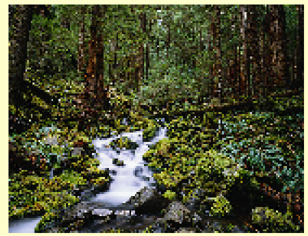
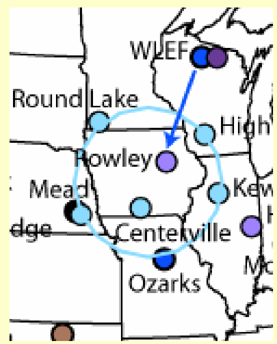
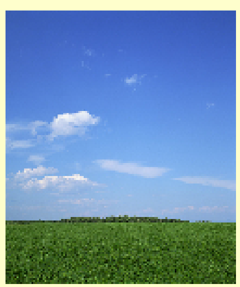
Field Testing and Error Analysis of Cavity Ringdown Spectroscopy Instruments Measuring CO2

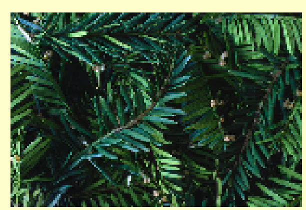
Scott J. Richardson, Natasha L. Miles, Kenneth J. Davis, and Eric. R. Crosson



RING 2







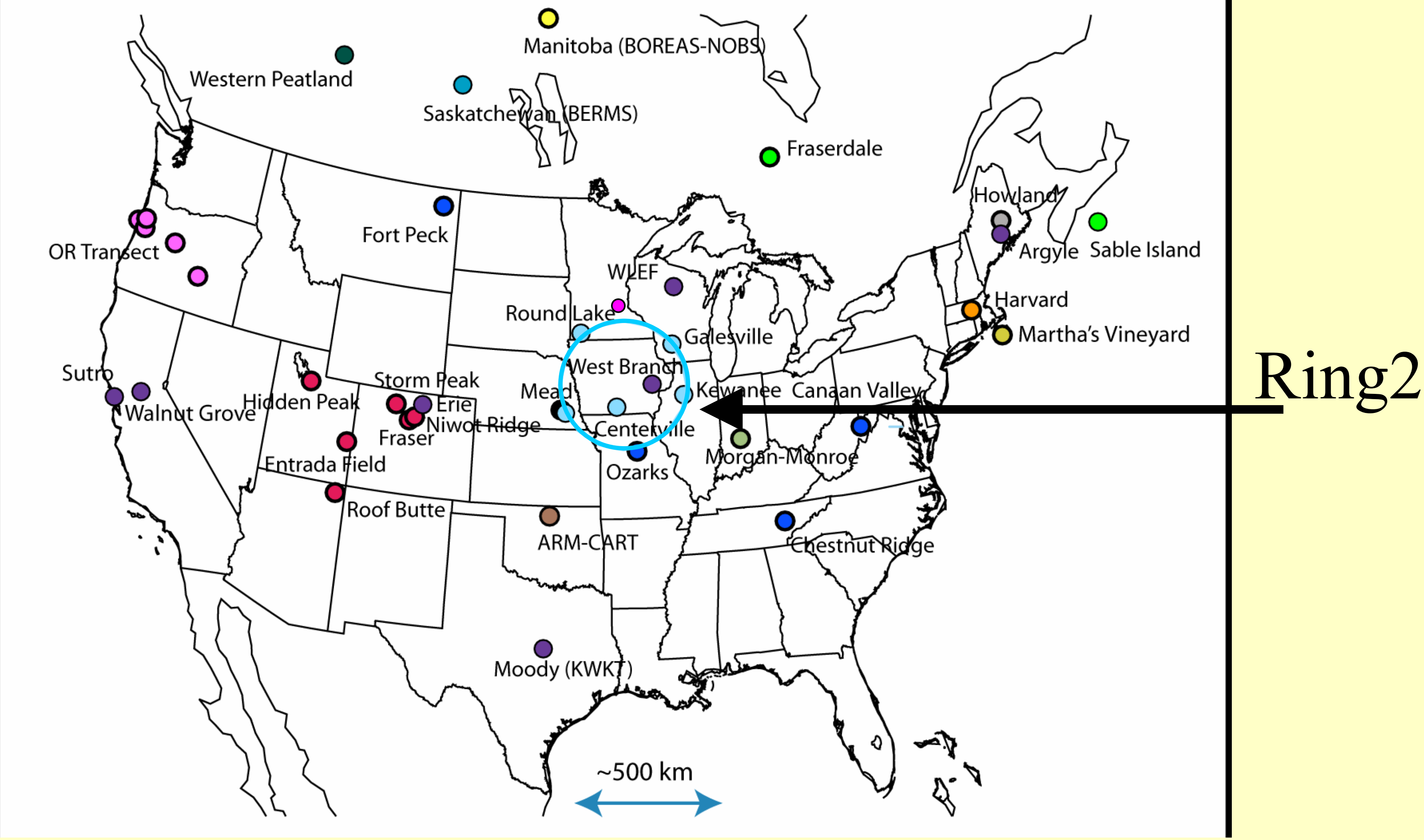
PENNSTATE

ring2.psu.edu

Field Testing of CRDS Systems

- Five CRDS systems deployed as part of the North American Carbon Program (NACP) Mid Continent Intensive (MCI)
- Termed “Ring2”
  - “Ring” of towers around the state of Iowa

Continuous, Well-Calibrated CO_2 Measurements in North America



Field Testing of CRDS Systems

- Five CRDS systems deployed as part of the North American Carbon Program (NACP) Mid Continent Intensive (MCI)
- Termed “Ring2”
  - “Ring” of towers around the state of Iowa
- Systems tested and calibrated at PSU facility
- Two NOAA tanks deployed with each system
  - Sampled every 22 hours
  - Used to account for system drift
  - Examine long-term stability of each system

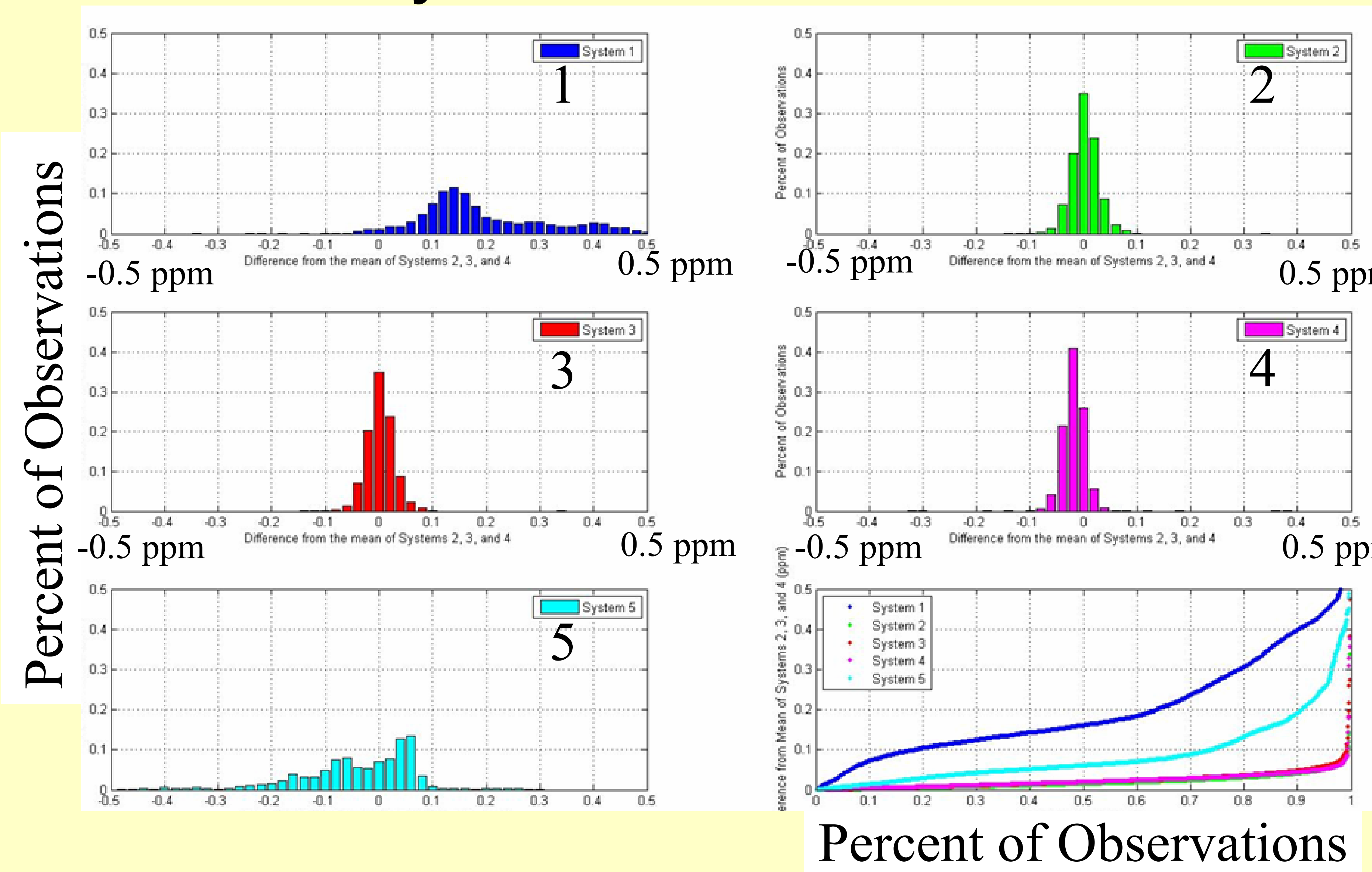
Field Testing of CRDS Systems

- Early CADS (CO_2) systems used in Ring2
  - SN 01 through 10
- Measure H_2O using an HDO line instead of an H20 line
  - Will be important later in talk
  - Current systems measure H_2O line

Lab Testing of CRDS Systems

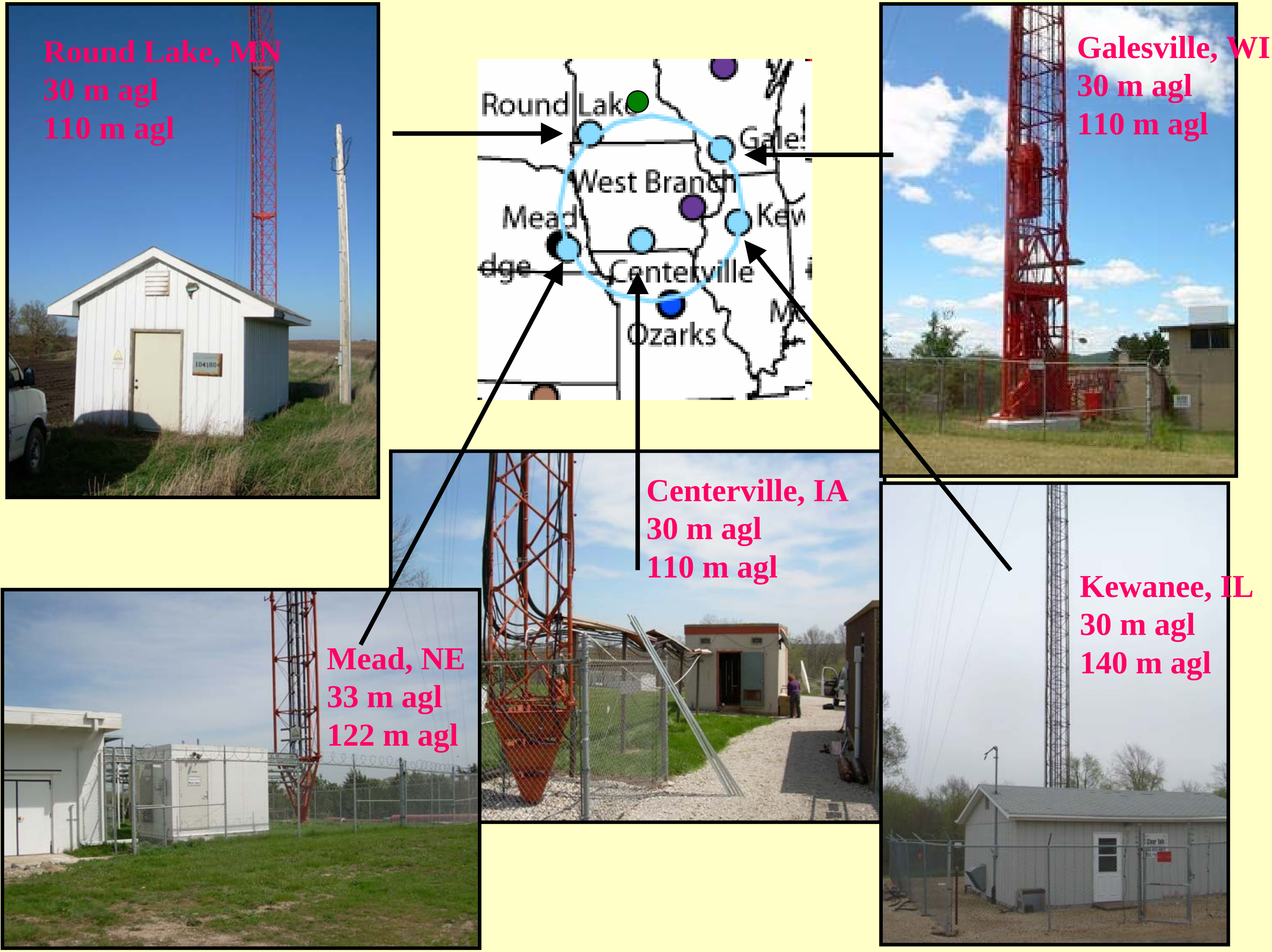
- CRDS systems calibrated using 4 NOAA calibrated CO_2 standards
  - April 2007
- 3 day lab test
  - No recalibration during 3 days
  - All 5 systems sample from 4 liter buffer volume
  - Air sample NOT dried

Difference from the mean using systems 2, 3 and 4

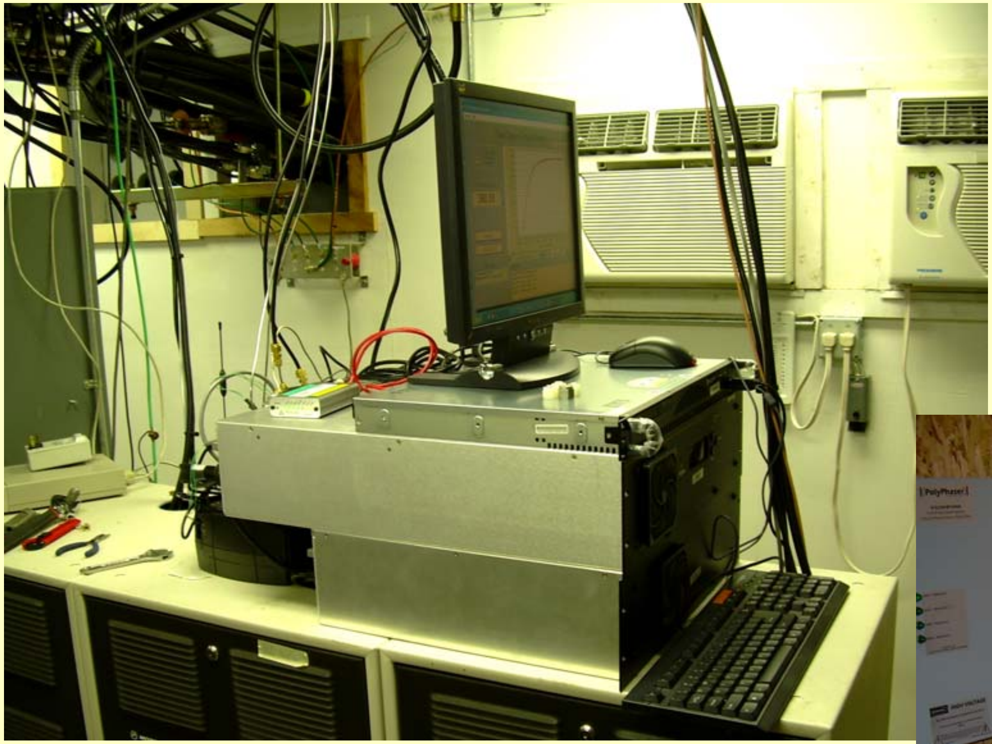


Deployment Method

- Systems deployed inside buildings
- Sample 2 levels
  - 110 to 140 m agl, 45 min of every hour
  - 30 m agl, 15 min every hour
- Real-time communications via cell phone data modems
  - Remote login for troubleshooting
- Daily data files automatically emailed
- Quick looks posted to web page


