AirCore: An Innovative Atmospheric Sampling System

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ABSTRACT

This work describes the AirCore, a simple and innovative atmospheric sampling system. The AirCore used in this study is a 150-m-long stainless steel tube, open at one end and closed at the other, that relies on positive changes in ambient pressure for passive sampling of the atmosphere. The AirCore evacuates while ascending to a high altitude and collects a sample of the ambient air as it descends. It is sealed upon recovery and measured with a continuous analyzer for trace gas mole fraction. The AirCore tubing can be shaped into a variety of configurations to accommodate any sampling platform; for the testing done in this work it was shaped into a 0.75-m-diameter coil. Measurements of CO_2 and CH_4 mole fractions in laboratory tests indicate a repeatability and lack of bias to better than 0.07 ppm (one sigma) for CO_2 and 0.4 ppb for CH_4 under various conditions. Comparisons of AirCore data with flask data from aircraft flights indicate a standard deviation of differences of 0.3 ppm and 5 ppb for CO_2 and CH_4, respectively, with no apparent bias. Accounting for longitudinal mixing, the expected measurement resolution for CO_2 is 110 m at sea level, 260 m at 8000 m, and 1500 m at 20 000 m ASL after 3 h of storage, decreasing to 170, 390, and 2300 m, after 12 h. Validation tests confirm that the AirCore is a robust sampling device for many species on a variety of platforms, including balloons, unmanned aerial vehicles (UAVs), and aircraft.

1. Introduction

An important constraint on the determination of land and ocean sources and sinks of carbon is an understanding of the distribution of CO_2 throughout the atmospheric column. To this end a variety of satellites are either currently making greenhouse gas measurements [Atmospheric Infrared Sounder (AIRS), Greenhouse Gases Observing Satellite (GOSAT), Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY), Tropospheric Emission Spectrometer (TES)] or planning to do so [Orbiting Carbon Observatory-2 (OCO-2), Active Sensing of CO_2 Emissions over Nights, Days, and Seasons (ASCENDS)]. Such satellite-based remote sensing missions provide column integrals of CO_2 or other trace gases, such as CH_4 or CO, across the globe, but suborbital measurements will be used to validate and help determine the altitude-weighting functions for the satellite data. One source of validation of spaceborne instruments is a network of ground-based upward-looking spectrometers, such as the Total Column Carbon Observing Network (TCCON), which is an array of Fourier transform spectrometers (FTS; see Petersen et al. 2008; Warneke et al. 2005). However, such spectral methods must also be validated and calibrated by in situ measurements, such as aircraft measurements. Although some effort has been made to validate these in the past (Washenfelder et al. 2006), validation measurements must continue in an ongoing fashion if spectrometers are to be used to continuously verify satellite measurements. Profiles to high altitudes are particularly valuable in these validation efforts because they do not require as much

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extrapolation and interpolation of measurements at levels above the aircraft ceiling, reducing the uncertainty in the column integral.

Altitude profiles are not only important for satellite and total column measurements, but they also serve as either a direct or indirect way to estimate regional fluxes. For example, regularly sampled vertical profiles of CO_2 from National Oceanic and Atmospheric Administration (NOAA)/Earth System Research Laboratory's (ESRL's) airborne flask network have been used to quantify North American carbon exchange directly (Crevoisier et al. 2006, 2010; Stephens et al. 2007; Yang et al. 2007), while aircraft measurements from various intensive campaigns have been used to quantify or constrain greenhouse gas sources and sinks on a continental or regional scale as well (Chou et al. 2002; Gerbig et al. 2003; Isaac et al. 2004; Kort et al. 2008; Martins et al. 2009; Mays et al. 2009; Miller et al. 2007; Sawa et al. 2004). Regular greenhouse gas sampling from commercial aircraft has provided another valuable dataset (Machida et al. 2008). Aircraft profiles provide an important capability for validating both inverse and forward models (Peters et al. 2007; Stephens et al. 2007; Yang et al. 2007). Although some inversion efforts have included the limited routine aircraft profiles that are available (Baker et al. 2006), many inverse models quantify carbon sources and sinks by using only ground-based in situ measurements, coupled with meteorological transport models, to produce estimates of net carbon sources and sinks (Gurney et al. 2004, 2002; Peters et al. 2005, 2007). The use of ground measurements only for model data assimilation forces inverse methods to rely on the correct parameterization of vertical transport to determine the flux of carbon into the atmospheric boundary layer. Because low-resolution transport models used for these studies often either fail to resolve the boundary layer height accurately or misrepresent vertical and horizontal transport, they can significantly contribute to error associated with the derived fluxes.

Vertical profile measurements of atmospheric trace gases have proved invaluable for validating inverse models and quantifying their associated error (Bakwin et al. 2003; Stephens et al. 2007; Yang et al. 2007). Profile measurements to altitudes higher than typical aircraft flights have also provided information about tropospheric–stratospheric exchange and stratospheric transport (Andrews et al. 1999, 2001; Daube et al. 2002). Vertical profile and high-altitude measurements of trace gases thus make a vital contribution to carbon cycle science, either directly through source and sink quantification, or indirectly through their use by inverse models and for remote sensing data validation.

In this study we validate an idea originally developed by Pieter Tans of NOAA/ESRL (Tans 2009): that a long tube descending from a high altitude with one end open and the other closed can sample and retain a mole fraction profile of a gas to be analyzed at a later date. The concept is based on the fact that molecular diffusion of air is relatively slow and that no other mixing occurs in the tubing (i.e., convection). For instance, a molecule of CO_2 in air will have a root-mean-square travel distance of approximately 1.6 m in a single day at 20°C resulting from molecular diffusion. By storing a concentration profile in a long tube it is possible to minimize resolution loss; after 1 day, the profile would still consist of 47 independent measurements (assuming a 150-m tube and diffusion in both directions, or 3.2 m).

Although other methods for filling the long tube with a sample are possible, this study is focused on the simplest approach in which the tube, open at one end, is allowed to equilibrate with ambient pressure. As the tube falls through the atmospheric column, ambient air is forced into the tube by the positive change in pressure. At the bottom of the profile the tube is sealed until it can be analyzed. In this simple configuration the AirCore can be launched on multiple platforms, including airplanes, balloons, and unmanned aerial vehicles (UAVs). From this perspective the AirCore is poised to make a significant contribution to airborne datasets because of its capability to capture a continuous profile (in contrast with discrete flask sampling), and its ability to be deployed to high altitudes (up to 30 km in a balloon). Its ability to sample at high altitudes, on either high-altitude aircraft or balloons, where in situ continuous analyzers cannot perform without expensive alterations (Daube et al. 2002), make it an ideal sampler for measuring close to the full column of a trace gas. Although a continuous, precise analyzer is necessary for analysis of the sample on the ground, the same analyzer would not be able to be deployed on a balloon with a 12-kg weight limit. We also envision that in the future, multiple AirCore samplers could be deployed and return to a central location for analysis, eliminating the need for multiple analyzers. The AirCore sample could also, in theory, pass through the first analyzer and on to another continuous analyzer for a different trace gas, yielding multiple gas measurements with only one sample.

The simplicity of the AirCore translates into a sampling method that is less expensive and easier to deploy in more places than other aircraft or balloon instruments. It can be used to make measurements of CO_2, CH_4, and other trace gases when deployed on weather balloons, aircraft, or any other vehicle to the high accuracy and precision required. The AirCore can produce column profiles of atmospheric greenhouse gases that

FIG. 1. The AirCore with magnesium perchlorate driers and shut-off valves attached on each end.

can be used for inverse models as well as for the validation of satellite column integral data. Given the simplicity and robustness of the AirCore, measurements can be made easily and more affordably than with other trace gas measurement systems.

