Field Testing And Error Analysis Of Cavity Ringdown Spectroscopy Instruments Measuring CO_2

PENNSTATE 1855

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PICARRO

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Continental atmospheric CO_2 observational network

Prevalent methods for making tower-based measurements of CO2 mixing ratio, notably non-dispersive infrared spectroscopy, require frequent system calibration and drying of the sample gas. Wavelength-scanned cavity ringdown spectroscopy (WS-CRDS) is an emerging laser-based technique for detecting trace quantities of gases, eliminating or significantly reducing the frequency of calibration and the need to dry the sample gas. We present results from ~24 months of field measurements from five WS-CRDS systems in MN, WI, IA, NE, and IL. These five systems, termed Ring2 (see Fig. 1 and Table 1), were deployed in support of the North American Carbon Program's Mid Continent Intensive from April 2007 to November 2009. Analysis and results include an examination of long-term stability, discussion of overall uncertainty, and the effects of using the water vapor correction instead of drying the sample gas.

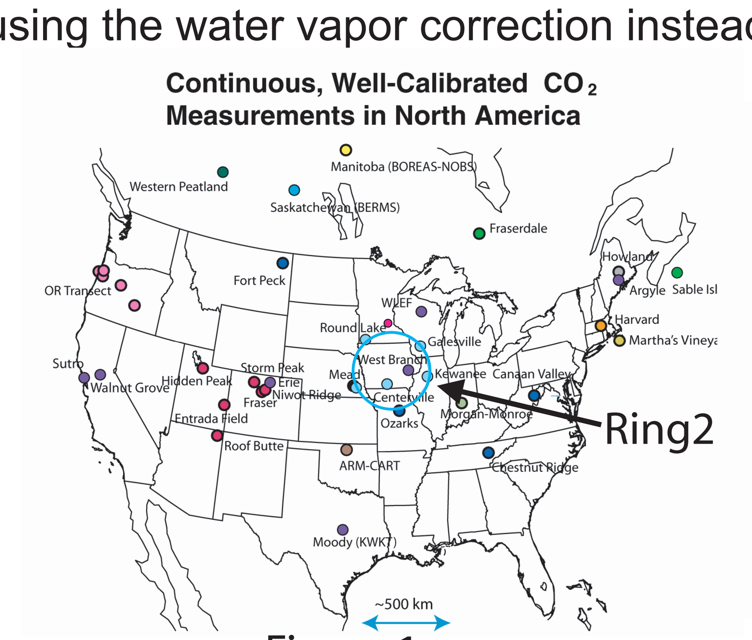


Figure 1

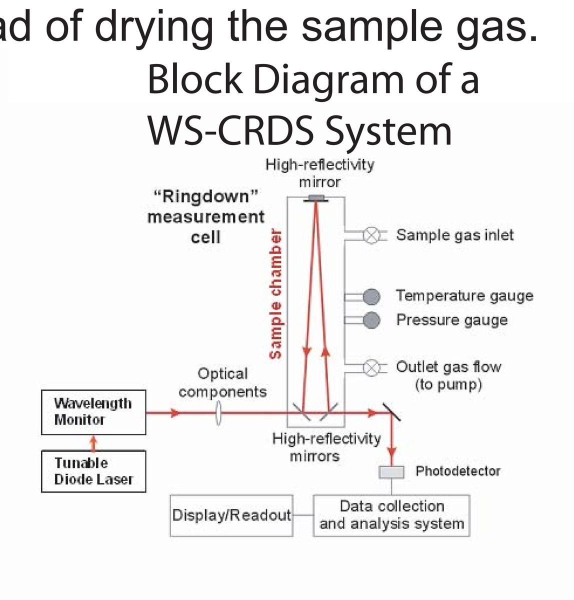


Figure 2

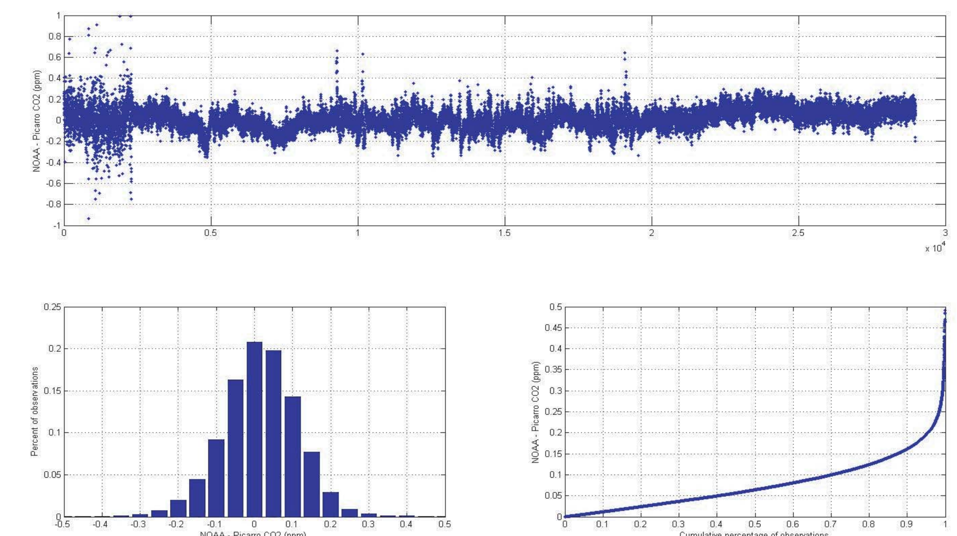
Five early model Picarro Inc. WS-CRDS systems were purchased for a regional deployment around Iowa. These systems were developed as part of a Small Business Innovative Research grant and are the basis for the current G1301 systems. Instrument performance is nearly identical to the current models with one significant difference: the systems deployed in this work measure water vapor content of the air sample using an HDO line instead of an H2O line, and this has significant impact on the water vapor measurement accuracy as will be shown.

