An Evaluation of Calibration Techniques for In Situ Carbon Dioxide Measurements Using a Programmable Portable Trace-Gas Measuring System

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ABSTRACT

The construction and deployment of a portable trace-gas measurement system (TGaMS) is described. The air-collection system (dubbed HYDRA) collects air samples from 18 different locations and was connected to either one or two LI-COR LI-7000 gas analyzers to measure CO2. An in situ “field calibration” method, that uses four calibration gases with an uncertainty on the order of ±0.1 μmol mol⁻¹ relative to the WMO CO2 mole fraction scale, revealed CO2 output from the LI-7000 had a slightly nonlinear relationship relative to the CO2 concentration of the calibration gases. The sensitivity of the field-calibrated CO2 to different forms of the field-calibration equation is investigated. To evaluate TGaMS performance, CO2 from collocated inlets, portable gas cylinders, and nearby independent CO2 instruments are compared. Results are as follows: 1) CO2 measurements from HYDRA multiple inlets are feasible with a reproducibility of ±0.4 μmol mol⁻¹ (based on the standard deviation of the CO2 difference between collocated inlets when HYDRA was operating with two LI-7000s); 2) CO2 differences among the various field-calibration equations were on the order of ±0.3 μmol mol⁻¹; and 3) comparison of midday hourly CO2 measurements at 30 m AGL between TGaMS and an independent high-accuracy CO2 measurement system (within 300 m of TGaMS) had a median difference and standard deviation of 0.04 ± 0.81 μmol mol⁻¹ over two months.

1. Introduction

Measuring trace gases to understand and to monitor the earth for climate change has become an important and common task within the biogeoscience community (Hansen et al. 2007). Within the past several decades the World Meteorological Organization (WMO) and other organizations around the world have invested a considerable amount of effort examining the accuracy of trace-gas measurements. Since the late 1970s, the WMO has organized 13 meetings of the so-called Experts on Carbon Dioxide Concentration to discuss CO2 and trace-gas-measurement-related topics (Worthy and Huang 2005; Miller 2006). One of the recommendations by this group is that interlaboratory comparisons of CO2 on the global network be on the order of ±0.1 μmol mol⁻¹. Historically these discussions have focused on the accuracy of long-term CO2 measurements (Bakwin et al. 1995; Trivett and Köhler 1999) and air sampling with flasks; however, recent discussions have included recommendations for in situ CO2 measurements (Miller 2006) as well as examples of continuously measuring, multi-inlet systems using a single sensor (e.g., Manning 2005; Stephens et al. 2006).

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Atmospheric CO2 measurements typically have one of three goals: 1) to make highly accurate measurements of CO2 that can be used in long-term CO2 monitoring or regional CO2 budget studies, 2) to measure CO2 fluctuations and calculate CO2 fluxes using the eddy-correlation method (Baldocchi et al. 1988; Berger et al. 2001; Massman and Lee 2002), or 3) to measure CO2 differences from multiple inlets using a single infrared gas analyzer (IRGA) with excellent reproducibility to measure changes in local CO2 gradients. Each measurement goal requires different emphasis on the instrumentation as well as processing techniques. For example, calculating the CO2 flux requires a fast-response instrument, high flow rates (for a closed-path gas analyzer), and good short-term repeatability, whereas a study of temporal changes of mean CO2 concentration over multiple years requires a high-accuracy sensor or a methodology to correct for sensor drift over time (e.g., by the use of calibration gases). The term “CO2 accuracy” refers to the accuracy of a CO2 measurement relative to the WMO CO2 mole fraction scale (hereafter WMO CO2 Scale) that is currently maintained at the National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Division (GMD) as described by Zhao and Tans (2006). Because accuracy is a qualitative expression, we will use the so-called combined standard uncertainty to show the degree of accuracy (expressed as ±1 standard deviation such that there is a 67% probability the true value is within the uncertainty range). Definitions of “reproducibility” and “repeatability” are given toward the end of this section.

One use of multi-inlet CO2-measurement systems that has recently received a lot of attention in the ecosystem flux community is determining the effect of horizontal CO2 advection on the local CO2 budget (e.g., Aubinet et al. 2003; Staebler and Fitzjarrald 2004; Sun et al. 2007; Yi et al. 2008, among many others). Horizontal advection is typically determined by estimating the horizontal divergence or convergence of CO2 through the “sides” of an imaginary control volume around a tower that measures the vertical CO2 flux. Because estimation of CO2 advection requires accurate measurements of spatial CO2 gradients, reproducibility of the mean CO2 differences among inlets is much more important than a high-accuracy CO2 measurement. To study the problem of horizontal CO2 advection, a portable trace-gas measurement system was developed at the National Center for Atmospheric Research (NCAR) Earth Observing Laboratory (EOL). The NCAR trace-gas measurement system (TGaMS) comprises an 18 inlet air-sampling system (hereafter “HYDRA”) connected to either one or two analysis systems that house a LI-COR LI-7000 CO2–H2O nondispersive infrared (NDIR) dual-cell IRGA (LI-COR Inc. 2005). TGaMS has been deployed in several field campaigns to study the horizontal transport of CO2 in a Colorado subalpine forest: the 2002 pilot study (NIWOT02) and the 2004 Carbon in the Mountains Experiment (CME04). TGaMS was also used in conjunction with another CO2 measuring system (based on a LI-COR LI-820 IRGA) to measure vertical and horizontal CO2 gradients in the Wavelet Detection and Atmospheric Turbulent Exchange Measurements 2003 (WALDATEM-2003) experiment that studied the turbulent exchange processes in a tall spruce forest at the FLUXNET station Waldstein-Weidenbrunnen in northeastern Bavaria (Thomas and Foken 2007; Thomas et al. 2004). During the winters of 2003–04 and 2004–05 TGaMS was used in the UNDERSNOW projects to study gradients of CO2 within the snowpack of a subalpine forest (Monson et al. 2006a,b). The use of TGaMS in NIWOT02 and CME04 is the focus of our study.