Round Lake, MN
30 m agl
110 m agl
Galesville, WI
30 m agl
110 m agl
Centerville, IA
30 m agl
110 m agl
Kewanee, IL
30 m agl
140 m agl
Mead, NE
33 m agl
122 m agl
West Branch
Mead
Centerville
Ozarks

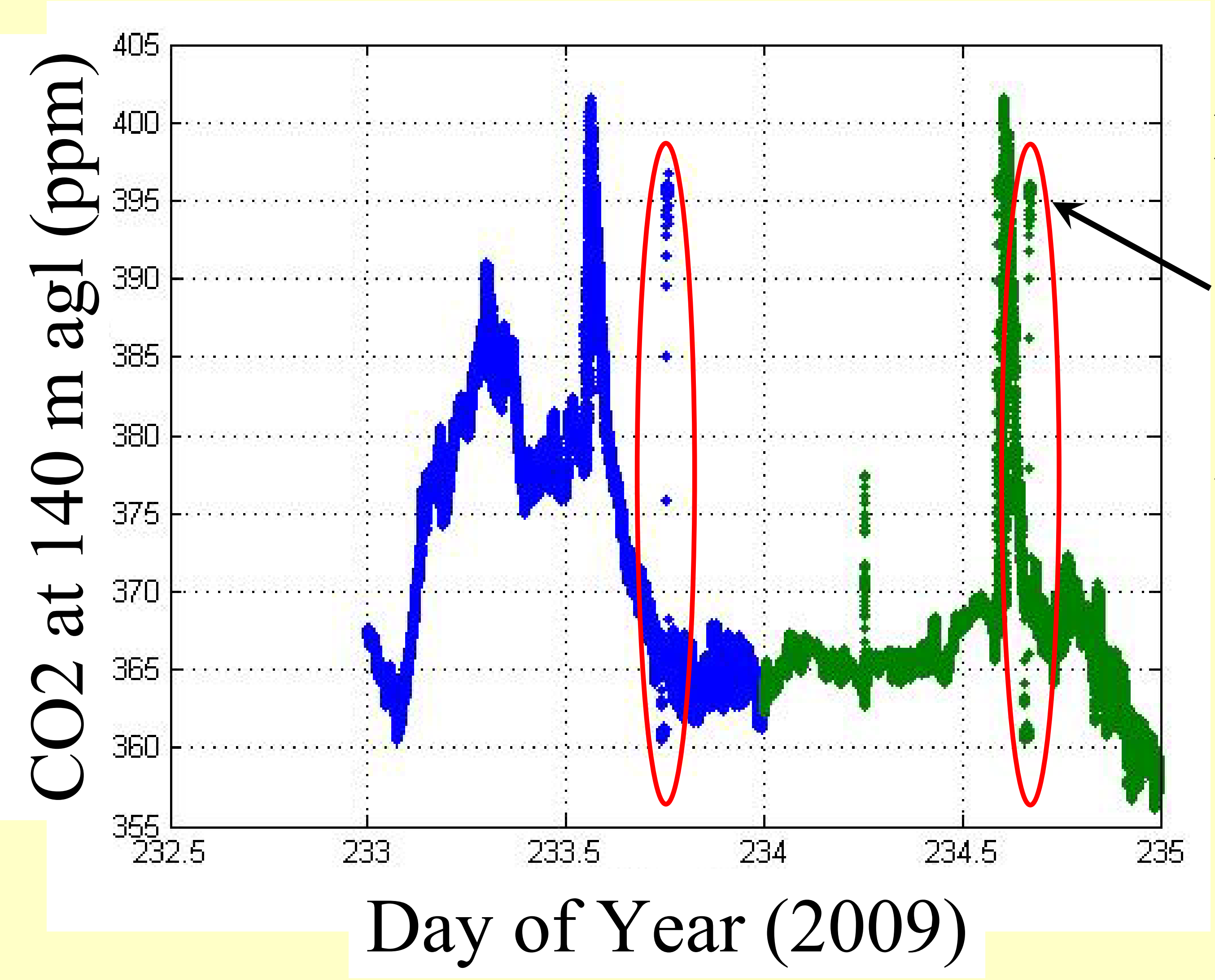
Typical Deployments



Kewanee, IL

Round Lake, MN

Sample 2-Days of Data

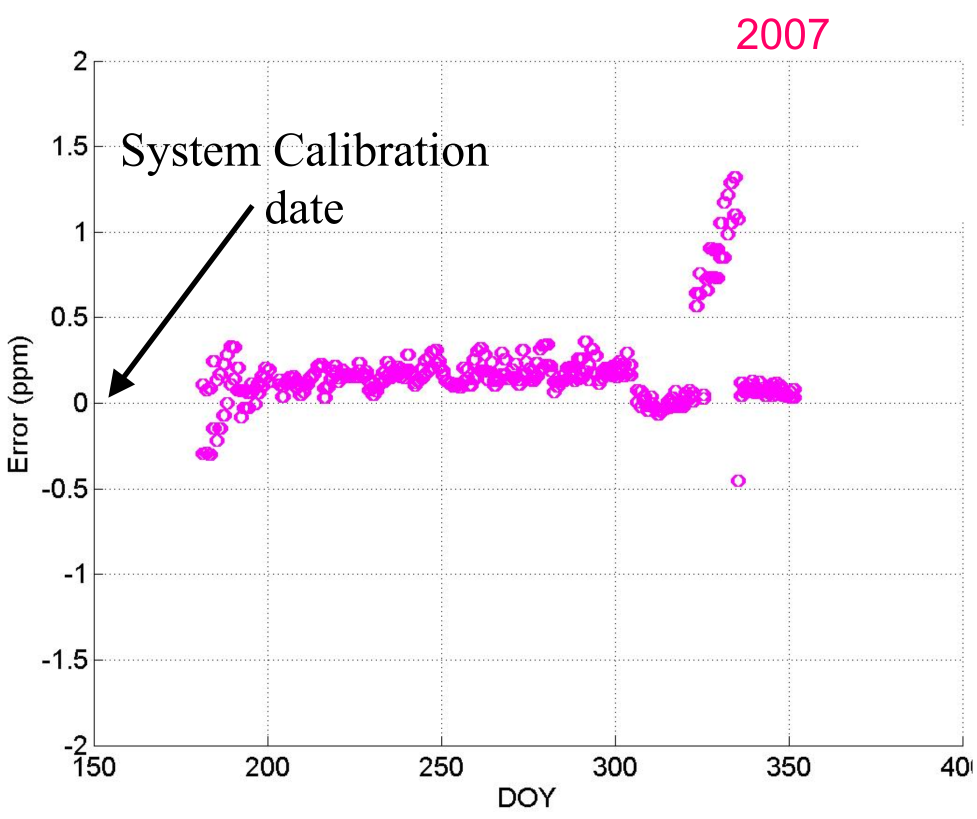


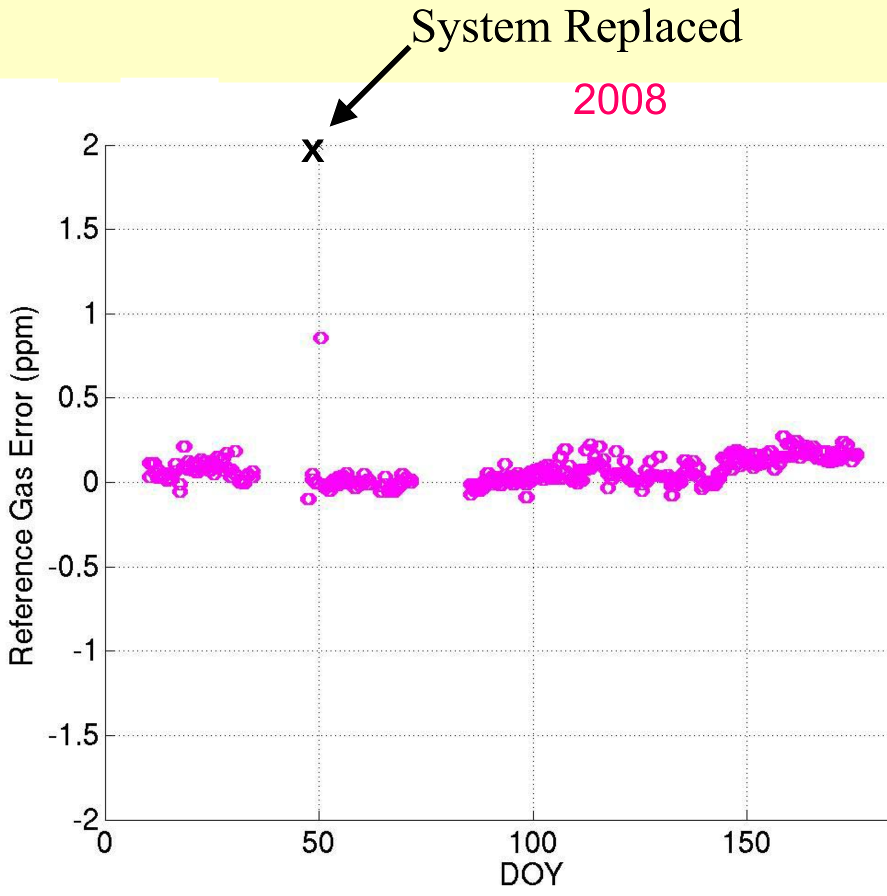
Raw ~1 Hz data

Calibration Gas sampled every 22 hours

Reference gas error using April 2007 calibration

Galesville (CADS08, CADS10)

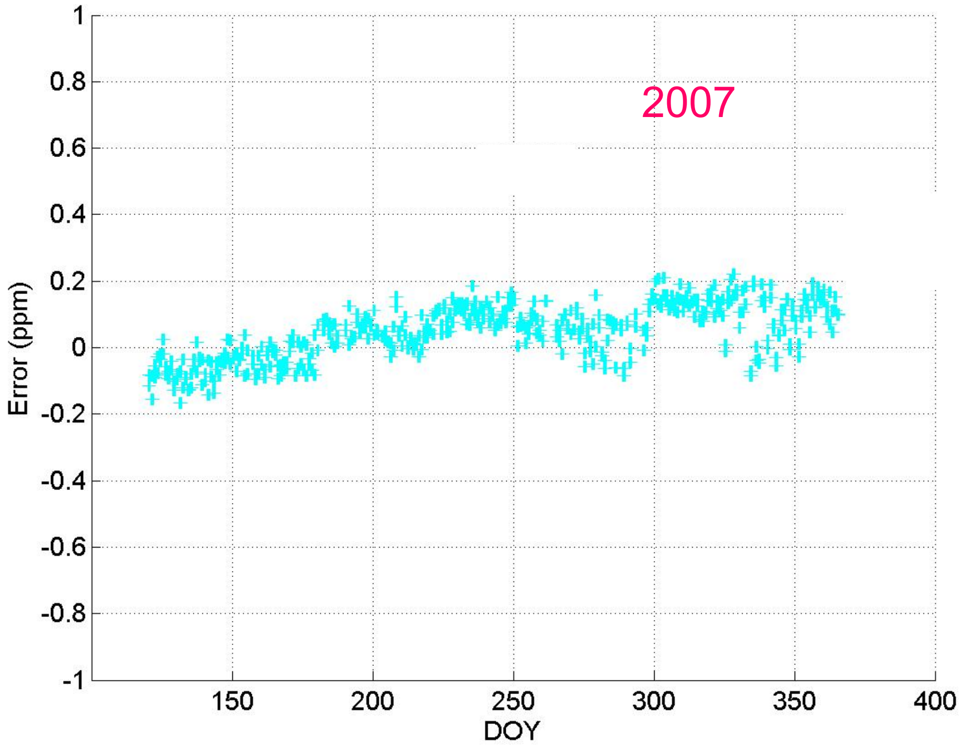


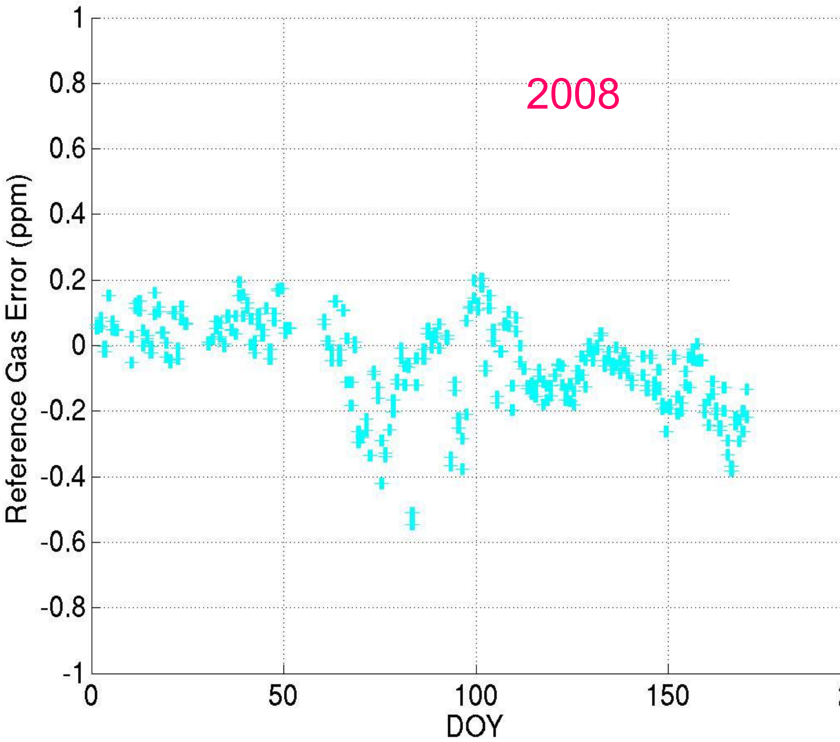


- Daily difference between 2 reference tanks and known values
- Result is applied to daily field calibration

Reference gas error using April 2007 calibration

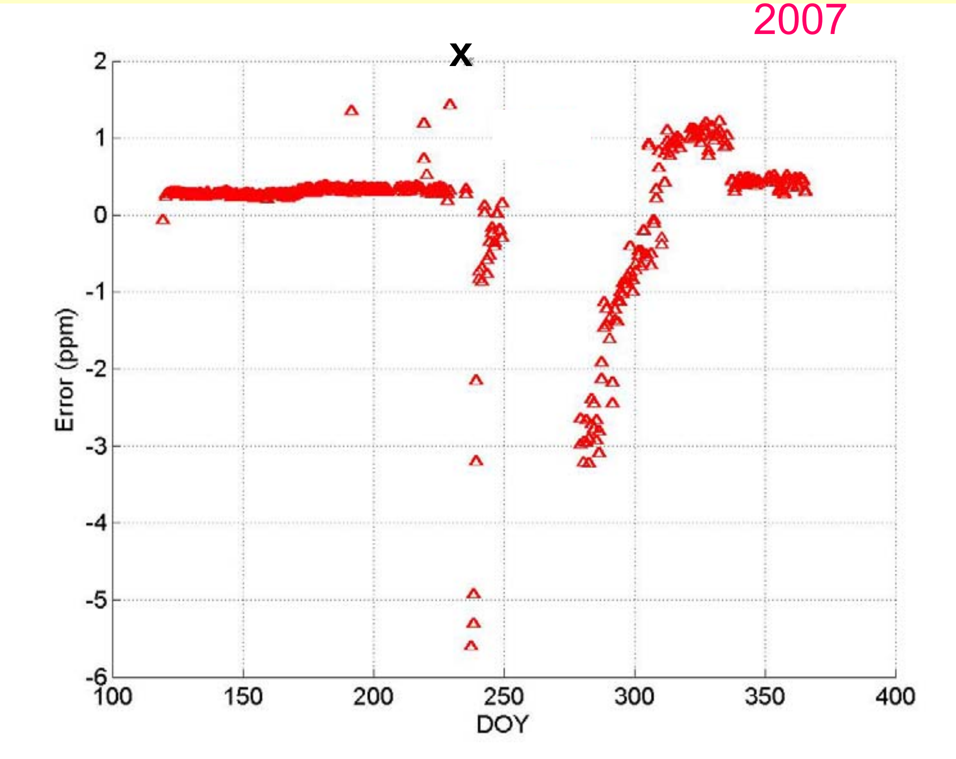
Centerville (CADS06)