The deployment strategy was to locate the five WS-CRDS systems at existing communication towers which had climate controlled facilities and line power. In addition, and to enable real-time trouble shooting and daily data downloads, it was necessary to have Verizon Wireless cell phone coverage (Airlink Raven EVDO were used to communicate with the WS-CRDS systems). Each tower had to be at least 100 m tall; the table below shows the location and sampling heights of each tower.

Figure 2 shows a block diagram of the WS-CRDS analyzer. The WS-CRDS analyzer utilizes a telecom-grade distributed feedback (DFB) laser measuring a single 12C16/16O2 spectral feature at a wavelength of 1603 nm and a single H2O spectral feature near 1603 nm (Crosson 2008). In WS-CRDS, light from a continuous-wave laser is injected into a precisely aligned optical cavity consisting of three very high reflectance mirrors (>99.995%). The light intensity inside the cavity then builds up over time and is monitored using a photo detector. The "ring-down" measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially in time. This exponential decay is typically characterized using the characteristic decay time constant, (Crosson and Davis 2006). The typical empty-cavity decay constant is 30 µsec.

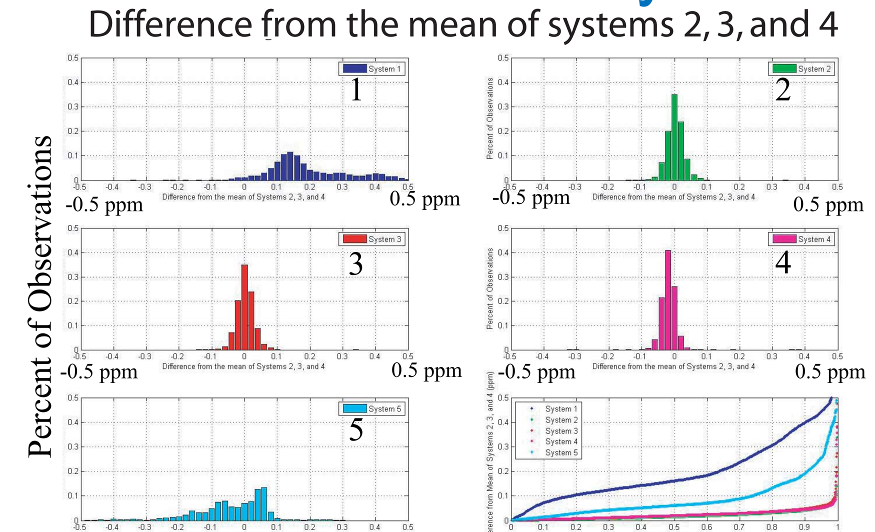
Site	Kewanee, IL	Centerville, IA	Mead, NE	Round Lake, MN	Galesville, WI
Latitude	41.2762 N	40.7919 N	41.1386 N	43.5263 N	44.0910 N
Longitude	89.9724 W	92.8775 W	96.4559 W	95.4137 W	91.3382 W
Elevation (m above MSL)	247	286	358	469	251
Installation date	26-Apr-07	27-Apr-07	30-Apr-07	1-May-07	29-Jun-07
Sampling heights, AGL	30/140 m	30/110 m	30/122 m	30/110 m	30/122 m

