Field Testing of Cavity Ring-Down Spectroscopy Analyzers Measuring Carbon Dioxide and Water Vapor

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ABSTRACT

Prevalent methods for making high-accuracy tower-based measurements of the CO_2 mixing ratio, notably nondispersive infrared spectroscopy (NDIR), require frequent system calibration and sample drying. Wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) is an emerging laser-based technique with the advantages of improved stability and concurrent water vapor measurements. Results are presented from 30 months of field measurements from WS-CRDS systems at five sites in the upper Midwest of the United States. These systems were deployed in support of the North American Carbon Program's Mid-Continent Intensive (MCI) from May 2007 to November 2009. Excluding one site, 2σ of quasi-daily magnitudes of the drifts, before applying field calibrations, are less than 0.38 ppm over the entire 30-month field deployment. After applying field calibrations using known tanks sampled every 20 h, residuals from known values are, depending on site, from 0.02 ±0.14 to 0.17 ±0.07 ppm. Eight months of WS-CRDS measurements collocated with a National Oceanographic and Atmospheric Administrations (NOAA)/Earth System Research Laboratory (ESRL) NDIR system at West Branch, Iowa, show median daytime-only differences of −0.13 ±0.63 ppm on a daily time scale.

1. Introduction

The interest in deploying regional measurement networks to quantify carbon dioxide (CO_2) fluxes, both biogenic and anthropogenic, is growing as the need to regulate CO_2 emissions grows. Inverse studies of CO_2 mixing ratio have traditionally been conducted at coarse spatial and temporal resolution because of both computing restraints and a scarcity of measurements. Until fairly recently the majority of high-accuracy field CO_2 measurements have been made using sensors based on nondispersive infrared (NDIR) spectroscopic gas detectors (e.g., Zhao et al. 1997; Bakwin et al. 1998). Wavelength-scanned cavity ring-down spectroscopy (WS-CRDS), however, has several key advantages over the NDIR technique, including improved stability (resulting in the reduced need for calibration gases) and concurrent water vapor measurements, potentially eliminating the need for drying (Busch and Busch 1997; Crosson 2008). Consequently, the simpler field deployment requirements are facilitating deployment of regional greenhouse gas measurement networks (e.g., Miles et al. 2012). These data will be used to address the need, as described by Wofsy and Harriss (2002) and the National Research Council (2010), to better quantify regional fluxes, both biogenic and anthropogenic, using atmospheric inversion methods.

Crosson (2008) documents a 45-day trial, comparing WS-CRDS with National Oceanographic and Atmospheric Administrations (NOAA)/Earth System Research Laboratory (ESRL) NDIR measurements. Even

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without sample drying, the root-mean-square difference was less than 0.18 ppm, and the drift is less than 0.4 ppm over the duration of the trial. Using laboratory tests, Chen et al. (2010) developed a general equation to account for water vapor effects on the CO_2 and CH_4. Separate calibration of each instrument for water vapor may improve the CO_2 accuracy by a small but significant amount, however. Chen et al. (2010) demonstrate the mean difference to be 0.22 ±0.09 ppm CO_2 between WS-CRDS and NDIR for flights over the Amazon rain forest during the Balanço Atmosférico Regional de Carbono na Amazônia (BARCA) phase B campaign before applying any field calibrations for the WS-CRDS. The average error is reduced after applying calibrations at the end of the campaign using synthetic calibration gases (accounting for isotopic effect and pressure broadening effect resulting from variations of compositions in air).

The North American Carbon Program (NACP) Mid-Continent Intensive (MCI) was designed as a methodological test to compare atmospheric inversions with agricultural and forest inventory estimates of regional CO_2 emissions (Ogle et al. 2006). Evaluating both strategies to estimate regional fluxes is a key element of the NACP Science Implementation Strategy (Denning et al. 2005). This paper describes instrument performance of five Picarro, Inc. (Sunnyvale, California), WS-CRDS systems, deployed near Centerville, Iowa; Galesville, Wisconsin; Kewanee, Illinois; Mead, Nebraska; and Round Lake, Minnesota, in support of the NACP MCI from May 2007 to November 2009. Predeployment calibrations and deployment details are described, followed by results from laboratory precision tests, round-robin field tests, analyzer drift, and, finally, an 8-month comparison of WS-CRDS to NOAA/ESRL NDIR measurements.

2. Instrument and deployment description

The WS-CRDS systems described in this paper (Picarro, Inc., CADS models CADS01, CADS03, CADS05, CADS06, CADS07, CADS08, CADS09, and CADS10) were developed as part of a small business innovative research grant, and they are the basis for the company's current G1301, G2301, G2302, and G2401 systems.