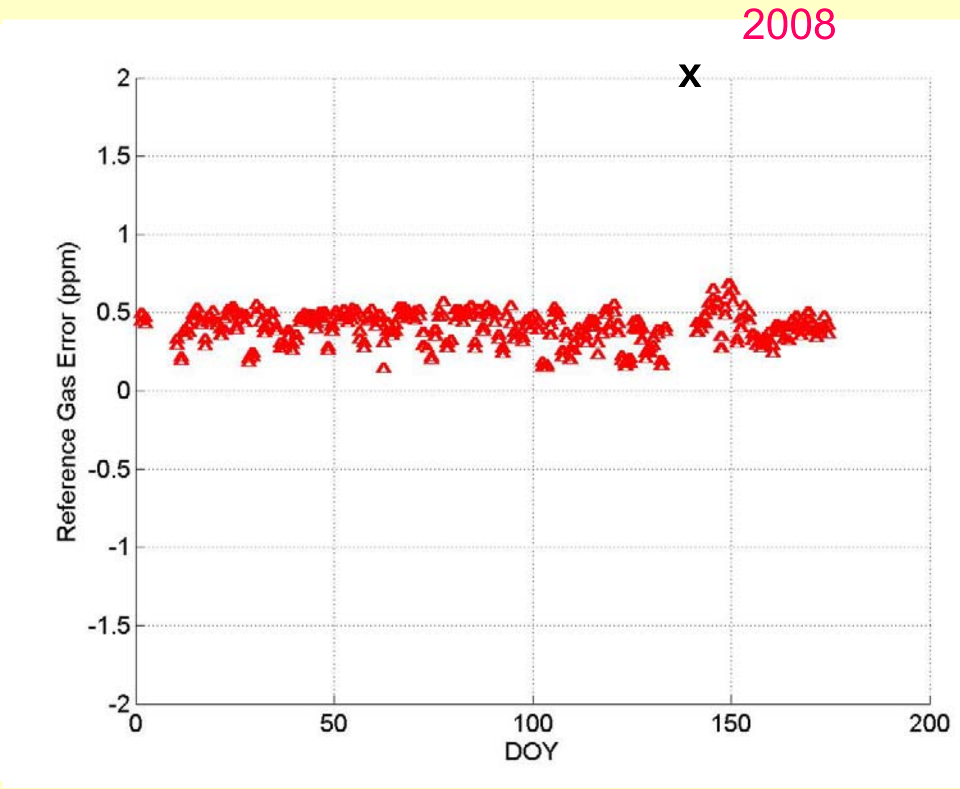




Reference gas error using April 2007 calibration

Kewanee (CADS05)

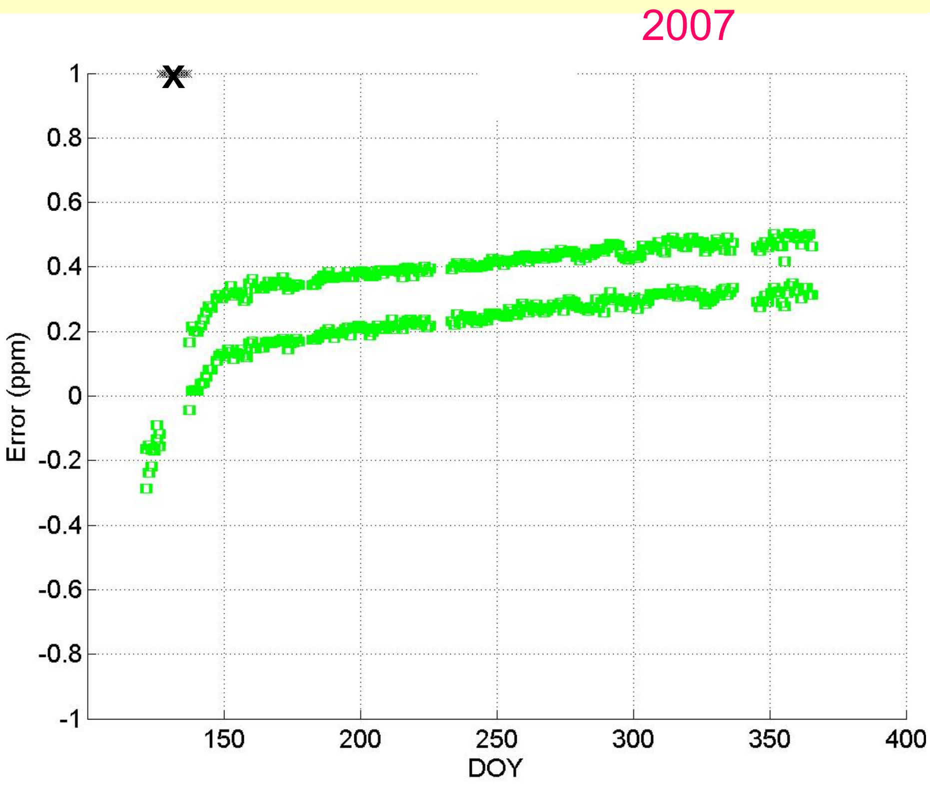


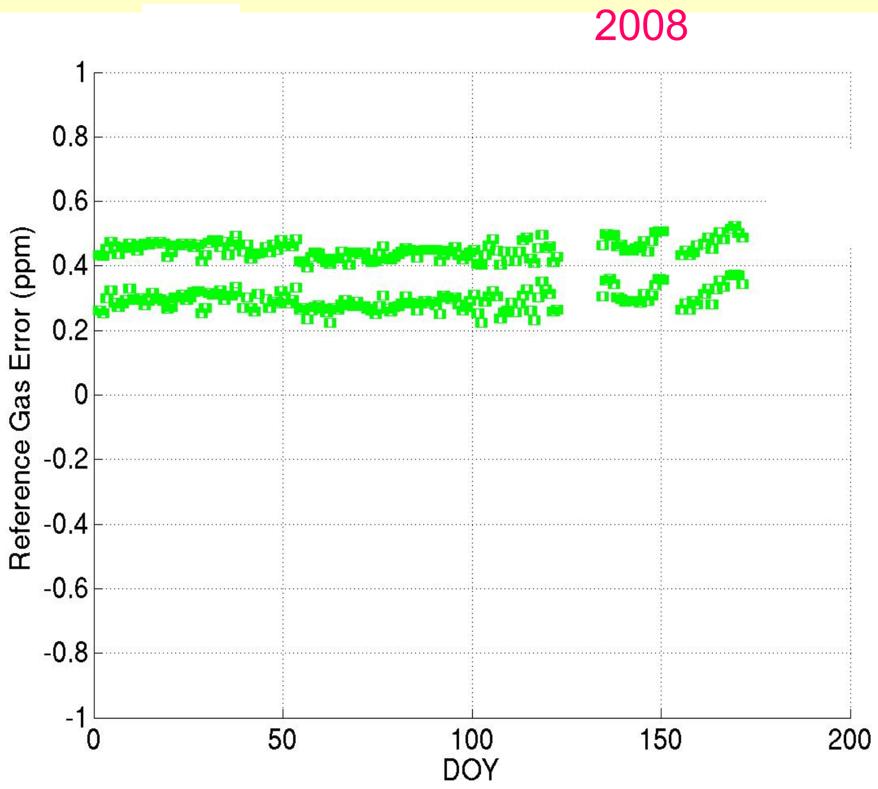


- Water problems

Reference gas error using April 2007 calibration

Mead (CADS01, CADS07)

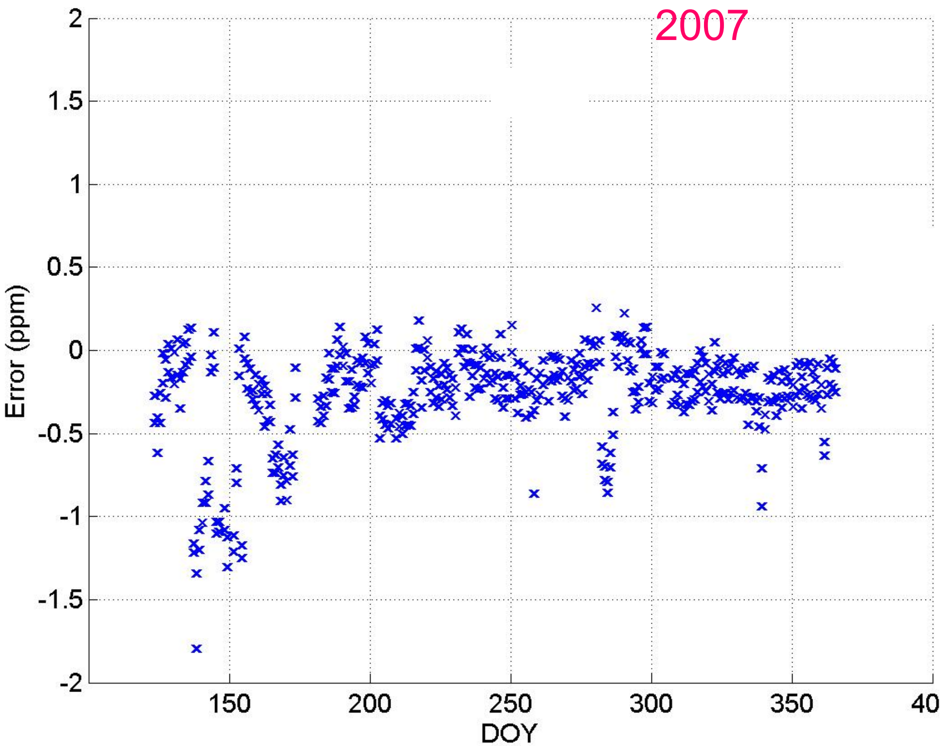


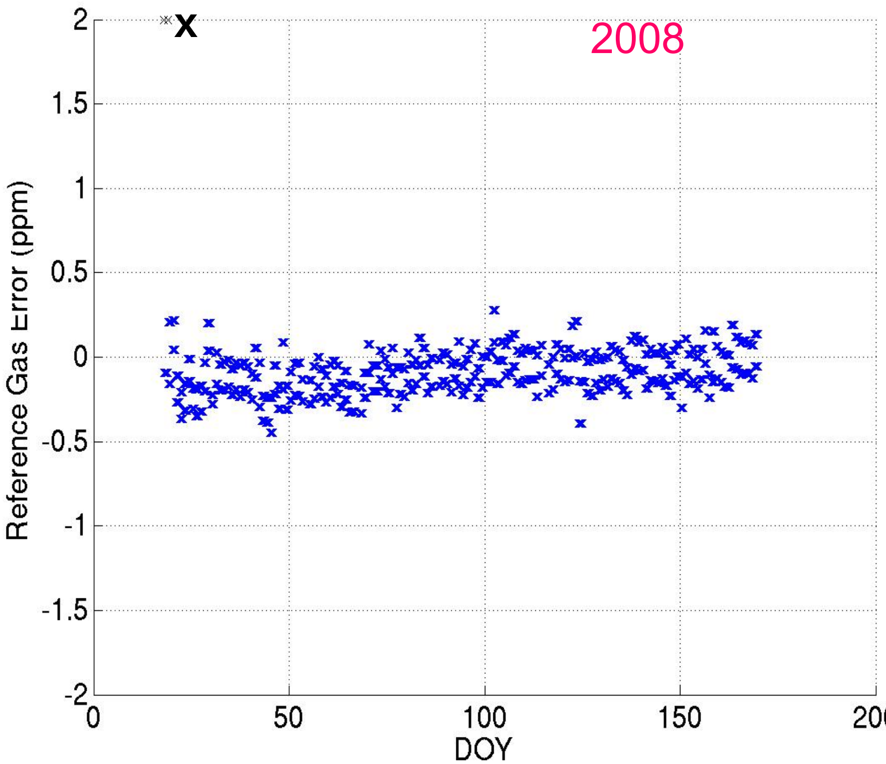


May 15

Reference gas error using April 2007 calibration

Round Lake (CADS03, CADS02, CADS09)





July 1 Oct 31

Round-Robin Tests

- 4 NOAA-calibrated tanks brought to each site
  - February 2008
  - April 2009
- Average errors for each site and each tank are less than 0.15 ppm
- Does not test water vapor correction

Round robin test, Feb 2008

Site	Tank 1 error (ppm)	Tank 2 error (ppm)	Tank 3 error (ppm)	Tank 4 error (ppm)	Mean
Kewanee	-0.097	-0.115	-0.049	-0.279	-0.135
Centerville	-0.155***	0.020	-0.158 ***	Unstable	-0.098
Mead	-0.071	-0.074	0.093	-0.093	-0.036
Round Lake	-0.047	Not tested	-0.210	Not tested	-0.129
Galesville	-0.174	-0.162	-0.018	-0.190 ***	-0.093
Mean	-0.109	-0.083	-0.068	-0.13	

*** Only 1 cal cycle

Blue: > 0.1 ppm

Red: > 0.2 ppm

Error Estimates

Contributions to analytical uncertainty	**PSU CRDS**	**NOAA-ESRL NDIR**
Calibration scale uncertainty	0.1 ppm	0.07 ppm
Standard equilibration uncertainty	0.05 ppm	0.05 ppm
Curve fitting errors	0.05 ppm	0.05 ppm
CO2 isotopic effects	0.05 ppm	
Errors due to water vapor effects		0.05 ppm
Analyzer drift uncertainty		0.1 ppm
Cavity pressure control error		
Cavity temperature control error		
Error due to HDO/H2O isotopic ratio		-
Total analytical uncertainty with HDO		**0.1**
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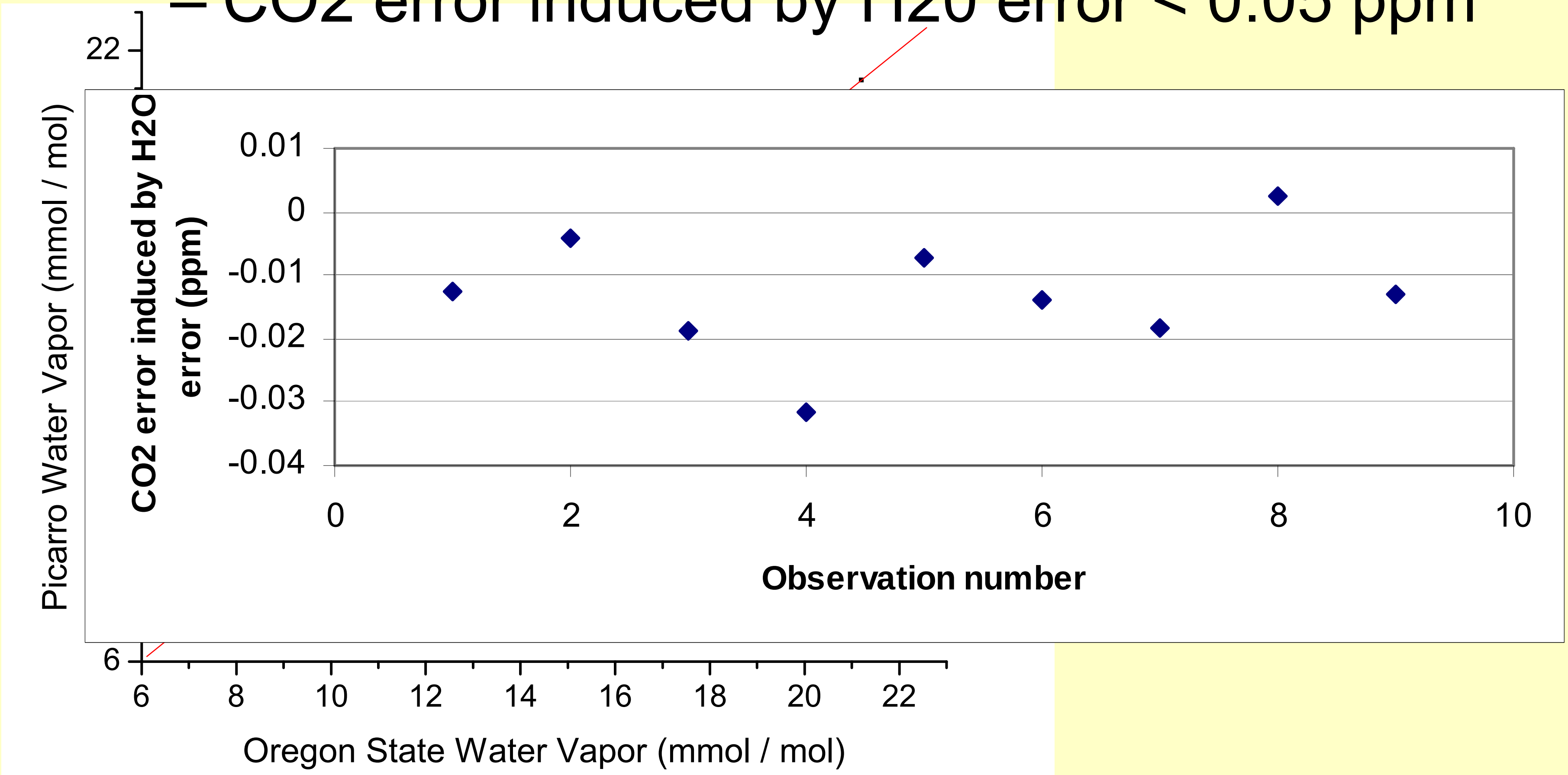
Accuracy of H20 Measurement