2. Method

a. AirCore description and preparation

The AirCore used for this validation study was 152-m (500 ft)-long, 304-grade stainless-steel tubing, with an outer diameter of 0.64 cm ($\frac{1}{4}$ in.) and a wall thickness of 0.025 cm (0.01 in.), treated by Restek, Inc., with their Sulfinert coating (Fig. 1). The thin wall was necessary to limit AirCore's weight for use on weather balloons (the approximate weight with valves and dryers is 6.7 kg). Prior to testing or field deployment, the AirCore tubing was dried by flowing hot, dry gas through the insulation-wrapped coil at 50 l min^{-1} for 12 h, achieving an exit temperature of 100°C. Short (15 cm) lengths of stainless steel tubing filled with fresh magnesium perchlorate powder were attached to either end of the AirCore tubing, to ensure that no moisture entered the tubing during any testing or sampling.

b. Picarro CRDS continuous analyzer

All gas analyses were performed using one of two wavelength-scanned cavity ring down-spectroscopy (CRDS) trace gas analyzers by Picarro, Inc., models G1301 and G1301-m (Crosson 2008). Laboratory AirCore testing was conducted using bottled natural air mixtures with World Meteorological Organization (WMO)-traceable calibrations for CO_2 and CH_4. The following abbreviations are used for measured mole fractions:

ppm = μmol mol^{-1} and ppb = nmol mol^{-1}. In the laboratory, the CRDS analyzer's precision, as indicated by one standard deviation of the measurements of a single calibration gas standard at 0.5 Hz with no averaging time, is 0.05 ppm for CO_2 and 0.5 ppb for CH_4 at all flow rates between 40 and 300 sccm (standard cubic centimeters per minute). The analyzer tightly controls the pressure and temperature in its measurement cell [187 hPa (140 torr) and 45°C], to achieve the above precision (Crosson 2008). The sample flow rate was adjusted by user-selectable parameters within the Picarro analyzer software before measurements began.

Picarro's model G1301-m, a flight-ready analyzer, was used on board an aircraft along with the AirCore for a comparison of the results. This analyzer's precision (defined as the standard deviation of continuous measurements of a single gas) in flight is 0.08 ppm for CO_2 and 1 ppb for CH_4, as determined from flight tests conducted at NOAA/ESRL. Similar precision has been reported by other groups (Chen et al. 2010). For aircraft flights, the analyzer flow rate was set to 300 sccm. This is the highest flow rate that the manufacturer recommends for the best performance in flight. Lower flow rates would not be desirable in flight because of the long lag time of pulling air through the inlet line.

c. AirCore analysis method

An experimental apparatus was constructed for laboratory testing and AirCore sample analysis using the Picarro CRDS analyzer (Fig. 2). Two calibration gas standards in cylinders were used along with a multiport valve (Vici Valco multiposition valve and microelectric actuator, Product EMT2SD8MWE) that could select one of two gases or none at all. An arrangement of valves and quick-connect fittings was designed to allow flexibility in performing the various laboratory tests and sample analysis while minimizing the potential for the introduction of room air and moisture into the tubing.

For analysis of an AirCore sample collected during flight, the end of the tubing that had been closed during sampling was opened and connected to one of the gas standards, and the other end was connected to the analyzer. The analyzer pump pulled the sample through the analyzer with both ends of the tube open, such that the standard gas was pulled through after the sample finished. To minimize pressure transients during analysis, the experimental apparatus incorporated a T fitting in the plumbing arrangement between the gas cylinder and AirCore, with one branch of the T connected to a flowmeter and open to the room beyond that. The flowmeter was monitored to ensure that flow was always positive and no room air was introduced. The plumbing arrangement allowed the CRDS analyzer to pull the
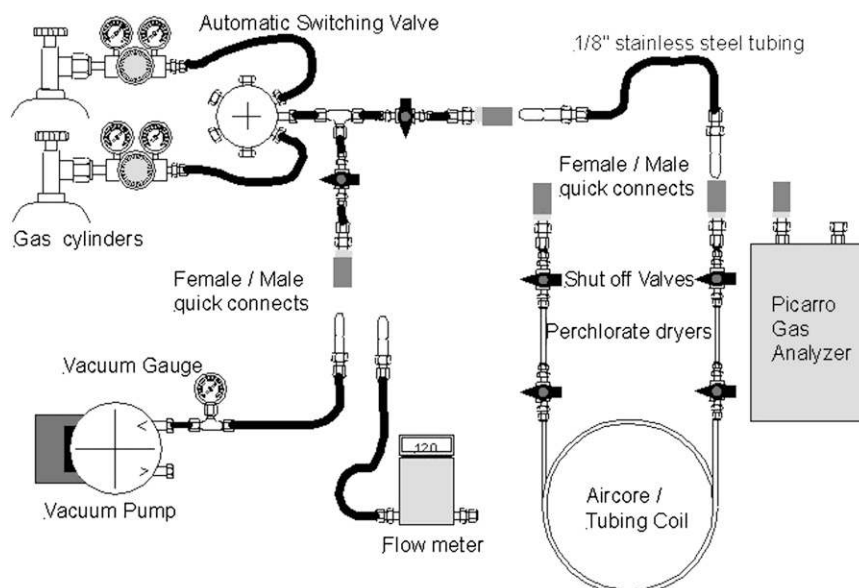
Fig. 2. Diagram of AirCore testing apparatus in the laboratory, showing the different components. The flowmeter was connected to the line for regular analysis, while the vacuum pump was used for the evacuation experiments described in section 3. Quick connections were also optional for taking the AirCore out of the analysis line to measure a gas cylinder directly with the Picarro CRDS gas analyzer.

sample at ambient pressure, so that there was no over-pressure from the gas cylinder regulator.

During testing and analysis, the flow rate was varied between 40 and 300 sccm. Lower flow rates were desirable during analysis of the AirCore sample to maximize the resolution of measurements, given the finite volume of air in the AirCore tubing (about 4 l in total). The AirCore samples from all of the flights were analyzed at 40 sccm, except for that of the 13 June flight, which was analyzed at 110 sccm. Section 3b describes the effect of flow rate on measurement resolution in detail. Some laboratory tests were done at the higher flow rates of 120 and 300 sccm to save time in repeated testing and to confirm that the results were not flow-rate dependent in any way.

After each flight, the AirCore was analyzed by the continuous CRDS analyzer on the ground with the sample that entered the AirCore last going into the analyzer first. Thus, the air sampled closest to the ground, within the planetary boundary layer, experienced the smallest loss of resolution from longitudinal mixing.

Once the AirCore had been analyzed, the time trace of analysis was converted into a mole fraction profile as a function of atmospheric pressure. Because of the method in which the AirCore sampled the ambient atmosphere, each unit of length in the AirCore tubing represented a constant unit of pressure in the atmosphere. The same mass of air entered the tubing at each increment of

ambient pressure during sampling, provided that the tubing temperature did not vary significantly during sampling. The tubing was wrapped in insulation for deployment on the balloon flight, and its measured temperature was found to vary by less than 10 K throughout the descent. Similarly, the temperature in the aircraft was controlled within 10 K as well.