The LI-7000 determines the CO2 concentration of an air sample by comparing absorption within the “sample” cell to absorption within the “reference” cell that contains either CO2-free air or air of constant CO2 concentration. It is well known that CO2 concentration measured by an IRGA depends on cell temperature and pressure following the ideal gas law (McDermitt et al. 1993). The LI-COR factory calibration uses a fifth-order polynomial to take into account cell temperature and pressure changes, and the LI-7000 is specified to have a nominal error on the order of ±1% over a range 0–3000 μmol mol−1 (LI-COR Inc. 2005). Researchers that desire high-accuracy CO2 measurements often control the temperature and pressure within the sample cell in order to minimize any imperfections in the factory calibration, as well as reducing errors due to the thermal micro-expansion–contraction of the optical bench and temperature effects on the internal electronics (D. Anderson 2007, personal communication). Another way to improve the IRGA CO2-measurement accuracy, is by an in situ “field calibration”; achieved when air with varying CO2 concentrations (so-called calibration gases) are sequentially passed through the sample cell (Trivett and Köhler 1999). Trivett and Köhler (1999) noted that a linear expression could be applied to correct the IRGA with the calibration gases, but the true calibration curve is nonlinear, which requires three or four calibration gases to characterize. Zhao et al. (1997) described a technique for processing data from a single-inlet CO2-measuring system that used four calibration gases, a LI-COR IRGA (model LI-6251), and a second-order polynomial to convert the raw CO2 voltage into CO2 concentrations. They estimated the uncertainty of their system to be better than ±0.2 μmol mol−1 by
considering the residuals in the second-order polynomial fit and errors in the CO2 concentration of the calibration gas. Following the methodology presented by Zhao et al. (1997), other researchers have used similar data-processing techniques for their CO2-measuring systems (e.g., Haszpra et al. 2001; Daube et al. 2002; Stephens et al. 2006). Ocheltree and Loescher (2007) used a LI-7000 and calibration gases prepared by NOAA/GMD to determine a third-order polynomial calibration curve over a range of 330–500 μmol mol⁻¹ in the laboratory. In the field, they calculated the CO2 concentration from the raw CO2 output by the LI-7000 (using the laboratory-determined coefficients) and an in situ linear field calibration using two calibration gases. Ocheltree and Loescher estimated an uncertainty of ±0.6 μmol mol⁻¹ for CO2 by considering the following: residuals in the laboratory-determined third-order polynomial, uncertainty in the calibration gases (relative to the WMO scale), and the digital-to-analog conversion of the CO2 data.

If a CO2 measurement does not require high accuracy, then LI-COR IRGAs can be used with two calibration gases (or one calibration gas and one CO2-free gas) and the LI-COR factory-determined calibration polynomial (Xu et al. 1999; Mölder et al. 2000; Monson et al. 2002; Liang et al. 2003). Most of these studies are more interested in reproducibility of CO2 differences so accuracy relative to the WMO CO2 Scale is not a primary concern.

Our study follows the International Organization for Standardization (ISO) definitions for accuracy, comparability, repeatability, and reproducibility (ISO/IEC 1995, 2007). “Comparability” refers to the ability to compare a measurand between two independent measuring systems using a common reference or scale (in our case the measurand is CO2, and the common reference is the WMO CO2 Scale). Comparability is a qualitative expression and we use empirical comparisons to express the degree of comparability—unless otherwise noted, this is done with a mean or median difference plus or minus the standard deviation of the difference. These comparison statistics will usually be influenced by real differences in the measured data, as well as any systematic and random measurement errors. Precision is defined as “the closeness of agreement between independent test results obtained under stipulated conditions” and is typically expressed by an estimate of the dispersion of the measurement, such as the variance or standard deviation (Taylor and Kuyatt 1994). Precision is called repeatability if the environmental conditions during the measurement do not change; otherwise it is labeled “reproducibility.” In general, precision without any qualifier should be taken as a synonym for repeatability (Taylor and Kuyatt 1994). For our study, reproducibility refers to the ability of TGaMS to maintain consistent CO2-difference measurements among the inlets as the environmental conditions change.

TGaMS was designed for studying horizontal advection—this requires excellent reproducibility among inlets, but not necessarily high accuracy. Previous advection studies around individual towers with a single IRGA and long tubing have proven successful (Aubinet et al. 2003; Staebler and Fitzjarrald 2004), but as these studies expand to “carbon-shed” or regional scales then the use of long tubing becomes impractical, and CO2 measurements at the ±0.1 μmol mol⁻¹ uncertainty level suggested by WMO becomes necessary in order to calculate CO2 differences from independent CO2-measuring systems. One of the goals of our study is to determine whether TGaMS should be considered a high-reproducibility or high-accuracy CO2-measuring system.

2. Instrumentation details

TGaMS consists of an air-sampling system, HYDRA, that collects air from 18 inlets (Fig. 1), and an analysis system, which is housed in a separate weatherproof box (Fig. 2). HYDRA and the analysis system are wired together for communication and power sharing. TGaMS was designed to be portable with a total weight of about 70 kg (Fig. 3, top-right photo). For our projects TGaMS had access to line power, and power consumption by TGaMS is on the order of 0.4 kW (primarily due to the pumps). A general description of TGaMS is given below, details specific to CME04 and NIWOT02 are in section 3.

Each of the HYDRA inlet lines was covered by a 1-μm Gelman filter (part #9967-008, LI-COR, Inc.) and air was drawn through a length of composite aluminum-polyethylene tubing (Type 1300 tubing, Synflex, inner diameter = 0.625 cm) that varied between 5 and 300 m for our experiments. The flow rate of the sample air from each inlet was typically set to 2 L min⁻¹ (lpm) by a valve (model MFVB6, OMEGA Engineering, Inc.), and monitored with a rotameter flowmeter (FL-1800 Series, OMEGA Engineering, Inc.). Upon leaving the Synflex tubing, the air sample entered a buffer volume that was a 2-L mason jar packed in foam at the bottom of the HYDRA box (Fig. 3, middle photo). The buffer volumes were fitted with stainless steel lids that had two 0.95-cm and one 0.635-cm bored-out Swagelok bulkhead fittings (models 600-61 and 400-61, Swagelok Co.) inserted through them. Tubing to one of the 0.95-cm fittings was from the inlet, while the other fitting connected the suction manifold. The 0.635-cm bulkhead fitting was for
the tube that led to the analysis system. The tubing ends within the buffer volumes were arranged to maximize mixing as shown in Fig. 1. The suction manifolds were short lengths of PVC tubing (~70 cm long) with Swagelok fittings tapped along the length of the tube to connect to the buffer volumes. One of the capped ends of each suction manifold was drilled out and equipped with a barbed connector and flexible tubing to attach a vacuum pump (model RAA-V210-EB, Gast Manufacturing, Inc.) that created a sufficient pressure drop for drawing the air samples into HYDRA. By wiring the power supply for the Gast pumps into the control system, the
pumps can be turned on and off by the TGaMS software to allow for periodic flushing of the buffer volumes (useful for measuring CO2 within snow). Whenever the Gast pumps are turned off, a “snapshot” of the CO2 concentration field is captured within the buffer volumes and can subsequently be sampled by the LI-7000. If one analysis system is used in TGaMS, a three-way solenoid valve can be used to connect the manifolds A and B as shown in Fig. 1b.

Air samples were drawn from the buffer volumes into the analysis system by a KNF diaphragm pump (model UN89, KNF Neuberger, Inc.) that was housed within the analysis system (Fig. 2). After the air sample was expelled by the KNF pump it passed through a normally open solenoid valve (model HS02M1H00V5, Numatics, Inc.) into a manifold. Whenever this valve was closed, one of the solenoid valves for the calibration gases was opened so that the manifold contained either an air sample or one of the calibration gases. Positive pressure within the manifold was created by either the KNF pump or the two-stage regulator attached to the calibration gas cylinders. The flow rate within the analysis system was controlled by an OMEGA valve and rotameter located upstream of the LI-7000 sample cell and typically set to 0.2 lpm. Before the air sample reached the LI-7000 sample cell it was dried in a section of Nafion counterflow gas-drying tubing (model MD-110, Perma Pure LLC). Dry air for the Nafion tubing was created by an additional pump that pushed ambient air through a canister of DRIERITE dessicant. The flow rate of the dry air within the Nafion tubing was controlled by a second valve and rotameter within the analysis system, and was set to match the air sample flow rate (Fig. 2). A third valve and rotameter controlled the flow rate in the LI-7000 reference cell. Air exiting, the LI-7000 reference and sample cells were exhausted at atmospheric pressure.