- NOAA-calibrated system tested at Oregon State
  - CO2 error induced by H20 error < 0.05 ppm



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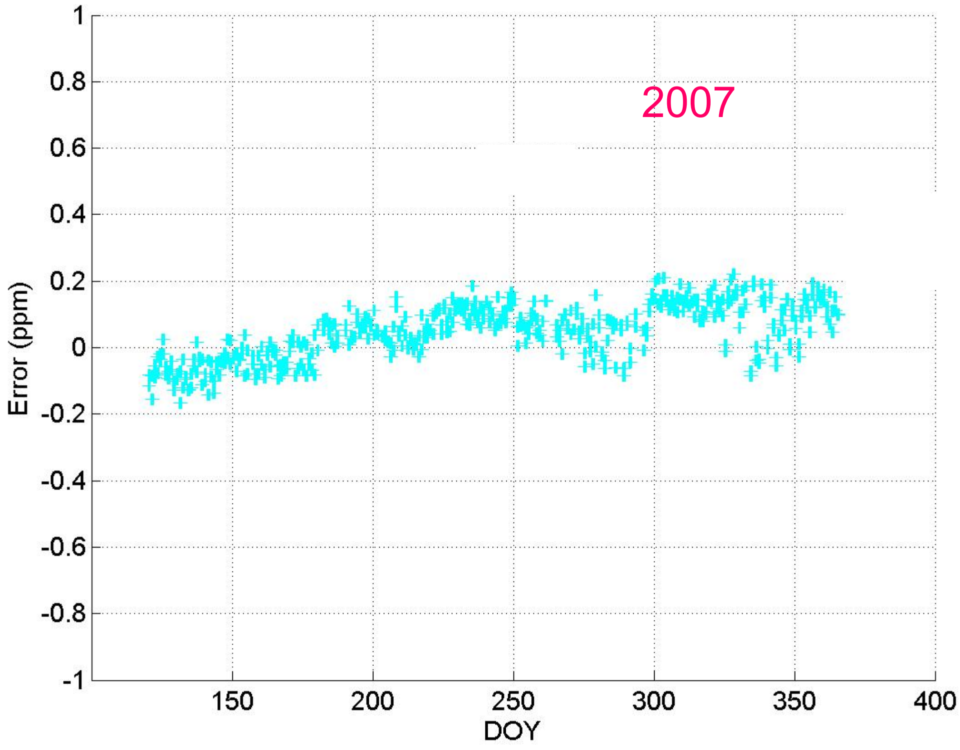
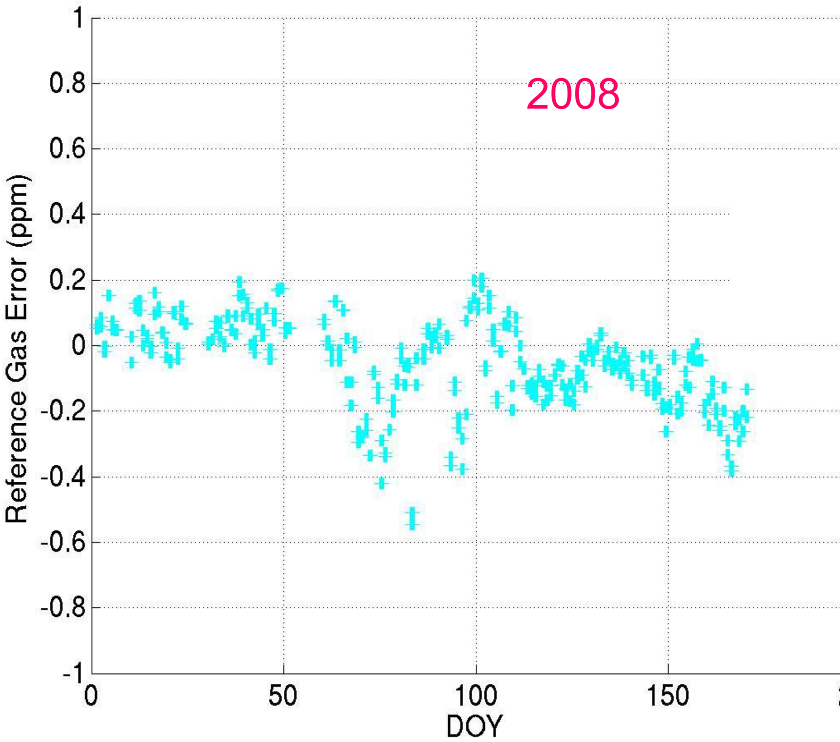
Reference gas error using April 2007 calibration

Centerville (CADS06)

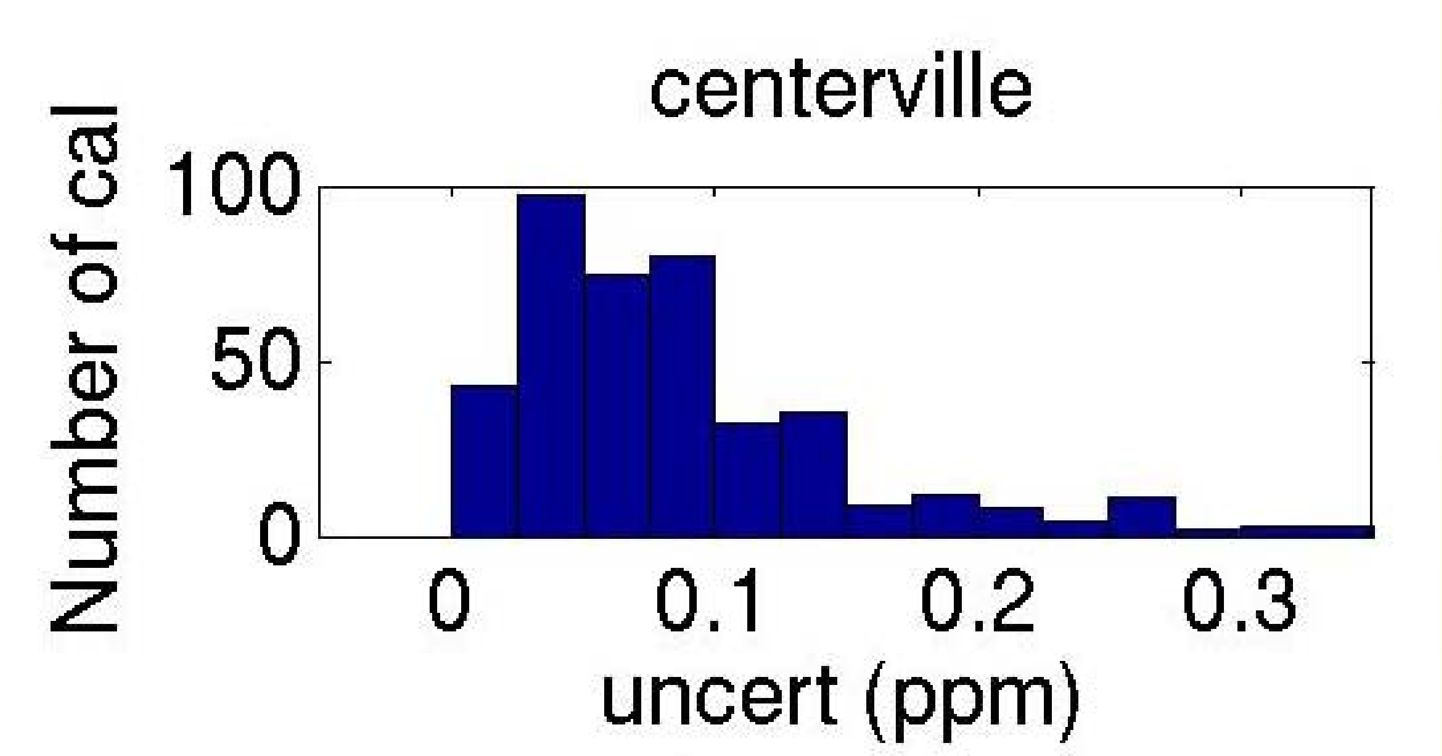




- Daily difference between 2 reference tanks and known values
- Result is applied to daily field calibration
- Difference between daily calibrations gives us info about analyzer drift error

Analyzer Drift Uncertainty

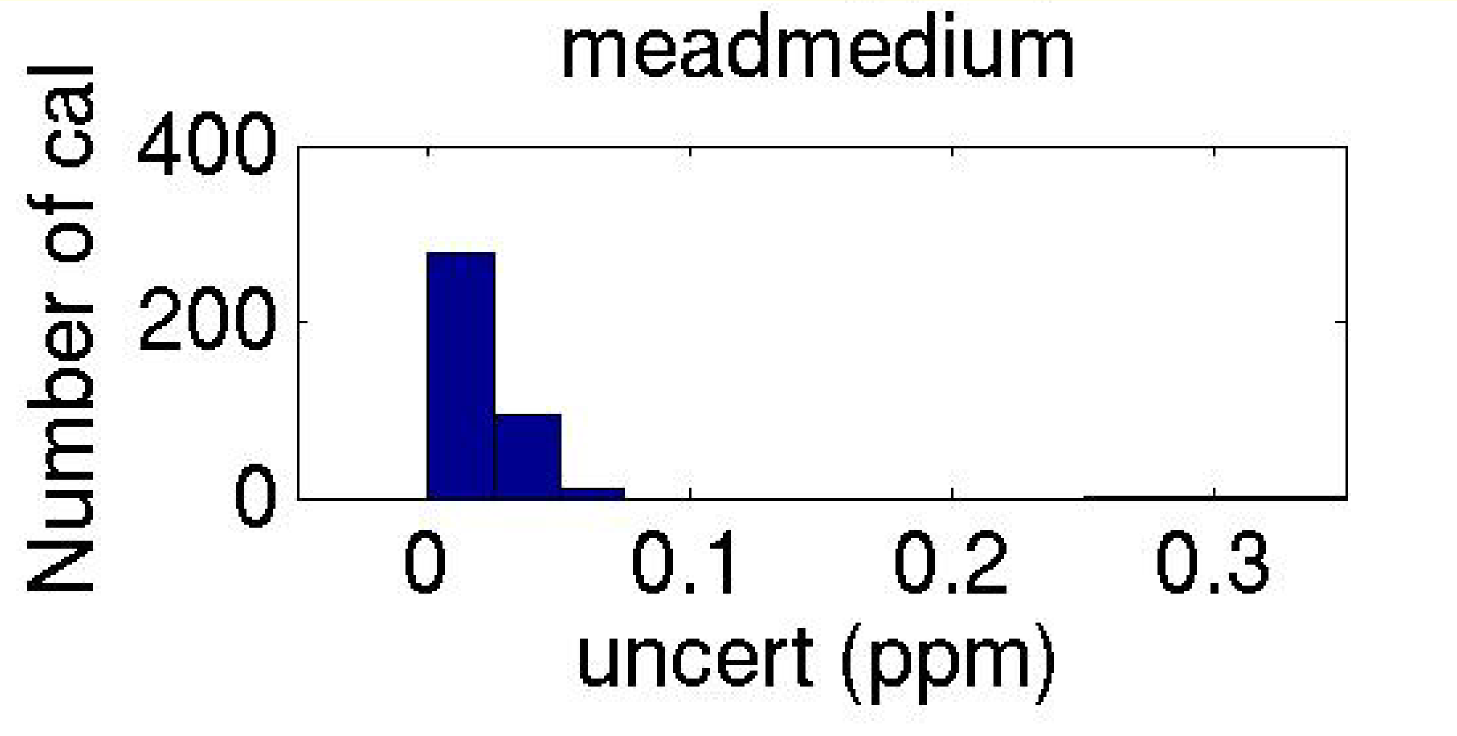
May 2007 - July 2008



- Drift uncertainty
  - Majority of points < 0.15 ppm uncertainty using daily calibrations
  - Improved system performance with software upgrades

Analyzer Drift Uncertainty

May 2007 - July 2008



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Intrinsic strength of CRDS technology is that measurements are absolute within the limits of the temperature and pressure control of the gas.

