Atmospheric Measurement Techniques Discussions

Atmospheric CO$_2$ monitoring with single-cell NDIR-based analyzers

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B. B. Stephens et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶▮

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

We describe CO$_2$ concentration measurement systems based on relatively inexpensive single-cell non-dispersive infrared CO$_2$ sensors. The systems utilize signal averaging to obtain precision (1-σ in 100 s) of 0.1 parts per million dry air mole fraction (ppm), fre-
5 quent calibrations and sample drying in order to achieve state-of-the-art compatibility, and can run autonomously for months at a time. Laboratory tests indicate compatibility among four to six systems to be ±0.1 ppm (1-σ), and field measurements of known reference-gases yield median errors of 0.01 to 0.17 ppm with 1-σ variance of ±0.1 to 0.2 ppm. From May to August 2007, a system co-located with a NOAA-ESRL
10 dual-cell NDIR system at the WLEF tall tower in Wisconsin measured daytime-only daily averages of CO$_2$ that differ by 0.26 ± 0.15 ppm (median ± 1 σ), and from August 2005 to April 2011 a system co-located with weekly NOAA-ESRL network flask collection at Niwot Ridge, Colorado measured coincident CO$_2$ concentrations that differed by −0.06 ± 0.30 ppm ($n = 585$). Data from these systems are now supporting a wide range
15 of analyses and this approach may be applicable in future studies where accuracy and initial cost of the sensors are priorities.

1 Introduction

Use of atmospheric CO$_2$ concentration measurements to estimate CO$_2$ fluxes has become finer scale in recent years, moving from global scale with coarse-resolution mod-
20 els (e.g., Enting et al., 1995; Fan et al., 1998; Bousquet et al., 2000; Gurney et al., 2002), to continental (Peylin et al., 2005; Peters et al., 2007, 2010; Schuh et al., 2010) and finer regional scales (Matross et al., 2006; Tolk et al., 2009; Lauvaux et al., 2009). Current attempts to infer surface CO$_2$ fluxes from concentration measurements are limited by both errors in modeling atmospheric transport (Lin et al., 2004; Stephens et
25 al., 2007; Houweling et al., 2010) and sparseness in the available data (Gurney et al., 2002; Butler et al., 2010).

The compatibility (see definition in WMO, 2011) requirements for useful CO$_2$ concentration data are demanding. For example, comparing two sites at 500 km spacing, assuming an average wind speed of 5 m s^{-1} and an average mixing depth of 1.5 km, a bias at one site of 0.2 parts per million dry air mole fraction (ppm) would result in an error of 50 g C m^{-2} yr^{-1} in inferred fluxes. By comparison, annual terrestrial ecosystem flux magnitudes averaged over 10^6 km regions of North America are thought to range from 0 to 120 g C m^{-2} yr^{-1} (Peters et al., 2007; CarbonTracker, 2010). For this reason, continental CO$_2$ concentration measurements are commonly undertaken with a goal of 0.1 ppm compatibility, which is also consistent with the long-standing WMO goal for Northern Hemisphere laboratories (WMO, 2011).

With the exception of a few long-running continuous instruments (Keeling et al., 1960; Lowe et al., 1979; Peterson et al., 1986), the majority of atmospheric CO$_2$ measurements have historically come from flask-collection programs. The few long-running high-accuracy in situ CO$_2$ measurements, and those deployed in increasing numbers over the past 15 years, have primarily been achieved using analyzers based on dual-cell nondispersive infrared (NDIR) spectroscopic gas sensors (e.g., Bakwin et al., 1995; Zhao et al., 1997; Trivett and Kohler, 1999) that are relatively expensive and require fairly intensive calibration schemes.

In the mid-2000s, we began developing and deploying alternative measurement systems, based on a relatively inexpensive NDIR sensor. In comparison to more expensive models, this sensor has a single detection cell, non-focusing optics, no chopper motor, and no gas-filter cells, but does require the same level of calibration effort and greater signal averaging. Since 2007, laser-based instruments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) and off-axis integrated cavity output spectroscopy (ICOS) have become commercially available and have been field tested (Winderlich et al., 2010; Richardson et al., 2011; WMO, 2011). These CO$_2$ instruments have much better stability than NDIR sensors, with the benefit of more moderate calibration requirements, and with stable ancillary H$_2$O measurements provide the possibility of measuring moist sample air. The initial cost of these laser-based

instruments is, however, greater.

We anticipate that the benefits of the new laser-based instruments will often outweigh their greater initial cost and will lead to their increasing use in atmospheric CO_2 monitoring. However, it is important to describe and report the performance of current
NDIR systems because (1) data from these systems are supporting a wide range of analyses and publications (Obrist et al., 2008; Burns et al., 2009, 2011; De Wekker et al., 2009; CarbonTracker, 2010; Strong et al., 2011; Miles et al., 2011; Brooks et al., 2011), (2) a number of these systems are still operating in the field and will continue to do so for years to come, and (3) systems like these may still find favor over laser-based
systems in applications where initial cost is a priority, and (4) many of the gas-handling, sample drying, calibration, and intercomparison issues we discuss are relevant to any atmospheric CO_2 measurement system regardless of sensor type.

In this paper, we describe two similar systems developed in loose collaboration, one at The Pennsylvania State University referred to here as the PSU system, and one at
the National Center for Atmospheric Research (NCAR) referred to here as AIRCOA (autonomous inexpensive, robust, CO_2 analyzer; Stephens et al., 2006). We also present examples of their performance as assessed through laboratory tests and both laboratory and field intercomparisons. In the United States, versions of these systems are currently operated by PSU at Ameriflux sites located in Canaan Valley (WV), Chest-
nut Ridge (TN), Missouri Ozarks (MO), and Mead (NE), and operated by NCAR as part of the Regional Atmospheric Continuous CO_2 Network in the Rocky Mountains (Rocky RACCOON, raccoon.ucar.edu) at Fraser Experimental Forest (CO), Niwot Ridge T-Van Site (CO), Storm Peak Laboratory (CO), Hidden Peak (UT), and Roof Butte (AZ). Instruments based on the designs described in this paper are also deployed in Oregon
(Göeckede et al., 2010) and at Morgan-Monroe State Forest (IN) (Schmid et al., 2000).