The WS-CRDS instruments scan a $^{12}C^{16}O_2$ line of carbon dioxide, which is used to infer the total carbon dioxide content of the sample gas. Variations in the isotopic content of the sample gas will cause a systematic, but very small, error in the total carbon dioxide, because $^{13}C^{16}O_2$ and other isotopologues are not measured by the instrument. The $^{13}C^{16}O_2$ exists at approximately 1.1% of the total carbon dioxide in the atmosphere; typical daily and seasonal variations of that ratio are 1‰–2‰. The resulting error is thus up to 2.2×10^{-5} of the reported carbon dioxide mixing ratio, which at 400 ppm corresponds to an error of less than 0.01 ppm. The next most abundant isotopologue $^{12}C^{16}O^{18}O$ is 2.5 times less abundant, and has a 3.6 ppb systematic shift for a 2‰ change in the isotopic ratio.

The instruments described in this paper are nearly identical in concept to the current models. One significant difference, however, is that the systems deployed in this work measure water vapor content using an HDO line instead of an H_2O line, necessitating an empirical correction to the data to be discussed in section 3e.

a. WS-CRDS laboratory calibration

Prior to deployment for the MCI, the WS-CRDS systems were tested in The Pennsylvania State University (PSU) CO_2 calibration facility, and a calibration was developed using four NOAA/ESRL CO_2 calibration standards with values of approximately 340, 370, 400, and 430 ppm CO_2. All five systems simultaneously sampled the same calibration gas using ⅛″ OD stainless steel tubing and three-way compression fittings to split the flow. Parker, Inc. (Cleveland, Ohio, Part 003-0216-900), valves and Scott Specialty Gas [now Air Liquide (Plumsteadville, Pennsylvania) Model 51-14B-590] regulators were used for gas handling. Each calibration gas was sampled for 8 min, and the first 3 min of data were ignored to allow for the equilibration of the sample. Six complete cycles through the four calibration gases were used to develop linear calibration equations that were used for the 30-month MCI deployment.

b. Water vapor correction to CO_2

Because the air sample is not dried during the MCI deployment of the PSU WS-CRDS systems, the water vapor dilution and line broadening effects are accounted for by measuring the water vapor content and correcting the raw CO_2 measurement. Therefore, any error in the water vapor measurement results in an error in the corrected CO_2. An HDO line was originally chosen to measure water vapor because of its proximity to the line used for CO_2. The measured HDO was calibrated to H_2O in a manner that inherently assumed a constant isotopic ratio. However, during the deployment, errors associated with the use of an HDO line became apparent. In section 3e, we develop an empirical correction based on measurements of both H_2O and HDO using one of the WS-CRDS instruments relocated to the NOAA/ESRL West Branch, Iowa, tall tower site after the conclusion of the MCI. This empirical relation accounts for the fact that, in general, the deuterium isotopic ratio is correlated to concentration, that is, more enriched deuterium tends to occur at higher levels of humidity.

To correct for water vapor effects we use the following relationship (Chen et al. 2010):

$$\mathrm{CO}_{2\mathrm{dry}} = \mathrm{CO}_{2\mathrm{wet}}/(1 - 0.012H - 2.674 \times 10^{-4}H^2),$$

with H in percent. We note that, to first order, the correction of CO_2 resulting from H_2O dilution and line broadening effects is $0.012\mathrm{CO}_{2\mathrm{wet}}H$.

The expression above found in Chen et al. (2010) uses the same carbon dioxide spectral line as the five instruments used in this study but a different ${}^{1}\mathrm{H}_2^{16}\mathrm{O}$ line. An additional laboratory test was performed on a specially modified G1301 to obtain the cross calibration of these two spectral lines. This work resulted in the following linear expression:

$$H = 1.021\,33H_{\mathrm{H2O}},$$

where H_{H2O} is the measurement of ${}^{1}\mathrm{H}_2^{16}\mathrm{O}$ used in these five instruments, and H is the H_2O calibrated to the G1301 instruments.

With these two measurements, it is possible to correct the carbon dioxide data reported by the instrument to obtain the dry mole fraction when the instrument is measuring the ${}^{1}\mathrm{H}_2^{16}\mathrm{O}$ line. To correct the data that are collected when the instrument was measuring the HDO line (nearly all of the results reported here), we generated an empirical correction factor using in situ data collected at West Branch with a modified instrument running in a mode where both water lines were scanned. This correction is described in greater detail in section 3e.

c. *Deployment details*

The initial laboratory CO_2 calibration was used for the duration of the project, with further field calibration performed at each site using two NOAA/ESRL CO_2 calibration standards (see Table 1 for calibration tank values) sampled every 20 h for 10 min each. The field standards were prepared by NOAA–ESRL (and thus contain near-atmospheric values of CO_2 isotopic ratios) and were calibrated at PSU. Predeployment tests sampling a tank for 5 days indicated typical drifts of 0.004 ppm day^{-1}; thus, quasi-daily calibrations are sufficient for the purpose of correcting for drift. The 20-h field calibration cycle was chosen such that the calibration time propagated throughout the day in order to detect time-of-day-dependent calibration errors; none were detected. As for the length of time to sample each of the calibration tanks, Allan variance (Allan 1966) plots of 5-day predeployment tank tests indicate an optimal calibration averaging time of 30–60 min. However, 2σ

TABLE 1. Location, elevation, installation date, sampling heights, and calibration tank values for the PSU WS-CRDS sites during the MCI.

