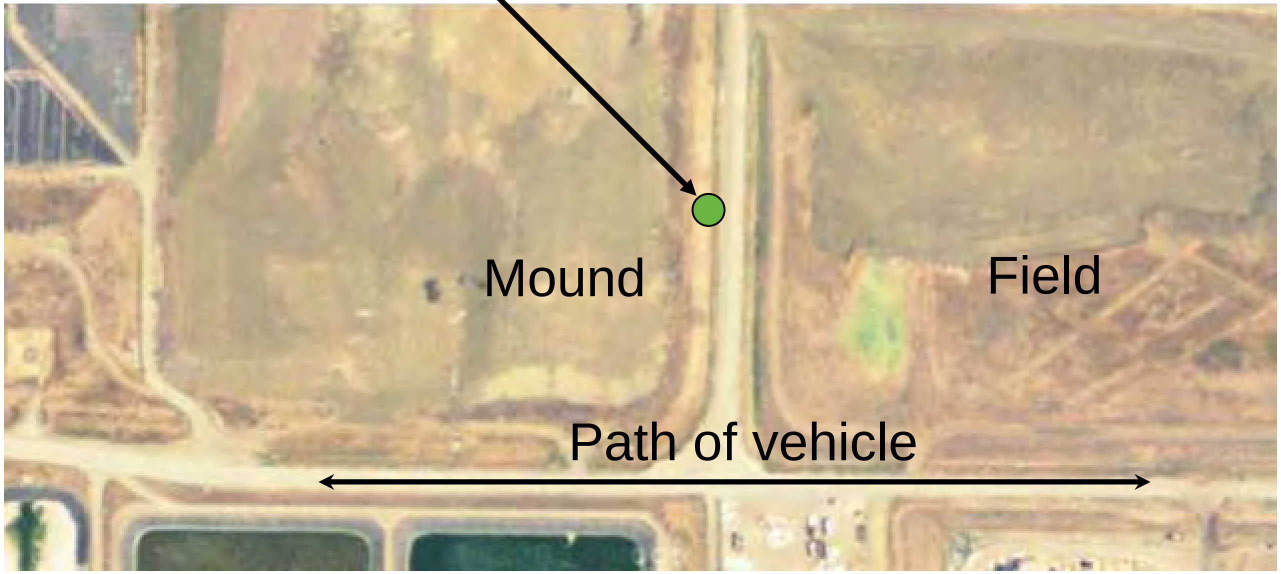


Field Trial at Landfill

Sunny, clear conditions,
Light winds from NNW-N, <5 mi/hr

Release point, CH_4 and C_2H_2

100m



Both gases released at approx 10 L/min

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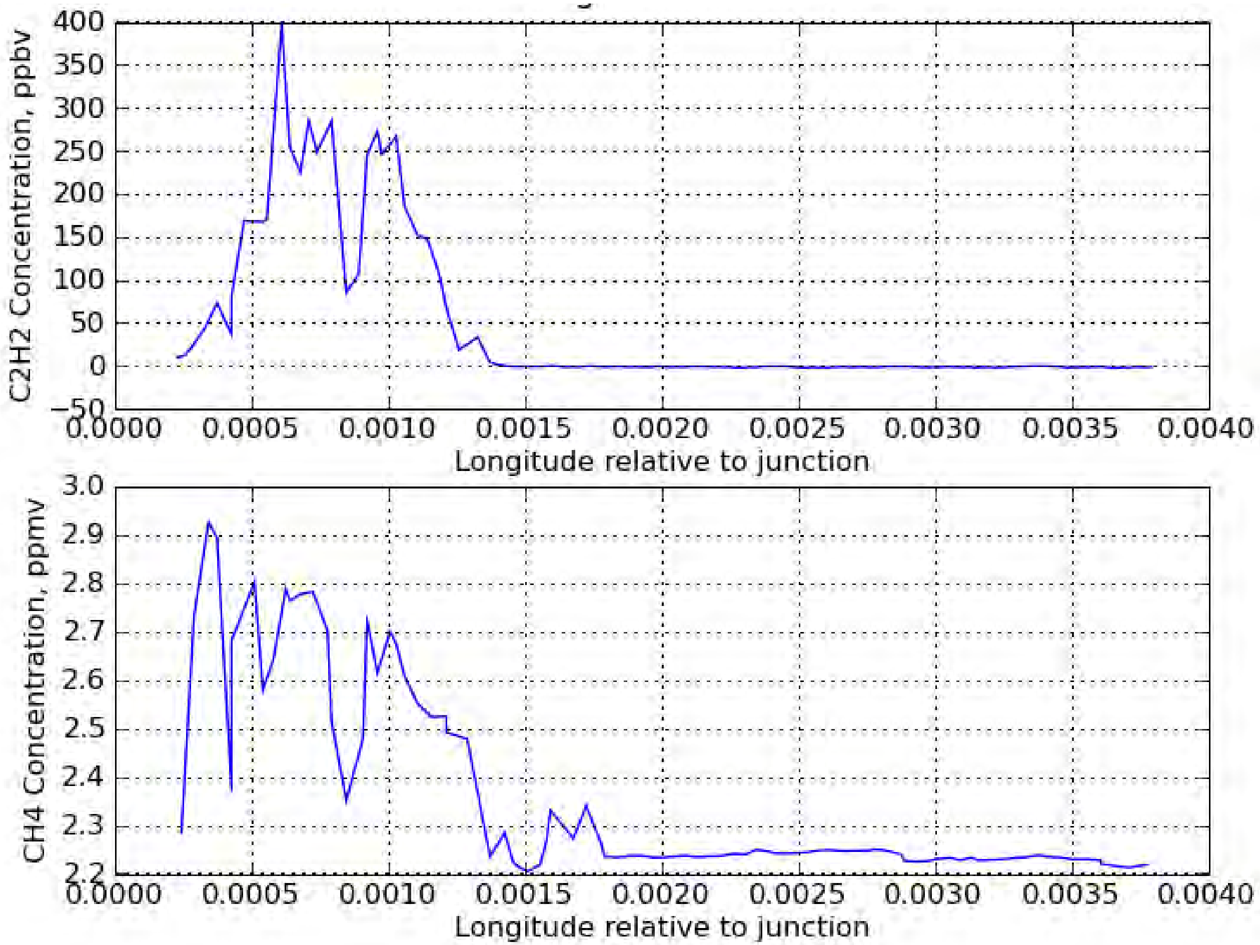
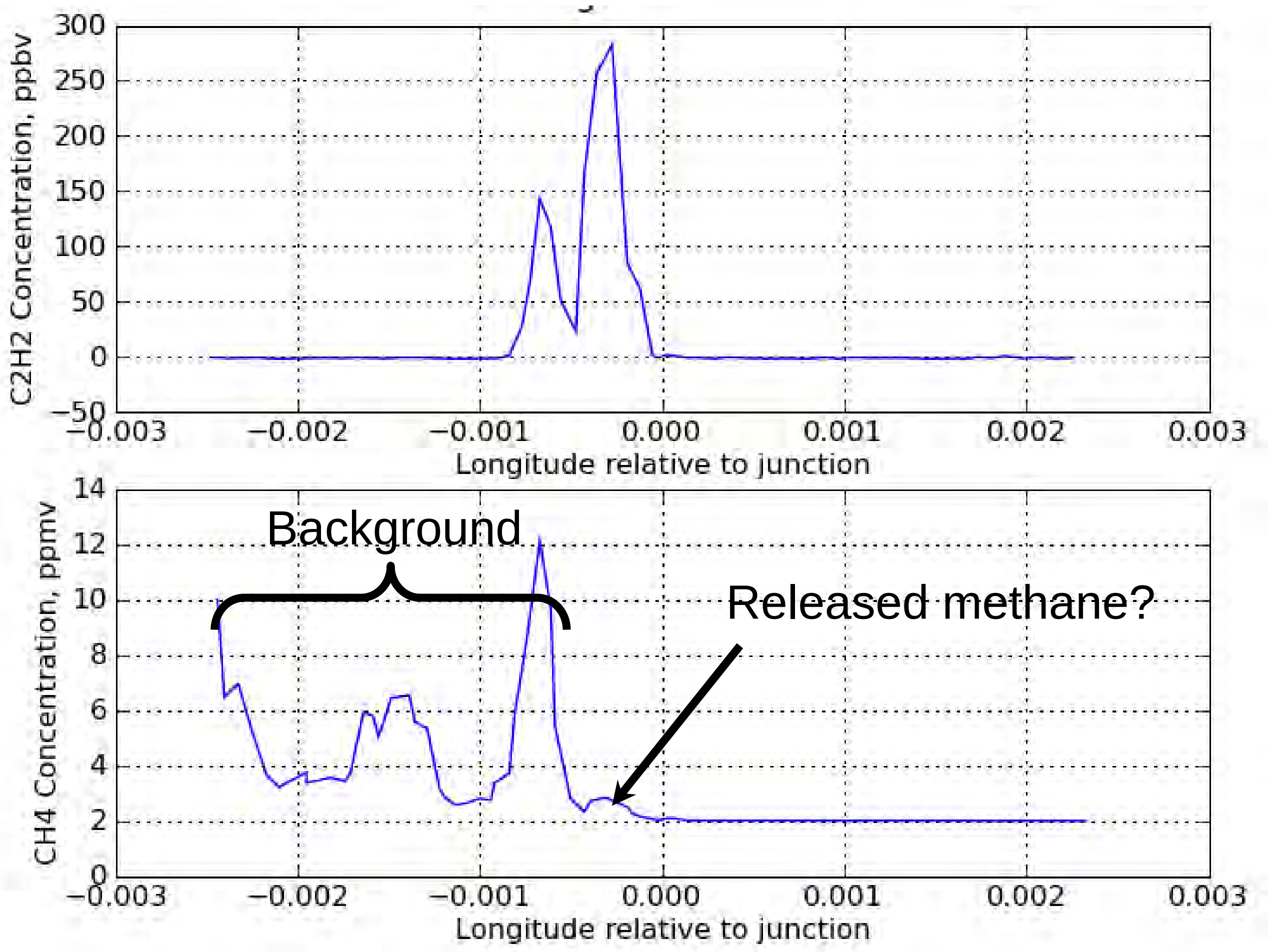
Field Trial – Example Results