- Cavity TEMP controlled to << 20 mK
  - Error of 0.004 ppm (1-sigma)
- Cavity PRES controlled to < 0.03 Torr
  - Error of 0.006 ppm (1-sigma)

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Error due to HDO/H2O isotopic ratio	**???**	-
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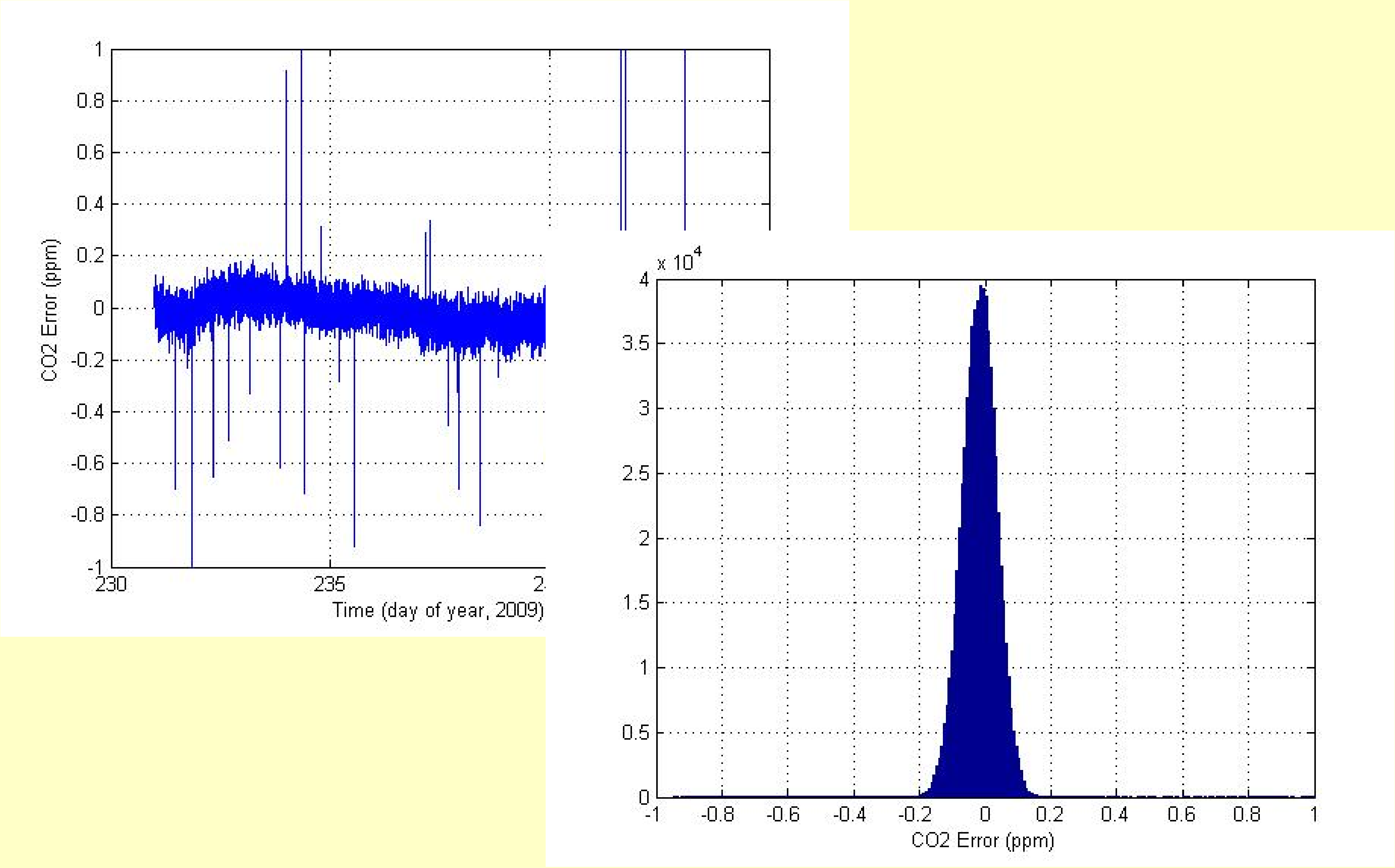
HDO Effects

- Earliest CRDS measured HDO line instead of H_2O line
- Atmospheric variability of HDO/H_2O isotopic ratio results in an error in the H_2O measurement
- Results in CO_2 error
  - Different from "normal" water vapor error
- 2 CRDS systems now measuring both H_2O and HDO to examine variability and CO_2 error
  - 50 part in 1000 change in HDO/H_2O isotopic ratio = 0.2 ppm CO_2 error

HDO Effects



Error Estimates

<table>
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<tr><td>Error due to HDO/H2O isotopic ratio</td><td>0.25 ppm ***</td><td>-</td></tr>
<tr><td>Total analytical uncertainty with HDO</td><td></td><td>0.1</td></tr>
<tr><td>Total analytical uncertainty without HDO</td><td></td><td>0.1</td></tr>
</table>

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Error due to HDO/H_2O isotopic ratio	0.25 ppm ***	-
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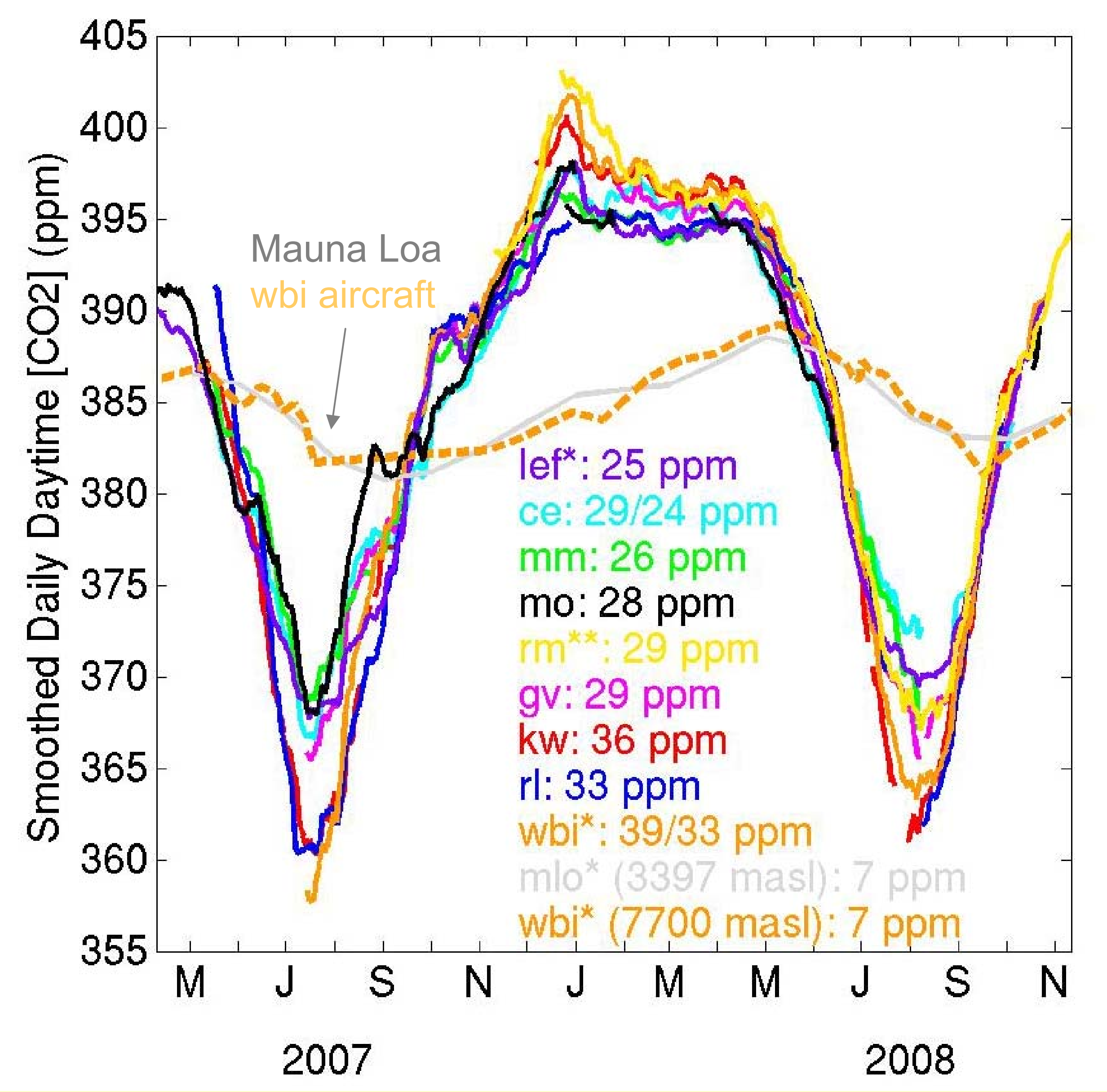
Analyzer drift uncertainty	0.1 ppm	
Cavity pressure control error	0.006 ppm	0.1 ppm
Cavity temperature control error	0.004 ppm	
Error due to HDO/H2O isotopic ratio	0.25 ppm ***	-
Total analytical uncertainty with HDO	**0.3**	**0.1**
Total analytical uncertainty without HDO	**0.1**	**0.1**

Conclusions

- 5 CRDS systems deployed early 2007
- Will remain in the field until Dec. 2009
- Round-robin tests verified accuracy
- Excellent long-term stability of systems
- Overall system error ~0.3 ppm
  - Post calibrations should decrease error
- CRDS error today ~0.1 ppm

Seasonal cycle



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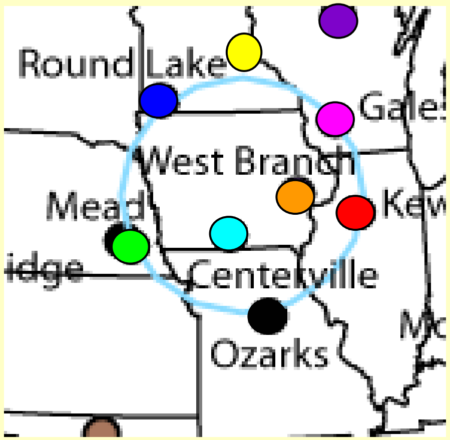
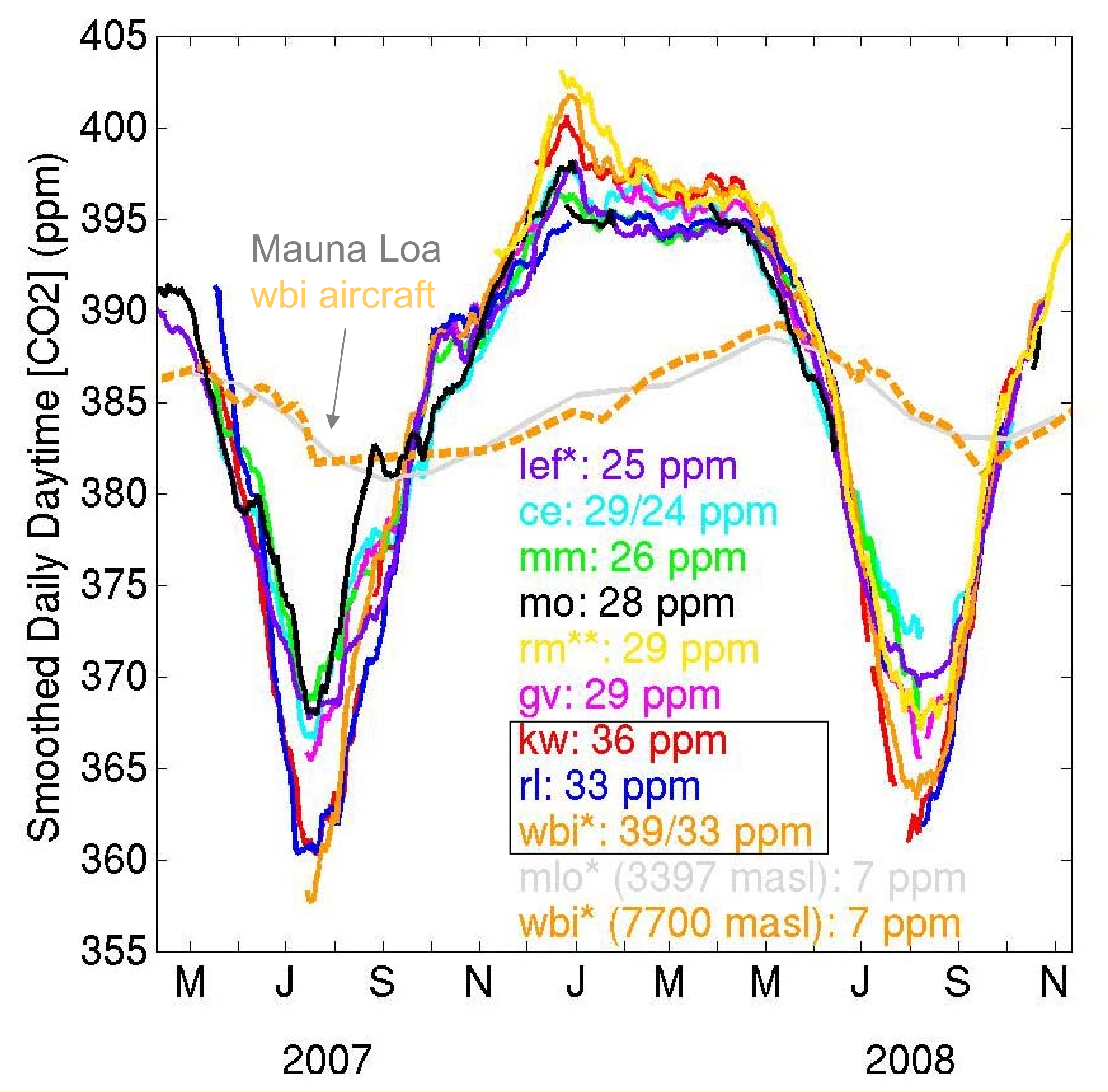
- N. Miles – data analysis and comparison to models
- A. Schuh – MCI overview, model results
- K. Corbin – modeling results



* NOAA (Andrews/Sweeney) ** U of Minn (Griffis)

Seasonal cycle



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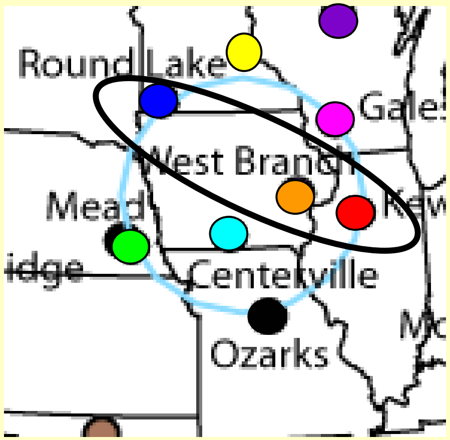

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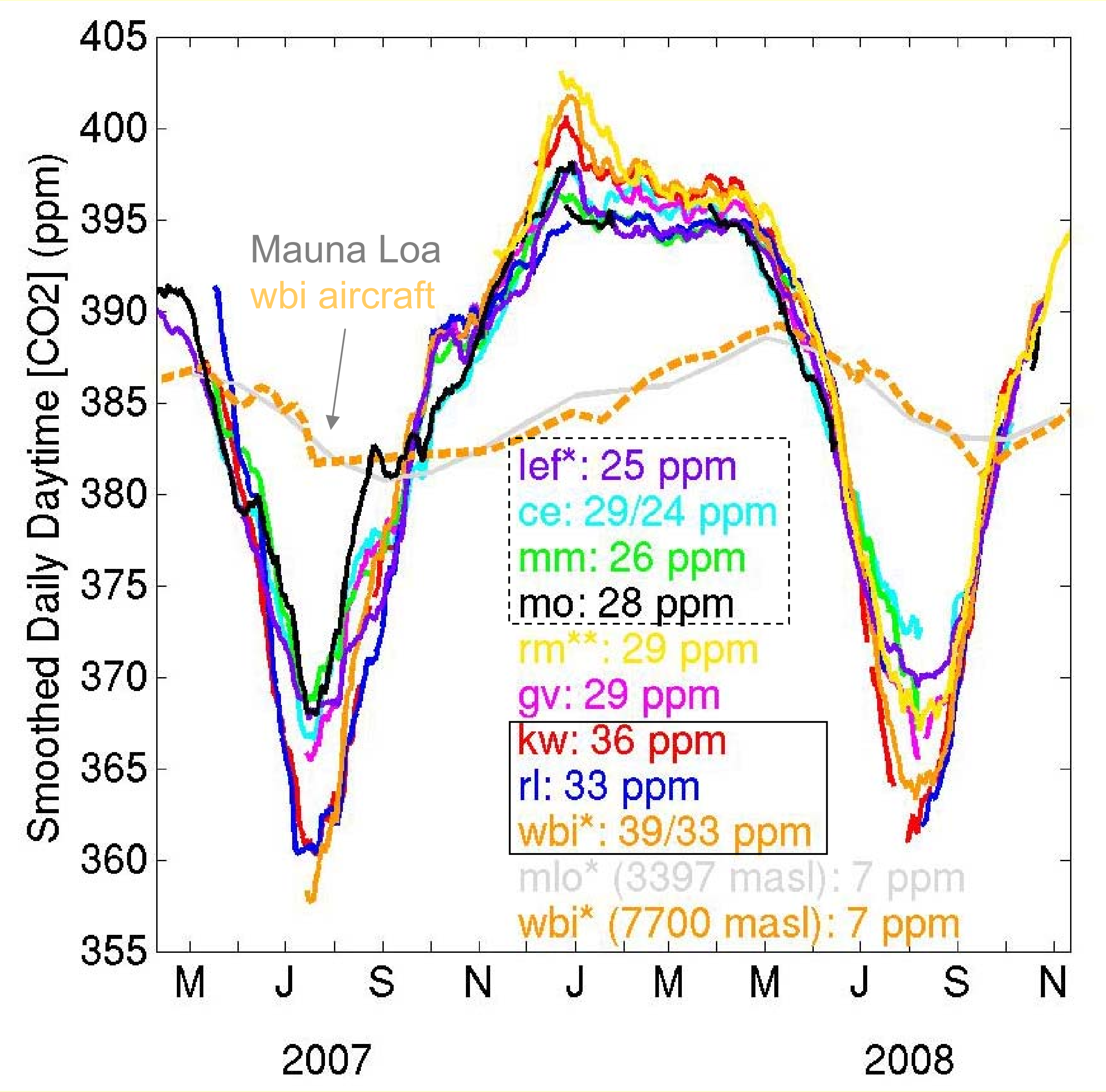