2 Methods

Both the PSU and AIRCOA systems and their calibration schemes were based in concept on those described by Bakwin et al. (1995), Zhao et al. (1997), and Trivett and Kohler (1999) but with design changes to lower the cost and size of the systems to
5 facilitate their deployment in multiple-system networks, while maintaining compatibility within these networks and to the WMO CO_2 scale (WMO, 2011). We first describe the PSU system, including elements common to AIRCOA, in detail, and then describe differences in the AIRCOA system. We also note differences between two versions of the PSU design. We next describe the two similar calibration strategies, and then present a
10 list of potential sources of noise or systematic bias in atmospheric CO_2 measurements along with brief statements of how we have addressed them.

2.1 PSU measurement system description

Figure 1a shows a schematic of the sampling and measurement components of the PSU system. Air is drawn from a single inlet through 4.3 mm ID polyethylene-lined
15 tubing (Eaton Corp, Synflex model 1300-04403) to ground level using a DC brushless micro-pump (KNF Neuberger, Inc., model NMP015B). The air is filtered using a 1-µm filter (Pall, model 4003). The flow rate is adjusted to about 150 cc min^{-1} using a miniature inline regulator (Beswick Engineering, model PRD-3N1-0-VIX) and needle valves (Swagelok, model B-1RS4-A). One needle valve, immediately upon entering the
20 enclosure from the tower, adjusts the sample line pressure and the other, preceding the CO_2 analyzer, makes a further adjustment of both the calibration and sample gas flows. The flow rates are monitored at the upstream and downstream ends of the system with flow meters (Honeywell, model AWM3300V). Three-way valves (Numatics, model TM101V12C2) are utilized to select between the sample and calibration gases. The
25 valve manifold for the calibration gases blocks one port on each valve such that they function as 2-way on/off valves. The regulators on the calibration gases are two-stage (Scott-Specialty, model 14B; Air-Liquide, model Alphagaz 1001) set to deliver 0.6 atm,

similar to the delivery pressure of the micro-pump. The sample air is purged when the calibration cylinders are being analyzed; a needle valve on the sample valve manifold (Beswick Engineering, model NLV-10-2-V) ensures that the flow from the tower and pressure in the Nafion drier remains constant.

Two 2.44 m by 2.8 mm ID Nafion driers (Perma Pure, model MD-110-96) are used in series, the first to dry the sample air and the second to further dry the sample air and to slightly moisten the calibration gases. We use the measured gas as the counter flow purge on the Nafion driers, after it has been dried prior to each stage by molecular sieve 13X. Most of the moisture in the ambient air exits the first Nafion without ever reaching the molecular sieve driers. We use 200 ml molecular sieve driers which last 6 to 18 months depending on outside humidity. Typical moisture levels at the sensor are 2600 ± 800 ppm as measured by a T/RH sensor (Campbell Scientific, model CS500-l, a modified version of a Vaisala Humitter 50Y). Measured differences of H_2O concentration between the sample and calibration gases are less than 100 ppm.

The CO_2 levels are measured using a single-cell sensor employing NDIR absorption spectroscopy (LI-COR, model LI-820). The LI-820 actively and precisely controls the optical bench to 50 °C and has good stability with respect to ambient temperature of around 0.1 ppm °C^{-1}. The LI-820 also provides a measurement of cell pressure and applies its own internal concentration-dependent pressure correction. We set the LI-820 to use an internal 0.5 Hz digital filter and then record values at 1 Hz. The sensor has unfiltered 1-σ noise of 1.0 ppm in 1 s, which averages to 0.1 ppm over 100 s. Following the LI-820 is a normally-open two-way valve (Numatics, model LS02LS00V), used for leak-checking purposes.

The components are mounted on an L-shaped backplane in an enclosure. The enclosure, operating typically in a climate-controlled environment, is temperature controlled to 30 °C (Minco, models CT15021, HK5174R294L12B, and S665PDZT24B), with a fan to minimize temperature gradients. Daytime temperatures do, however, frequently exceed the set-point in the summer; temperatures can thus vary by 0.0 ± 1.3 °C between calibrations. Choosing a higher set-point could be advantageous, but may

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

adversely affect the electronics. The Missouri Ozarks system does not have active temperature control, but is in a temperature-controlled building. The temperature variations between calibrations are similar to the actively controlled sites. Flow restrictions downstream of the LI-820 are minimal and sample cell pressure is closely tied to ambient. Pressure differences in the LI-820 cell between calibration gases and sample air in the field are typically less than 0.1–0.3 kPa. Pressure differences in the LI-820 cell between subsequent calibrations are 0.0 ± 0.3 kPa. A data logger (Campbell Scientific, model CR10X) is used for data acquisition and system control.

We make considerable efforts to minimize and monitor system leaks. Because of silicone seals in the LI-820, plastic fittings and viton o-rings on the Nafion driers, viton seals in the solenoid valves and manifolds, and plastic and viton seals in the micropump it is not practical to completely eliminate them. Automated leak tests are performed following every calibration cycle, both at high pressure for leaks to ambient air using the entire system volume ($\sim$40 ml) and at ambient pressure for leaks of calibration gases through the valves using the volume downstream of the valve manifold ($\sim$25 ml), with a goal in both cases that the pressure changes be less than 0.05 kPa min^{-1}. In the case of a leak of calibration gas through a valve, with concentration 100 ppm higher than ambient and a sample flow rate of 100 ml min^{-1}, this magnitude of leak would cause a bias of 0.01 ppm.