Comparison with NOAA-ESRL



A pre-deployment field trial (Crosson, 2008) at NOAA-ESRL in Boulder, CO compared the performance of a WS-CRDS system with a LICOR-7000. The total length of the test was 45 days, with 24 days in an "operational" mode, sampling the same sample air. For the LICOR-7000 system, four calibration gases were sampled every six hours, and the sample was dried. The WS-CRDS system was calibrated once over the duration of the field trial and the air sample was NOT dried. The largest difference between the mean of the measurements of each of the four calibration gases during the 24-day operational period and the known value of the tanks was 0.07 ppm. During a 60-hour test period, the root-mean-square difference between the WS-CRDS and LICOR-7000 systems was 0.064 ppm; over the entire 45-day trial the root-mean-square difference was less than 0.018 ppm. The majority of this difference is attributable to a slow drift (less than 0.8 ppb per day) of the WS-CRDS system, and can be easily corrected using reference gases sampled with a daily, or less, frequency.

Comparison of five WS-CRDS Systems



An additional pre-deployment field trial was performed at PSU in which all five systems sampled from the same 4-L buffer volume for three days. The CO2 mixing ratio varied from as low as 390 ppm to as high as 485 ppm. Histograms 1-5 in the figure above show the differences from the mean of systems 2, 3, and 4; systems 1 and 5 had known problems and were not deployed but tested nonetheless. The difference from the mean for the one-minute averages are less than 0.1 ppm for 98% of the values, and less than 0.2 ppm for essentially all the data.

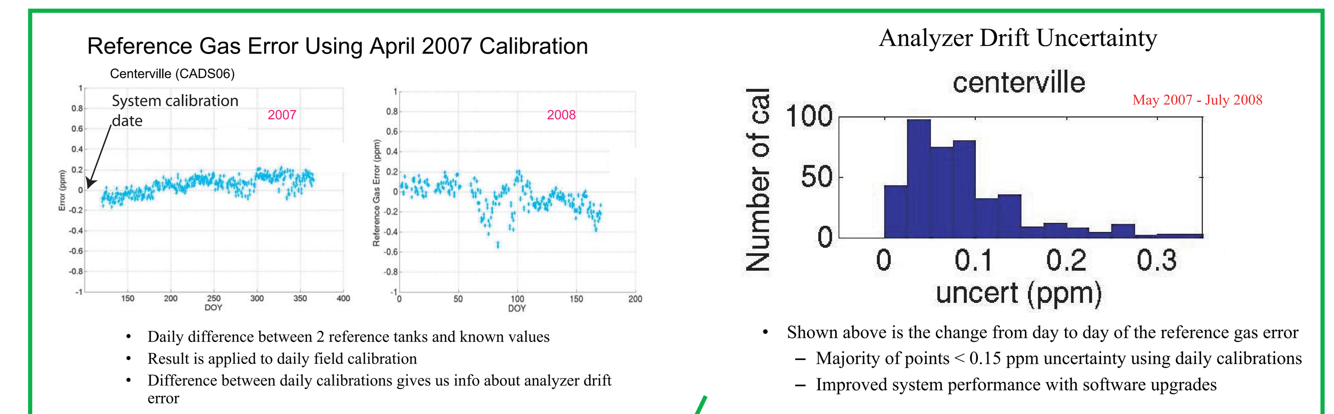
Round Robin Tests

Round-robin tests, in which four NOAA-ESRL calibration tanks were sampled at each of the Ring2 sites, were performed in February 2008 (see table below). An additional round robin was performed in November 2008, with similar results (not shown). With the exception of two, all of the measured CO2 mixing ratios are within 0.2 ppm of the known values. The means of the difference from the known values, for each site and for each tank, are between −0.14 and −0.04 ppm.