Therefore, the beginning of the concentration time trace during measurement represented the last pressure sampled (when the valve was closed upon recovery); the end of the AirCore sample time trace, signaled by when the chase standard gas came through the analyzer, represented the lowest pressure encountered during flight. The concentration profile was then converted to a pressure profile, because each unit of time going through the analyzer (at a constant flow rate) represented a unit of length along the AirCore tubing, which in turn represented one unit of pressure in the atmosphere. For the 150-m-long AirCore used in this study, each meter of the tubing represented 1/150 of approximately 0.8 atmospheres (atm) (the ambient pressure when it was sealed upon landing), or 5.4 hPa.

d. Flask package

NOAA/Earth System Research Laboratory's flask packages with 12 glass flasks were used to compare with AirCore results on aircraft flights. These flask packages are used routinely on aircraft for collecting air samples

as part of the NOAA/ESRL/Global Monitoring Division's Carbon Cycle and Greenhouse Gases Group. Samples are collected with a two-component system: the programmable compressor package (PCP) contains pumps and batteries, and the programmable flask package (PFP) contains 12 sample flasks and a manifold. Flasks are cylindrical, 0.7 l in volume, and constructed of borosilicate glass with a glass piston, Teflon O-ring-sealed stopcock on each end. Before deployment, flasks are evacuated, leak checked, flushed, and pressurized to 1.4 atm with synthetic air containing approximately 330 ppm CO_2 and no detectable CH_4. This composition is chosen to ensure that the flask surfaces and O rings are conditioned with near-ambient CO_2, and to indicate when the flask is insufficiently flushed (indicated by low CH_4 mole fractions).

Samples collected in PFPs were analyzed at NOAA/ESRL for CO_2 and CH_4 on one of two nearly identical automated analytical systems. These systems consist of a custom-made gas inlet system, gas-specific analyzers, and system control software; they use a series of stream selection valves to select an air sample or standard gas, pass it through a trap for drying maintained at $\sim -80°C$, and then to an analyzer. Carbon dioxide was measured by a nondispersive infrared analyzer (± 0.03 ppm; Conway et al. 1994), and CH_4 was measured by gas chromatography (GC) with flame ionization detection (± 1.2 ppb; Dlugokencky et al. 1994). Other gases are measured in the flasks as well, but are not discussed in this work. All measurements are reported as dry-air mole fractions relative to internally consistent standard scales maintained at NOAA.

3. Results

Results from testing the AirCore are presented below. These include laboratory tests in which calibrated air standards were used to fill the AirCore as well as flight tests on a balloon and aircraft.

a. Evacuation tests

Evacuation tests were conducted in the laboratory to ensure the preservation of sample mole fraction after the tubing had been evacuated and slowly filled, mimicking the loss in pressure as the AirCore rises to altitude when deployed in the field. Before evacuation, the AirCore was filled with a dry calibrated gas (henceforth referred to as the initial fill gas) by simply flowing this gas through the tubing and then closing the valves on either side. A pump was then used to evacuate the tubing from one end while the other end remained closed, to approximately 300 hPa, analogous to approximately 8 km of altitude. The tubing was then filled with a different standard gas

TABLE 1. Summary of reproducibility of a standard reference gas in the AirCore under various conditions. The first row shows the precision of the CRDS Picarro analyzer itself for comparison.

Test condition	CO_2 (ppm)	CH_4 (ppb)
CRDS analyzer precision at 0.5 Hz	0.05	0.5
Standard gas flow through AirCore	0.04	0.2
Storage of standard gas of 13h	0.07	0.3
Evacuation and fill standard gas	0.04	0.3
Initial fill gas preservation after aircraft flights	0.04 avg, 0.07 max	0.3 avg, 0.7 max

(referred to as the sample fill gas) in a controlled fashion at approximately 100 sccm, a typical average fill rate during flight, until the air inside the tubing reached ambient pressure, and was sealed. The AirCore thus contained a gas sample including the initial fill gas, which was compressed at the closed end of the tubing after filling, as well as the sample fill gas that entered the tubing after evacuation. The AirCore contents were then analyzed, and the measurements were compared to measurements of the initial fill gas and the sample fill gas because they had been previously measured directly on the same analyzer. Results from repeated evacuation tests showed that the CO_2 and CH_4 mixing ratios of both the initial and sample fill gases were preserved to within 0.04 ppm for CO_2 and 0.3 ppb for CH_4 (Table 1).

b. Flight tests

In-flight comparisons of CO_2 and CH_4 were made by the simultaneous operation of a Picarro flight-ready (unit CFADS30, model G1301-*m*) gas analyzer, the AirCore, and the discrete 12-flask sampling package (PFP) in a single-engine private airplane (Cessna T210) as part of NOAA's Carbon Cycle and Greenhouse Gases Group aircraft sampling program in Boulder, Colorado. Additional flights of the AirCore alone on a helium balloon were conducted as part of the Edge of Space Sciences (EOSS; available online at http://www.eoss.org) program.

1) AIRCRAFT FLIGHTS

A Cessna T210 regularly flies for NOAA's Carbon Cycle and Greenhouse Gases Group. The flights depart between 0900 and 1000 LT from the Boulder Municipal Airport (1600 m ASL) in Boulder, Colorado, and perform a descending profile over Briggsdale, Colorado, from 7900 m ASL down to 2000 m ASL, leveling off at 12 altitudes to collect a flask sample while circling. On the return to Boulder, the aircraft maintains a generally constant altitude. Three such aircraft flights were conducted with the AirCore, a Picarro CRDS continuous analyzer, and a 12-flask sampling package on 7 May 2009, 27 May 2009, and 13 June 2009. Each of the three systems

FIG. 3. The Cessna T210 used in light aircraft flights. Right photo shows inlet locations.

was provided its own dedicated inlet, located under the starboard wing of the aircraft (Fig. 3). Sample air was drawn from the inlet through approximately 5 m of Kynar (AirCore and the flasks) or polytetrafluoroethylene (PTFE; the CRDS analyzer) tubing. Both kinds of tubing were tested in the laboratory in advance to ensure there was no effect on CO_2 and CH_4 mole fractions for the lengths and flow rates used during sampling.

The Picarro CRDS flight-ready CO_2–CH_4–H_2O analyzer (model G1301-m) was installed in the aircraft along with a reference gas tank calibrated at NOAA/ESRL on the WMO standard scale with CO_2 and CH_4 mole fractions close to ambient. The analyzer pulled air from the wing-mounted inlet continuously at 300 sccm and measured at 0.5 Hz, sampling from the reference tank once every 20 min for 1.5 min. The air sample was not dried prior to measurement by the analyzer. The CO_2 and CH_4 data were corrected for water vapor postflight using a correction that was determined using the same analyzer unit in the laboratory. For CO_2 this calibration is consistent with the manufacturer's correction within 0.1 ppm (Picarro does not provide a correction for CH_4). The correction is also consistent to within 0.1 ppm for CO_2 and 1 ppb for CH_4 with that found by another group testing the same analyzer (Chen et al. 2010). The resulting flight data were corrected first by a linear calibration performed in the laboratory with five standard tanks prior to the flight, and then by a single offset using the value of the in-flight reference tank, linearly interpolated with time.

The AirCore data did not require water correction because the sample was dried by magnesium perchlorate driers to less than 100 ppm of water at the AirCore tubing inlet. Reference gases were run through the Picarro CRDS analyzer prior to and after the AirCore analysis for calibration purposes. The AirCore data were corrected first by the linear calibration for the CRDS analyzer as determined in the laboratory, and then by the offset found in the initial fill gas that remained in the AirCore at the end of the flight profile. For the aircraft

flights to approximately 300 hPa, approximately 1/3 of the AirCore remained filled with the initial fill gas. For all three flights the initial fill gas, when analyzed post-flight, had retained its original value within 0.07 ppm for CO_2 and 0.7 ppb for CH_4 (Table 1). A reference gas was also run before the AirCore analysis and used as the chase gas for analysis. The measured value of this standard gas did not drift significantly between the pre-AirCore measurement and the measurement after the AirCore was analyzed; it was within 0.05 ppm for CO_2 and 0.5 ppb for CH_4.