- Closest distance to source 120m. $10^{-3}\deg \approx 70\text{m}$



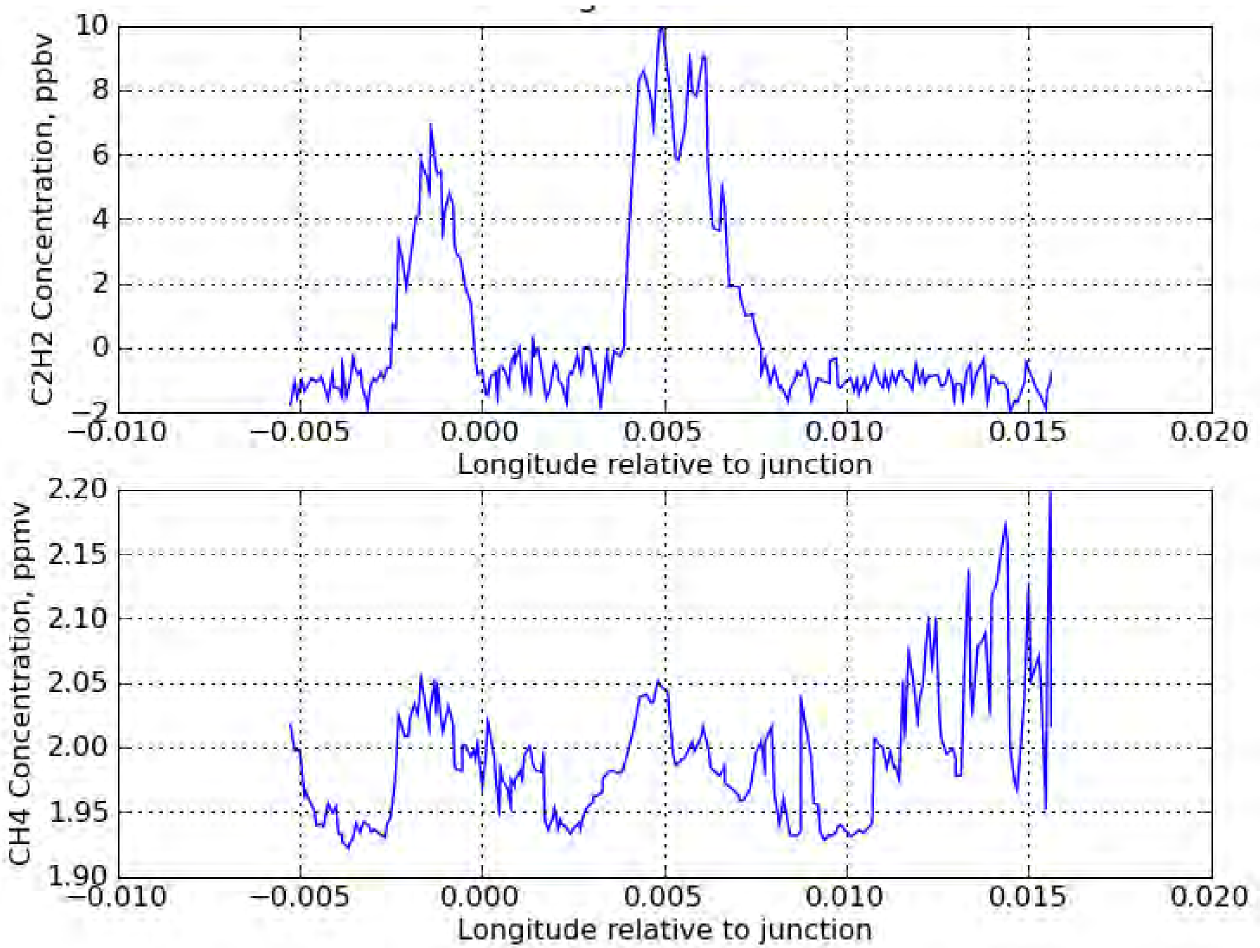
Field Trial – Example Results

- Released methane sometimes swamped by ambient levels



Field Trial – Example Results

- Acetylene still readily visible at 800m south of release

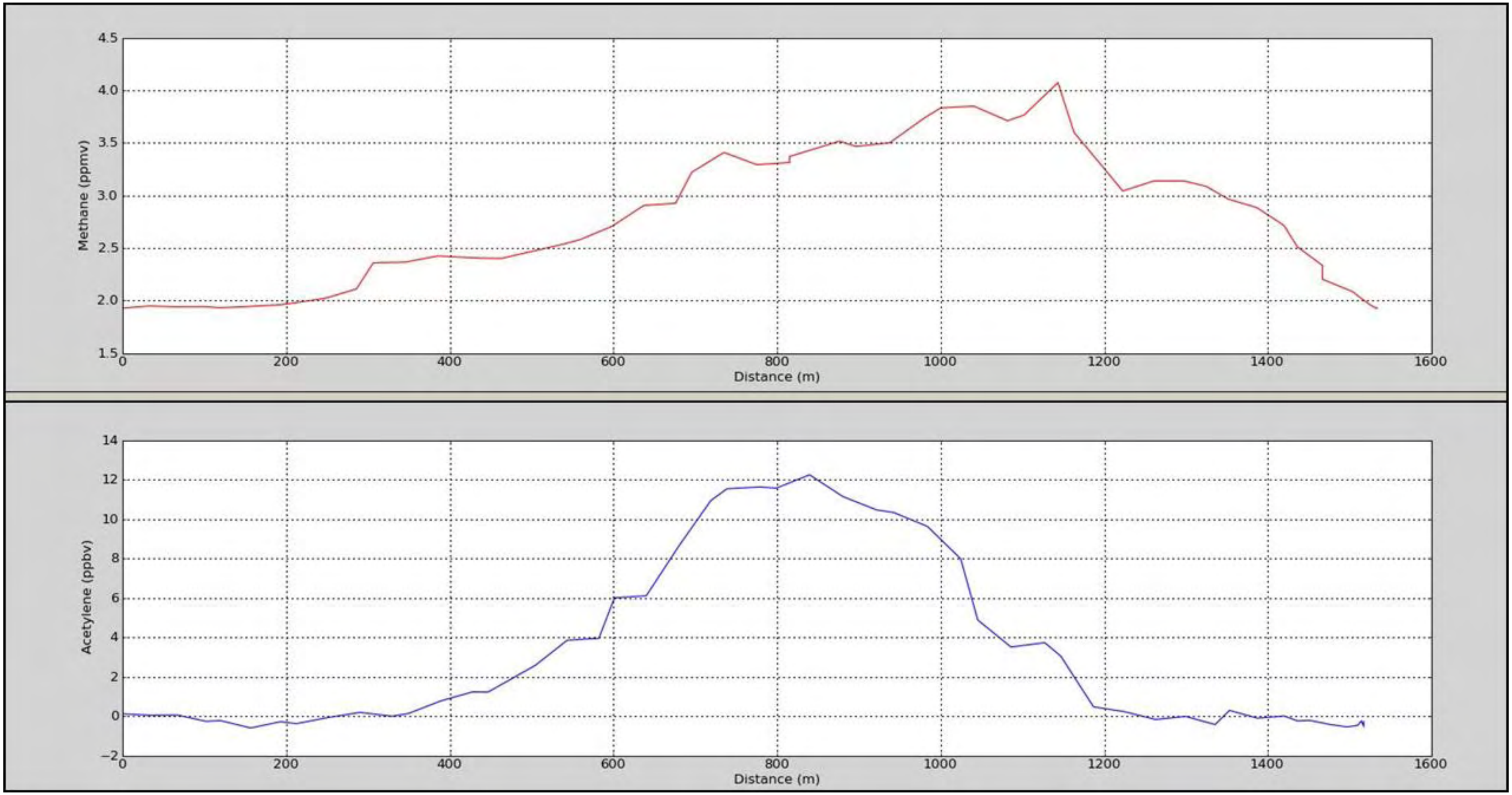