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 2007	27 Apr 2007	30 Apr 2007	1 May 2007	29 Jun 2007
Sampling heights (m AGL)	30/140	30/110	30/122	30/110	30/122
Calibration tank values (ppm CO_2)	360.84 and 395.48	361.00 and 396.14	361.82 and 417.40	337.76 and 364.16	360.54 and 422.89
Picarro CADS serial number	CADS05	CADS06	CADS01: April–May 2007 CADS07: May 2007–November 2009	CADS03: May–June 2007 CADS01: June–October 2007 CADS09: October 2007–November 2009	CADS08: June–October 2007 CADS10: October 2007–November 2009

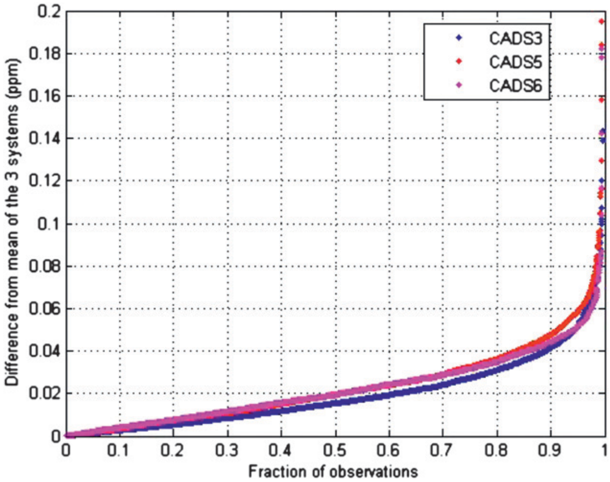

FIG. 1. The CO_2 mixing ratio cumulative difference from the mean of the three WS-CRDS systems available for testing. All units sampled from a 4-l buffer volume during a 3-day laboratory test. No further calibrations were performed beyond the initial characterization. Results shown are 1-min averages.

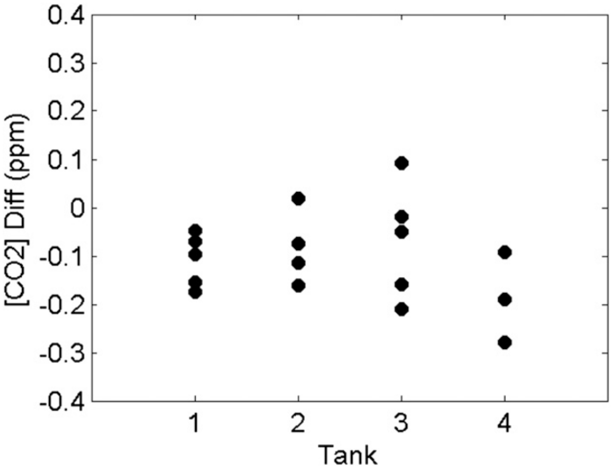

FIG. 2. Differences between calibrated results and known values (measured − known) for each PSU site during a round-robin test completed in February 2008. Tanks 2 and 4 were not tested at Round Lake and unequilibrated tests are not shown. The CO_2 levels are 338.81, 369.39, 401.68, and 431.78 ppm for tanks 1, 2, 3, and 4, respectively.

of even the native (1.5 s) data are within 0.06 ppm of the mean and, as the averaging time is increased, 2σ of the averages are within 0.03 ppm for 3-min averages. We chose a 10-min calibration sampling time in order to allow more-than-sufficient time for transitions. For each day, the mean of the residuals of the two tanks was used to correct for the zero drift of the instrument. Although it is likely that the slope and zero of the linear calibration drifted over the deployment period, the error associated with correcting with an offset rather than a slope and offset is small (e.g., 0.03 ppm at Kewanee and 0.02 at Mead over a 370–400 ppm range). In addition, a zero drift correction was chosen over a linear correction because only two calibration tanks were deployed with each instrument. Except during hours in which the field standards were sampled, the upper level (110–140 m AGL, see Table 1) at each site was sampled for 45 min and the lower level (30 m AGL) was sampled for 15 min. Parker, Inc., (Cleveland, Ohio, Part 091-0094-900) valves and ¼″ OD Synflex tubing (Part 1300-04403) from the sample level on the towers to the instrument were used.

Table 1 shows the location, elevation above sea level, installation date, sampling heights, and calibration tank values for all five PSU MCI sites. The deployment strategy was to locate the five WS-CRDS systems at existing communication towers that were at least 100 m tall, with climate-controlled facilities and line power. To enable real-time trouble shooting and daily data downloads, Verizon Wireless cell phone coverage and Airlink Raven Evolution-Data Optimized (EVDO) modems were used.