A "target" cylinder with a known CO_2 concentration is sampled every hour, and must be replaced every 9–12 months, while an "archive" cylinder is sampled daily and is expected to last 20 years. Calibration, target, and archive cylinders are sampled for 2.5–5 min, and 1 min of data following the valve is ignored while the system flushes. Data is transferred electronically on a daily to weekly basis and we process and display the data and system diagnostics on an ongoing basis. Problems such as pump failure, LI-820 source failure, and target cylinder depletion can then be remedied quickly. The final data is subjected to automated and manual quality control.

Results from "PSU Version 1" systems are presented in Sects. 3.1 and 3.3. These systems did not incorporate the automated leak tests or target and archive cylinders.

Also, the systems used nitrogen as a Nafion purge gas and did not have temperature control of the enclosure. Results from "PSU Version 2" systems are presented in Sect. 3.2.

2.2 Differences in AIRCOA system

Figure 1b shows a schematic of the sampling and measurement components of the AIRCOA system. This system is similar to the PSU system described in Sect. 2.1, with some notable differences. The AIRCOA system samples air from three or five heights on a tower (three-inlet version shown in Fig. 1b) and thus has a second valve manifold to select among inlet lines. The AIRCOA sample flow is somewhat slower, at $100\,\text{ml min}^{-1}$. The AIRCOA system purges all sample lines not in use at 500 to $1000\,\text{ml min}^{-1}$ using a brushless DC diaphragm pump (KNF Neuberger, model N89), and like the PSU system purges the upstream Nafion drier with sample air at its normal pressure and flow when calibration gas is being analyzed. The sample inlets include 30-µm polypropylene filters (Millipore, model AN3H04700) in polypropylene filter holders (Cole-Palmer, model A-06623-22), but with additional 5-µm metal filters (Beswick Engineering, CF-1010-05) immediately upstream of the sample needle valves, solenoid valves, and inline regulator and a 40-µm metal filter (Beswick Engineering, CF-1010-40) before the downstream leak-check valve. The micropump is a custom project version of the same pump specified to be leak tight (KNF project number MPU1870-NMP015).

The needle valves used are smaller (Beswick Engineering, NVL-10-2), with the exception of the main flow-control valve (Swagelok, B-SS2), the solenoid valves are all one type (Numatics, model TM101V12C2), and the T/RH sensor is from a different vendor (Vaisala, model Humitter 50Y). Laboratory tests show lower humidities at the LI-820 of 350–650 ppm with inlet dew points of 10–26 °C, and any humidity differences between sample and calibration gases downstream of the LI-820 are below the detection limit of the sensor. These lower humidities may in part result from slower flow rates

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Atmospheric CO$_2$ monitoring with NDIR-based analyzers

B. B. Stephens et al.

and lower ambient pressure, while the lack of measurable humidity differences may result from shorter calibration gas cycles.

A long-term surveillance gas is sampled through the entire AIRCOA inlet system to detect problems with the system, and especially any problems with the first stage of the drying system. The regulator on this cylinder is set to approximately 20 kPa above ambient and a needle valve is used to match sample pressures in the first Nafion drier. This long-term surveillance gas is measured every 8 h.

The AIRCOA system switches the gas being analyzed every 150 seconds and the data-processing software ignores the first 50 seconds after each switch to allow for flushing of gases through the system. The system cycles between the 3 (or 5) inlet lines on a 7.5 (or 12.5) min schedule. The data-processing software makes a calculation based on measured flows of how long the sample gas takes to get from the inlet to the sample cell and adjusts the times of reported measurements accordingly. A PC104-based computer running Linux performs automated data acquisition and valve control. With the exception of the Niwot Ridge site, the AIRCOA do not control the temperature of the instrument enclosure.

The AIRCOA data-processing software uses measured temperature variations and changes in pressure during leak checks to define monthly empirical temperature and concentration-dependent pressure effects on the LI-820 data. Analysis of calibration cycles has shown a consistent memory effect due to inadequate system flushing of -7×10^{-4} ppm/Δ-ppm, where Δ-ppm is the change in concentration from the previous to the current 2.5 min measurement. We apply corrections for these empirically derived temperature, pressure, and flushing effects to all AIRCOA data before fitting the reference-gas calibration curves.

Over the past 6 years, several AIRCOA have experienced water-ingestion events during wet weather conditions, which has necessitated replacing the Nafion dryers and cleaning the LI-820. It is not clear if liquid water entering the inlet or condensation within the instrument is at fault, but we are considering the addition of hydrophilic filters upstream of the driers to prevent this in the future.

Full Screen / Esc

We access this system through a dedicated internet connection and retrieve, process, and display data and system diagnostics in near real time. If any of the automated diagnostics suggest a problem, we are then able to perform more detailed troubleshooting interactively. This direct connectivity and rapid processing is invaluable for maintaining the systems and producing high-quality CO$_2$ measurements.

2.3 Calibration using field standards

Even with internal or post-processing temperature and pressure compensation, the LI-820 CO$_2$ calibration typically drifts by 0.3 ppm day^{-1} with fluctuations of similar magnitude possible over several hours. Thus, frequent calibration is necessary to characterize and remove changes in the zero, slope, and nonlinear components of the sensor calibration, as well as to minimize the effects of unaccounted pressure and temperature effects. Four field standards, contained in high-pressure aluminum cylinders with brass, packless, taper threaded valves (Ceodeux), are measured every 4 h by the systems for 2.5 min each. Depending on site access, these cylinders are either 10 or 30 l. The PSU standards nominally span 335–435 ppm, while the AIRCOA standards nominally span 360–480 ppm. These four known values are used to develop a second-order linear regression between the LI-820 output and CO$_2$ concentration. Both systems alternate the sequence of the 4 gases to detect and characterize any problems associated with dead-volumes or incomplete flushing of the LI-820 cell. Every 30 min the AIRCOA systems also analyze one of the four calibration gases to estimate short-term drift in the LI-820 zero offset.