Both the CO_2 and CH_4 mole fraction profiles from the three flights from all three methods are shown in Figs. 4–6. The tops of the AirCore profiles are mixed with the initial fill gas (values of the fill gases for each flight are indicated in the figure captions), resulting in the lack of agreement with the top-most flask. The CRDS analyzer profiles for all three flights show considerably more variability in CO_2 than the AirCore. There are two possible reasons for this variability: 1) AirCore smoothes the profile by way of diffusion and flow mixing, as examined in further detail below; and/or 2) the flight pattern requires that the aircraft maintains a given altitude for a minute or two while flask sampling is occurring, possibly passing through atmospheric variability that the AirCore will not capture because it samples only at the time of the last pressure decrease at any pressure point. The flight on 7 May 2009 (Fig. 4) shows particularly significant variability during level flight. Because previous tests with the same CRDS analyzer measuring a single gas during a flight shows significantly less variability in flight (0.08 ppm CO_2 and 1 ppb CH_4 standard deviations) than when sampling ambient air, it is believed that the variability is real atmospheric variability and not instrument noise.

The AirCore profiles from the flights on 27 May 2009 and 13 June 2009 show brief enhancements in methane at the pressure levels close to 400, 700, and 750 hPa (27 May) and 650 hPa (13 June). These enhancements neither correspond with enhancements in the in situ analyzer
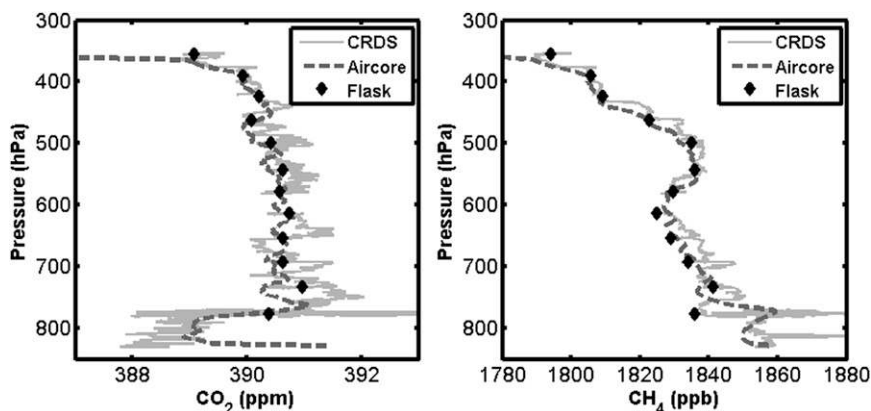
FIG. 4. Pressure profiles for (left) CO_2 and (right) CH_4 by three different methods from a profile Cessna flight on 7 May 2009. AirCore initial fill gas value was 362.82 ppm for CO_2 and 1706.5 ppb for CH_4.

data nor in the CO_2 concentration. After the flight experiments had been completed, extensive laboratory testing showed that the quick-connect fittings used to connect the AirCore to the CRDS analyzer were causing these CH_4 enhancements during the analysis stage. The short time scale of the spikes indicates that they had not experienced smoothing consistent with being introduced into the AirCore itself during sampling. Rather, they were introduced directly into the CRDS analyzer during AirCore sample analysis. The effect was later replicated in the laboratory (both with and without AirCore) and was found to originate at the quick-connect fittings when they were moved. When the connections were moved during the analysis, they produced a spike in methane but not CO_2 or water vapor, indicating that the enhancements were not caused by a leak in the system, but rather by outgassing either from the O ring or grease used in the quick connects (by Swagelok). This outgassing did not affect the mean CH_4 value of a standard gas running through the system and only occurred when the connection was turned or pulled. We remain confident that the flight data are not compromised other than at those specific points in the profile. Those particular fittings will not be utilized in future deployments of the CRDS analyzer or AirCore analysis.

(i) Analysis of flask offsets

Offsets between measurements made by NOAA/ESRL flasks, the Picarro CRDS analyzer, and AirCore profiles have been calculated for the three aircraft flights. For the continuous methods, the measurements were averaged over 10 hPa surrounding the atmospheric pressure of each of the 12 flask samples. The 32 (11 flasks for each of two flights, excluding the topmost 12th flask because of mixing with fill gas, and 10 flasks for the third flight, excluding the lowest because of extremely high variability) AirCore flask offsets have a mean value ($\pm$ one standard deviation) of -0.11 ± 0.29 ppm and 1.2 ± 5.1 ppb for CO_2 and CH_4, respectively (Fig. 7 and Table 2). Offsets calculated in the same manner between the AirCore and

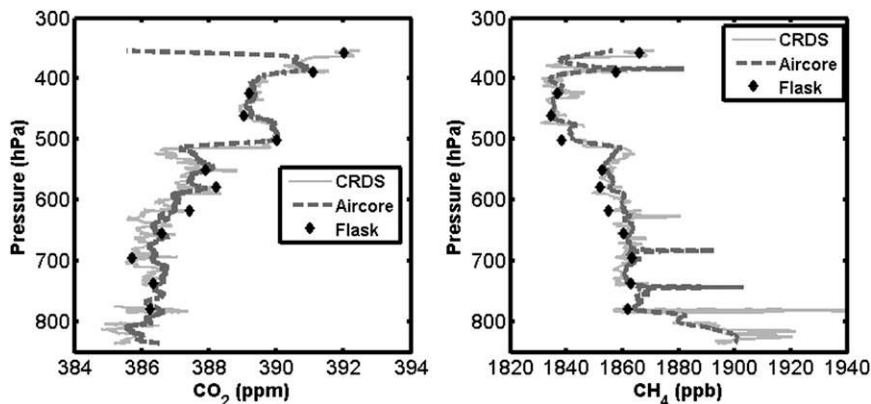FIG. 5. As in Fig. 4, but for 27 May 2009. AirCore initial fill gas value was 384.34 ppm for CO_2 and 1856.3 ppb for CH_4.
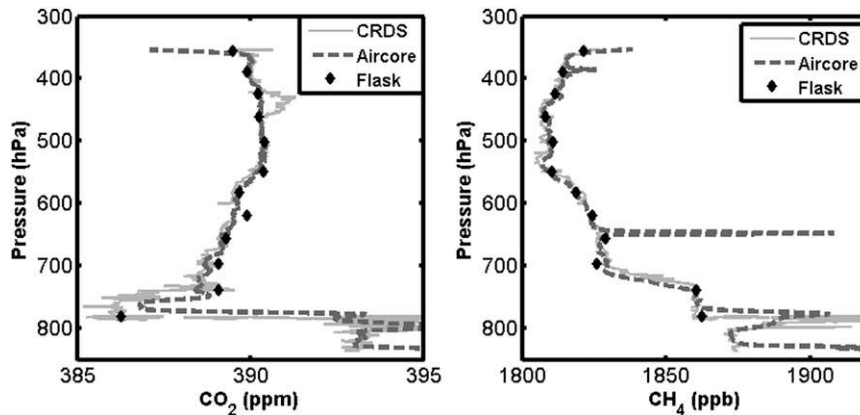
FIG. 6. As in Fig. 4, but for 13 Jun 2009. AirCore initial fill gas value was 384.34 ppm for CO_2 and 1856.3 ppb for CH_4.

the CRDS in situ values at the flask sampling locations show a mean offset of 0.00 ± 0.34 ppm and -0.5 ± 3.1 ppb for CO_2 and CH_4, respectively (Fig. 8 and Table 2).