3. Results

a. Predeployment laboratory testing

In April 2007, prior to field deployment, the performance of the WS-CRDS instruments was assessed via laboratory tests. Three WS-CRDS systems (CADS03, CADS05, and CADS06) sampled indoor air from a 4-L buffer volume for 3 days. The CO_2 mixing ratio varied from 390 to 485 ppm and water vapor ranged from approximately 0.4% to 1%. The difference from the mean of the 1-min averages is less than 0.1 ppm for 98% of the values (Fig. 1).

b. Round-robin field testing

Round-robin tests were performed in February and November 2008, in which four standard tanks that were filled and calibrated by NOAA/ESRL were tested at each of the five PSU MCI sites. The tanks are considered unknowns and corrected using the field standards using the same method applied to atmospheric samples. Results from the February tests are shown in Fig. 2; similar results were obtained from the November tests. Each tank was sampled 2–4 times at each site for 5 min. Tests that, upon postanalysis, did not equilibrate are not included in the mean. The mean difference between the field-calibrated round-robin tanks and the known values is –0.11 ±0.09 ppm.

c. Long-term stability

Errors associated with the use of an HDO line became apparent during the deployment, although the magnitude

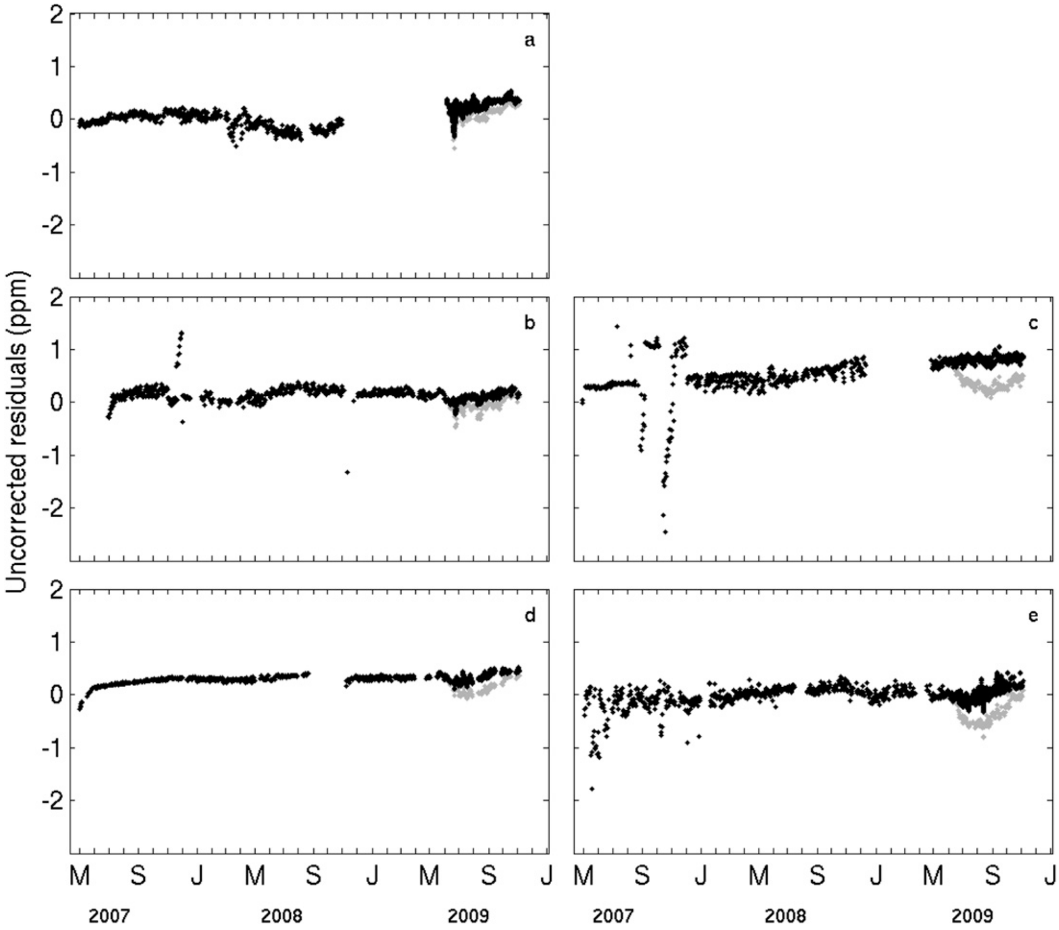

FIG. 3. Residuals (measured − known) for the higher of two NOAA/ESRL field standards sampled every 20 h at (a) Centerville, (b) Galesville, (c) Kewanee, (d) Mead, and (e) Round Lake. These data are used to apply quasi-daily field calibrations. Beginning in June 2009, Nafion dryers humidified the field standards, and the residual values prior to empirical correction are indicated (gray symbols). Large deviations in the residuals on 17–30 Nov 2007 and 2 Nov–3 Dec 2008 at Galesville and 18 Aug–30 Nov 2007 at Kewanee are believed to be associated with errors in the wavelength-tracking algorithms that were corrected by the manufacturer in late 2007.