The field standards are purchased from Scott-Marrin Inc. and calibrated with respect to the WMO CO$_2$ scale by laboratory comparison to other cylinders following the general methods and practices recommended by WMO (2011). At PSU, this is done using four NOAA-ESRL-calibrated standards with a LICOR-7000, while at NCAR six NOAA-ESRL-calibrated primary cylinders are used to calibrate five in-house secondary standards, which are then used to calibrate field-standards with a Siemens Ultramat 6F. Drift in cylinder CO$_2$ concentration can be significant (Kitzis, 2009; Langenfelds et al.,

2005). The drifts reported by Kitzis (2009) are typically less than 0.02 ppm yr^{-1}, but some cylinders can exhibit drifts of greater than 0.045 ppm yr^{-1}. We nominally stop using field standards when they reach 20 atm in pressure, calibrate them in laboratory before and after use, and interpolate these calibrations in time to minimize drift effects. The AIRCOA systems generally have the cylinders oriented horizontally, which is known to minimize drift (Keeling et al., 2007).

In the 4th World Meteorological Organization round-robin reference gas intercomparison (WMO, 2009), the PSU values differed from the NOAA-ESRL averages by +0.05, −0.04, and −0.05 ppm and the NCAR values differed from the NOAA-ESRL values by +0.04, 0.00, and 0.01 ppm for the three tested cylinders. Note that we compare to the NOAA-ESRL measurements closest in time, rather than the mean over 5 to 6 years as was done in the WMO report (WMO, 2009), because the round-robin cylinders drifted by up to 0.1 ppm over this period. Based on these results and repeatability measured in the laboratory, we assess the uncertainty in assigning concentrations to our field standards to be less than 0.1 ppm.

As a large portion of the CO$_2$ in the Scott-Marrin-purchased field standards is derived from natural gas extraction, the isotopic ratio differs from natural air, with ^{13}C ratios typically in the range of −30 to −40 ‰. In this case, if the field measurements are made using a sensor that has a different ^{13}CO$_2$ sensitivity than that used for laboratory transfer calibrations, biased measurements may result (Lee et al., 2006). LiCor NDIR analyzers are approximately 1/3 as sensitive to ^{13}CO$_2$ as they are to ^{12}CO$_2$ (McDermitt et al., 1993). For the PSU system, with field standards calibrated and used on two different LiCor sensors, this is likely not a factor, but for the AIRCOA system, with field standards calibrated on a Siemens Ultramat 6F that is essentially blind to ^{13}CO$_2$ (Lee et al., 2006), this effect requires a correction of approximately −0.04 ppm to field measurements. This correction is smaller than that reported by Lee et al. (2006) because we are comparing to an analyzer with 1/3 rather than 100 % ^{13}CO$_2$ sensitivity and we are not considering offsets in ^{18}O. Laboratory tests have confirmed the sign and approximate magnitude of this effect, but to date our corrections have relied on assumed

^{13}C values for CO$_2$ in the field standards, and have not included potential ^{18}O differences. Future plans call for measuring the ^{13}C and ^{18}O of CO$_2$ in all field standards. Laser-based CO$_2$ sensors are usually blind to ^{13}CO$_2$ and also require consideration of isotopic biases or the use of NOAA-ESRL calibration cylinders with near-ambient levels of ^{13}CO$_2$, as in Richardson et al. (2011).

2.4 Potential causes of measurement error and their solutions

Here we briefly summarize the potential sources of instrument noise and bias that we have considered in the design of our systems, and how we have addressed them.

2.4.1 Short-term LI-820 noise

We average for ≥100 s to get 1-σ precision on sample-air and calibration measurements of ±0.1 ppm or better.

2.4.2 Drift in LI-820 sensitivity

We use 4-hourly 4-point calibrations, and for the AIRCOA systems also 30-min 1-point calibrations.

2.4.3 Drift in LI-820 pressure sensitivity

As the LI-820 calibration drifts, its internal pressure correction becomes less accurate. The AIRCOA system applies an additional empirical pressure correction based on observed effects during automated leak checks. These corrections are typically around 0.5 ppm kPa^{-1}, but differences in LI-820 cell pressure between the sample and calibration gases is typically 0.2 kPa or less, limiting the correction to 0.1 ppm.

2.4.4 Drift in LI-820 temperature sensitivity

The PSU system controls the temperature of the instrument enclosure to 30 °C, with changes between calibrations of 0.0 ± 1.3 °C. The AIRCOA system applies an additional empirical temperature correction derived monthly from calibration gas and temperature measurements inside the enclosure but outside the LI-820. These corrections are typically around -0.1 ppm °C^{-1}, even though the LI-820 optical bench itself is temperature controlled. The errors associated with uncorrected temperature variations in PSU Version 2 systems are estimated to be 0.0 ± 0.07 ppm. For PSU Version 1 systems exposed to outdoor temperature variations (notably the NOAA-ESRL comparison at WLEF), large temperature changes not captured by the 4-h calibration cycle may have resulted in errors in CO_2 of 0.25 ppm.

2.4.5 Leaks through fittings and valves

The systems perform automated sealed positive pressure and ambient pressure checks to monitor and detect leaks to ambient and leaks of calibration gases through solenoid valves. We also filter sample air to minimize small particles from affecting solenoid valve seals.

2.4.6 Incomplete drying of air

We use relatively slow flow (100 to 150 ml min^{-1}) and two stages of 2.44 m Nafion driers. We also measure relative humidity downstream of our CO_2 sensor to verify drier performance and monitor mole-sieve saturation.

2.4.7 Incomplete flushing of cell or dead-volumes

We avoid very slow flow and ignore 50 to 60 s of data after switching between sample or calibration gases. We plumb solenoid manifolds such that air exhausts from both ends and flushes the entire manifold regardless of position selected. Both systems

alternate the sequence of calibration gases to check for memory effects in the sensor. In AIRCOA data post-processing, we apply an empirical correction equivalent to +0.07 ppm following a step change of +100 ppm.