Two peaks probably due to changing wind direction

Methane/Acetylene Tracer Measurement at a Landfill

Methane (ppmv)

Acetylene (ppbv)



Distance (m)

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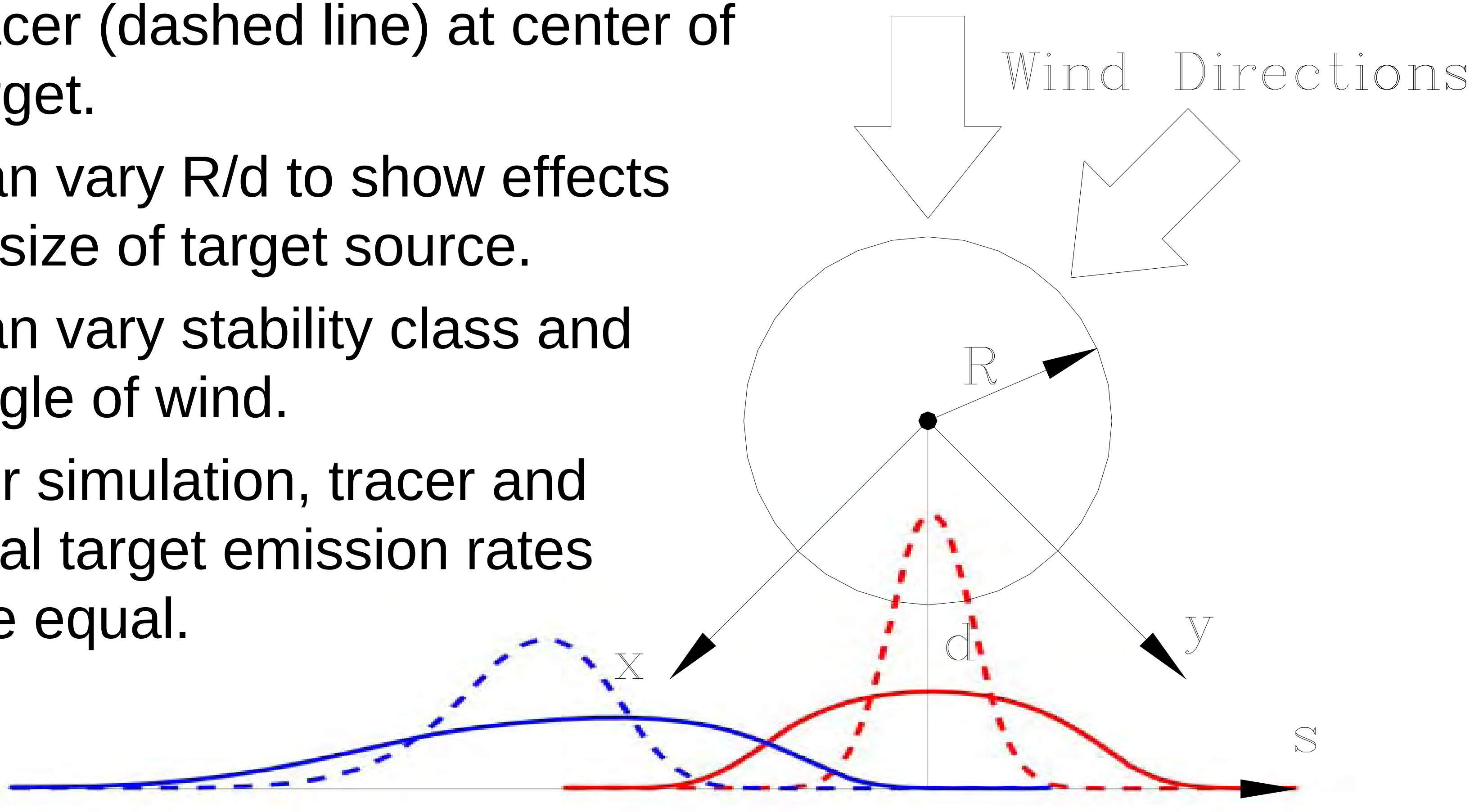
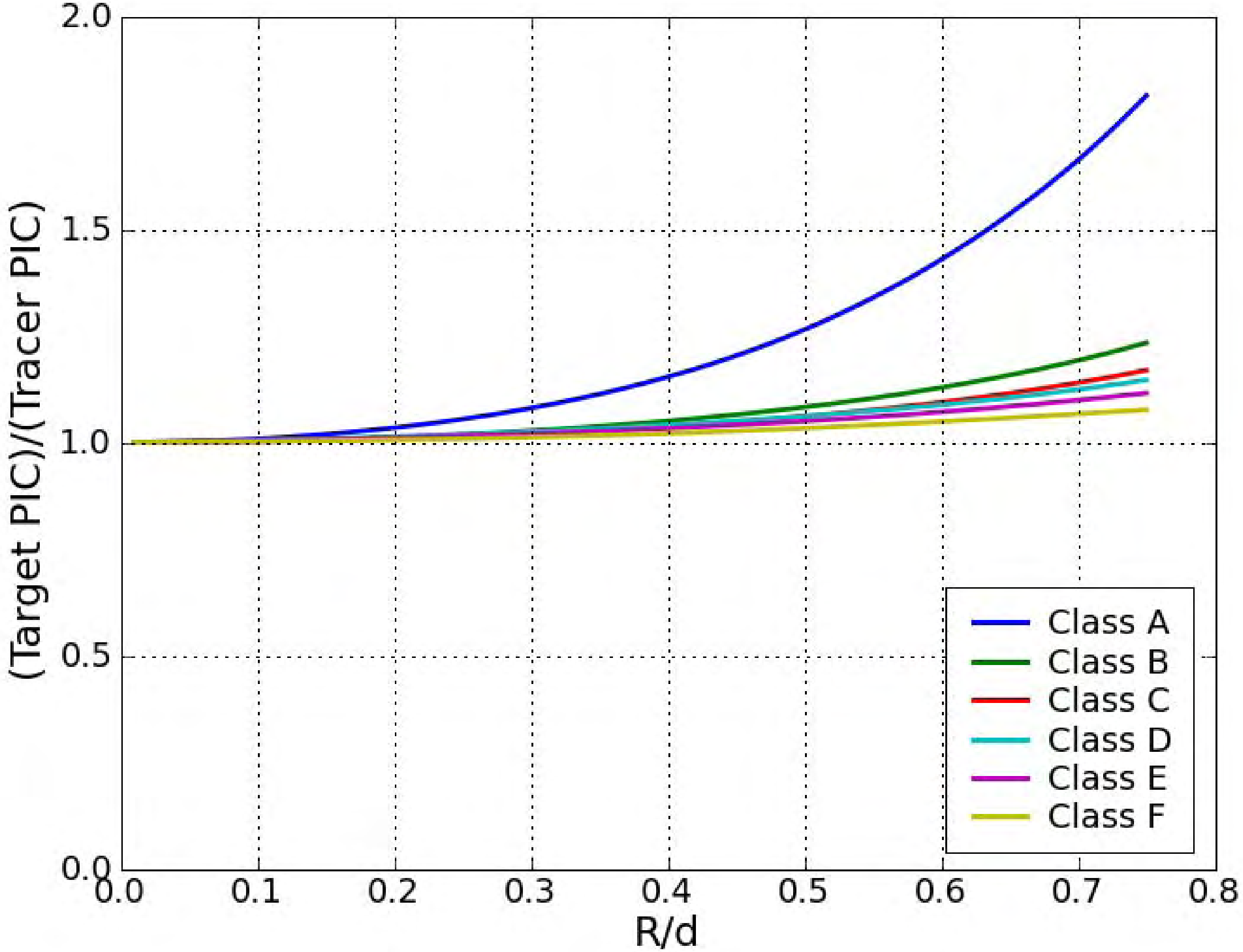
Simulation of Bias