was not yet determined. In April 2009, Nafion dryers (Permapure, Toms River, New Jersey, Part MD-110-24S-2) with molecular sieves [Air Liquide America Specialty Gases (formerly Scott Specialty Gases, Plumsteadville, Pennsylvania)], to provide dry counterflow, were used to dry the sample air and (slightly) humidify the dry field calibration standards. By June 2009, the molecular sieve was depleted and the field standards were subsequently humidified to the ambient moisture levels, leading to differences between the measurements and known tank values of up to 0.6 ppm (Fig. 3). Moistening the field standards reduces the reported CO_2 between June and November 2009. The error is strongly correlated with the water vapor mixing ratio, and an empirical correction (the quadratic fit of the error as a function of water vapor) was applied to the residuals for June–November 2009 for each site. Note that the equilibration time for Nafion dryers is on the order of days, and therefore the standards and the sample gas had essentially the same water vapor content, thus calibrating out effects of the moist Nafion dryers.

The long-term stability of the WS-CRDS instruments is demonstrated by the residuals for NOAA/ESRL field standards using only the initial, predeployment calibration (Fig. 3). The residuals typically change slowly and do not, in general, have a unidirectional trend over the duration of the deployment. Large deviations in the residuals on 17–30 November 2007 and 2 November–3 December 2008 at Galesville and 18 August–30 November 2007 at Kewanee are believed to be associated with errors in the wavelength-tracking algorithms that were corrected by the manufacturer in late 2007.

After applying the empirical correction for HDO effects, the residuals averaged over the 30-month field deployment are 0.03 ±0.20, 0.16 ±0.16, 0.54 ± 0.40, 0.29 ±0.09, and −0.03 ±0.21 ppm for the Centerville, Galesville, Kewanee, Mead, and Round Lake sites, respectively (Fig. 3). At Kewanee, the calibration shifted by 0.3 ppm upon deployment, contributing to its comparatively large mean residual. Excluding Kewanee, 2σ of the magnitude of the uncorrected drifts are less than 0.38 ppm. By the end of the 30-month deployment, the instruments had drifted by 0.2–0.8 ppm from the initial laboratory calibrations. The measured drifts without field calibrations, while large compared to the WMO target accuracy of 0.1 ppm (WMO 2009), are very small compared to the alternative NDIR systems, which typically drift by 0.3 ppm day^{-1} (Stephens et al. 2011). Even in situations for which accuracy better than 1 ppm is not required, however, field calibrations are still recommended as a means of testing for software and hardware problems.

An estimate of the *calibrated* residuals is given by the magnitude of the median difference between the residuals of the two references gases and is 0.02 ±0.14, 0.07 ±0.13, 0.04 ±0.15, 0.17 ±0.07, and 0.17 ±0.07 ppm for Centerville, Galesville, Kewanee, Mead, and Round Lake, respectively; 95% (2σ) of the points are within 0.20, 0.23, 0.22, 0.32, and 0.38 ppm, respectively.

d. Uncertainty resulting from analyzer drift

Because the tower data are corrected using the 20-h residuals from the NOAA/ESRL field standards, the uncertainty resulting from analyzer drift is related to the change between the field calibrations. For example, if the residual is 0.5 ppm on day 1 and 0.6 ppm on day 2, assuming the instrument drifts steadily in between the measurements, an estimate of the error resulting from drift between calibrations is the difference between the two, or 0.1 ppm. For these data we simply applied the field calibration as a zero shift to the tower data for that day. Probability distributions of the uncertainty resulting from analyzer drift are shown in Fig. 4. The instrument at Mead (CADS07) had significantly less noise than the other instruments; 1σ of the differences between subsequent quasi-daily residuals are less than 0.06 ppm, and 2σ of the differences are less than 0.36 ppm.

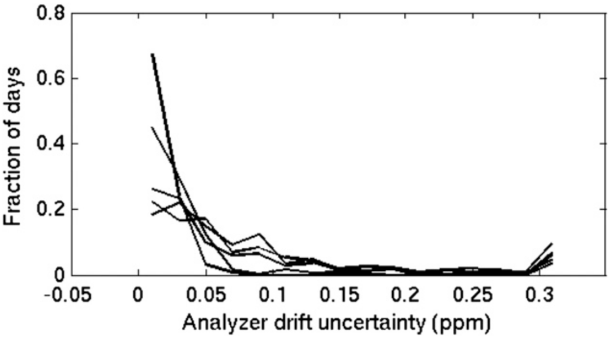

FIG. 4. Probability distributions of the difference between each field calibration and the subsequent field calibration performed 20 h later, as an estimate for the uncertainty resulting from analyzer drift. Shown are probability distributions for each of the five instruments (for the higher of the two field standards). The bin size is 0.02 ppm and the largest bin contains all of the points larger than 0.3 ppm.

e. Comparison of NOAA/ESRL NDIR and PSU WS-CRDS measurements of CO_2 mixing ratio at West Branch