Offsets between the CRDS in-flight data and the flasks were also calculated using the pressure averaging method and also do not suggest any bias; the mean values ($\pm$ one standard deviation) of these offsets are -0.06 ± 0.35 ppm and 1.6 ± 5.1 ppb for CO_2 and CH_4, respectively. A weighted time average of the CRDS-obtained mole fractions over the fill time of the flask sample is used to compare with the flask mole fractions as well, to provide a better match between the flask timing and the analyzer data. These offset means and standard deviations were -0.01 ± 0.30 ppm and -0.1 ± 2.4 ppb for CO_2 and CH_4, respectively. Finally, the AirCore pressure profile was compared with the smoothed CRDS analyzer pressure profile (see section 3b for the smoothing method) for each of the three flights. The highest and lowest pressures were excluded from the offset calculation

because of the mixing with the fill gas and the very high variability in the lowest 50 hPa of the profile. The means and standard deviations of the profile offsets were averaged over the three flights and are -0.07 ± 0.42 ppm for CO_2 and 0.1 ± 5.2 ppb for CH_4 (Table 2).

AirCore offsets among all three flights compare favorably with the offsets of the continuous CRDS analyzer. Notably, offsets between all three systems are smaller for the flight on 13 June 2009 (standard deviations of the offsets are approximately 0.2 ppm for CO_2 and 2 ppb for CH_4), where less atmospheric variability was observed in the vertical profile (Fig. 6). The average variability measured by the CRDS analyzer, defined as the standard deviation of the measurement over a 10-hPa range, was 0.29 ppm for CO_2 and 2.9 ppb for CH_4. It seems to be apparent that atmospheric variability plays a large role in the offsets seen in flights and is at least part of the reason that offsets in the laboratory with calibrated standards are significantly smaller for both
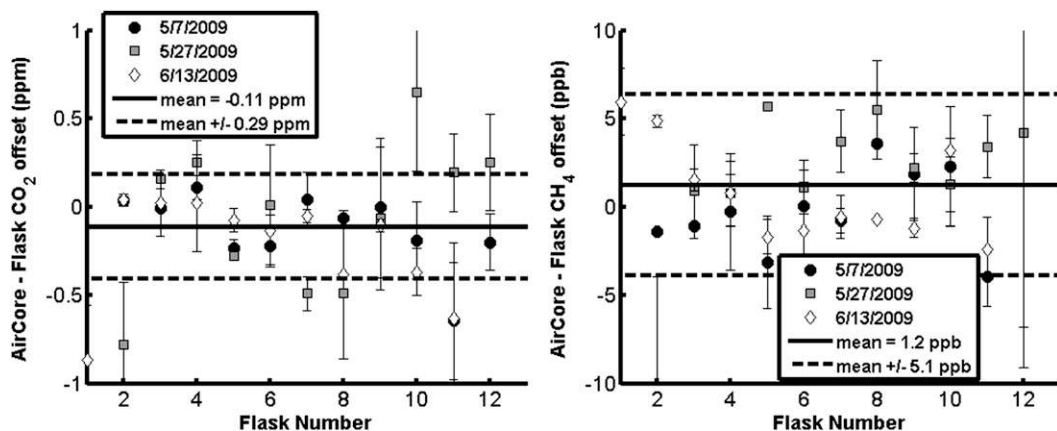

FIG. 7. AirCore–flask offsets for all three flights for (left) CO_2 and (right) CH_4. Error bars represent the variability observed by the Picarro CRDS continuous in situ analyzer, expressed as the standard deviation of the measurement for ± 5 hPa around the pressure at which the flask was sampled.

TABLE 2. Offsets with flasks and CRDS continuous analyzer for three profiles from aircraft flights over Briggsdale, CO. The value shown represents the mean ± one standard deviation of the set of 36 (12 flasks for each of three flights) offsets between each method and the flasks. The offset of the topmost flask is excluded for the AirCore, because the top of the profile is compromised by mixing with the initial fill gas. The lowest-altitude flask was also excluded for the 13 Jun flight for both the AirCore and the Picarro CRDS continuous analyzer because of the high (~6 ppm) offset caused by large variability at that altitude on that flight. The CRDS data offset was calculated both by comparing the data at the pressure of the flask sample (as it was for the AirCore), but also by comparing the time trace data at the time of the flask sample. The final column indicates the mean and average standard deviation of the offsets between the smoothed CRDS analyzer signal (see section 3b) and the AirCore at all the pressures, excluding the same regions as were excluded in the flask comparisons (very high and very low altitudes).

Mean ± standard deviation of offsets	CRDS vs flasks with time	CRDS vs flasks with pressure	AirCore vs flasks	AirCore vs CRDS at flask locations	AirCore vs CRDS (370–760 hPa)
CO_2 (ppm)	−0.01 ± 0.30	−0.06 ± 0.35	−0.11 ± 0.29	0.00 ± 0.34	−0.07 ± 0.42
CH_4 (ppb)	−0.1 ± 2.4	1.6 ± 0.1	1.2 ± 5.1	−0.5 ± 3.1	0.1 ± 5.2

gases. It would seem that variability in the atmosphere limits the absolute reproducibility between the various measurements in a field experiment.

(ii) Column average

The pressure-weighted column average and standard error over the entire pressure profile were calculated for each of the three methods (the onboard Picarro CRDS analyzer, the AirCore, and the flasks) for the 27 May 2009 flight (Table 3). These averages constitute the kind of data product that would be used to validate satellite data. The averages of the CRDS analyzer and the AirCore match well, within less than 0.1 ppm for CO_2 and 2.2 ppb for CH_4. The data at the top of the profile (where fill gas mixing occurs) were not included in the average for the AirCore, so one might expect some bias, but it is not apparent in the final average. The flask average is 0.7 ppm higher than the AirCore average in CO_2 and 5 ppb lower in CH_4. The flask average is based only on the 12 flask samples, so one would not expect an exact match with the two continuous methods. Further and more extensive flight testing is planned in the future, both to gather more statistics on AirCore accuracy and for validation to higher altitudes.

2) BALLOON FLIGHTS

Edge of Space Sciences (online at http://www.eoss.org) is a Denver, Colorado, group of scientists and engineers interested in balloon launching and tracking. EOSS provided a platform for AirCore testing using a helium balloon that could accommodate a 9-kg payload package. The AirCore payload was flown on 9 May 2009. Figure 9 shows a photograph of the AirCore, wrapped in insulation, after recovery from the balloon flight. The box in the center of the coil is the meteorological data package [designed by KalScott Engineering as part of a National Aeronautics and Space Administration (NASA)-funded Small Business Innovation Research (SBIR)], collecting ambient and coil temperatures, relative humidity, ambient pressure, and GPS data during flight.