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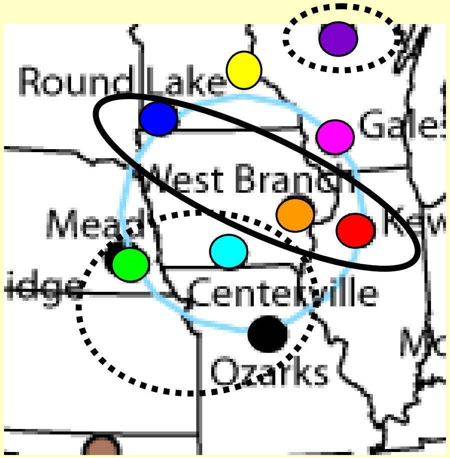

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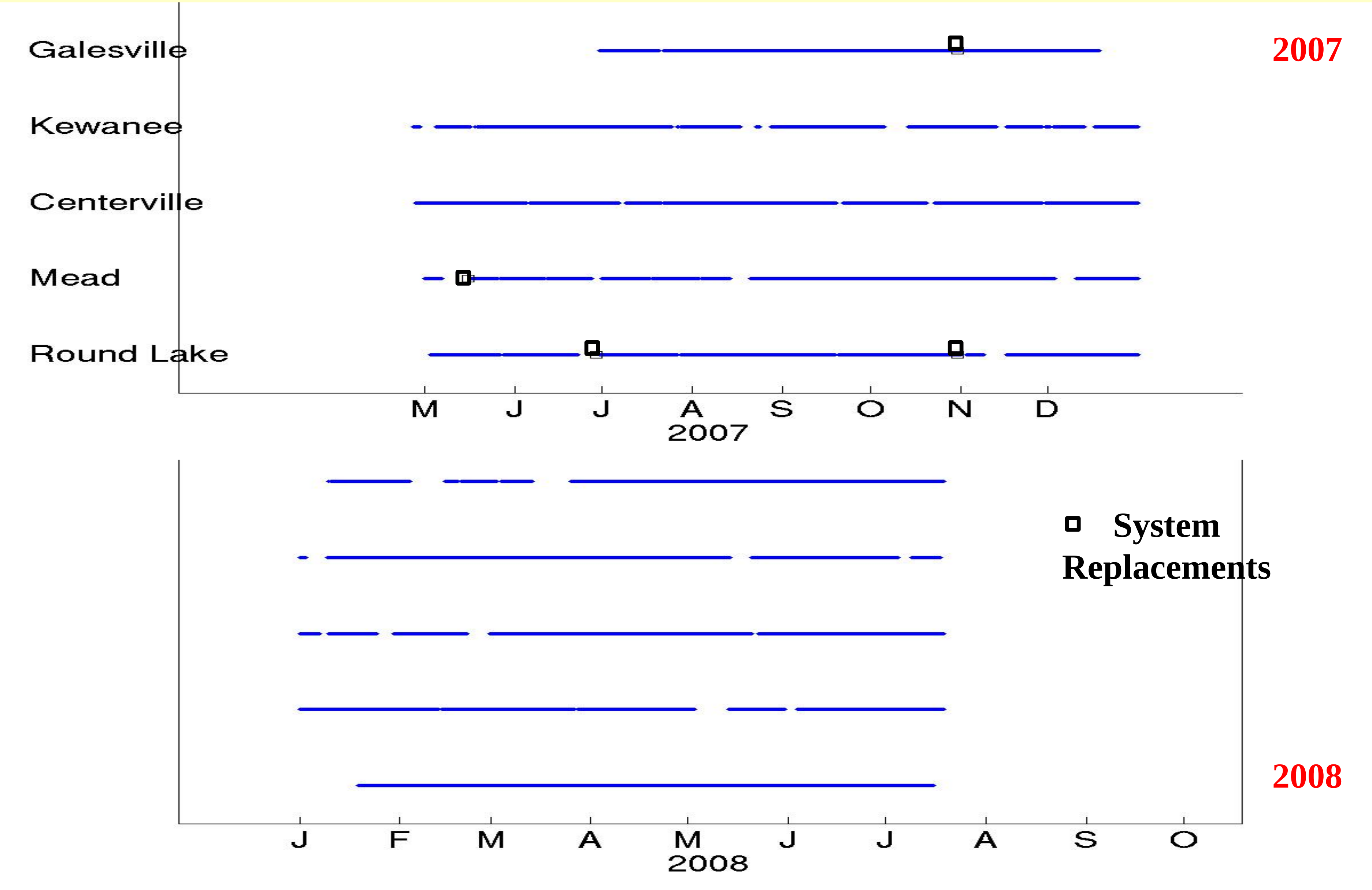
End

Data availability



Summary

- 5 CRDS systems deployed in early 2007
- Satellite measurements to provide much more frequently sampled [CO_2] in the free troposphere
- Ring 2 network designed to over sample the region; large gradients observed within the ring in 2007 and 2008
- Will be used to calculate the regional flux for comparison with bottom-up methods
- Ring 2 slated to be discontinued as of Oct 2008, but could be used to evaluate satellite [CO_2] results

How do Ring 2 analytical uncertainties compare?

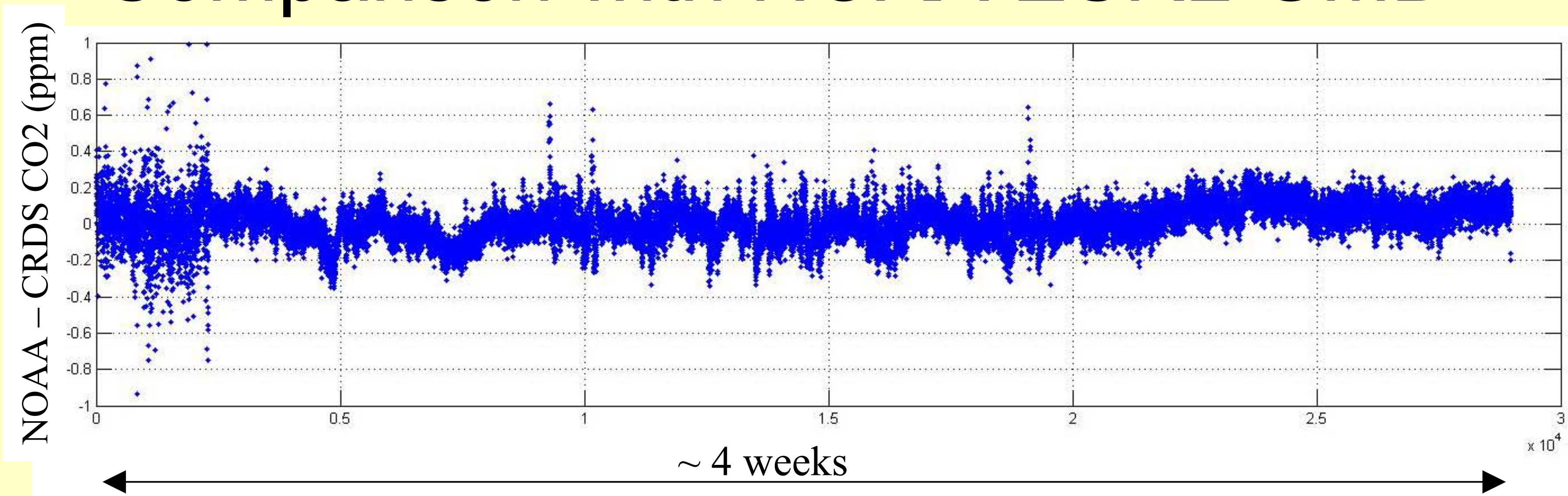
Comparison with NOAA ESRL GMD

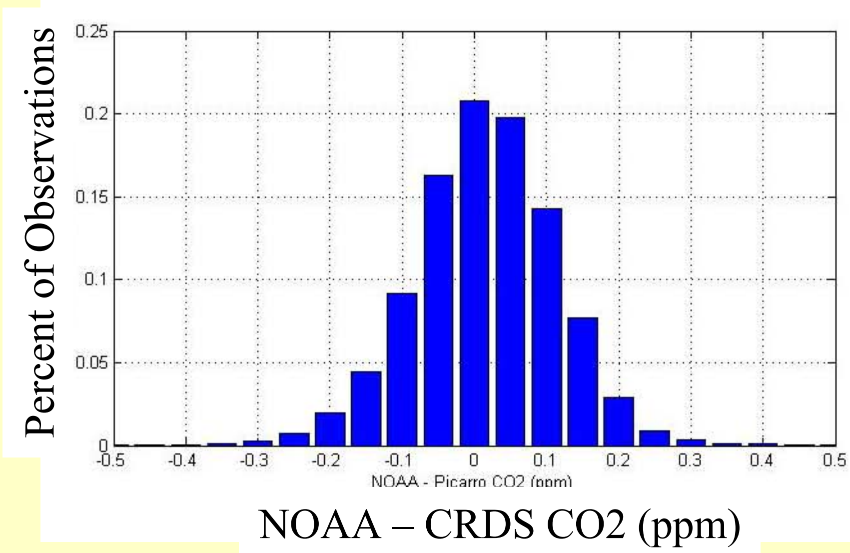
- One system tested at NOAA ESRL for ~45 days
- NOAA Licor-based system air sample dried
- CADS system did not dry sample
  - Water vapor content measured using a water line
  - Corrected CO2 for moisture
- Difference between the two measurements < ~0.15 ppm for 90% of measurements
  - Some error due to timing of systems
- RMS difference over 45 days = 0.02 ppm

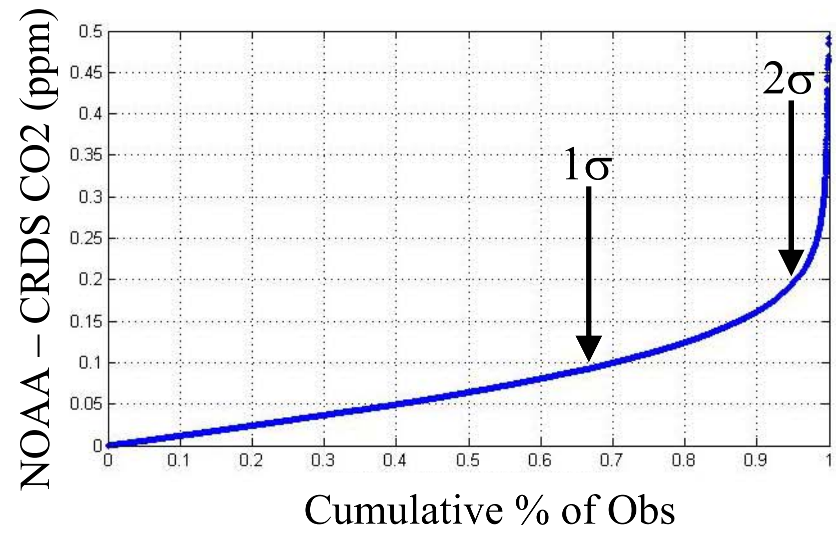
+

= analyzer drift uncertainty + 0.07 ppm calibration scale uncertainty + smaller terms
Does not include sample equilibration error or real atmospheric variability