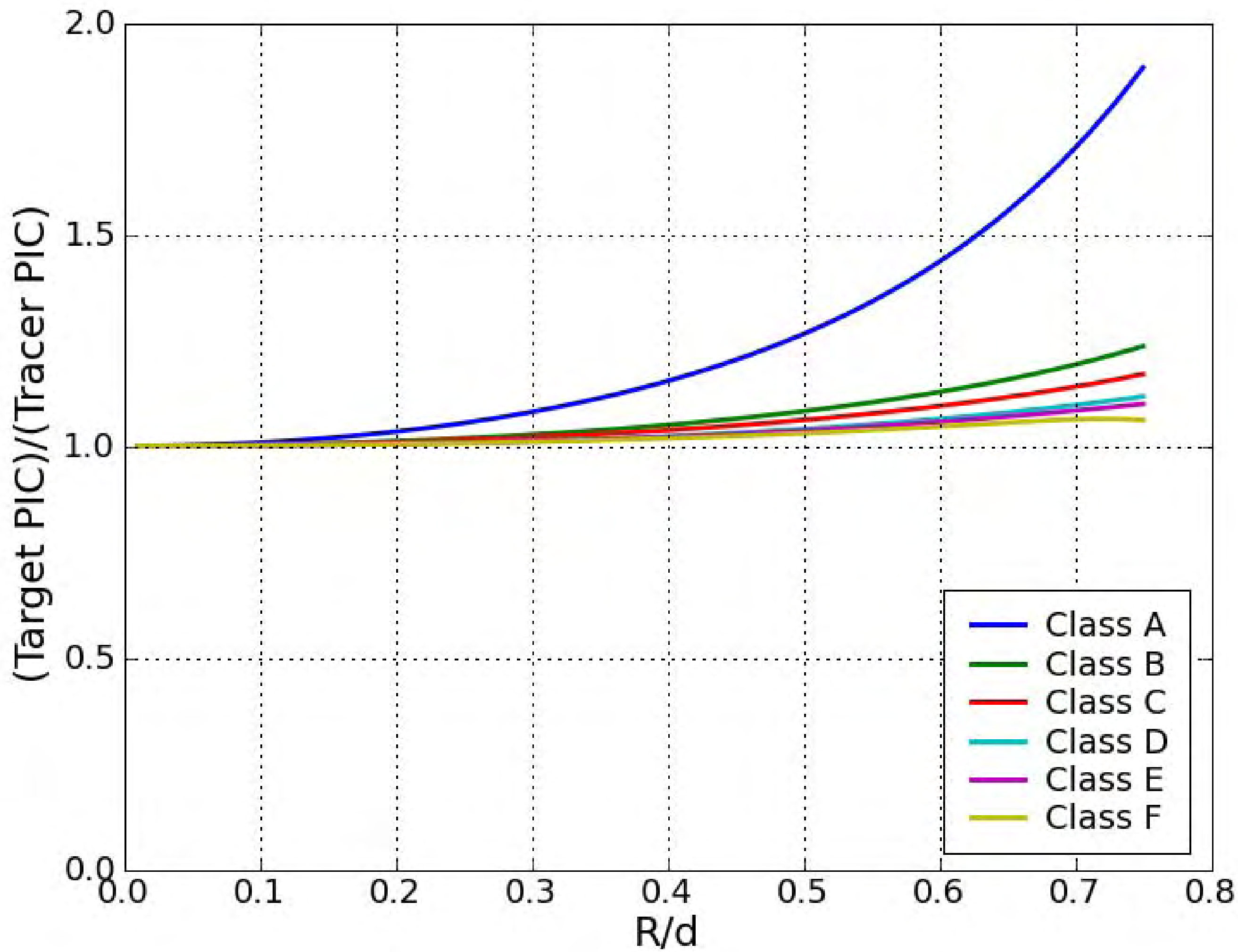
- Calculate integrated concentration along path for circular, uniform, extended target source (solid line) and for a point tracer (dashed line) at center of target.
- Can vary R/d to show effects of size of target source.
- Can vary stability class and angle of wind.
- For simulation, tracer and total target emission rates are equal.