In part to assess the range of isotopic values measured in the region, the Kewanee instrument (CADS05) was, upon the conclusion of the MCI, relocated to the NOAA/ESRL tall tower site at West Branch. The software was also updated to enable the instrument to measure both HDO and H_2O. Shown in Fig. 5 are the CO_2, H_2O, and isotopic ratio between HDO and H_2O. Here the isotopic ratio of HDO to H_2O (δD) is defined in the typical way as

$$\delta D = (R/R_{\mathrm{standard}} - 1) \times 1000,$$

where R is the ratio of HDO to H_2O, and R_{standard} is the international standard reference ratio [Vienna Standard Mean Ocean Water (VSMOW)]. Previous in situ measurements of δD in water vapor have been limited, but recently WS-CRDS and related off-axis integrated cavity output spectroscopy have been evaluated for this use (e.g., Gupta et al. 2009; Wang et al. 2009; Worden et al. 2010). Although Gupta et al. (2009), for example, calibrated δD every few hours with known liquid water standards, the current data were not field calibrated because their primary purpose was to correct the CO_2 mixing ratios. The initial laboratory calibration was performed by measuring water vapor from a room temperature liquid water bubbler containing −62‰ liquid water. A shift of −100 ±20‰ was applied to this calibration because of the known shift in δD upon the evaporation from liquid to vapor (Cappa et al. 2003). Although this shift is an estimate, it affects only the reported δD, not the CO_2. The resulting δD shown in Fig. 5c varies widely, between −280‰ in the winter and −40‰ in the summer, and is highly correlated with the H_2O. These values of δD are reasonably consistent with values typically seen in other studies (e.g., Lawrence et al. 2004). The empirical relationship between the water vapor measured on an H_2O line (H_{H2O}) and that measured on an HDO line and converted to H_2O (H_{HDO}) is found to be (Fig. 6a)

$$H_{\mathrm{H2O}} = -0.029H_{\mathrm{HDO}}^{2} + 1.0H_{\mathrm{HDO}} + 0.028.$$

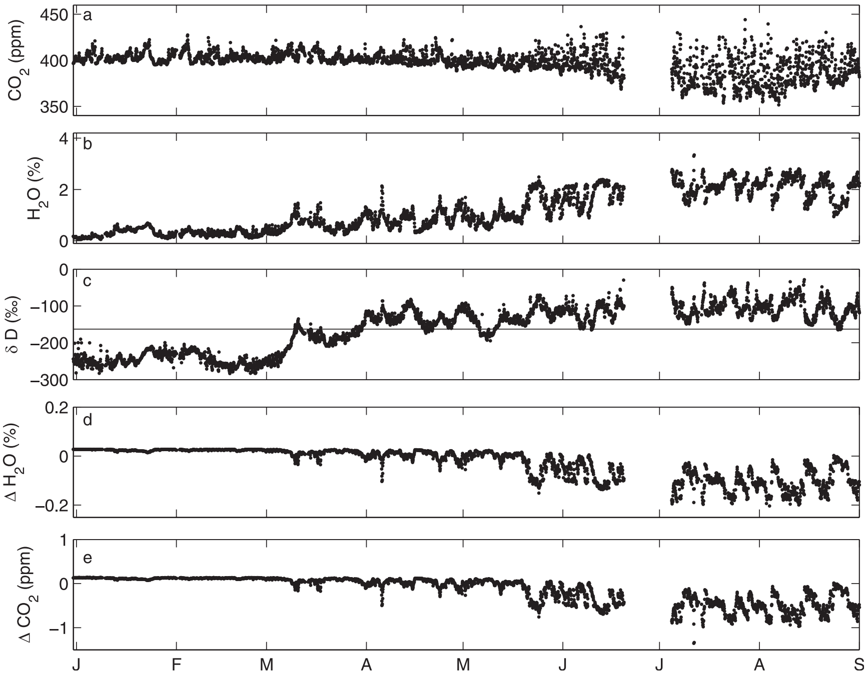

FIG. 5. The (a) CO_2 mixing ratio measured at West Branch for January–August 2010 at 99 m AGL; (b) H_2O mixing ratio; (c) HDO/H_2O isotopic ratio, where the horizontal line indicates the value of isotopic ratio of the laboratory calibration (−162‰). Beyond the initial laboratory calibration on a single instrument, the water measurements are uncalibrated. (d) Corrections to the reported water vapor and (e) carbon dioxide resulting from the empirical HDO correction are unique to this dataset.