For our experiments, the LI-7000 was not temperature or pressure controlled; however, to improve the CO2 accuracy and reproducibility, an in situ field calibration was achieved by periodically passing a series of calibration gases through the sample cell. A summary of the calibration gases used in NIWOT02 and CME04 is in Table 1. An accurate, rigorously tested calibration gas (i.e., gases with CO2 uncertainty on the order of $\pm 0.1$ $\mu$mol mol$^{-1}$ or better) is the foundation of any
high-accuracy CO$_2$ measurement. In our study we focus on the sensitivity of the CO$_2$ field calibration procedure and equations on the calculated CO$_2$ with the assumption that the CO$_2$ concentration assigned to each calibration gas has no systematic error. In reality there is, of course, some uncertainty in the concentration value assigned to each calibration gas. Zhao and Tans (2006) provided a detailed description of how the concentrations are assigned to calibration gases, and estimated an uncertainty of 0.071 $\mu$mol mol$^{-1}$ relative to the WMO CO$_2$ Scale for the “working standards” (calibration gases that are prepared by NOAA/GMD and used in the field with CO$_2$-measuring systems). Because the CO$_2$ concentration of the calibration gases used in NIWOT02 and CME04 were calculated with different methods, this information is discussed in section 3.

The coordinator of TGaMS was a computer-controlled microprocessor [16-channel B1 (digital) Optomux Protocol Brain Board, Opto 22, Inc.] that was bolted to the inside of the wooden HYDRA box. The control board energized solid state optically-isolated OAC5 relays that determined which buffer volume was sampled within HYDRA, as well as controlling whether the LI-7000 measured a calibration gas or an air sample within the analysis system. To easily determine the state of the Opto 22, LEDs were connected to the relays and set

![Diagram showing site topography and tower layout at the NWT site.](image)

**FIG. 3.** Site topography and tower layout at the NWT site. The Long-Term Ecological Research (LTER) C-1 site is a long-term climate station within the Niwot Ridge Biosphere Reserve. Elevation contours at 5-m intervals are from the USGS 7.5-min DEM. The Como Creek data are from the “Hydrography–Streams” data available from the Boulder County GIS Web page (see online at http://www.co.boulder.co.us/gis/). All tower locations are differentially corrected measurements with a Trimble GPS Pathfinder Pro XL system. The photos show (left) outside of HYDRA box, (middle) inside of HYDRA box, and (right) HYDRA being transported through the forest.
into the outside of the HYDRA box. The software used to communicate with the Opto 22 control board and also collect the 1-Hz serial output from the LI-7000, was the UNIX-based NDAQ software designed by the NCAR EOL Integrated Surface Flux Facility (ISFF) group. The NDAQ software has been implemented on several platforms and is available on request from ISFF.

### Table 1. Details of the NCAR CO₂-measuring system (TGaMS) during the NIWOT02 and CME04 projects. (For an overview of the NIWOT02 and CME04 projects visit the NCAR EOL Web page at http://www.eol.ucar.edu/rtf/projects/.)

<table>
<thead>
<tr>
<th>Project</th>
<th>NIWOT02</th>
<th>CME04</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of LI-7000s</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Reference cell CO₂ concentration</td>
<td>323.16 ±0.11 (4)</td>
<td>363.23 ±0.02 (6)</td>
</tr>
<tr>
<td>Calibration gas CO₂ concentrationᵃ</td>
<td>283.38 ±0.11 (4), 360.06 ±0.04 (4), 419.52 ±0.10 (4)</td>
<td>335.09 ±0.02 (11), 349.51 ±0.03 (8), 398.23 ±0.02 (8), 417.96 ±0.02 (6)</td>
</tr>
<tr>
<td>Calibration gas uncertainty</td>
<td>±2³ μmol mol⁻¹</td>
<td>±0.1 μmol mol⁻¹</td>
</tr>
<tr>
<td>Calibration frequency</td>
<td>Hourly</td>
<td>Either hourly or every 2.5 h</td>
</tr>
<tr>
<td>Sampling strategyᵇ</td>
<td>Continuous flow</td>
<td>Continuous flow</td>
</tr>
<tr>
<td>Flushing</td>
<td>CAL GASES: 215 s</td>
<td>CAL GASES: 116 or 40 s</td>
</tr>
<tr>
<td>Timeᶜ</td>
<td>AIR SAMPLES: 55 s</td>
<td>AIR SAMPLES: 90 or 40 s</td>
</tr>
<tr>
<td>Sampling timeᶜ</td>
<td>25 s</td>
<td>10 s</td>
</tr>
</tbody>
</table>

ᵃ Calibration gas CO₂ concentrations all have units μmol mol⁻¹ and include plus or minus the standard deviation of the N-independent samples (N is shown in parentheses). For CME04 the mean from the pre- and postproject values determined at the NCAR O₂/CO₂ calibration facility (see online at http://www.eol.ucar.edu/~stephens/CALFAC) were used.

ᵇ The uncertainty estimate for NIWOT02 gases is a rough estimate based on repeatability considerations and CO₂ field comparisons.

ᶜ A “continuous flow” sampling strategy refers to whether or not the pump for the inlets (Gast) is running at the same time the air is sampled from the buffer volumes by the KNF pump.

d "Flushing time" is the amount of time allowed to flush out the system before statistics are calculated. "CAL GASES" are the times used when calibration gases are measured, while "AIR SAMPLES" are the times used for atmospheric air samples. An example calibration period is shown in Fig. 7, where the flushing time is 215 s and the sampling time is 25 s.

c "Sampling time" is the length of the time used to calculate the mean CO₂ values (and other statistics). This is equivalent to the sampling time period shown in Fig. 7.

### 3. Field deployments

Most TGaMS deployments have taken place near the Niwot Ridge Forest AmeriFlux site (NWT; Fig. 3, more information available online at http://public.ornl.gov/ameriflux/) where measurements of vertical profiles of mean CO₂ with a LI-COR LI-6251, and CO₂ flux at 21.5 m with a LI-COR LI-6262 have been made since November 1998 (Monson et al. 2002; Turnipseed et al. 2002). The NWT LI-CORs are field calibrated with two gases—a “span” gas that has a CO₂ concentration of around 400 μmol mol⁻¹, and one with ultra-high purity Nitrogen (the N₂ gas is also used in the reference cell of each of the NWT LI-CORs). The span gas concentration is determined with a LI-6251 and a NOAA/GMD “secondary standard” gas cylinder in a trailer at the site; N₂ is first passed through the sample cell, followed by the GMD secondary standard gas, followed by the gas with the unknown concentration. The procedure is repeated several times to assign a concentration to the span gas. In the field, NWT CO₂ is calculated from the factory calibration combined with in situ linear coefficients from field calibrations that occur every 4 h (Monson et al. 2002). Another tall tower making multiyear measurements at the Niwot Ridge forest site is managed by the U.S. Geological Survey (USGS). The USGS system has a LI-7000 located between the USGS and NWT towers and inlets located on both the USGS and NWT towers; the USGS calibration gas concentrations were determined in the laboratory using a NOAA/GMD standard gas and a LI-COR LI-6262 (Yi et al. 2008). The CO₂ data from both the NWT and USGS systems are used in section 5b.