Results, wind normal to path



Results, wind at 45°to path



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Conclusions

- Tracer methods using mobile monitoring platforms are promising tools for measuring total methane emissions. They exploit the averaging properties of atmospheric dispersion in the far field

- Method works best when winds are steady, and do not change much on the timescale of the measurement

- Presence of extraneous sources too close to the measurement path are the main cause of inaccuracies

- Cavity Ring Down Analyzers have several properties that make them well-suited for these measurements
  - (i.e. stability, sensitivity, multi-species capable, no species crosstalk)

Methane concentration excess

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~ Fin ~

Thank you!

Backup Slides

Regional Scale Measurements

CO_2/H_2O Analyzers for

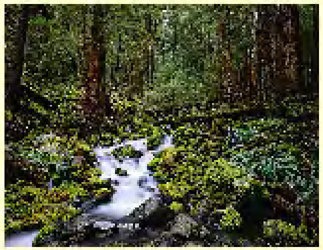
Atmospheric Inversion Measurements

Natasha Miles, Scott Richardson and Ken Davis

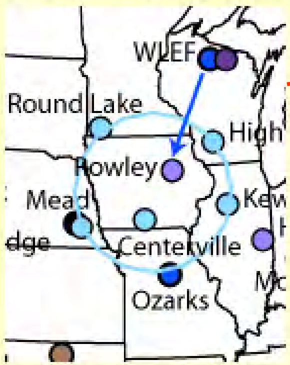
Pennsylvania State University, Department of Meteorology,
University Park, PA, USA

"Ring 2": High-precision, high-accuracy CO_2 mixing ratio measurements in support of the NACP Mid Continent Intensive

ring2.psu.edu



RING 2



Colorado State University   PENNSTATE 1855

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The role of Ring 2 in the Mid-Continent Intensive

- Add a regional network of 5 communications-tower based atmospheric CO_2 observations in the mid-continent intensive region
  - April 2007 through October 2008 (+)
  - In addition to the planned long-term atmospheric CO_2 observing network
    - Tall towers
    - Aircraft profiles
    - Well-calibrated CO_2 measurements on AmeriFlux towers

- The communications towers will "oversample" the atmosphere in the study region for more than a full year

- A coupled atmosphere/terrestrial carbon model and a Lagrangian particle dispersion model will be used to conduct an atmospheric inversion and convert these mixing ratio measurements into highly data-constrained regional carbon balance estimates

- Goal is to produce a map of **sources** and **sinks** (fluxes) of **CO_2** for US

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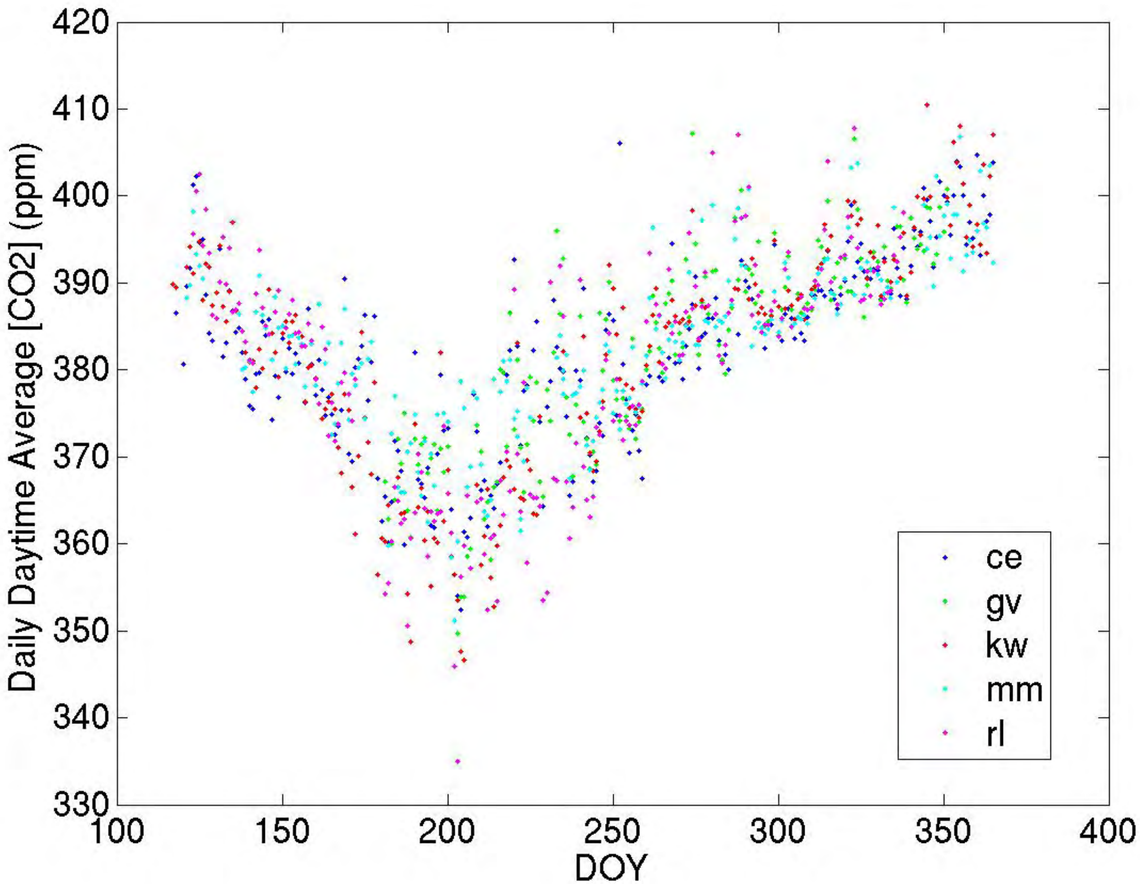
Daily Daytime Average (all 5 Ring 2 sites)



- 50 ppm drawdown!
  - Typical forest signal is 20-30 ppm
  - Agriculture (esp corn) has huge signal

- Large spatial gradient!
  - as large as continental-scale sites despite being separated by 500 km at most