Unfortunately, there were no collaborating data flown along with the AirCore on the balloon. Profiles from the aircraft flight on 7 May 2009, 2 days prior to the balloon flight (also shown in Fig. 4), are shown in Fig. 10, along with the balloon profiles for reference. The column averages of the balloon profiles from 850 to 400 hPa are 0.7 ppm higher for CO_2 and 20 ppb higher for CH_4 than the aircraft flight. They illustrate the similarity of the
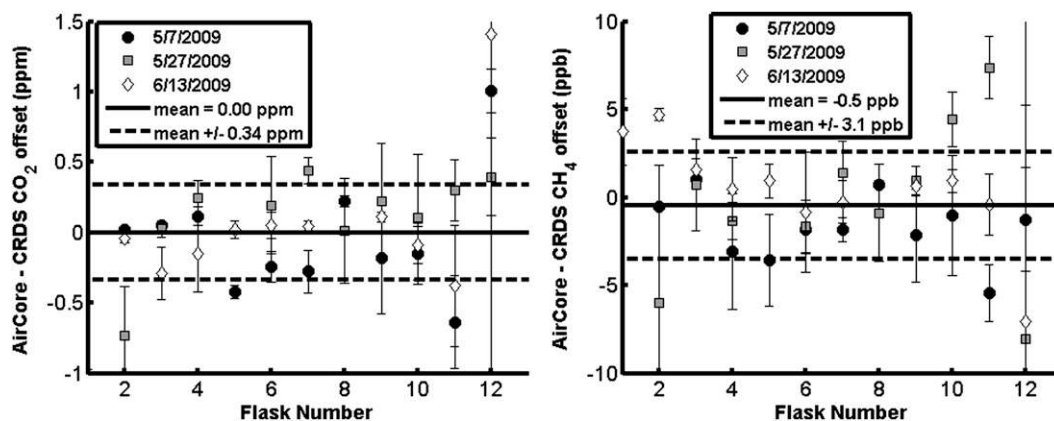

FIG. 8. As in Fig. 7, but for AirCore–CRDS analyzer offsets at the 12 flask locations.

TABLE 3. Column average dry mole fractions obtained by three different methods for the aircraft flight on 27 May 2009. Note that the second value is the standard error (not the standard deviation as in other tables), meaning the standard deviation divided by the square root of the number of independent measurements.

Column average ± standard error	Flasks	Picarro CRDS	AirCore
CO_2 (ppm)	388.3 ± 0.6	387.6 ± 0.05	387.6 ± 0.22
CH_4 (ppb)	1853.7 ± 3.1	1856.2 ± 0.4	1858.4 ± 2.5

FIG. 9. Photograph of AirCore as packaged for the 9 May 2009 balloon flight.

profiles on two different days and in different locations in Colorado; the landing site of the balloon was approximately 80 km from the location of the aircraft profile. Aside from the aircraft profile, the only validating diagnostic in this case is the value of the original fill gas, which remained in a very small quantity at the closed end of the AirCore. In the case of this flight, there was very little gas remaining in the tubing after evacuation to 30 km at the flight maximum altitude, but the value obtained for its CO_2 mole fraction from a few measurement points upon analysis was still within 0.5 ppm of the baseline value.

Just as for the aircraft flights, the CRDS analyzer measurements of the sample mole fraction were corrected by the laboratory calibration of the analyzer. However, not enough initial fill gas remained for use as an additional correction to the data, as was used for the aircraft flights. Instead, the AirCore sample mole fractions were corrected by the small offset found in the chase gas (<0.02 ppm CO_2 and <0.3 ppb CH_4), to account for any analyzer drift since its initial laboratory calibration. If this 150-m AirCore was to be deployed operationally, the flight altitudes should ideally be limited to 22 km so that enough initial fill gas is recovered to provide a validation or a check on every flight. If higher altitudes are desired, the AirCore will have to be lengthened to allow for fill gas recovery.

The uppermost section (below 30 hPa, or above approximately 20 km) of the profiles shown in Fig. 10 has been compromised by mixing with the initial fill gas. For example, the methane mole fraction reaches a minimum (1470 ppb) at that altitude and then sharply increases. The initial fill gas was at 1707 ppb, and that gas mixed with the sample at the top, increasing the value above that point. Although less diffusive mixing occurs in the CO_2 mole fraction because of the lower diffusivity of CO_2 in the air, mixing can be assumed to be occurring with the fill gas (at 363 ppm), causing the sharp drop at the top of the profile.

c. Plug tests

To understand mixing and bias resulting from storage and analysis, several plug tests were conducted, for which

the tubing was filled in alternating slugs with NOAA/ESRL-calibrated standard dry gases of two different CO_2 values. The AirCore was then analyzed either immediately (as a flow-through test) or after a period of time (as a storage test). The objectives were 1) to confirm that the mole fractions of CO_2 and CH_4 were preserved, and 2) to confirm that molecular diffusion and the flow-induced mixing could be predicted by simple analytical theory.

1) CONCENTRATION PRESERVATION OF SAMPLE

In flow-through testing, two different alternating gas standards were pulled through the AirCore with the CRDS analyzer, and then pulled through the analyzer directly, bypassing the coil. In repeated experiments, mean measurements obtained in each case agreed within 0.04 ppm for CO_2 and 0.2 ppb for CH_4. This agreement was 0.07 ppm for CO_2 and 0.3 ppb for CH_4 after 13 h of storage in the tubing. Table 1 summarizes the results from the laboratory testing and standard gas mole fraction preservation under a variety of conditions.

Additional flow-through and storage testing was conducted on tubing that had not been dried before use and on different tubing materials, including Synflex (also known as Dekoron) and untreated 304-grade stainless steel. It was not until dried Restek Sulfinert–treated 304 tubing with magnesium perchlorate chemical dryers attached was used that we could eliminate significant bias in our results.

2) DIFFUSION AND LONGITUDINAL MIXING

To analyze the resolution loss from storage and analysis of gas in the AirCore, multiple plug tests were performed by alternating two standards through the analyzer only; the analyzer and magnesium perchlorate tubes;
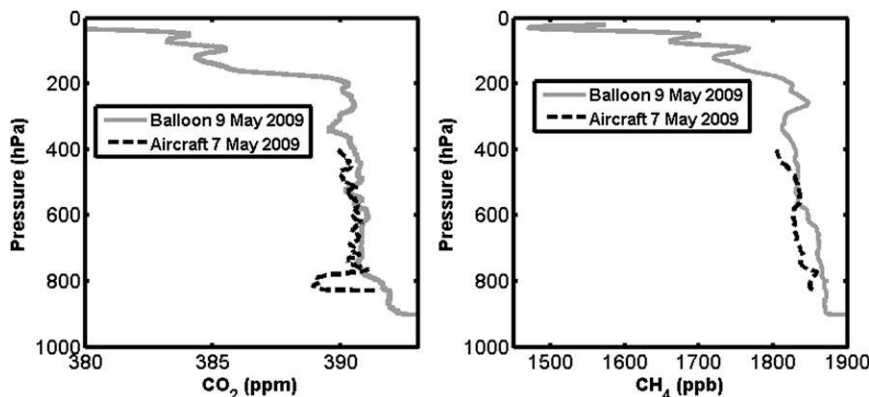
FIG. 10. (left) CO_2 and (right) CH_4 pressure profiles from AirCore deployed on a balloon flight on 9 May 2009. AirCore initial fill gas value for the balloon deployment was 362.82 ppm for CO_2 and 1706.5 ppb for CH_4. The AirCore profiles from the aircraft flight 2 days prior are also shown in black dashed lines for reference.

and the analyzer, magnesium perchlorate tubes, and AirCore, at 4-min intervals at 120 sccm. First, a baseline mixing condition was determined by running slugs directly into the analyzer, documenting mixing occurring in the tubing connecting the gas cylinders to the analyzer and in the analyzer itself, without the AirCore in line (black solid line in Fig. 11). Alternate gas slugs were run through the magnesium perchlorate driers (gray dashed line in Fig. 11) and showed no difference in recovery time from that exhibited when running through the analyzer alone. More significant longitudinal mixing was observed by flowing slugs through the 152-m AirCore and the perchlorate tubes (shown in the black dashed line in Fig. 11). When the 4-min slugs were stored over a 13-h period in the AirCore, the mixing of the original signal was further increased (solid gray line in Fig. 11).