Several different sampling strategies have been employed with TGaMS. A typical sampling sequence from NIWOT02 (with two LI-7000s) and two different sampling strategies from CME04 (with one LI-7000) are shown in Fig. 4. The initial CME04 sampling strategy (middle panel) was chosen for sequential sampling of the inlets. On 10 September 2004 the sampling scheme was modified (bottom panel) so that the spatial location of the inlet was prioritized (starting at the southern inlets and ending at the northern ones). It was preferable to reprogram the inlet-sampling software rather than physically moving the inlets or reconfiguring the tubing at the HYDRA box.
a. NIWOT02 experiment

In September 2002 the first field deployment of TGaMS took place at the NWT site as part of an effort to study the effect of horizontal transport of CO₂ on the overall CO₂ budget within a forested mountainous region (Sun et al. 2007). During NIWOT02 the 18 HYDRA inlets were spread over a 300 m × 300 m section of the forest at locations shown in Fig. 3 and at various heights above the ground listed in Table 2.

Two LI-7000 gas analyzers (designated LI-A and LI-B) were running in parallel to increase the time–space resolution of the CO₂ measurements. The two identical analysis systems (Fig. 2) were connected to HYDRA as shown in Fig. 1a. Tees were used to connect the same calibration gases to both LI-A and LI-B, and the Opto 22 control board activated the valves in both analysis systems simultaneously (i.e., A1 and B1, A2 and B2, etc., were sampled at the same time). Figure 5a shows 12 h of the raw CO₂ data from both LI-A and LI-B with a 12-min calibration time period (4 min for each gas) that appears in the time series as “steplike” changes in the CO₂ values. Atmospheric inlets were each sampled for 80 s. All 18 inlets were sampled every 12 min, and a full cycle,
consisting of a calibration followed by 4 cycles of atmospheric sampling, took 1 h. For comparison and evaluation of the CO2 measured by TGaMS, 1-m AGL collocated inlets were placed at the NWT, USGS, and NCAR towers (the A1 and B1 inlets were collocated at the NCAR tower and sampled at the same time as shown in Fig. 5).

The CO2 concentration of the three NIWOT02 calibration gases (Table 1) were estimated using the same method as that used for the NWT calibration gas (as described above). The uncertainty of this method is probably on the order of ±2 μmol mol⁻¹ relative to the WMO CO2 Scale.

**b. CME04 experiment**

The CME04 experiment took place during summer 2004 in the same forest as the NIWOT02 experiment, but with expanded coverage from three additional above-canopy towers that included the north side of Como Creek [see Burns et al. (2006) for an overview of the CME04 instrumentation]. TGaMS was located at the “Pine” tower with inlets running in a north–south line across Como Creek, vertically up the Pine tower, and along Como Creek about 100 m southeast and southwest of the tower (Fig. 3). Because only a single LI-7000 was available to use with TGaMS, manifolds A and B were connected to each other by a three-way distribution valve (Fig. 1b). A fourth calibration gas was added to TGaMS by attaching a fifth solenoid valve to the analysis system manifold. The two other CME04 towers (“Aspen” and “Willow”) were equipped with Autonomous Inexpensive Robust CO2 Analyzers (AIRCOA) that were designed and assembled at the NCAR/EOL Research Aviation Facility (Stephens et al. 2006).

In an effort to minimize inconsistencies between systems, the concentrations of the calibration gases used by NWT, TGaMS, and the AIRCOAs were determined at the NCAR O2/CO2 calibration facility (see online at http://www.eol.ucar.edu/~stephens/CALFAC) using a Siemens Ultramat-6F NDIR gas analyzer along with 6 primary standards (with CO2 concentrations determined by both NOAA/GMD and the Scripps Institution of Oceanography) and 12 secondary standards. Six of the secondary gases were used to assign CO2 concentrations to cylinders with unknown concentrations. The cylinders are all housed horizontally in an insulated enclosure. The system uses active pressure and flow control (MKS Instruments, Wilmington, Massachusetts) to maintain a constant flow rate of 100 standard cubic centimeters per minute (scm). The air is dried to a dewpoint of −95°C before being measured. The system samples each cylinder for 7.5 min, such that one pass through six known and six unknown cylinders takes 1.5 h. This is repeated 6–8 times in a pyramidal pattern so that the sampling order is varied (Komhyr et al. 1985). The CO2 concentration of the unknown cylinder is then determined using a third-order polynomial fit of the six known CO2 concentrations. The assigned CO2 concentration of the air within the unknown cylinders was reproducible to ±0.05 μmol mol⁻¹ with an estimated uncertainty of ±0.1 μmol mol⁻¹ relative to the WMO CO2 Scale. A postproject calibration of each CME04 cylinder was performed to look for any significant changes to the CO2 concentrations (none were found).

**4. Data-processing details**

A list of practical considerations and possible problems associated with running continuous-measuring CO2 systems can be found in Trivett and Köhler (1999), Miller (2006, his recommendation R9.3) and Stephens et al. (2006, their Table 1). For our study the focus is on the following items: the selection of appropriate CO2 calibration gases, the form of the equation used to field calibrate the CO2 output by the LI-7000, how the calibration coefficients are applied to the data between calibration periods, and the travel time of the air sample from the inlet to the buffer volume. Each of the TGaMS data-processing steps are described in detail below.
a. LI-7000 settings and the field-calibration equation

The LI-7000 instrumentation manual and LI-COR online documentation provide a description of the LI-COR factory calibration and how to apply a field calibration (McDermitt 1997). The LI-7000 uses digital filtering with a range of selectable averaging times (from 0 to 20 s) that reduce the noise in the CO2 data. If no filtering is used, the peak-to-peak noise level is around 1.1 µmol mol⁻¹ (at 370 µmol mol⁻¹), whereas an averaging time of 20 s reduces the peak-to-peak noise to 0.039 µmol mol⁻¹. For our experiments the averaging period was set to 1 s, which has a LI-COR-specified peak-to-peak noise level of 0.17 µmol mol⁻¹. The 1-s averaging time was chosen as a trade-off between response time and noise reduction (for a 1-s averaging period).
period the delay time is less than 1 s compared to a 10-s delay for a 20-s averaging period).