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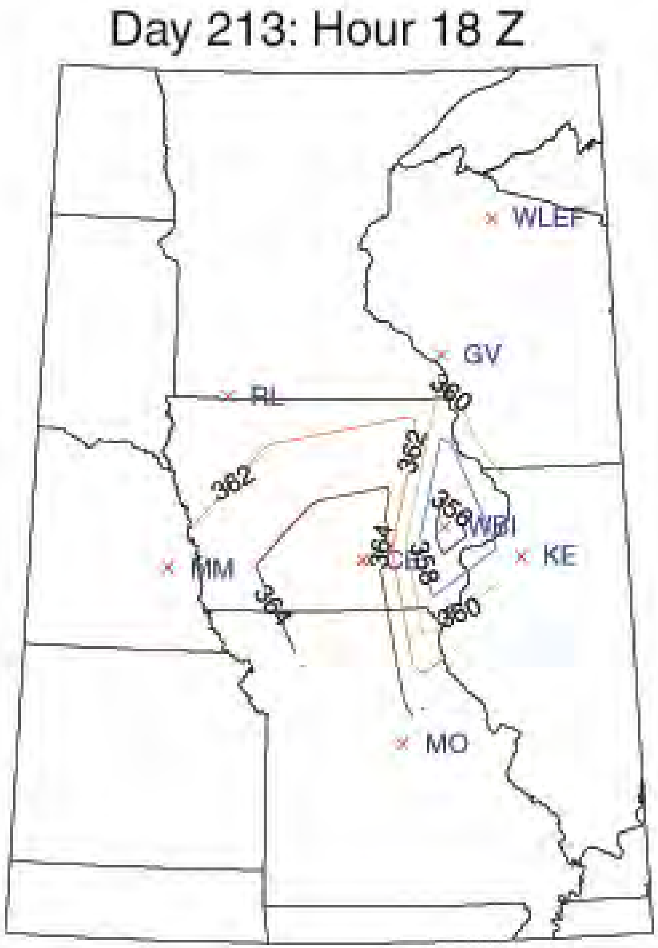
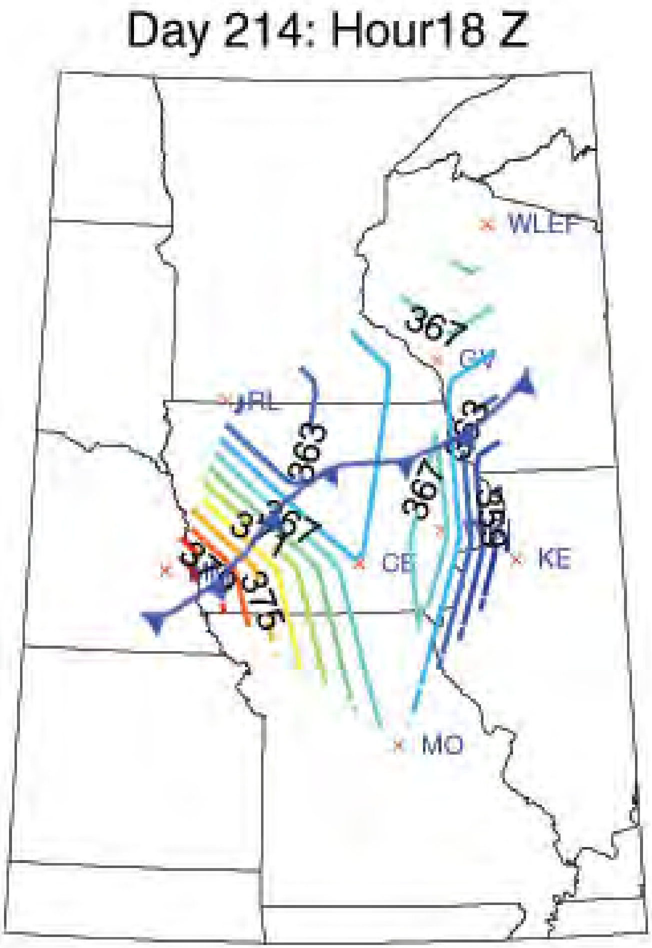
CO_2 "weather maps"

Day with small spatial gradient
6 ppm difference



Day with large spatial gradient
20 ppm difference



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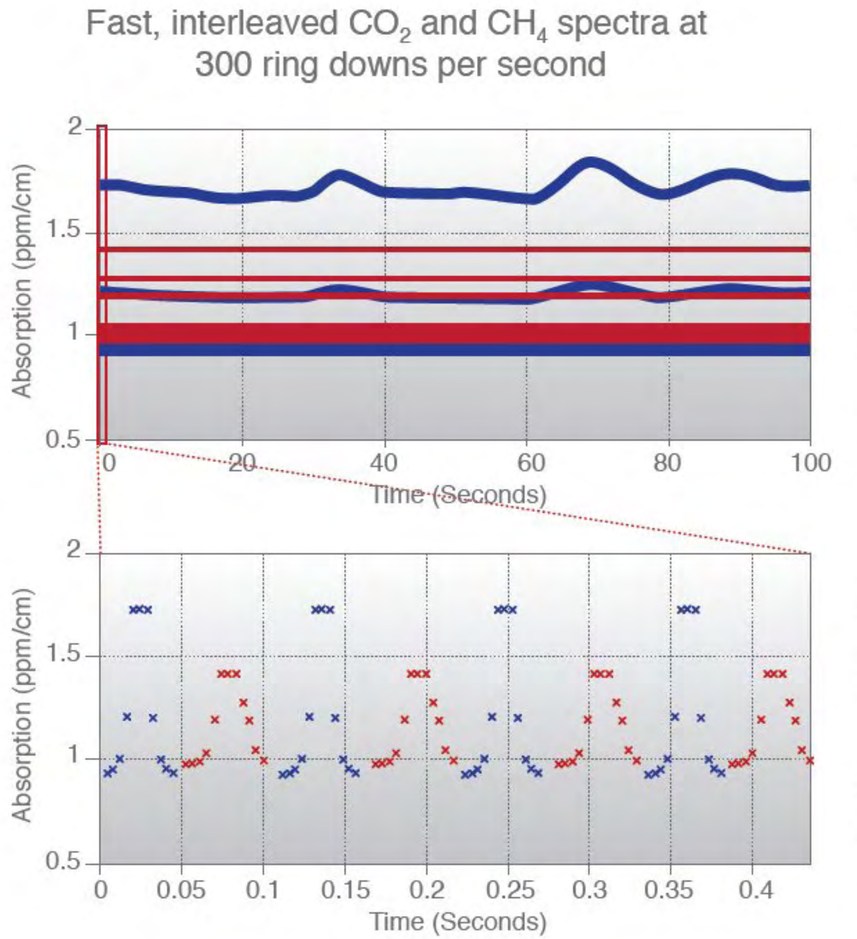
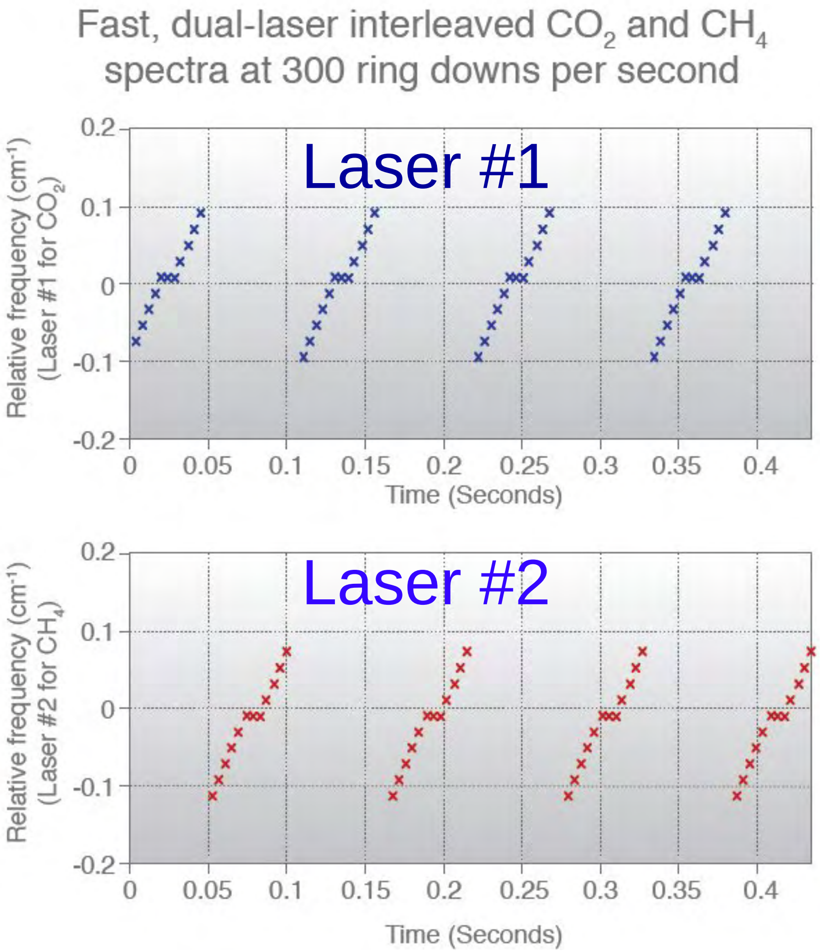
How multiple gases are measured simultaneously in the 2-laser Picarro flux analyzer