2.4.8 Drying system affecting CO_2

We maintain constant pressures and flows in the Nafion driers, and avoid large humidity changes when switching between calibration and sample gases, in order to minimize surface interactions that may affect CO_2 concentrations. We also use Nafion purge flow gas with ambient CO_2 levels in case of leaks between the sample and purge streams. The maximum difference in H_2O between the PSU system sample and calibration gases of 100 ppm corresponds to a dilution error in CO_2 concentration of 0.03 ppm.

2.4.9 Other plastics affecting CO_2

We minimize changes in pressure at the AIRCOA inlet filter holder and other plastic components to avoid transients associated with CO_2 absorption and desorption.

2.4.10 Calibration gases made with synthetic air

We use calibration gases with bulk natural air that includes ambient levels of O_2 and Ar to prevent differential pressure-broadening of the IR absorption features, and we either use laboratory calibration and field instruments with similar $^{13}CO_2$ sensitivities (PSU), or we apply a correction for non-ambient $^{13}CO_2$ levels in calibration gases (AIRCOA).

2.4.11 Regulator temperature effects

Laboratory tests suggest such effects are negligible for our selected regulators and ambient temperature fluctuations.

2.4.12 Regulator flushing effects

We analyze all calibration gases frequently, to minimize stagnation effects that may result from surface or elastomer interactions in the regulators. Laboratory tests suggest this effect is negligible for our calibration gas frequencies, however it may still have an influence on less-frequently analyzed surveillance gases.

2.4.13 Drift in field calibration cylinders

We measure our field cylinders before and after use and interpolate these values in time. We also nominally stop using field cylinders when they have reached 20 atm.

2.4.14 Independent diagnostics and verification of links to WMO scale

We analyze known cylinders multiple times per day (PSU: target sampled every hour and archive every 24 h; AIRCOA: surveillance sampled every 8 h). These cylinders are treated as unknowns in the data-processing and checked against laboratory-assigned values. In the case of AIRCOA this gas runs through the entire inlet/drying system. The PSU systems are periodically checked for biases from the inlet/drying system using gas from a calibrated cylinder plumbed into a 0.1 l mixing volume and sampled as an unknown. At selected sites we also have conducted long-term intercomparisons with independent NOAA-ESRL measurement programs.

2.4.15 Development of problems in the field

We use near real-time data retrieval, processing, diagnostic checking, and display software to detect and correct problems as soon as possible after they arise.

3   Results

To further check for biases in our measurements and to support our results, we have compared measurements of common air among multiple analyzers, of known cylinders to laboratory-assigned values, and to co-located NOAA-ESRL measurements.

3.1   Side-by-side system comparisons

Six PSU Version 1 systems were tested at PSU for compatibility (WMO, 2011); all systems sampled outdoor air in parallel from a 4-l mixing volume which had a fan actively circulating the air. An LI-7000 was connected in series with one of the six LI-820 systems to reveal any possible systematic bias associated with the use of the LI-820. In test "A" all of the systems used common calibration gases. In subsequent tests, however, each system utilized its own set of calibration gases, in order to detect potential biases associated with calibration transfer. The individual differences from the mean of the seven systems have 1-σ variability of less than 0.1 ppm (Fig. 2a).

As various AIRCOA systems were built during the 2004 to 2006 period, a collection of side-by-side comparisons were made, totaling over 200 days of testing. Pair-wise system comparisons are shown as median ±1-σ differences in Fig. 2b. The 2005 and 2006 intercomparisons were done in a laboratory sampling outside air in Broomfield, Colorado, USA through a 400 l mixing volume and using the same set of calibration gases for all AIRCOA. The first two points in 2004 represent comparisons done during the 2004 Carbon in the Mountains Experiment (Burns et al., 2011) on Niwot Ridge at the Willow site, in which the AIRCOA were outside and exposed to ambient temperature fluctuations of 20 °C, used separate sets of calibration gases, and sampled from the same inlets but with no mixing volume. Without a mixing volume, small differences in sample timing can lead to large variability, so the results for these two tests are shown for daytime samples from the highest inlet (17 m) only. Of the 58 pair-wise differences from 17 comparison periods, 57 are within 0.2 ppm, 51 are within 0.1 ppm

and 36 are within 0.05. Collectively, these median differences have 1-σ variability of ±0.07 ppm.

3.2   Known cylinder measurements

As an example of the typical reproducibility of the PSU systems relative to PSU laboratory measurements, long-term archive cylinder residuals are shown in Fig. 3a, for PSU Version 2 systems. While the cylinder tests do not test for any problems associated with water vapor, they provide valuable information related to system accuracy. The medians of the residuals (Fig. 3a) are 0.13 ± 0.17 ppm, 0.06 ± 0.17 ppm, and -0.11 ± 0.21 ppm for the Canaan Valley, Mead, and Missouri Ozarks sites, respectively.

Figure 3b shows long-term surveillance cylinder results compared to laboratory assigned values for four AIRCOA units operating autonomously at field sites from late 2005 to early 2009. This figure includes data from periods when the field and laboratory measurements differed noticeably and alerted us to problems with the field measurements. Some of the larger differences result from impacts of the inlet and drying system, such as internal leaks between sample and purge gas within the upstream Nafion, highlighting the value of running surveillance gas through the entire inlet system. Note that in the case of such an internal Nafion leak, the effect will be much larger on the surveillance gas, which differs from ambient concentrations, than on the sample gas itself because the Nafion purge gas CO_2 concentration is usually equal to ambient. Over the entire period shown, the medians ± 1-σ of these differences were 0.01 ± 0.18 ($n = 2831$) for the Niwot Ridge T-Van site, -0.17 ± 0.14 ($n = 3480$), for Storm Peak Laboratory, -0.15 ± 0.16 ($n = 2405$) for Hidden Peak, and -0.07 ± 0.11 ($n = 3482$) ppm for Fraser Experimental Forest. The tendency for a low bias in the surveillance gas measurements is the subject of ongoing investigations, and may be related to regulator stagnation effects for the less-frequently run surveillance gas or switching between wet and dry air entering the upstream Nafion drier.