Why use field calibrations rather than the factory-calibrated CO$_2$ output from the LI-7000? The LI-COR factory calibration covers a CO$_2$ range of 0–3000 μmol mol$^{-1}$ and has been found to drift by several μmol mol$^{-1}$ depending on changes in cell temperature and pressure. By using our own calibration gases we can measure CO$_2$ with greater accuracy over the range of CO$_2$ concentrations specific to our project, and also take into account any environmental changes or other unforeseen factors (e.g., dust getting into a cell or drift in the electrical components) that might affect the factory calibration. The equation used to “field calibrate” the internally calculated CO$_2$ output by the LI-7000 can be expressed in a general form as

$$\text{CO}_2 = A_3 (\text{CO}_2)_{\text{raw}}^3 + A_2 (\text{CO}_2)_{\text{raw}}^2 + A_1 (\text{CO}_2)_{\text{raw}} + A_0, \tag{1}$$

where $(\text{CO}_2)_{\text{raw}}$ is the digital CO$_2$ output from the LI-7000, and $A_3$, $A_2$, $A_1$, and $A_0$ are empirical calibration coefficients determined from each field calibration time period by fitting $(\text{CO}_2)_{\text{raw}}$ to the CO$_2$ concentration of the external calibration gases (Fig. 6). Although the relationship between $(\text{CO}_2)_{\text{raw}}$ and the known values of the calibration gases may appear linear (Fig. 6a), its slight nonlinearity is shown by their differences (Fig. 6b). As a general guideline for CO$_2$ measurements, Miller (2006) recommends that the number of calibration gases ($N$) should exceed the order of the polynomial fit by 2 [e.g., if there are $N = 4$ calibration gases available, a second-order polynomial should be used for Eq. (1)]. In general, for $N$ data points, a $N - 2$ order polynomial will not fit the data exactly so that differences, so-called residuals, exist between the data calculated using the polynomial equation and the $N$ data points; a $N - 1$ order polynomial, however, will always fit $N$ data points with residuals of zero (Devore 1987). Part of our study was to investigate the magnitude of the differences if a linear ($N - 3$), piecewise linear ($N - 1$), second-order polynomial ($N - 2$), or third-order polynomial ($N - 1$) form of Eq. (1) is used (Table 3).

b. Flushing time of the analysis system

Flushing the previous air sample (or calibration gas) from within the tubing, manifolds, and solenoid valves of the system depends on tubing length and flow rate, and needs to be checked for each unique setup. CO$_2$ concentrations should only be calculated after flushing has been achieved; therefore, we will designate the time period used for calculating CO$_2$ as the “sampling time period.” The flushing and sampling times used in NIWOT02 and CME04 are listed in Table 1. A calibration time period from NIWOT02 is shown in Fig. 7 with the 25-s “sampling time period” marked by vertical lines and a linear fit of the CO$_2$ data versus time shown as a solid line. (Note that the solid line extends outside the sampling time period for reasons explained below.) If the slope of the “CO$_2$ versus time” line is near zero it indicates that the stale air has been flushed out. After 240 s of sampling the 283 μmol mol$^{-1}$ calibration gas, both LI-A and LI-B had a slope larger than −0.18 μmol mol$^{-1}$ min$^{-1}$ indicating that stale air was still present. Since the 283 μmol mol$^{-1}$ gas is at a much lower concentration than the other calibration gases, any flushing problem would be most obvious for this gas. It should also be noted that for each calibration gas, the peak-to-peak range of CO$_2$ within the sampling time period RNG$_{CO_2}$ was at or below the LI-COR specified peak-to-peak noise of 0.17 μmol mol$^{-1}$.

Using CME04 data, the flushing time period was systematically investigated by examining changes in the CO$_2$ statistics as the flushing time was varied for fixed sampling time periods of 10 and 50 s (Fig. 8). Based on the median slope values (Fig. 8b), the vast majority of the air is flushed out by around 40 s; however, the standard deviation of the slope does not level off until a flushing time of around 60 s. In Fig. 8c it is noteworthy that the residuals of the second-order polynomial fit tend to decrease as the flushing time is increased (this was also observed for the other three CME04 calibration gases). This result, coupled with the long flushing time necessary for the 283 μmol mol$^{-1}$ gas in NIWOT02, indicate that some residual air remained within the system likely due to either slow flushing of dead volumes or surface effects of CO$_2$ absorbing and desorbing from the internal plumbing surfaces. These flushing issues add to the uncertainty of the CO$_2$ concentrations assigned to the calibration gases and are an important consideration in relation to the field calibration equation. To evaluate a system for the existence of incomplete flushing, a method recommended by Komhyr et al. (1985) and Trivett and Köhler (1999) is to run the calibration gases in a “pyramidal” pattern where the sampling order of the calibration gases is constantly being altered (i.e., from highest to lowest concentration during one calibration, and then from lowest to highest concentration for the next, etc). A pyramidal calibration pattern was not used with TGaMS in CME04 (or any of the other TGaMS projects), but will be used in future field projects.

We found that the median of the CO$_2$ versus time slopes for the 50- and 10-s sampling time periods were similar (Fig. 8b); however, the standard deviation of the slopes is larger for the 10-s sampling time period, which is why slopes from 50-s periods are shown in Fig. 7.
c. Determination of the field-calibration coefficients

The CO₂ concentrations of the lowest CME04 calibration gases (335 and 349 μmol mol⁻¹) were about 20 and 10 μmol mol⁻¹ below the lowest CO₂ concentration observed in the atmosphere and differed from each other by only 14 μmol mol⁻¹ (Fig. 6a). If a 375 μmol mol⁻¹ gas were included (rather than either the 335 or 349...
\( \mu \text{mol mol}^{-1} \) gas, it would have created a more evenly spaced distribution among the calibration gases, and added a gas that was approximately the median \( \text{CO}_2 \) concentration of the air sampled throughout the project. It also would have also been better if the 418 \( \mu \text{mol mol}^{-1} \) calibration gas was closer to 450 \( \mu \text{mol mol}^{-1} \) so the highest calibration gas would have bracketed the largest observed \( \text{CO}_2 \) concentration.

Frequency distributions of the differences between the calibration gas concentration and the calculated \( \text{CO}_2 \) data from 893 CME04 calibration time periods are shown in Fig. 9. These distributions are the 1-Hz \( \text{CO}_2 \) observations (Fig. 9) that were obtained using a second-order calibration equation. The reason for the discrepancy between the residuals with our LI-7000 and those from Zhao is not known, however, the IRGA setup in the laboratory likely had an advantage of minimal dead volumes and a slowly varying (or controlled) temperature environment. Although these features could be added to a field-based instrument, they were not used within the TGaMS system. To minimize dead volumes, a rotary valve system could be used rather than solenoid valves and manifolds; rotary valves, however, are more sensitive to dirt in the lines, tend to leak after extensive use, and are more expensive (Trivett and Köhler 1999). It is also possible to have a design that flushes the manifolds in a more efficient manner by drawing air from both sides of the manifold rather than from just one end (Bakwin et al. 1995; Stephens et al. 2006).