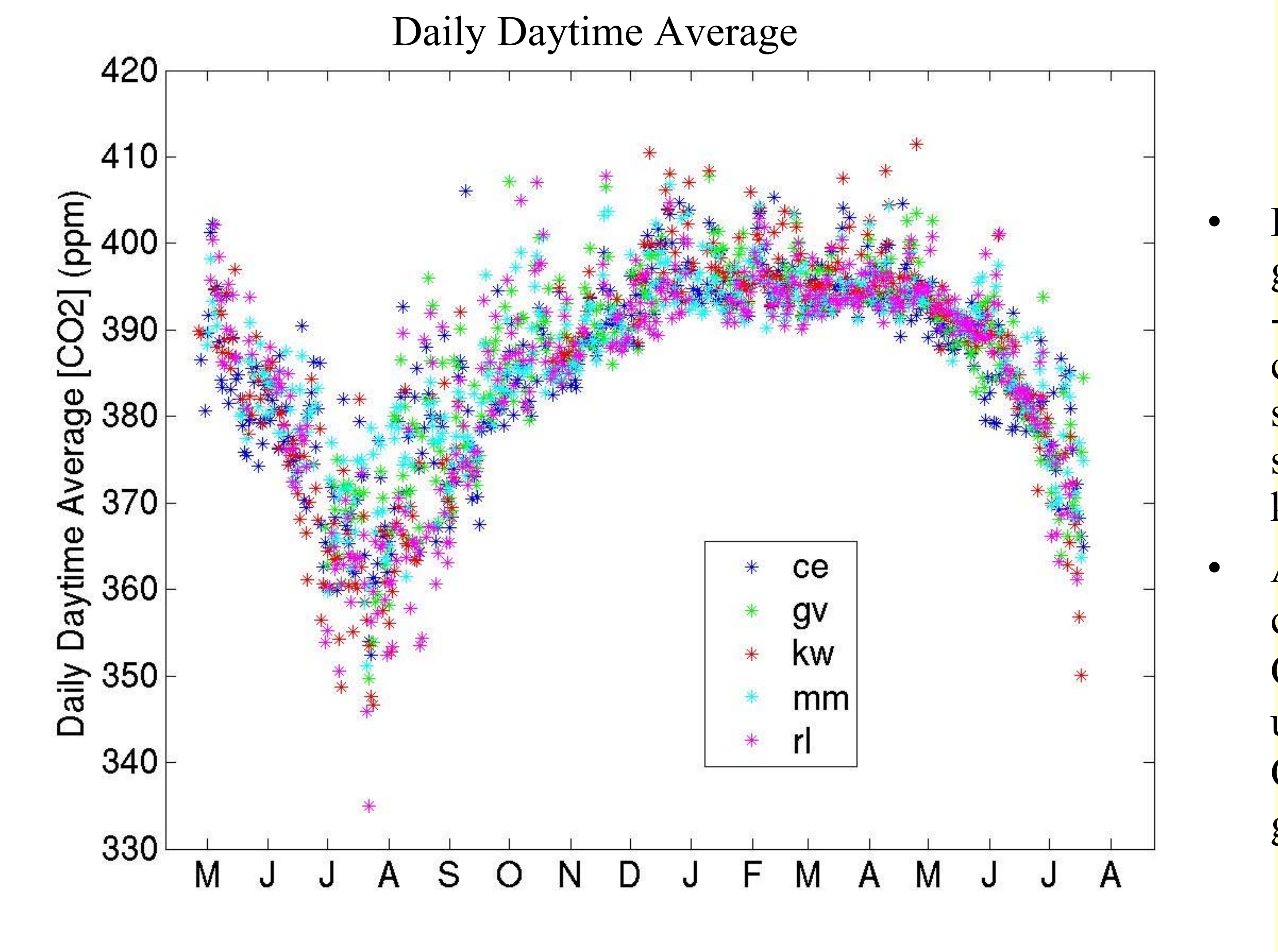
Comparison with NOAA ESRL GMD







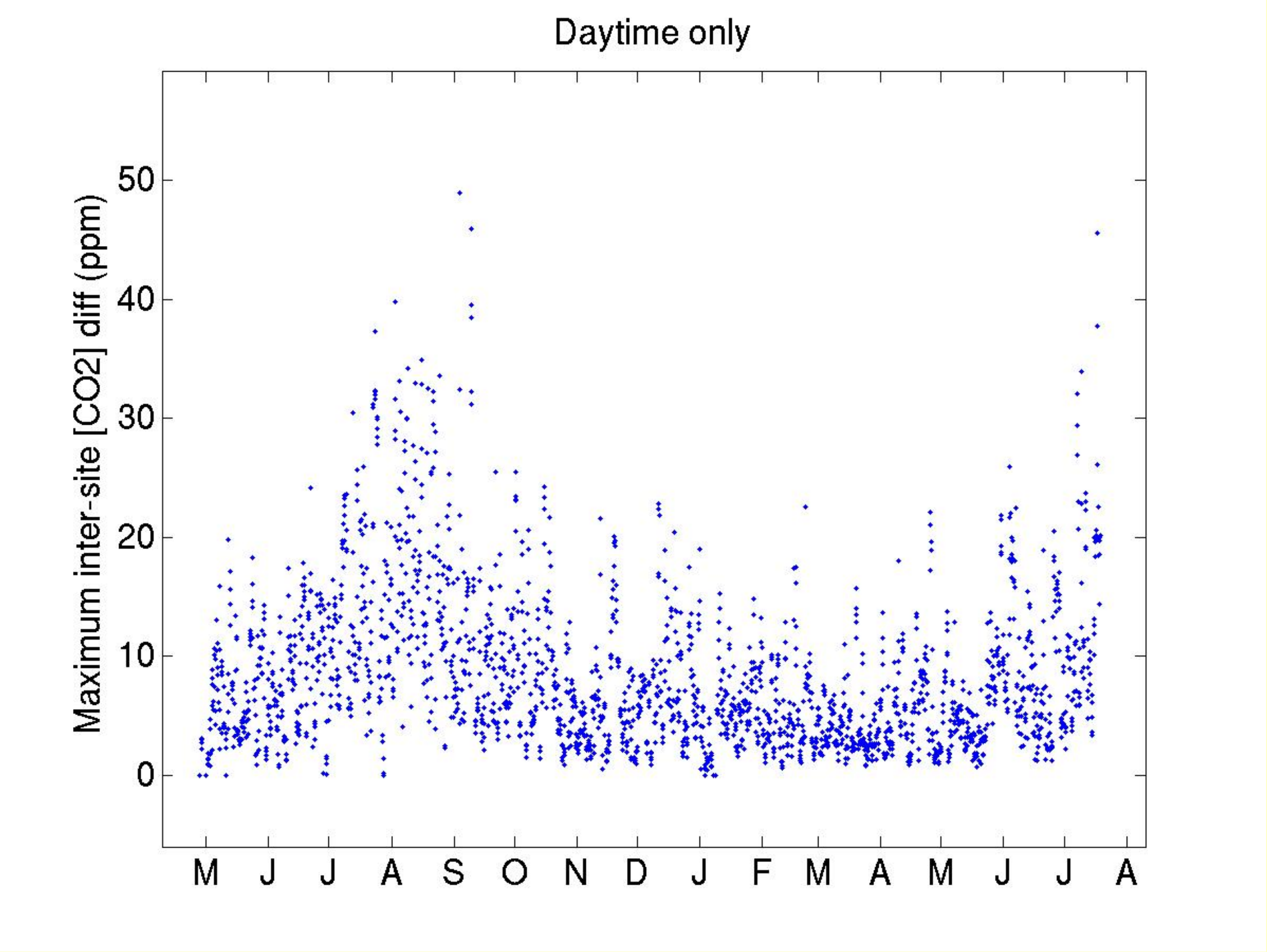
Most points < 0.15 ppm with calibrations every four hours



- Large spatial gradient!
  - as large as continental-scale sites despite being separated by 500 km at most
- Associated changes in FT CO_2 are unknown; satellite CO_2 can fill this gap

- Strong coherent seasonal cycle across stations; synoptic variance
- 50 ppm drawdown!
  - Typical forest signal is 20-30 ppm
  - Agriculture (esp corn) has huge signal

Spatial gradients



2007 **2008**

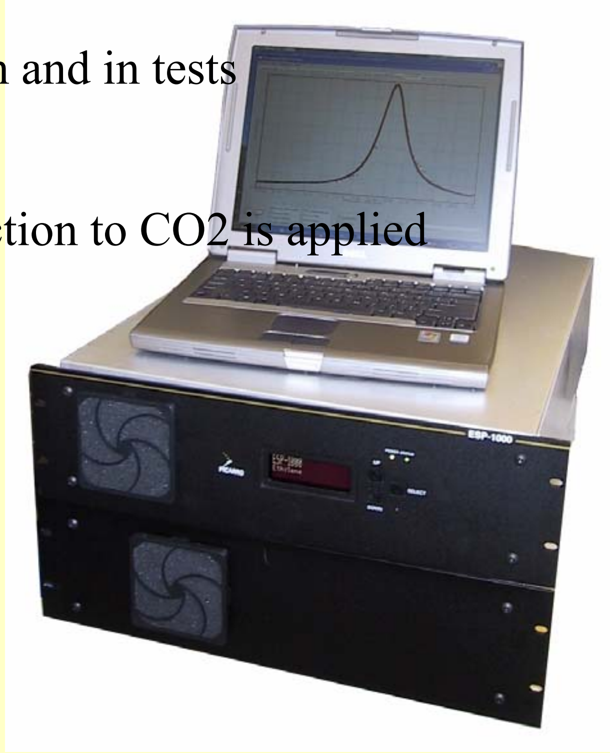
Differences as large as 40 - 50 ppm between Ring 2 sites!

On other days, the difference is less than 5 ppm

Example of model results of high- and low-gradient day

Cavity Ring-Down Spectroscopy

- Picarro, Inc. has developed an ultra-sensitive trace gas monitoring system. Advantages include:
  - •High precision and accuracy
    - < 0.1 ppm accuracy
    - Long-term stability: days to weeks
    - 1.5-sec sample precision and accuracy of ≤ 0.2 ppm and in tests
  - •Measurement rate in seconds rather than minutes
  - •No drying is required; water vapor is measured and correction to CO_2 is applied
  - •Stable and robust long-term measurement




Round Lake, MN
100 ft agl
360 ft agl


Centerville, IA
100 ft agl
360 ft agl


Galesville, WI
100 ft agl
360 ft agl


Kewanee, IL
100 ft agl
460 ft agl


Mead, NE
100 ft agl
400 ft agl

Outline

- Seasonal patterns of CO_2 mixing ratios
- Profiles
- Synoptic variability
- Spatial variability / coherent response to climate
- NACP's Mid-Continent Intensive
- Ring 2: network of CO_2 measurements
  - Reliability, precision/accuracy of Cavity Ring-Down Sensors
  - Uncertainty estimates, water vapor correction
  - Spatial gradients observed in region

How do satellite measurements fit in?

The role of Ring 2 in the Mid-Continent Intensive

- Add regional network of 5 communications-tower based atmospheric CO2 obs in the midcontinent intensive region
  - April 2007 through November 2009
  - In addition to the long-term atmospheric CO2 observing network
    - NOAA CMD all towers
    - Aircraft profiles
    - Well-calibrated CO2 measurements on AmeriFlux towers
- Plan: to "oversample" the atmosphere in the study region for more than a full year
- Inversions to produce maps of fluxes of CO2 for region (CSU)

North American Carbon Program Mid-Continental Intensive

Cavity Ring Down systems

- Kewanee, IL
- Centerville, IA
- Mead, NE
- Round Lake, MN
- Galesville, WI

PSU Ameriflux systems

- Ozarks, MO
- Mead, NE

NOAA Tall Towers

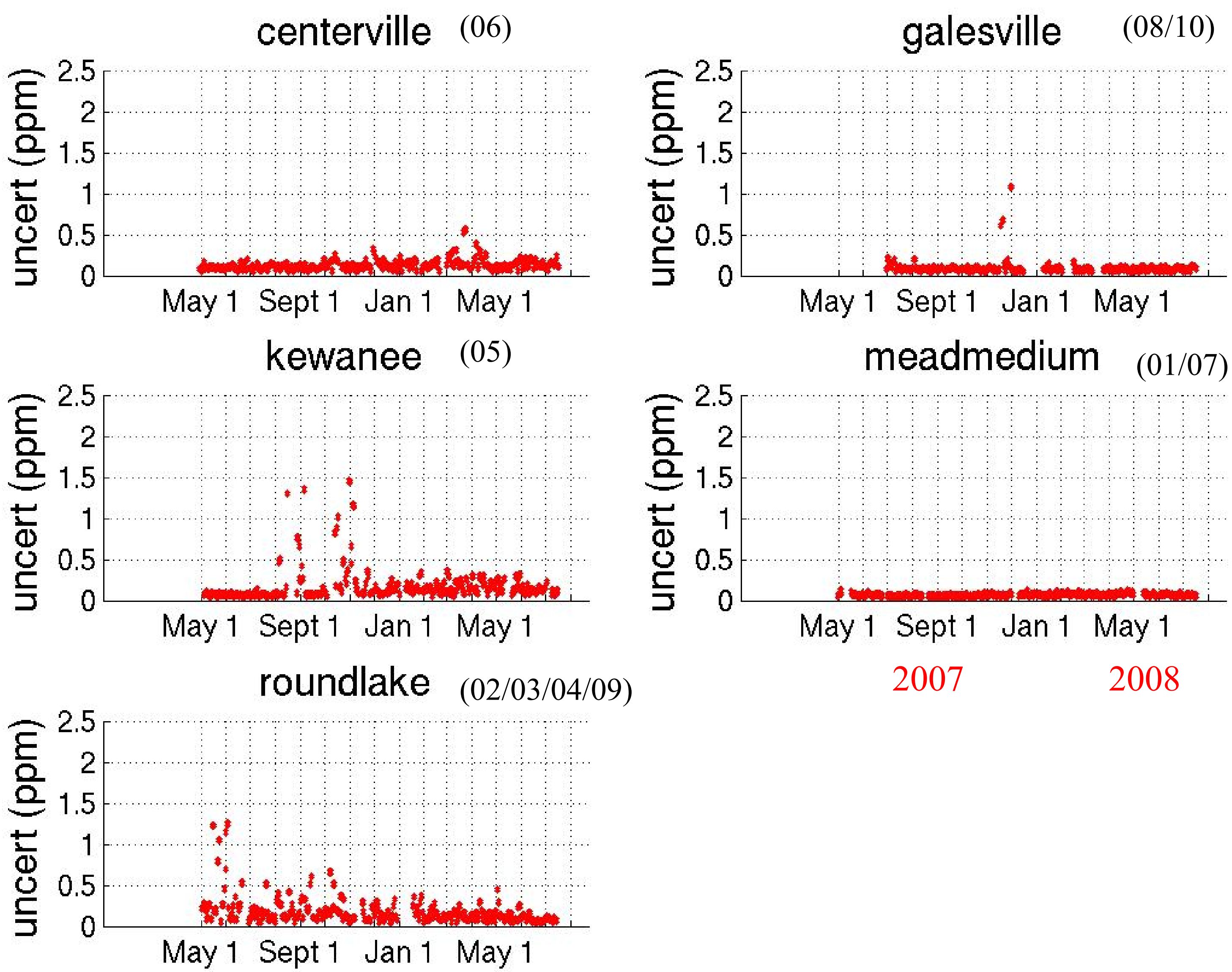
- West Branch, IA
- WLEF, WI

Uncertainty estimates (NOAA; A. Andrews)

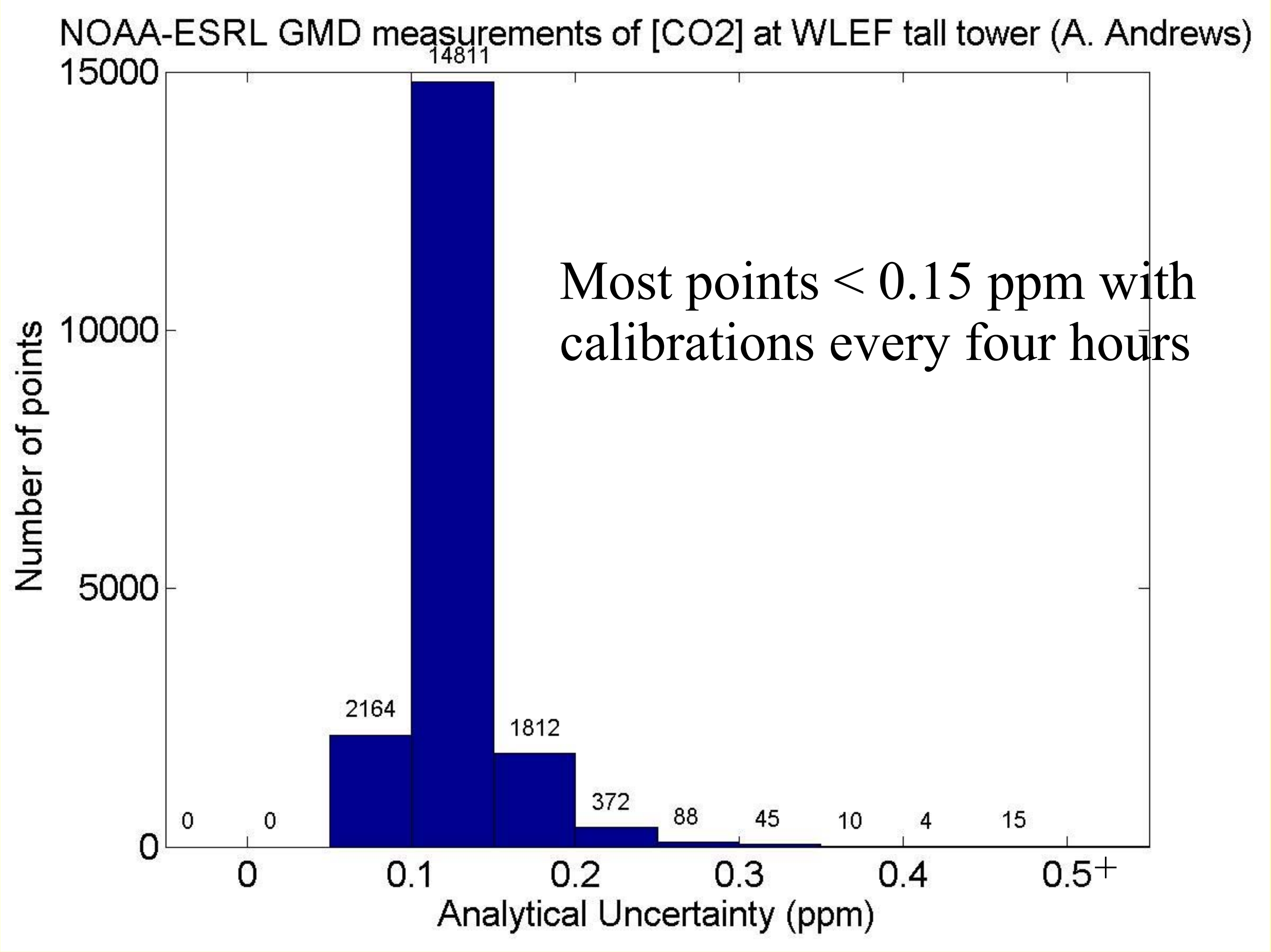
- Analytical uncertainty
  - Calibration scale uncertainty (0.07 ppm)
  - Analyzer drift uncertainty (typically < 0.1 ppm)*
  - Standard equilibration uncertainty (typ <0.05 ppm)
  - Curve fitting errors (typ <0.05 ppm)
  - Differences in water content between sample and standards (typ < 0.05 ppm)*
- Total uncertainty = analytical uncertainty + sample equilibration error and real atmospheric variability