3.3 Comparisons to co-located NOAA-ESRL measurements

As a further means to evaluate the performance of the systems, one system (PSU Version 1) was deployed at the WLEF tower near Park Falls, Wisconsin, USA for the period May–August 2004. NOAA-ESRL measurements of CO_2 concentrations have been made at the WLEF site since 1994 (Bakwin et al., 1998). The PSU system sample line branched off the NOAA-ESRL system 76-m sample line at the base of the tower. The PSU system, including the calibration cylinders, was located outdoors, and thus subjected to environmental temperature and pressure changes. The NOAA-ESRL and PSU systems had independent filtering and, more importantly, drying, with the NOAA-ESRL system using a refrigerated, continuously purged liquid water trap, followed by a Nafion drier (Bakwin et al., 1998). A Hygrometrix relative humidity sensor was used to monitor residual moisture levels. The NOAA-ESRL system used a LI-6251 two-cell NDIR sensor. The differences between the daily mean PSU value and the daily mean NOAA-ESRL value (Fig. 4a) were 0.08 ± 0.10 ppm. The daytime-only (12:00–17:00 LST) average differences were larger; 0.26 ± 0.15 ppm. While the differing flow rates are accounted for with an appropriate shift of the data, timing issues may also contribute to the error, as noted in Richardson et al. (2011). Also, this PSU Version 1 system did not temperature control the enclosure or apply any temperature correction between calibrations, and the enclosure was exposed to outdoor temperature variations.

An AIRCOA system has been located at the Niwot Ridge T-Van site since late August 2005. This site has been a weekly flask collection site for NOAA-ESRL since 1967, using paired 2.2 l glass "Network" flasks. Also, since 2005 NOAA-ESRL 0.7-l flasks have been collected at sub-weekly intervals using the NOAA Portable Flask Package (PFP). The second highest inlet height for the AIRCOA is co-located with the 3.5 m inlet used for flask sampling. Figure 4b shows the differences between AIRCOA and NOAA-ESRL data for this site, where the AIRCOA data, with an approximate 7.5 min sampling frequency for this inlet, has been interpolated to the time of flask collection.

After filtering to exclude flasks when the ±15-min CO_2 range was greater than 3.0 ppm (6 Network and 18 PFP flasks) and when the remaining differences were greater than 3σ (37 Network and 49 PFP flasks), we obtain median ($\pm1\sigma$) AIRCOA − Network Flask differences of -0.06 ± 0.30 ppm ($n = 585$) and AIRCOA − PFP Flask differences of 0.17 ppm ± 0.38 ppm ($n = 745$). Note that the PFP results should not be considered representative as the storage times for these flasks is considerably longer than for other sites (Schaeffer et al., 2008). The 0.3–0.4 ppm variability in these comparisons likely results from not sampling the exact same air, and is typical of continental flask versus in situ CO_2 comparisons. The median AIRCOA − Network differences demonstrate good agreement with the WMO CO_2 scale over long periods of time.

4 Discussion and summary

In this paper we describe relatively inexpensive single-cell NDIR-based systems for measuring CO_2 concentrations and evaluate their performance. Making accurate CO_2 measurements requires careful attention to gas handling, numerous automated quality control diagnostics, and a suite of reference cylinders closely linked to the WMO CO_2 calibration scale. Our approach builds on those of Bakwin et al. (1995), Zhao et al. (1997), and Trivett and Köhler (1999), but with considerable changes. These systems are based on a simplified single-cell infrared gas analyzer, which dramatically lowers the cost but increases the short-term noise and instrument drift rate. We overcome the short-term noise with signal averaging, and as has been done previously for more expensive sensors we overcome instrument drift with frequent calibrations. Additional potential sources of CO_2 measurement bias that we address with automated diagnostics include: incomplete flushing of the sample cell and dead volumes, incomplete drying of the sample air, sensitivity to pressure broadening, sensitivity to temperature, leaks to ambient air, leaks of calibration gas through solenoid valves, and modification of CO_2 concentration by the drying system or plastic components (see Sect. 2.4).

Since the development of these systems, laser-based instruments (e.g., WS-CRDS and off-axis ICOS) have become commercially available and promise to find widespread applicability in studies where NDIR was once the only solution (Winderlich et al., 2010; Richardson et al., 2011; WMO, 2011). However, once calibrations are performed, the performance of less-expensive NDIR-based measurements is not dramatically disparate from that shown in field tests of early WS-CRDS systems (Richardson et al., 2011), and this is likely because many of the potential causes of error in CO$_2$ systems relate to things other than sensor stability (Sect. 2.4). To compare with the NDIR-based known-cylinder residuals presented in this paper, the median of the calibrated residuals for the WS-CRDS instruments in the Richardson et al. (2011) study are, depending on the site, 0.02 ± 0.14 ppm to 0.17 ± 0.07 ppm. There are notable disadvantages to the single-cell NDIR-based CO$_2$ measurements systems described in this paper, including labor-intensive initial system construction, considerable cost of replacing calibration gases on an annual basis, and less short-term precision than is attainable via other methods. Nonetheless, accuracy sufficient for many current applications can be achieved with low cost single-cell NDIR-based systems when initial cost of the sensor is a factor, and the systems currently in the field are contributing valuable measurements for carbon cycle studies.