We now consider the following question—is it better to fit the \( N \) calibration data points with a \( N - 1 \) or \( N - 2 \) order polynomial? If there were absolutely no systematic errors in the assigned calibration gas concentrations, the gas from each calibration cylinder was delivered cleanly (e.g., no errors due to incomplete flushing, etc.), and the true instrument response was not captured by a \( N - 2 \) order fit, then a \( N - 1 \) order fit could be considered. One might consider the residuals introduced by a \( N - 2 \) order fit to be a negative aspect of the calibration procedure because residuals are transferred to the final, calculated \( \text{CO}_2 \); however, rather than being detrimental, the magnitude of the residuals are actually a valuable indication of the “health” of a sampling system as well as an indication of the accuracy of the calibration gases. Because other IRGA systems have shown that the residuals can be very small [on the order of 0.02 \( \mu \text{mol mol}^{-1} \) (Zhao and Tans 2006) or 0.07 \( \mu \text{mol mol}^{-1} \) (van der Schoot et al. 2006)], the residuals on the order of 0.1 \( \mu \text{mol mol}^{-1} \) from CME04 may be an indication of dead

---

**Table 3. Different forms of the \( \text{CO}_2 \) field-calibration equation [Eq. (1)] that were examined in the postprocessing of the CME04 raw LI-7000 data, \(( \text{CO}_2)_{\text{raw}}\).**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Equation form</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3</td>
<td>Third-order polynomial</td>
<td>( A_3 - A_0 ) are determined at each calibration period. The coefficients are linearly interpolated between calibration periods.</td>
</tr>
<tr>
<td>P2_con</td>
<td>Second-order polynomial</td>
<td>( A_1 = 0 ). ( A_2 - A_0 ) are determined at each calibration period. These coefficients are used until the subsequent calibration period.</td>
</tr>
<tr>
<td>P2</td>
<td>Second-order polynomial</td>
<td>Same as P2_con, but the ( A_2 - A_0 ) coefficients are linearly interpolated for the time between the calibration periods.</td>
</tr>
<tr>
<td>L1</td>
<td>Linear</td>
<td>( A_1 = A_2 = 0 ). ( A_1 ) and ( A_0 ) are determined by a linear fit for each calibration time period using all four-calibration gases.</td>
</tr>
<tr>
<td>L2</td>
<td>Piecewise linear</td>
<td>( A_3 = A_2 = 0 ). ( A_1 ) and ( A_0 ) are determined by a linear fit for each calibration time period and between each pair of calibration gases. This method will result in a unique set of coefficients for each pair of calibration gases.</td>
</tr>
</tbody>
</table>

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L. Zhao 2007, personal communication; also see Zhao and Tans (2006), which is a factor of 5 smaller than the residuals we found in the field with the TGaMS LI-7000.
FIG. 7. Time series from NIWOT02 of the raw CO₂ output by (a1)–(a3) LI-A and (b1)–(b3) LI-B during time periods when the 419, 360, and 283 µmol mol⁻¹ calibration gases were being sampled (concentration of the calibration gas are indicated in the bottom left). The data used to calculate the mean CO₂ are indicated by the vertical lines and labeled, sampling time period. The standard deviation (σ) and peak-to-peak range (RNG) of the CO₂ from the sampling time period are shown within each panel along with the slope from a linear fit of CO₂ vs time (as indicated by the solid line). The flushing time period starts when the valve is switched (i.e., at t = 0). For NIWOT02 the flushing time was 215 s and the sampling time was 25 s (Table 1).
volumes affecting our ability to accurately measure the gas concentrations.

The CO₂ community recommends that independent monitoring of the CO₂ accuracy be performed by sampling from a long-term “surveillance” gas cylinder (i.e., a cylinder containing CO₂ in air that is not used in the calibration, but is sampled periodically by the system; Bakwin et al. 1995; Zhao et al. 1997; Trivett and Köhler 1999; Stephens et al. 2006; Miller 2006). The surveillance gas is supposed to last beyond the time period when the regular calibration gases are changed, to keep track of any changes that might be caused by changing a calibration gas or the introduction of a gas with a error in the assigned concentration value. The disadvantage of the surveillance gas is that it only checks the calibration curve at one specific CO₂ concentration. There was no independent surveillance gas available with the TGaMS system so we are not able to evaluate this aspect of the field calibration.

For NIWOT02, the initial attempt at data processing used all three calibration gases and a linear form of Eq. (1); however, when using all three gases, the calculated CO₂ did not agree well with the 360 μmol mol⁻¹ calibration gas. Because the 360 and 419 μmol mol⁻¹ concentration gases nearly bracketed the range of CO₂ observations during the experiment, it was decided not to include the 283 μmol mol⁻¹ concentration gas in the calibration. The time series of the linear coefficients [A₁

![Graphical representation of statistics from 283 different sampling time periods for the 398 μmol mol⁻¹ calibration gas as a function of flushing time for (a) the standard deviation (σ) of (CO₂)raw and (b) the slope of (CO₂)raw vs time within the sampling time period. (c) Median of the calibrated CO₂ data using a second-order polynomial (P2) form of the field-calibration equation. The solid and dashed lines indicate a 10- or 50-s sampling time period, respectively. Data shown are from CME04 between days 220 and 251; other calibration gases show similar results.](image-url)
and $A_0$ in Eq. (1) and changes in cell temperature $T_{\text{cell}}$ and pressure $P_{\text{cell}}$ are shown in Fig. 10. The $T_{\text{cell}}$ experiences the same diurnal temperature changes as the atmosphere, but stays about 10°C warmer. The atmospheric pressure and $P_{\text{cell}}$ closely follow each other because the pump is upstream of the sample cell. For LI-A, the changes in $T_{\text{cell}}$ caused $A_1$ to vary (by less than 1%), and $A_0$ to change by around 2 μmol mol$^{-1}$ (to compensate for the change in $A_1$). These variations in CO$_2$ with temperature are comparable to the quoted value of ±0.3 μmol mol$^{-1} \,$°C$^{-1}$ (LI-COR Inc. 2005). For LI-B, the connection between $A_1$ and $A_0$ was less obvious and both terms appear to have a slight drift. There was a jump in the LI-B offset value that occurred around day 259 (16 September 2002). This was a day LI-A and LI-B were visited with a set of portable calibration gas cylinders (section 5b), and it is possible something caused the calibration to change slightly when the portable gas cylinder was attached and removed from LI-B. This is an example of why it is useful to use a field calibration rather than rely on the factory calibration.

d. Application of the field-calibration coefficients to LI-7000 data

Typical methods for extending the calibration coefficients to the time between the calibration periods

![Graph](image-url)
used in previous studies are linear interpolation of the coefficients (Zhao et al. 1997) or using the average between calibration periods (Monson et al. 2002). If there is not too much change in the calibration coefficients between calibrations, one could simply apply the coefficients from each calibration until the following data cycle. However, we found that during NIWOT02 the drift in the calibration coefficients was too large to maintain an acceptable level of accuracy in the calibrated CO₂ data (to better than ±1 µmol mol⁻¹). To account for any change in the calibrations between calibration periods, the calibration coefficients were linearly interpolated and then applied to the (CO₂)raw data.

FIG. 10. Calculated calibration coefficients from NIWOT02 of the gain (Å₁) and offset (Å₀) from (a),(b) LI-A and (c),(f) LI-B. Each point represents the results of a linear calibration from one calibration period that occurred every hour. (c) The air temperature (T_air) and LI-A cell temperature (T_cell) and (d) the atmospheric pressure (P_baro) and LI-A cell pressure (P_cell). Note that second-order and third-order polynomials were not used in NIWOT02.
5. Results

The effect of using different forms of the field-calibration equation (as described in section 4) and methods of data processing on the final calculated CO₂ data are presented within this section. We also present in situ CO₂ field comparisons that were found to be useful in evaluating data quality.

a. Effect of the field-calibration equation on the calculated CO₂

Based on the discussion in section 4c (e.g., Figs. 6 and 9) we already have some insight into how the CO₂ data calculated with the different calibration equations will compare with each other. Figure 11b shows that the CO₂ differences among the various calibration equations were within 0.2 μmol mol⁻¹ of each other near the calibration gas concentrations. However, at CO₂ concentrations much greater than the highest calibration gas (418 μmol mol⁻¹), the linear (L1) and third-order polynomial (P3) equations quickly diverge (with differences over 1 μmol mol⁻¹) from the CO₂ calculated with the piecewise linear (L2) and second-order polynomial (P2) equations. The divergence is due to the range of the CO₂ measurements not being properly bracketed by the calibration gases.