This relationship was applied as part of the conversion from $CO_{2\mathrm{wet}}$ to $CO_{2\mathrm{dry}}$ described in section 2c. This empirical relationship derived directly from the observations captures the tendency of HDO to be enhanced at high levels of humidity, which, if uncorrected, would cause a tendency toward overestimation of the water vapor concentration at high humidity levels. A shift of +100‰ in δD, as an extreme example, results in 10% error in the reported water vapor, leading to a CO_2 correction of 1.4 ppm at 400 ppm CO_2 and 3% H_2O. The corrections to the reported water vapor and carbon dioxide resulting from the empirical HDO correction unique to this dataset are shown in Figs. 5d,e. Throughout the deployment, 95% (2σ) of the δD corrections to the hourly data are less than 0.4 ppm in magnitude. A random residual resulting from noise in the relationship between HDO and H_2O remains (Fig. 6a); 95% of the residuals induce an error of less than 0.3 ppm CO_2, using the relationship $0.012CO_{2\mathrm{wet}}H$ (Fig. 6b). While the empirical correction reduces the average magnitude of error by only a small amount, prior to the correction the error is a seasonally dependent bias, whereas afterward it is a random error.

We compare the CO_2 mixing ratio data after applying the isotopic ratio correction for January–September 2010. The NOAA/ESRL NDIR and PSU WS-CRDS data are independently quality controlled. The flow rate of the NOAA/ESRL measurement is ~8 L min^{-1}, while that of the PSU WS-CRDS systems is ~200 mL min^{-1}. Five-minute samples are used for both despite this difference in flow rate. The hourly daytime-only difference (PSU − NOAA) measurements at West Branch are shown in Fig. 7a. While the median difference (−0.12 ppm) is near the WMO recommended limit of 0.1 ppm for CO_2 (WMO 2009), the standard deviation is large, at 1.37 ppm. On a daily time scale (daytime only), the median difference is −0.13 ±0.63 ppm (Fig. 7b).

The total uncertainty includes atmospheric variability as well as measurement uncertainty and scale uncertainty (0.07 ppm). Over the duration of the comparison, the median of the hourly daytime-only NOAA/ESRL total uncertainty estimates is 0.13 ±0.68 ppm (Fig. 7c), with no clear seasonal dependence. Over the comparison as a whole, the median difference between the measurements is about the same as the median NOAA/ESRL uncertainty estimate.

The difference between PSU and NOAA/ESRL measurements tends to be larger during the growing season, when there are large deviations in CO_2 mixing ratio and higher humidity levels. Considering only 1600–1700 LST,

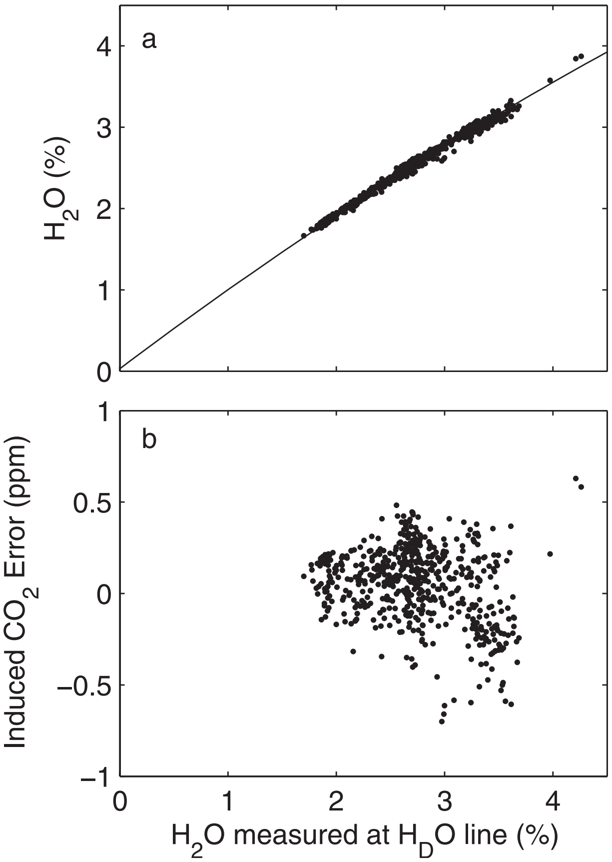

FIG. 6. (a) The random residual resulting from noise in the relationship between HDO and H_2O. (b) CO_2 error resulting from noise in the relationship between HDO and H_2O.

in order to sample when the atmosphere is well mixed and stable with time, the median of the differences is −0.33 ±0.83 ppm for July–August.

There are several factors that may contribute to the differences between the NDIR and WS-CRDS measurements at West Branch. There was a large difference in flow rates between the two instruments—approximately a factor of 50—compounding small errors in timing. Although the lag of maximum correlation changed by about 15 min from the beginning of the comparison to the end, for the sake of simplicity a single time shift was applied to the entire dataset to account for the difference in timing between the two systems. The MCI region is largely agricultural, with the local region surrounding West Branch being dominated by corn (Miles et al. 2012). Large local fluxes cause large deviations in CO_2, accentuating the small differences in timing and affecting the comparison of the two measurements.

For comparison, the 1992–99 NOAA–Commonwealth Scientific and Industrial Research Organisation (CSIRO) flask air intercomparison experiment indicated differences of 0.2 ±0.2 ppm for biweekly measurements at Cape Grim (Masarie et al. 2001), Australia. With predominant winds transporting well-mixed air over the Southern Ocean to the station, the range of CO_2 values was much smaller (<5 ppm seasonal drawdown) than that of the MCI region, reducing the effects of timing differences compared to the current study.