Multiple side-by-side laboratory tests of up to six of our systems showed median differences between systems that varied about zero by 0.1 ppm (1-σ). Field measurements of known reference-gases at seven sites resulted in median errors of 0.01 to 0.17 ppm with 1-σ variance of ± 0.1 to 0.2 ppm. A four-month field comparison of a PSU Version 1 system with established NOAA-ESRL measurements at the WLEF tall tower reveal daytime-only daily-averaged differences to be 0.26 ± 0.15 ppm without temperature control or corrections. An ongoing 6-year field comparison of an AIRCOA unit to NOAA network flasks showed agreement of -0.06 ± 0.30 ppm. The long-standing WMO goal for inter-laboratory compatibility in the Northern Hemisphere is 0.1 ppm (WMO, 2011), but it is worth noting that other long-running intercomparison activities, including those between flask and in situ analyzers maintained by the same lab,

typically see systematic biases on the order of 0.2 ppm (Masarie et al., 2001; WMO, 2009; Richardson et al., 2011). Thus, while we and the community as a whole still have work to do in resolving and improving remaining compatibility issues, including cylinder drift and modification of CO_2 concentration by sampling components, the inexpensive
5 sensors described here have compatibility as good as other methods.

We have learned a great deal about the performance and limitations of our CO_2 systems through the intercomparison activities described above. When possible, we have incorporated this new knowledge into system improvements, in particular in the changes made between the Version 1 (Sects. 3.1 and 3.3) and Version 2 (Sect. 3.2)
10 PSU systems. Of the remaining differences between the systems, many reflect choices for historical, personal preference, or site-specific reasons that do not significantly affect the performance of the systems. We do, however, recommend introducing target or surveillance gases through the entire inlet system, as is done for AIRCOA, to improve the detection of inlet-system problems. Also, the post-processing pressure, tempera-
15 ture, and flushing corrections used with the AIRCOA systems can improve the quality of the final data. Whatever individual design choices others make in deploying similar NDIR or laser-based CO_2 measurement systems, we strongly encourage a program of multiple intercomparison activities as detailed here. At a minimum, these should include side-by-side laboratory tests with like and different systems, using long-term
20 surveillance gases in the field, and field comparisons to co-located measurements by other laboratories.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

References

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Atmospheric CO_2 monitoring with NDIR-based analyzers

B. B. Stephens et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◀◀   ▶▶

◀   ▶

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Atmospheric CO_2 monitoring with NDIR-based analyzers

B. B. Stephens et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

28 March 2011, Helsinki, Finland, 2009.

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Atmospheric CO_2 monitoring with NDIR-based analyzers