An overall summary of the CO₂ differences among the methods used in our study is shown by frequency distributions with the median difference and standard deviation of the difference for each combination listed in the top-left corner of Fig. 11c. Since most of the atmospheric CO₂ measurements were within the 370–390 μmol mol⁻¹ range, the results in the frequency distributions will be heavily weighted to the differences at this CO₂ concentration, and is why the divergence in P3 and L1 at large values of CO₂ do not have a large impact on the frequency distribution of the difference. The frequency distribution of the P2_con-L2 difference (standard deviation = 0.53 μmol mol⁻¹) is more spread out than the difference of P2-L2 (standard deviation = 0.31 μmol mol⁻¹), which indicates the importance of linearly interpolating the coefficients between adjacent calibration periods.

b. Empirical data quality tests

The CO₂ measured by TGaMS was evaluated for accuracy, reproducibility, and comparability by empirical CO₂ comparisons among a set of portable cylinders, collocated inlets attached to independent CO₂-measuring instruments, and CO₂-measuring systems that are located near each other. For CME04, the TGaMS CO₂ data used in these comparisons are from the P2 field-calibration equation (Table 3).

During NIWOT02 a set of four 6-L calibration cylinders were prepared and brought to each CO₂-measuring system involved in the project. The CO₂ concentrations assigned to each portable gas cylinder (353, 369, 392, and 416 μmol mol⁻¹) were determined by comparison to gases from NOAA/GMD, and selected to span a large portion of the CO₂ range measured in the field. The comparison between LI-B and the portable cylinders is the most consistent (Fig. 12). Results for LI-A were similar to LI-B with a slightly larger variability (primarily due to the comparison on 19 September, which should probably not be considered because someone breathed into the A1 and B1 inlets causing the CO₂ to briefly go over 20 000 μmol mol⁻¹ 10 min before the LI-A comparison, and 20 min before the LI-B comparison). Based on these few comparisons, the CO₂ measured by LI-A and LI-B was 1–2 μmol mol⁻¹ larger than the CO₂ concentration within the portable cylinders.
It is possible that a CO₂ bias was introduced by the method used to determine the CO₂ concentration of the TGaMS calibration gases (described in section 3a). Over the range of portable cylinder CO₂ concentrations, the CO₂ difference varies on the order of 0.3–0.4 μmol mol⁻¹, which is consistent with the magnitude of differences found in the evaluation of the different field-calibration equations in CME04 (recall that a linear field-calibration equation was used for NIWOT02). The comparisons of the portable cylinders with NWT and USGS were more variable, perhaps due to the fact that the USGS and NWT systems used the LI-COR factory calibration and only two calibration gases (as described in section 3). Also, the calibrations of the NWT/USGS systems were performed less frequently than LI-A and LI-B (NWT calibrations were every 4 h, and USGS calibrations were every 2 h compared to every hour for TGaMS). On 18 September 2002 the calibration gas in

![Graph showing frequency distribution of CO₂ calculated using different forms of the field-calibration equation.](image)

**Fig. 11.** Plots of (a) the frequency distribution of CO₂ calculated using different forms of the field-calibration equation (each form is identified in the legend and described in Table 3), (b) the difference in CO₂ calculated with each calibration equation [relative to the piecewise linear L2 form of Eq. (1)], and (c) the differences from (b) shown as a frequency distribution (the median difference ± the standard deviation of the difference for each combination are shown in the upper left). The dashed vertical lines in (a) and (b) are the CO₂ concentration of the calibration gases (note that the two lower gases are beyond the x limits of the plot). These are CO₂ data from the 1-m inlet (A7) at the Pine tower during CME04 between days 220 and 280.
the USGS system was changed, which is the reason the first comparison was so different than the later ones.

Time series of 1-m CO₂ from the NIWOT02 collated inlets shows that each CO₂-measuring system captured a similar diurnal CO₂ pattern; however, there were some significant differences between the various systems (Fig. 13). The median and standard deviation of the CO₂ difference between the A1 and B1 inlets was \(2.02 \pm 0.42\) \(\text{mmol mol}^{-1}\) (Fig. 14e1), whereas the differences between A9 and NWT (0.66 \(\pm 2.7\) \(\text{mmol mol}^{-1}\)), and A8 and USGS (\(-3.99 \pm 1.7\) \(\text{mmol mol}^{-1}\)) were larger and more variable. It is not too surprising that A1–B1 agree better than NWT–A9 and USGS–A8, since LI-A and LI-B used the same calibration gases, were situated near the inlets (less than 5 m away), and the CO₂ data were processed in a similar manner. A difficulty with this comparison was the long tubing lengths used to reach the NWT and USGS towers. The air sample within the long tubing undoubtedly underwent additional mixing that likely has a detrimental effect when trying to compare CO₂ on a point-by-point basis over fairly short (order of 30 min) time scales. CO₂

![Figure 12](image_url)

**Fig. 12.** Differences in CO₂ between each continuous CO₂-measuring system—(top to bottom) LI-A, LI-B, NWT, and USGS—and the four transportable gas concentrations during NIWOT02 (note that the range of the y axis for the top two panels differs from the bottom two panels). The legend in the second panel identifies the date of the comparison. The IC2 comparison on 19 September for LI-A was affected by someone exhaling into the LI-A and LI-B collated 1-m inlet 10 min before attaching the portable cylinder to the LI-A system. Each CO₂-measuring system at the site was equipped with a three-way valve to allow the gas from the portable cylinders to be run through the system following the same pathway that the calibration gas would normally use (the line pressure with the portable calibration gases attached was matched as best as possible to that used by the calibration cylinders at each system).
reproducibility achieved with TGaMS is demonstrated by comparing the 1-m CO2 measured from inlet B1 at the NCAR tower with CO2 from the collocated 1-m inlet (A1–B1), the 1-m inlet at the West tower (B5–B1), and the 6-m inlet at the NCAR tower (A2–B1) (Fig. 14e2). From these frequency distributions it can be observed that the CO2 difference between the collocated inlets were all between $6 \pm 1$ mol mol$^{-1}$, whereas the horizontal and vertical CO2 differences observed in the environment ranged from $-30$ to over $10$ mol mol$^{-1}$ and are what one would expect to find (e.g., CO2 at 1 m was always greater than CO2 at 6 m, and CO2 upslope of the NCAR tower was usually smaller than CO2 at the NCAR tower, but the horizontal difference was of either sign). A detailed examination of CO2 in NIWOT02 can be found in Sun et al. (2007).