**Shown in red are the points most likely to be different with the Ring 2 systems

Analyzer drift uncertainty + 0.07 ppm calibration scale uncertainty

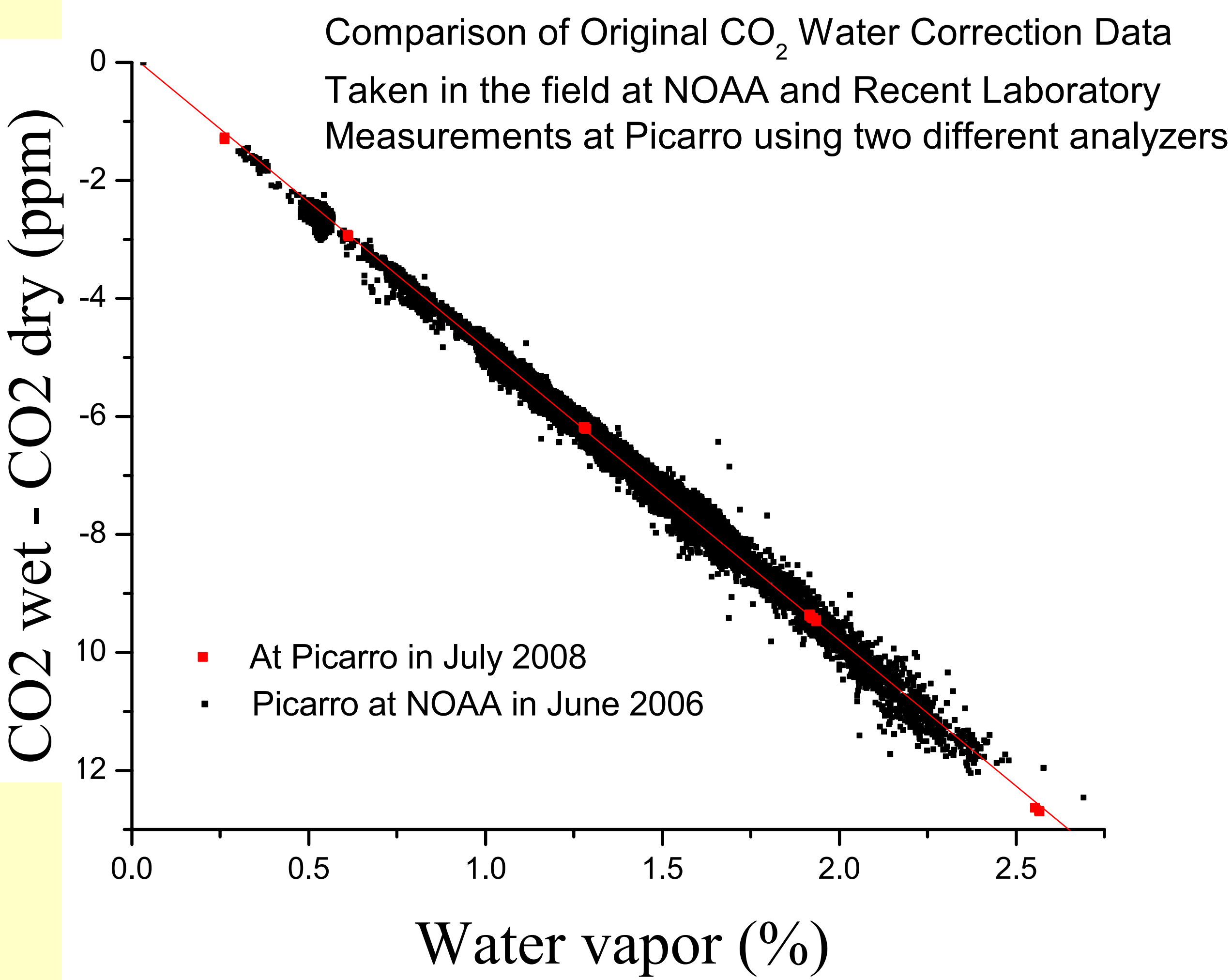


2006



= analyzer drift uncertainty + 0.07 ppm calibration scale uncertainty + smaller terms
Does not include sample equilibration error or real atmospheric variability

Water vapor correction



- Sample not dried; water vapor is measured and [CO2] is corrected
- Leads to additional uncertainty
- Further tests in progress
  - nafion dryer
  - bubbler

Continuous, well-calibrated CO2 Measurements in North America

Types of instrumentation

- **LICOR two-cell infrared absorption**
  - NOAA sites, Canadian sites, Harvard, ARM-CART
- **LICOR single-cell infrared absorption** (new low-cost systems)
  - PSU Ameriflux sites, NCAR sites, Oregon State, Indiana
  - Calibrated every 4 hours with 4 cal tanks
  - System must be dried
- **Cavity ring-down spectroscopy**
  - Ring 2

Introduction

- CO_2 concentration measurements
  - Commonly made using non-dispersive infrared spectroscopy (NDIR)
  - Requires dried air sample
  - Requires frequent (~hourly) system calibration
- Cavity Ringdown Spectroscopy (CRDS) proving to be a reliable method for trace gas monitoring
  - Picarro, Inc. systems discussed here

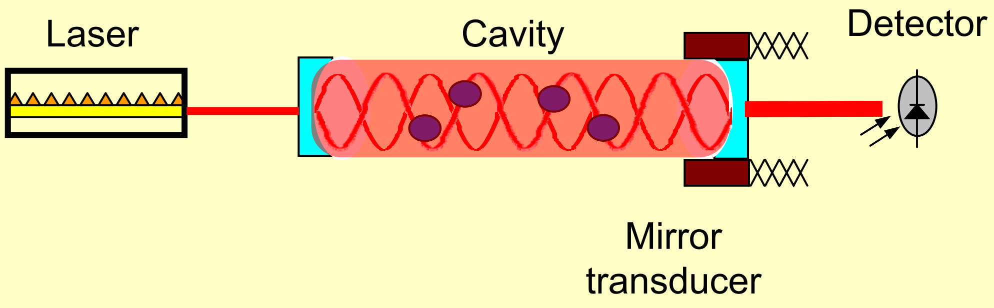
Cavity Ringdown Spectroscopy

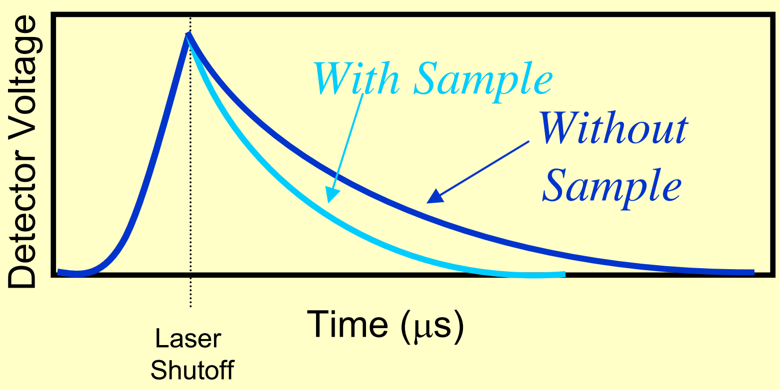
- Laser-based technique
  - High precision and accuracy
    - 1.5-sec sample precision and accuracy of ≤ 0.2 ppm
    - 1-min accuracy < 0.1 ppm
  - Long-term stability: days to weeks or months
  - No drying is required
    - water vapor is measured and correction to CO2 is applied
  - Stable and robust long-term measurement

Cavity Ringdown Spectroscopy

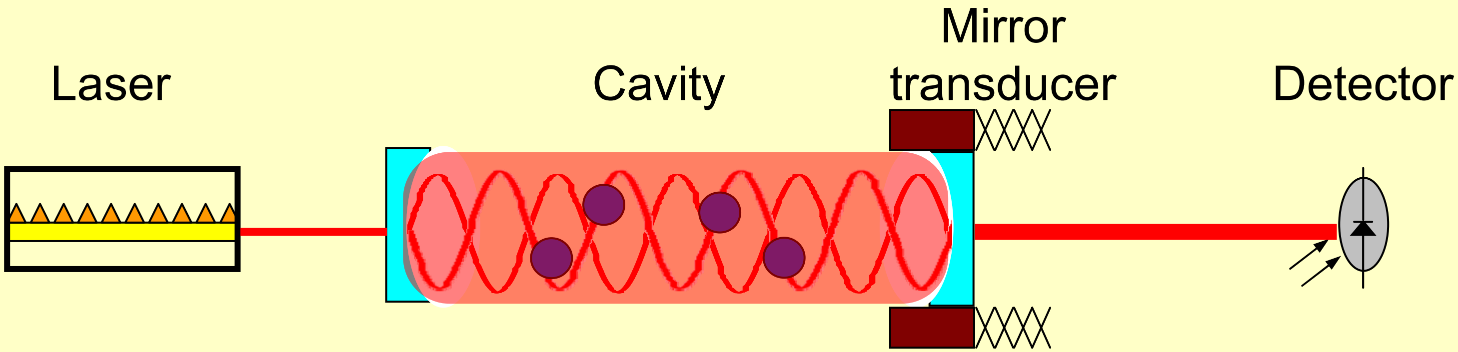
The basic measurement algorithm is:

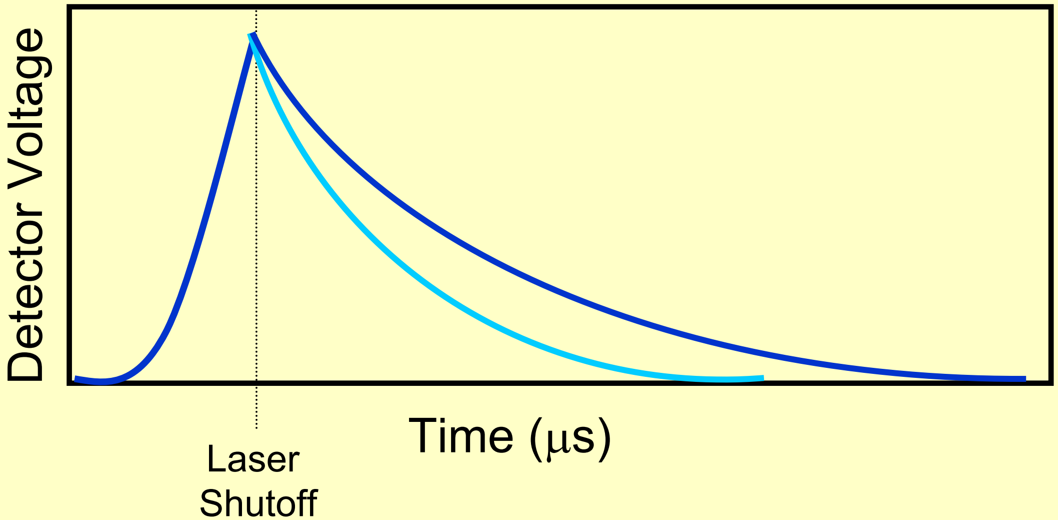
1. Tune laser and cavity to desired wavelength
2. Inject light into the cavity (laser resonant with cavity)
3. Once light circulating in the cavity hits a threshold, stop injecting
4. Measure decay time of light in cavity
5. Compare decay time to that of an off-resonance cavity
6. Repeat





Introduction of a gas sample





Ringdown curve dictated by cavity mirror loss

Ringdown time dictated by cavity mirror loss AND absorption by molecules; ringdown time shortens

CRDS → Very Long effective path length (~10-20 km)

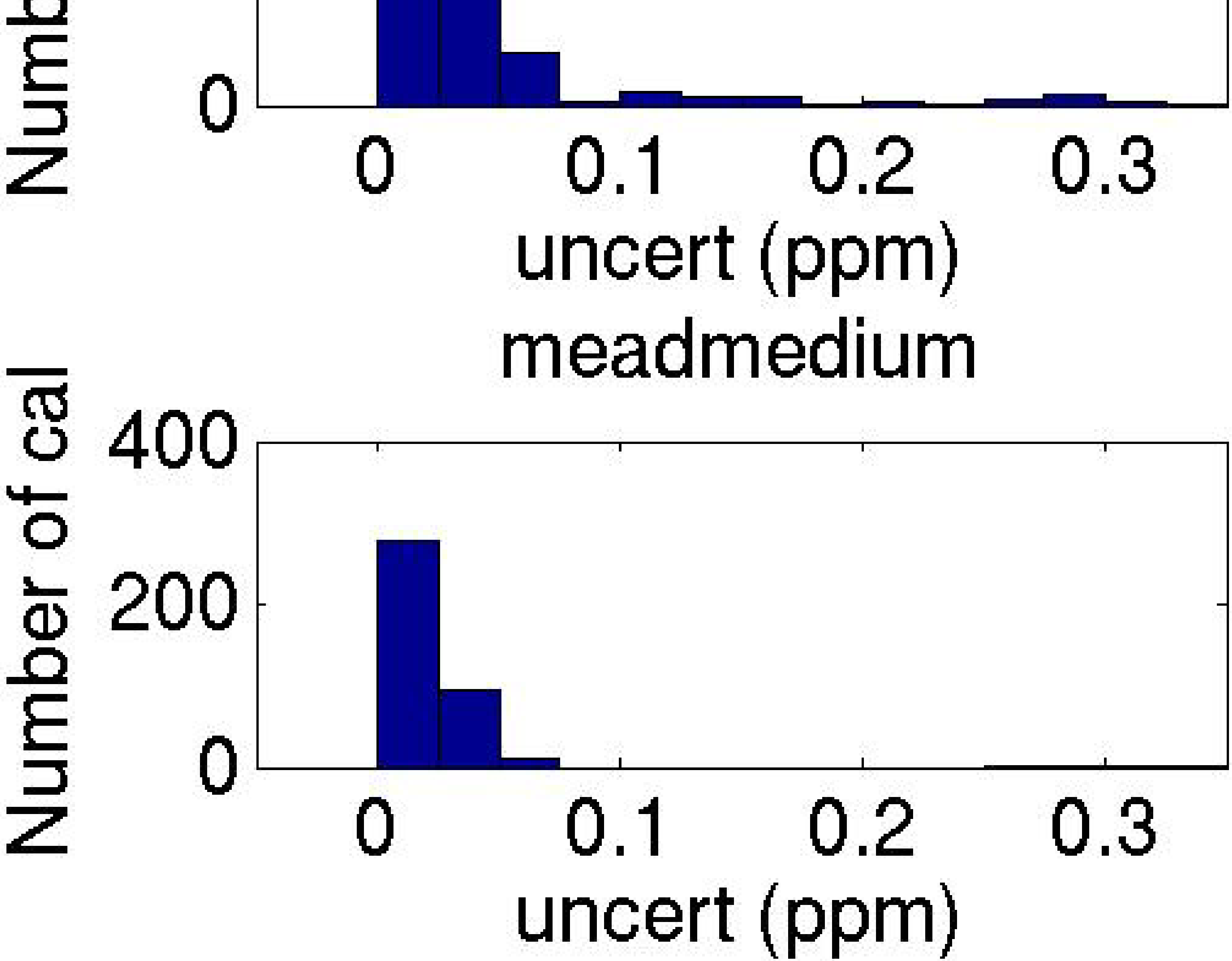
Round robin test, Feb 2008

Site	Tank 1 error (ppm)	Tank 2 error (ppm)	Tank 3 error (ppm)	Tank 4 error (ppm)	Mean
Kewanee	-0.097	-0.115	-0.049	-0.279	-0.135
Centerville	-0.155***	0.020	-0.158 ***	Unstable	-0.098
Mead	-0.071	-0.074	0.093	-0.093	-0.036
Round Lake	-0.047	Not tested	-0.210	Not tested	-0.129
Galesville	-0.174	-0.162	-0.018	-0.190 ***	-0.093
Mean	-0.109	-0.083	-0.068	-0.13	

Blue: > 0.1 ppm

Red: > 0.2 ppm

- 4 NOAA-calibrated tanks brought to each site
  - February 2008
  - April 2009
- Average errors for each site and each tank are less than 0.15 ppm
- Doesn’t test water vapor correction
- *** Only 1 cal cycle



Numb
0
0
0.1
0.2
0.3
uncert (ppm)
meadmedium
Number of cal
400
200
0
0
0.1
0.2
0.3
uncert (ppm)