4. Conclusions

The WS-CRDS instruments deployed during the Mid-Continent Intensive measured both carbon dioxide and water vapor, and used the water vapor measurement to correct the CO_2 for water vapor interference effects, including dilution and overlapping absorption bands. The H_2O measurement in this early version of the WS-CRDS was made at a HDO line, however, necessitating corrections during postprocessing; drying the air sample (e.g., via Nafion dryers) would have simplified data postprocessing, although we do not feel it is necessary in the current WS-CRDS instrument measuring CO_2 and CH_4 (G2301). If the sample is dried using Nafion dryers, then we plumb the system such that the calibration air also passes through the dryer. This both equilibrates the sample and calibration gas moisture levels to a similar value and provides a test for leaks in the drying system. If applying the water vapor correction to the carbon dioxide value, then it is recommended to perform periodic tests using moistened calibration gas to ensure data quality. Quasi-daily (20 h) measurements of field standards show that long-term instrument drift is less than 0.38 ppm (2σ) over a 30-month period. After applying a field calibration in which known tanks are sampled every 20 h, residuals from known values are, depending on the site, from 0.02 ±0.14 to 0.17 ±0.07 ppm. Finally, a comparison with NOAA/ESRL measurements at West Branch for 8 months shows a median daytime-only difference of −0.13 ±0.63 ppm on a daily time scale.

Other techniques to continuously measure CO_2 at remote, tower-based locations, including the two-cell NDIR-based method employed at the NOAA/ESRL towers and the single-cell NDIR-based method (e.g., http://www.raccoon.ucar.edu and amerifluxco2.psu.edu), are not commercially available as a completed unit. In addition, both require frequent calibration (on hourly instead of daily orders). The use of the WS-CRDS systems simplifies instrument development and deployment (i.e., there is no need to construct the system or use as many field calibration standards), but the up-front cost is higher. Stephens et al. (2011) points out that the benefits of laser-based instruments such as WS-CRDS may often outweigh their greater initial cost because of their better stability, more moderate calibration requirements, and

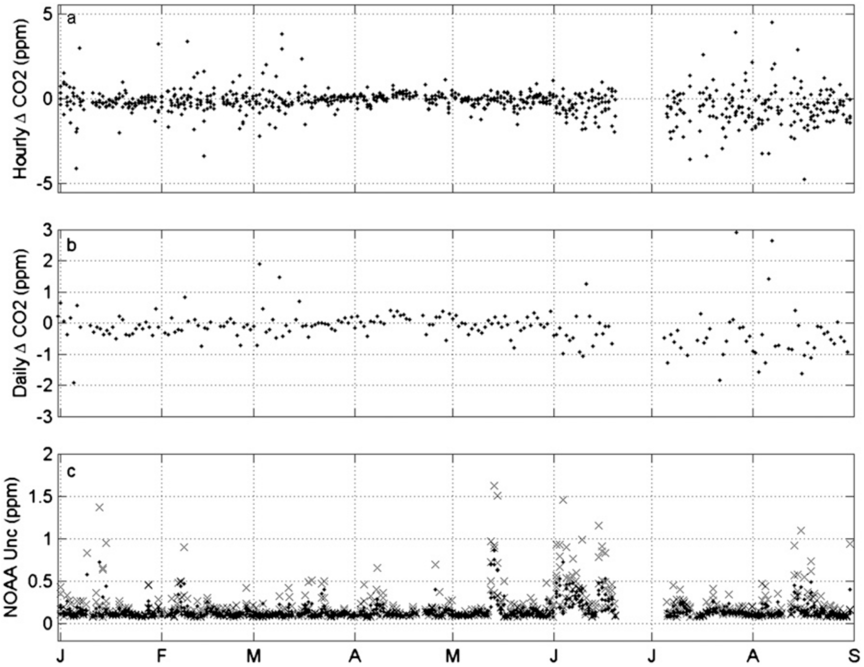

FIG. 7. (a) Daytime-only hourly differences between NOAA/ESRL NDIR and PSU WS-CRDS measurements of CO_2 mixing ratio for January–August 2010 at West Branch at 99 m AGL. (b) As in (a), but on a daily time scale. (c) NOAA/ESRL daytime-only hourly total uncertainty estimates (×) and daily mean total uncertainty (·). Note that three to five points in each subplot are outside of the range.

stable ancillary H_2O measurement, thereby enabling a moist air sample measurement.

The commercialization of WS-CRDS has made practical CO_2 measurement networks of unprecedented density (Lauvaux et al. 2011). Including two NOAA tall towers at West Branch, Iowa, and Park Falls, Wisconsin; The Pennsylvania State University/University of Missouri Ameriflux tower at Ozarks, Missouri; and the University of Minnesota Rosemount tower, there were nine towers within a 500 km × 800 km domain during the MCI.

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