4. Discussion

a. Analytical diffusion estimate

1) MOLECULAR DIFFUSION

The effect of molecular diffusion is well documented. The root-mean-square of the distance of molecular travel is $X_{rms} = (2Dt)^{1/2}$, where D is the molecular diffusivity of the molecule in the surrounding gas, and t is the time over which travel occurs. For CO_2 in air, D at 20°C and 1000 hPa is 0.16 cm^2 s^{-1}; for CH_4, it is 0.23 cm^2 s^{-1} (Massman 1998).

2) TAYLOR DISPERSION

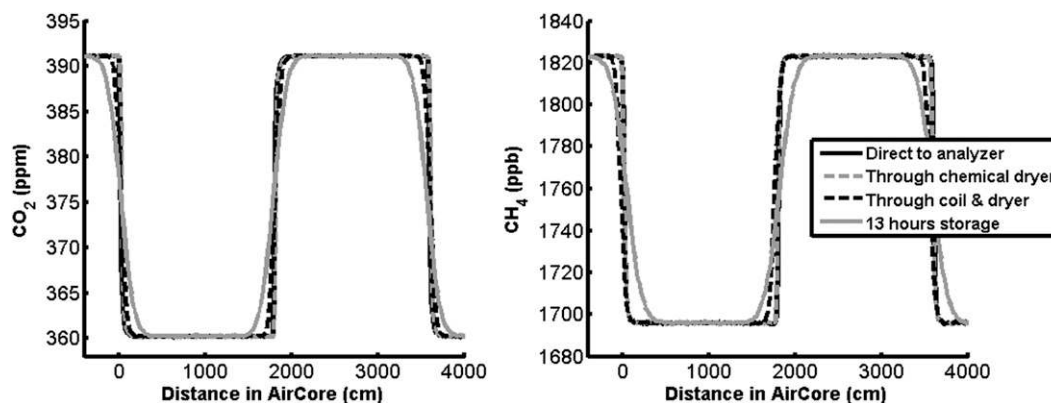The flow of air through the long coiled tubing of the AirCore is laminar for the tubing dimensions used here

FIG. 11. The CO_2 and CH_4 during a step change in concentration. The transition between the gases is shown when run directly through the analyzer (solid black line); mixing is likely due to the cell of the analyzer itself. Overlapping with this is the result when flowing gas also through a magnesium perchlorate chemical drier (gray dashed line). The boundary when the gases are run through the entire length of the AirCore tubing (black dashed line) is shown, as is the added diffusive mixing resulting from storage time of 13 h in the coil before analysis (solid gray line).

[0.64 cm (¼ in) OD with 0.025-cm (0.01 in)-thick walls] at flow rates of up to 9.5 l min^{-1}. Flow rates of gas entering the AirCore during a typical aircraft flight or balloon flight do not exceed 235 sccm as a sample enters the coil, and during analysis they are between 40 and 120 sccm. This range of flow rates falls well below flow rates required for a turbulent regime; thus, the flow is expected to be fully laminar inside the tubing. In laminar flow a parabolic velocity profile exists inside the tubing, producing longitudinal mixing, also known as Taylor dispersion, after Taylor's (1953) analysis on the subject. At low flow rates, Taylor dispersion and molecular diffusion (both in the longitudinal direction) are both considered; by combining the two an effective diffusion coefficient can be calculated as follows:

$$D_{\text{eff}} = D + \frac{a^2 \overline{V}^2}{48D},\qquad(1)$$

where D is the molecular diffusivity, a is the tube's inner radius, and $\overline{V}$ is the average velocity (Aris 1956). The first term accounts for molecular diffusion in the longitudinal direction, while the second term is the Taylor dispersion. It should be noted here that this diffusivity was derived for a fully developed laminar profile in a straight tube. This effective diffusivity was then used in the diffusion equation to solve for the mole fraction profile after a given amount of time.

To apply these principles to a laboratory test, the time over which diffusion occurred and the flow rate need to be prescribed. To compare the model to the test, the flow rate of analysis was chosen as the flow rate and the total time it took to pull air through the AirCore (33 min) was used as the time for the flow-through test. For the flow-through test, this is representative of the total time a parcel of air would have spent flowing through the coil.

Good agreement is seen in the comparison between a simple model and test data for the flow-through experiment (Fig. 12). The diffusion equation was applied to the baseline transition between standard gas concentrations by flowing directly to the CRDS analyzer, bypassing the AirCore (solid black line, Fig. 12). This baseline test illustrates an asymmetry in the transition resulting from mixing in the analyzer cell. Diffusion was modeled over the 33-min analysis time using first the molecular diffusivity alone (gray dashed line, Fig. 12), and then using the effective diffusivity of Eq. (1) (black dotted line, Fig. 12). The results show that molecular diffusion alone accounts for only part of the observed mixing of the transition, whereas the effective diffusivity including Taylor dispersion [Eq. (1)] provides a significantly better match between the data (solid gray line, Fig. 12) and the model (black dotted line, Fig. 12). This
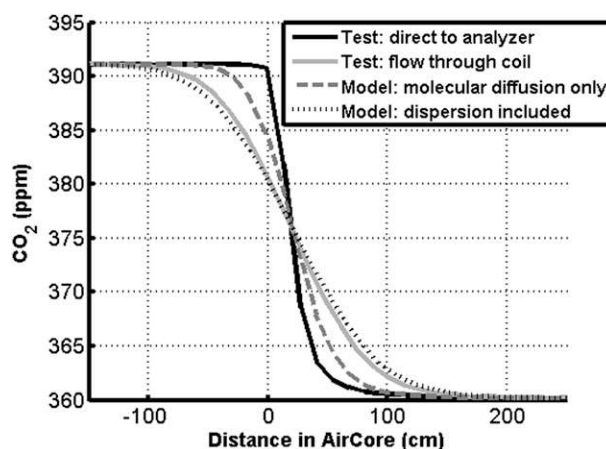

FIG. 12. Experimental comparison with expected diffusion for the flow-through test of a step change in concentration. The initial profile is indicated (solid black line); that profile was then smoothed by diffusion acting over the 33-min analysis time, using the effective diffusivity from Eq. (1). The resulting profile is shown (black dotted line). For reference, the result when molecular diffusion is considered alone is shown (dashed dark gray line); as is the test data (light gray solid line).

experiment clearly shows that both causes of mixing should be considered, and they are of equivalent magnitude when acting over a time of 33 min.