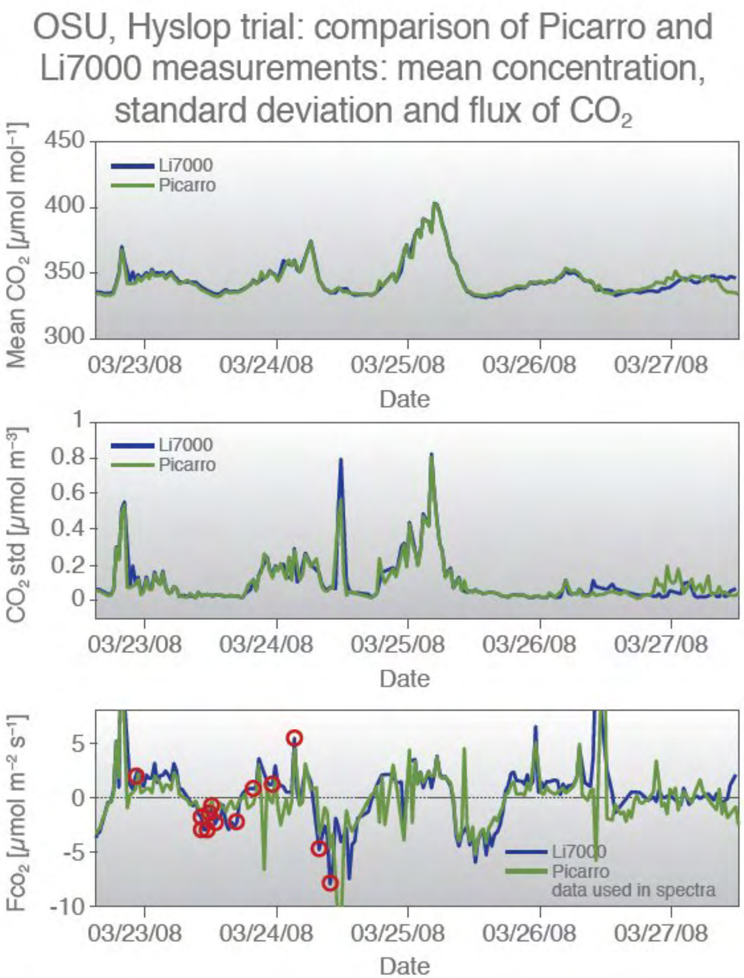


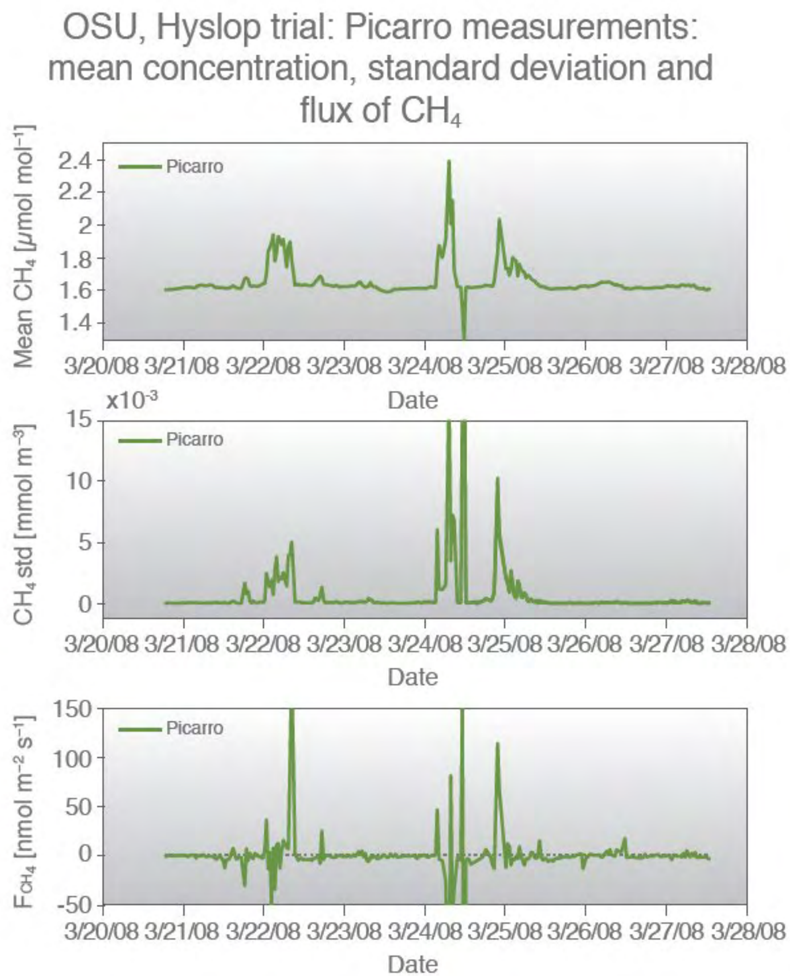


Interleaved tuning of dual-laser system over CO2 and CH4 spectral lines used to measure concentration. Inset shows Individual ring down measurements taken at specific locations along each peak, actively targeted by wavelength monitor control loop.

Frequency of each laser as a function of time as each is tuned across the spectral lines at left. Rapid switching between lasers allows high-speed measurements while maintaining high measurement precision.