In CME04, there were no collocated inlets, so the midday 1-h median from the upper level at each tower is used to cross compare CO2 from the various systems. Hourly CO2 time series from the top of each tower along with NOAA/GMD CO2 air samples collected with a flask system at the NWR site on Niwot Ridge (Conway et al. 1994) are shown in Figs. 14a1–a3. The NWR air-collection site is above tree line at 3523 m and...
3.4 km to the northwest of the CME04 forest towers and is included to give an estimate of how much CO₂ spatial variability existed. The hourly panels show the temporal variability on a given day. A comparison of the midday CO₂ measured at the top of the NWT tower with a tunable diode laser absorption spectrometer and the NWR flask CO₂ has been presented previously by Bowling et al. (2005, their Fig. 9), who found that CO₂ differences during summer 2003 were on the order of 0–4 μmol mol⁻¹. For CME04, the NWR CO₂ flask measurements were generally within 1 μmol mol⁻¹ of the tower CO₂ measurements indicating the high degree of atmospheric mixing present within the convective daytime boundary layer; however, local differences among the CME04 towers, were also sometimes on the order of 1 μmol mol⁻¹. It should be noted that the NWR flask samples were sometimes collected closer to 1100 MST rather than 1200 MST, so the time series of NWR and the CME04 tower CO₂ in Fig. 14b do not always have a consistent time stamp. To get an empirical estimate of the degree of CO₂ comparability among the various systems, the time series and frequency distribution of the midday CO₂ differences are plotted in Figs. 14c,d, and the median differences and standard deviations are: 0.04 ±0.81 μmol mol⁻¹ (Pine - Aspen), -0.27 ±0.73 μmol mol⁻¹ (Willow - Aspen), and -1.33 ±0.94 μmol mol⁻¹ (NWT - Aspen). It should be emphasized that these statistics include differences due to local meteorology and different underlying surfaces; the highest inlet at Willow was at 17 m surrounded by low shrubs, whereas the 30-m inlets at Pine and Aspen and the 21.5-m inlet at NWT were located above an 11-m-tall subalpine forest. The CO₂ measured by NWT was typically about 1–2 μmol mol⁻¹ lower than the other three systems and this systematic bias is probably due to the limitation of using two calibration gases and the LI-COR factory calibration.

6. Conclusions

The construction of a portable, 18-inlet, CO₂-measuring system (TGaMS) used in two different field projects was described. The air-sampling system, called HYDRA, was attached to either one or two analysis systems that used a LI-COR model LI-7000 to analyze the CO₂ concentrations of the air samples. To improve the accuracy of the measured CO₂, in situ "field calibrations" (i.e., short time periods when a series of high-accuracy calibration gases were passed through the LI-7000 sample cell) were used by fitting the raw CO₂ data output from the LI-7000 to the assigned CO₂ concentration of the calibration gases. CO₂ calculated using a third-order polynomial, second-order polynomial, linear, and piecewise linear form of the field-calibration equation [Eq. (1)] were compared. For N = 4 calibration gases, the second-order polynomial had residuals of the fit that were on the order of ±0.1 μmol mol⁻¹, whereas a linear fit had residuals on the order of ±0.3 μmol mol⁻¹ (Fig. 9). Part of our study explored the possibility of using a third-order fit to eliminate the residuals. Although the CO₂ concentrations from a third-order fit were within 0.2 μmol mol⁻¹ of the CO₂ calculated from the second-order fit, using a third-order fit was rejected for the following reasons: 1) any errors in the CO₂ concentrations assigned to the calibration gases are fit exactly with a N = 1 fit, 2) any dead volume or incomplete flushing of the system could bias the assigned CO₂ concentration, 3) the highly nonlinear nature of the N = 1 order fit makes extrapolation of the field-calibration curve inadvisable, and 4) although the N = 1 order fit was fairly well behaved for the calibration gas concentrations used in CME04, certain combinations of gas concentrations can produce nonlinear results between the calibration points. Rather than eliminating the residuals of the fit, we concluded that residuals act as an indicator of system integrity and large residuals might indicate some problem within the system or with a particular calibration gas. A few changes to TGaMS (listed below) might help to reduce the magnitude of the TGaMS residuals in future experiments.

Empirical comparisons were used to estimate how well TGaMS measured CO₂ during various field projects. In NIWOT02, a pair of side-by-side inlets (with one inlet attached to each LI-7000) was used to empirically
estimate the TGaMS CO₂ reproducibility; the CO₂ difference between the collocated inlets had a median and standard deviation of $-0.02 \pm 0.42 \, \text{μmol mol}^{-1}$ over 17 days (Fig. 14c). During NIWOT02 four portable cylinders with gas concentrations closely linked to the WMO CO₂ Scale were periodically sampled by TGaMS. These comparisons revealed a positive bias of $1\text{--}1.5 \, \text{μmol mol}^{-1}$ in the TGaMS CO₂ data, which is most likely due to the way CO₂ concentrations were assigned to the calibration gases in NIWOT02 (section 3a). Therefore, in NIWOT02 we conclude that TGaMS ran in a mode with acceptable reproducibility between inlets, but was not a high-accuracy system relative to the WMO CO₂ Scale.

In CME04, two high-accuracy CO₂-measuring AIRCOA systems (Stephens et al. 2006) were deployed within 400 m of TGaMS. The calibration gases used with TGaMS and AIRCOA were assigned CO₂ concentrations with an estimated uncertainty of $\pm 0.1 \, \text{μmol mol}^{-1}$ relative to the WMO CO₂ Scale by the NCAR CO₂/CO₂ Calibration Facility. The empirical assessment of how well TGaMS measured CO₂ was based on midday, above-canopy CO₂ comparisons. The 30-m CO₂ measured by TGaMS (at Pine tower) and AIRCOA (at Aspen tower) had a median difference and standard deviation of $0.04 \pm 0.81 \, \text{μmol mol}^{-1}$ based on data between 1000 and 1500 MST over 2 months. This result includes real variability in the CO₂ difference, but is comparable to the differences measured between the two AIRCOA systems (Fig. 14d). Therefore, we conclude that TGaMS in CME04 had improved CO₂ accuracy compared to NIWOT02.

For others interested in making highly-accurate CO₂ measurements (relative to the WMO Scale) we recommend the following guidelines: 1) high-accuracy calibration gases must be used, 2) calibration gases should fully span the expected range of environmental CO₂ and be approximately equally spaced within the range, 3) a long-term “surveillance” gas should be used to independently evaluate the system performance, 4) flushing of the system should be checked by examining the slope of “CO₂ versus time” during the calibration periods, and 5) the order of sampling the calibration gases should be varied to detect any flushing issues. Hardware changes that would improve TGaMS are as follows: 1) active temperature control of the LI-7000; 2) minimize dead volumes by better flushing of the system (this can be achieved by a redesign of the manifold as well as using a higher flow rate for flushing); 3) minimize internal plumbing surfaces that absorb–desorb CO₂; 4) develop a systematic way to check for tubing damage (i.e., cracks or holes), as well as leaks in valves, rotameters, fittings, etc. (as an example of this, in CME04 chunks of dry ice were dropped into the HYDRA box and revealed a leak in one of the internal connections for one inlet; such a method works for spot checks, but a more comprehensive leak-checking methodology should be developed); 5) measure the pressure, temperature, and humidity of the incoming air sample so that any blockage due to ice or debris can be detected; and 6) tubing should be insulated and/or heated to minimize condensation (or ice) formation on the inner walls of the tubing.

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