B. B. Stephens et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
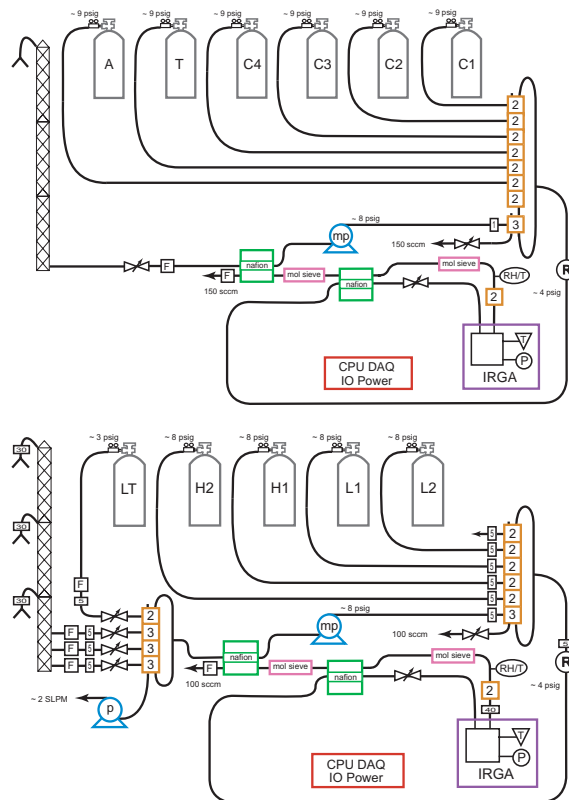
Fig. 1. Schematics of the single-cell NDIR-based CO$_2$ concentration measurement systems, **(a)** PSU system and **(b)** AIRCOA system. Components include sample air intakes with rain shields; mass-flow meters (F); 1, 5, 30, and 40-µm filters (1, 5, 30, 40); manual needle valves; three-way (3) and two-way (2) solenoid valves and manifolds; Nafion driers, molecular sieve driers; a sample micropump (mp) and purge pump (p); reference and archive, target, and surveillance cylinders; two-stage pressure regulators; a single-stage pressure regulator (R); a humidity and temperature sensor (RH/T); and a LI-820 single-cell NDIR sensor (IRGA).
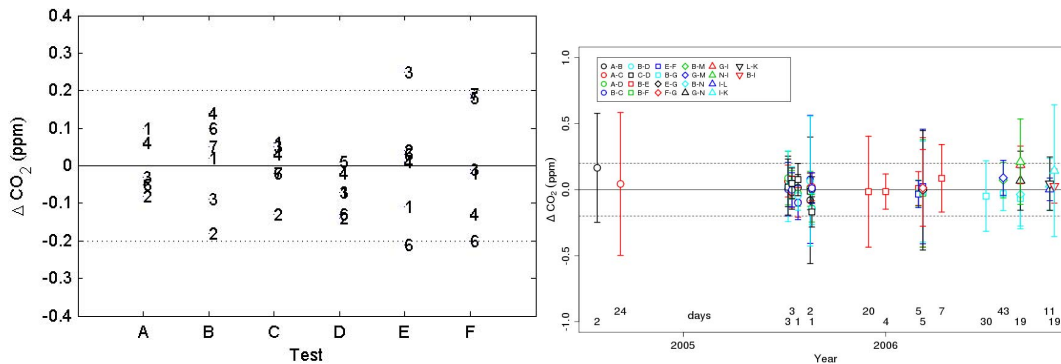
Fig. 2. Results from side-by-side system comparisons. **(a)** Time-averaged difference from the all-systems mean for PSU systems (1–6) sampling outdoor air in parallel, and one LI-7000 (system 7) sampling in series. Points above 415 ppm (more than 15 ppm above calibration gas range) are excluded. The time length of the tests vary between 75 and 400 min. In Test A all systems used one set of calibration gases, whereas in the remaining tests, all systems used their own set. Note that the tested systems are PSU Version 1 systems, with none of the upgrades added to later systems. **(b)** Pair-wise AIRCOA system differences in tests of 2–6 systems (letters A–L) for durations up to 6 weeks, shown as median differences and 1-σ variability. The first two tests were in the field with systems exposed to ambient temperature swings, independent calibration gases, and no mixing volume. All others were in the laboratory, with common calibration gases, and a 400 l mixing volume. The numbers at the bottom of the figure indicate the number of days for each test. See text for statistics on differences.
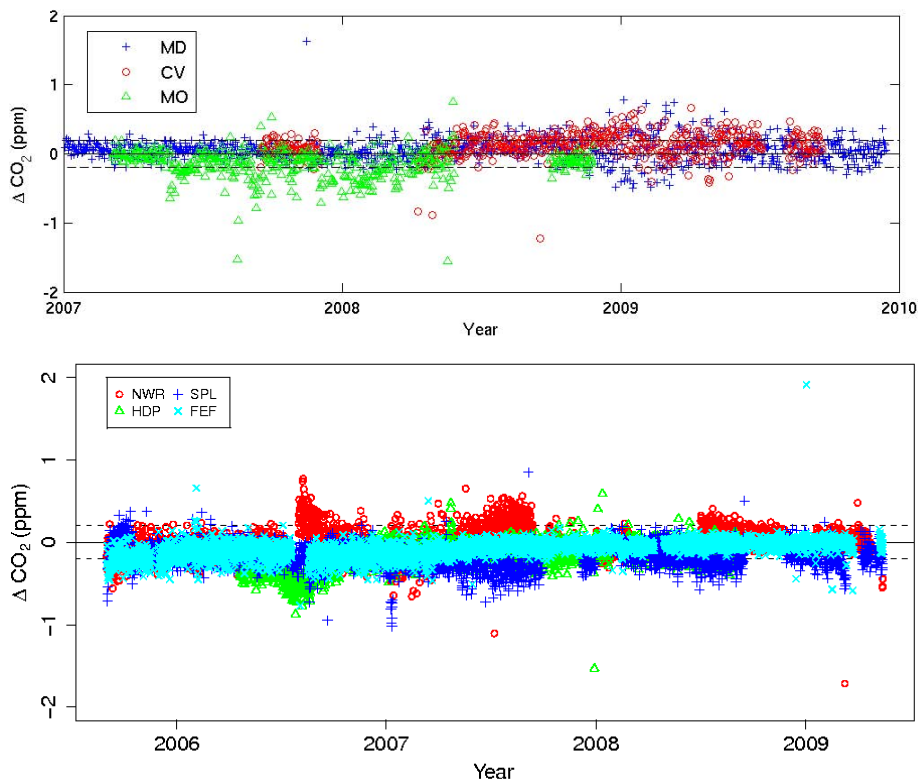
Fig. 3. Results from field measurements of cylinders of known concentration. **(a)** Residuals (measured – known) for daily measurements of the archive cylinder at the Mead (MD), Canaan Valley (CV), and Missouri Ozarks (MO) PSU Version 2 sites. **(b)** Residuals of 8-hourly long-term surveillance gas measurements made by 4 AIRCOA units from September 2005 through May 2009 in the field at Niwot Ridge (NWR), Storm Peak Laboratory (SPL), Hidden Peak (HDP), and Fraser Experimental Forest (FEF) sites. See text for statistics on differences.
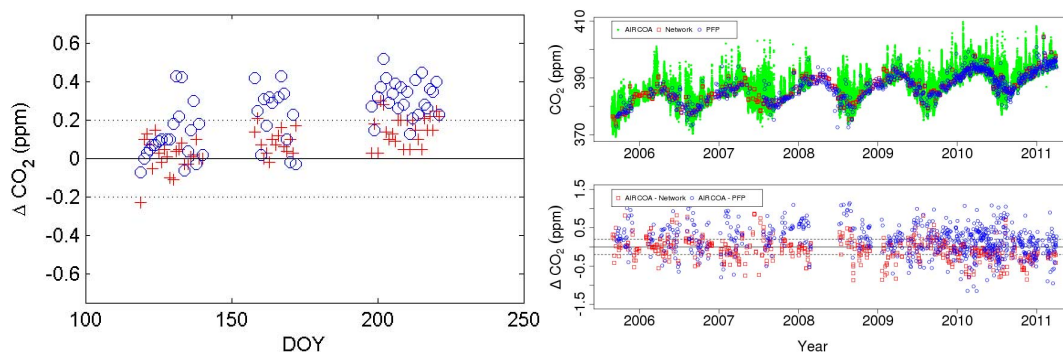
Fig. 4. Results from comparisons to co-located NOAA-ESRL measurements. **(a)** Difference between the CO$_2$ concentration measured by the PSU and NOAA-ESRL systems at the WLEF tower (76-m level) during periods in May–August 2004 when both measurements are available. Difference between the daily average (+) and the daily daytime (12:00–16:00 LST) average (open circles) CO$_2$ concentration measurements. Note that the tested system is a PSU Version 1 system with none of the upgrades added to later systems, including temperature control of the enclosure, target and archive cylinders, automated leak tests, and drying without nitrogen. This PSU system was also exposed to ambient temperature and pressure changes. **(b)** CO$_2$ concentration measured by the AIRCOA and NOAA-ESRL flasks at the Niwot Ridge T-Van site from September 2005 to March 2011, **(c)** Differences between the measurements in **(b)** shown for both NOAA-ESRL paired 2.2-L "Network" flasks and individual 0.7-L "Portable Flask Package (PFP)" flasks. Data points with ±15-min CO$_2$ ranges greater than 3.0 ppm and with remaining differences greater than 3σ are excluded. See text for statistics on differences.