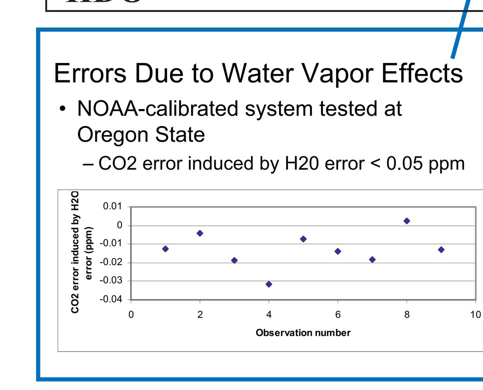
Site	Tank 1 Error (338.81 ppm)	Tank 2 Error (369.39 ppm)	Tank 3 Error (401.68 ppm)	Tank 4 Error (431.78 ppm)	*Mean (ppm)*
Centerville	–0.155 (1)	0.020 (2)	–0.158 (1)	N/A	*–0.098*
Galesville	–0.174 (2)	–0.162 (2)	–0.018 (2)	–0.190 (1)	*–0.093*
Kewanee	–0.097 (3)	–0.115 (3)	–0.049 (3)	–0.279 (3)	*–0.135*
Mead	–0.071 (2)	–0.074 (2)	0.093 (2)	–0.093 (2)	*–0.036*
Round Lake	–0.047 (4)	N/A	–0.210 (4)	N/A	*–0.129*
Mean (ppm)	*–0.109*	*–0.083*	*–0.068*	*–0.13*	

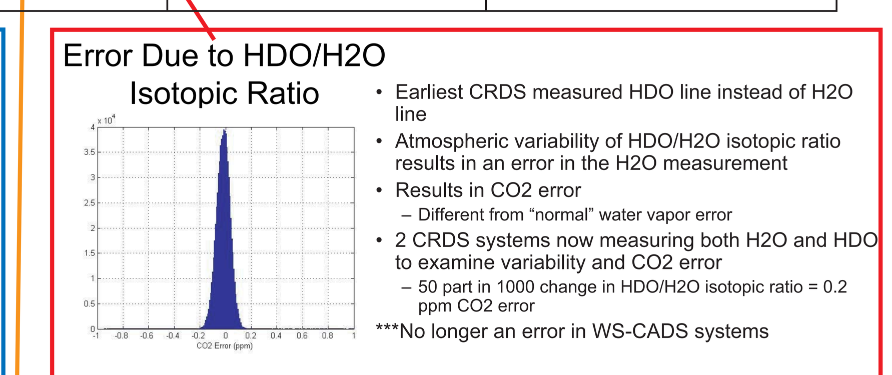
Assessment of Accuracy and Precision

In the table below are the various contributors to the analytical uncertainty for both the WS-CRDS system and the NOAA-ESRL NDIR system. Shown below and color coded are the uncertainty due to **analyzer drift**, **water vapor effects**, **temperature and pressure control**, and also the error, unique to these early Ring2 systems, due to the **atmospheric variability of the HDO/H2O isotopic ratio**.



Contributions to analytical uncertainty	PSU WS-CRDS systems	NOAA-ESRL NDIR systems
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
Errors due to water vapor effects	0.05 ppm	0.05 ppm
Analyzer drift uncertainty	0.1 ppm	0.1 ppm
Cavity pressure control error	0.006 ppm	
Cavity temperature control error	0.004 ppm	
Error due to HDO/H2O isotopic ratio	0.25 ppm ***	No Error
Total analytical uncertainty with HDO	**0.3**	**0.1**
Total analytical uncertainty without HDO	**0.1**	**0.1**





Strength of WS-CRDS technology is that measurements are theoretically 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)

Conclusions

- 5 WS-CRDS systems deployed early 2007
- Remained in the field until November 2009
- Round-robin tests verified accuracy (0.1 - 0.15 ppm)
- Excellent long-term stability of systems
- Overall system error ~0.3 ppm mostlly caused by HDO/H2O isotopic ratio effects
- Post calibrations should decrease error
- WS- CRDS error today ~0.1 ppm

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Galesville, WI: Dennis McSorley

Kewanee, IL: Dan Vandiver

Mean, NE: Roger Book and Rick Dodds

Round Lake, MN: Bob Cook

Related Sessions

B51E-0338. Mid-Continental Intensive Field Campaign Atmospher ic CO2 Observations Compared to Forward Models. L. I. Diaz; K. J. Davis; N. L. Miles; S. Richardson; A. E. Schuh; A. Denning; A. E. Andrews; A. R. Jacobson; K. Corbin

B53F-03. Atmospheric CO2 Inversions of the Mid-Continental Intensive (MCI) Region (Invited). A. E. Schuh; A. Denning; S. M. Ogle; K. Corbin; M. Uliasz; K. J. Davis; T. Lauvaux; N. Miles; A. E. Andrews; G. Petron; D. N. Huntzinger

B51E-0339. Comparison of Regional Carbon Dioxide Fluxes from Atmospheric Inversions and Inventories in the Mid-Continent

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