Time series of Picarro and LiCOR flux data

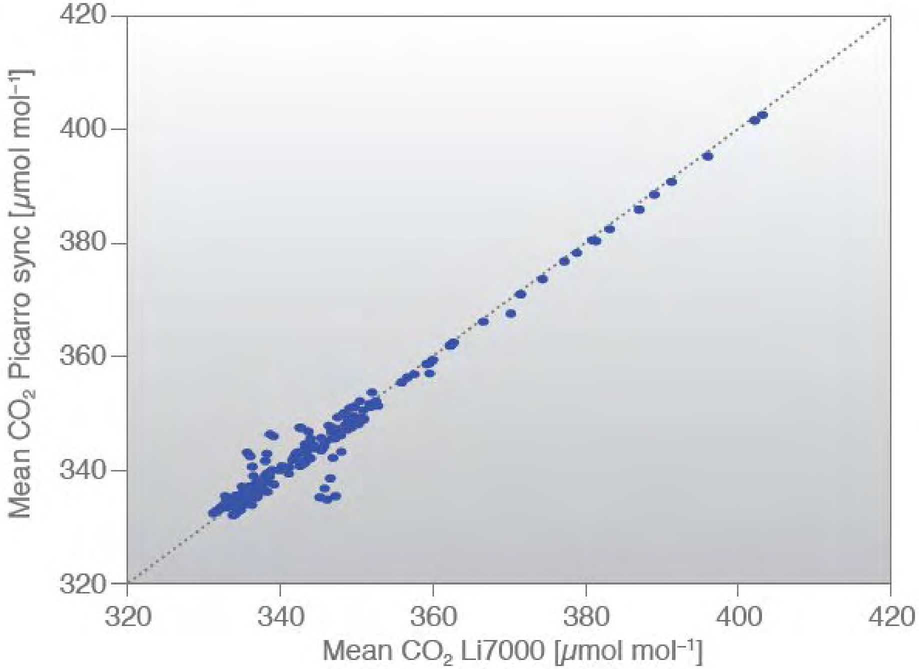




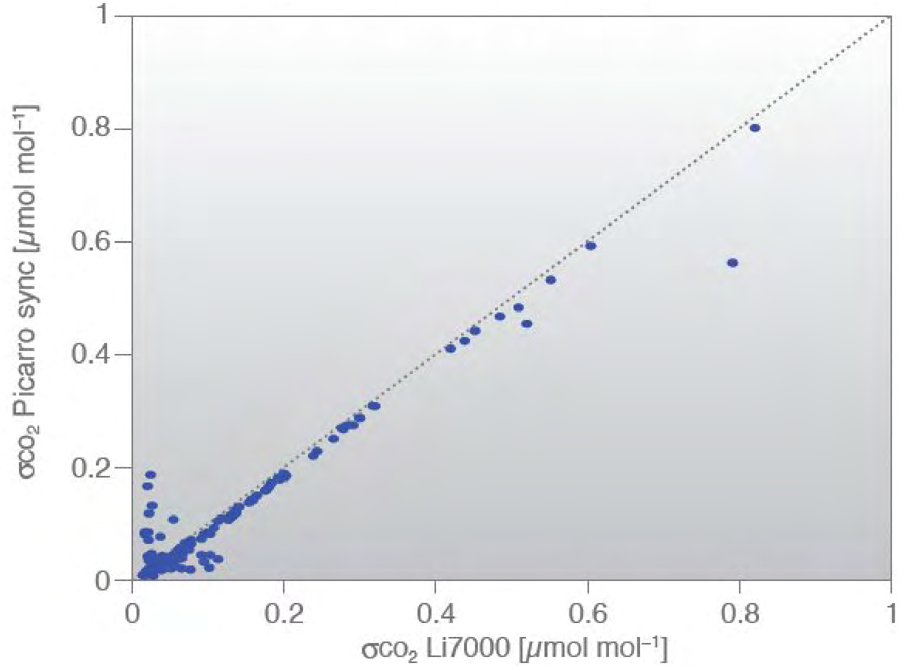
Time series plots of selected statistics and vertical fluxes for both closed-path analyzers. Circles in the bottom panel indicate data used in the computation of power- and cospectra (later slide).

Comparison of Picarro with LiCOR 7000

OSU, Hyslop trial: concentration time series data, Picarro vs. LiCOR7000. N=183



OSU, Hyslop trial: concentration standard deviation time series data, Picarro vs. LiCOR7000. N=183



Scatter plot of data shown as previous time series plot. The dotted lines indicate unity.

Very good agreement with LiCOR for CO_2

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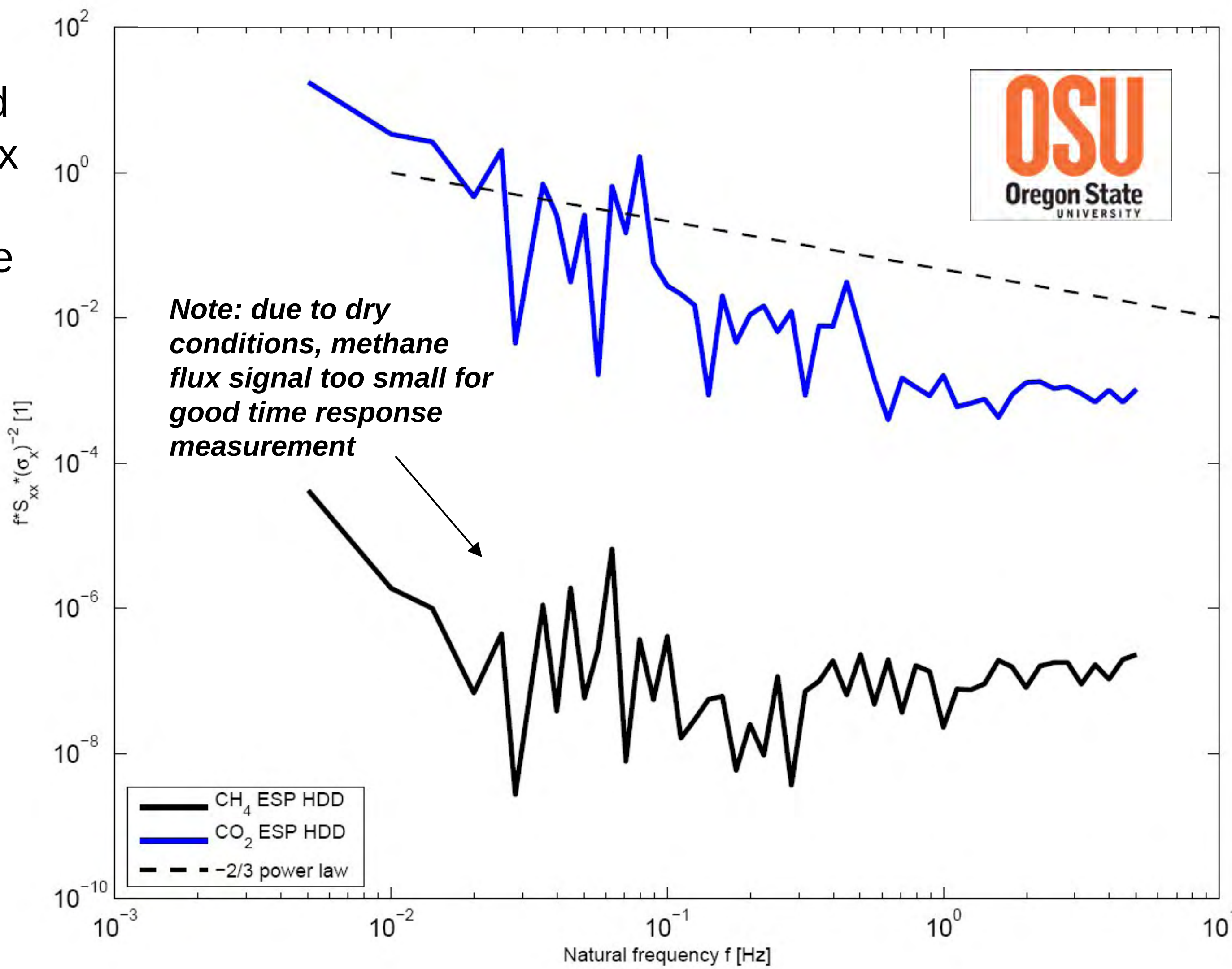
OSU Oregon State UNIVERSITY

Flux analyzer performance analysis

OSU analysis of field data from Picarro flux analyzer: Powerspectra of time series sampled at 10Hz

Measured instrument precision at 10Hz:
- 230 ppbv CO_2
- 1.2 ppbv CH_4

Analysis courtesy Dr. Christoph Thomas, OSU



GHG measurements over differing spatial scales

Quantifying GHG sources/sinks for accountability and regulation: point sources and regional/national sources need to be measurable with the same network