A similar analysis was performed for the case in which the slugs of alternating concentration are stored in the AirCore for 13 h before analysis (Fig. 13). It is clear from the model–data comparison that when a sample is stored for 13 h the molecular diffusion term (gray dashed line, Fig. 13) dominates, and adding the Taylor dispersion term during analysis (black dotted line, Fig. 13) does not change transition time significantly. Both match the storage test data (gray solid line, Fig. 13) very well. In both the flow-through and the storage experiments the modeled result matches the experiment closely enough that this simple representation for molecular and flow-induced mixing can be used to predict signal degradation for different storage times and analysis flow rates.

b. Effect of diffusion on flight data

The model for diffusion and Taylor dispersion in the AirCore was applied to the CRDS analyzer's continuous profile from the 27 May 2009 aircraft flight to examine the effect of longitudinal mixing on the profile. The AirCore storage time averaged to approximately 2 h before analysis, with an additional hour for the actual analysis. Dispersion and diffusion during sampling were not considered, only during analysis. The resulting smoothed in situ analyzer profiles were compared with the AirCore profile (Fig. 14). This analysis illustrates
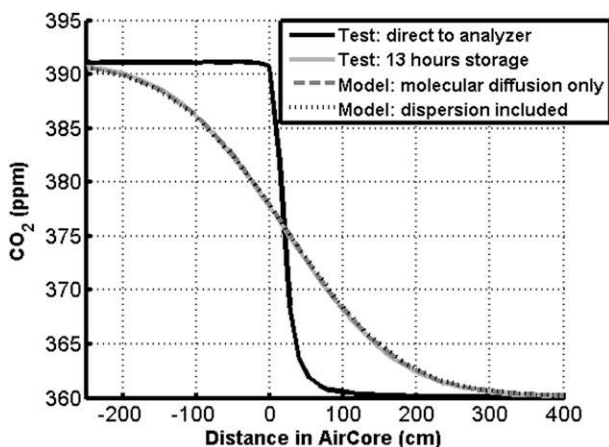
FIG. 13. Experimental comparison with expected diffusion for the storage test of 13 h. The initial profile that was then smoothed by molecular diffusion acting over 13 h is shown (solid black line). Modeled molecular diffusion over the storage time alone is shown (dashed dark gray line); the result when Taylor dispersion during analysis is also considered (black dotted line). Because of the long storage time, the added Taylor diffusion contributes negligibly to the mixing. Data points from the AirCore test are shown (solid light gray line); they lie beneath the two model lines.

that much of the small-scale variability that the onboard analyzer measured was smeared out, while larger gradients and features were preserved.

Based on the above analysis, the resolution of the AirCore measurements can be estimated as a function of the total length of the tubing L and the ambient pressure at the surface when the downstream valve is closed after sampling P_{max}. The distance of diffusion is expressed as $X_{rms} = (2Dt)^{1/2}$, which must be doubled in the resolution estimate to account for diffusion in both directions. Because the AirCore sample in the tubing is equalized in pressure as it descends, the fraction of the

tubing that $2X_{rms}$ represents is directly translated into a fraction of pressure in the atmosphere,

$$\Delta P = P_{max}(2X_{rms}/L),$$

where ΔP represents the effective resolution, in units of atmospheric pressure, of the coil in the atmosphere. It is assumed that diffusion is the limiting factor on resolution, meaning that the analyzer can pull the sample through the AirCore slowly enough to make at least (L/X_{rms}) independent measurements of the sample as it flows through the analyzer. The CRDS analyzer pulling the sample at 110 sccm and measuring at 0.5 Hz makes one measurement every 3.7 scc (standard cubic centimeters). The analyzer cell has a standard volume of approximately 6 scc [it is 35 cc in volume, but is maintained at 187 hPa (140 torr) and 45°C]. Therefore, the analyzer is oversampling at this low flow rate. As it is, 6 scc in the AirCore tubing and ambient pressure (0.8 atm in Boulder) represents 0.28 m, which is the root-mean-square distance that CO_2 molecules diffuse in air over 10 min. Thus, the flow rate of the analyzer and its effective cell size are not reducing the AirCore resolution; instead, molecular and flow dispersion are the limiting factors on the measurement resolution of the AirCore sampling system as currently configured. Longer AirCore tubing could be used to decrease the effect of diffusive mixing.

Figure 15 illustrates the resolution of CO_2 measurements with an AirCore 150 m long analyzed at 40 sccm descending to sea level pressure ($P_{max} = 1000$ hPa), as a function of altitude for various storage times, assuming a standard atmosphere. The analysis flow rate is only a factor resulting from the Taylor dispersion term in the total diffusion. The molecular diffusion coefficient of
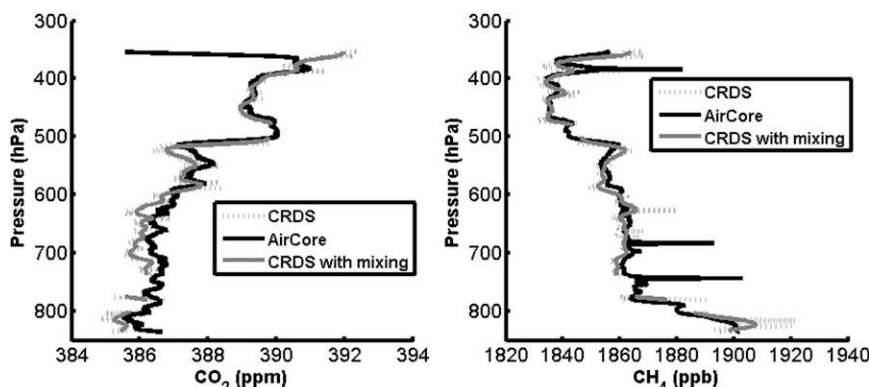

FIG. 14. Profiles of (left) CO_2 and (right) CH_4 from the aircraft flight on 27 May 2009. Results from the AirCore (black dashed line) are compared with the onboard Picarro CRDS continuous analyzer profile (light gray dotted line), which has been smoothed by a model of molecular diffusion and flow-induced mixing (solid gray line).
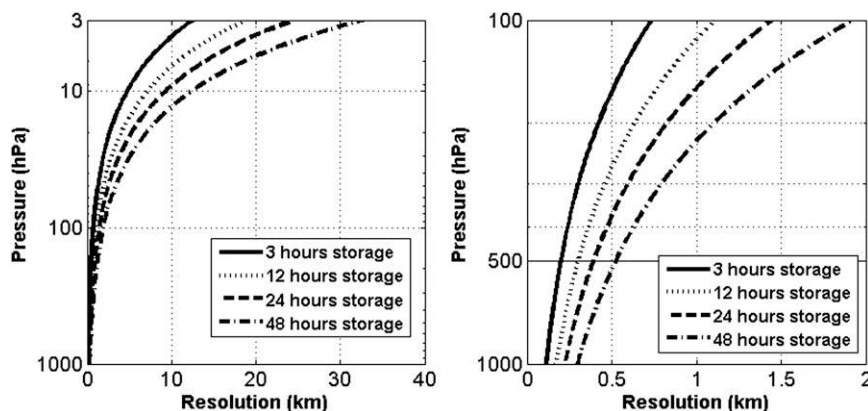
FIG. 15. Expected resolution of CO_2 measurements made with AirCore for different storage times. (left) The resolution at all atmospheric pressures down to 3 hPa and (right) a closer view of the resolution to 100 hPa.

methane in air is 40% greater than that of CO_2, leading to a corresponding decrease in resolution. The resolution of the AirCore for CO_2 is estimated to be 110 m at sea level, 260 m at 8 km ASL (350 hPa), and 1500 m at 20 km ASL (45 hPa) after 3 h of storage. After 12 h of storage the resolution decreases to 170, 390, and 2300 m respectively.

5. Conclusions

The AirCore has been shown to be a viable, unbiased sampling system for CO_2 and CH_4. Laboratory tests have shown repeatability and accuracy of better than 0.05 ppm for CO_2 and 0.4 ppb for CH_4. Deployment on three aircraft sampling flights along with a Picarro G1301-*m* flight CO_2–CH_4–H_2O analyzer and NOAA/ERSL flasks show very good agreement (standard deviation of differences of 0.3 ppm CO_2 and 5 ppb CH_4 with flasks, and 0.4 ppm CO_2 and 5 ppb CH_4 with the in situ analyzer). The AirCore has been fully validated for CO_2 and CH_4 in laboratory testing and on aircraft flights to nearly 8 km; further testing would be required for full validation under different environmental conditions at extreme altitudes, where low temperatures ($<-35°C$) and low pressure (<300 hPa) are prevalent, or for measurement of gases other than CO_2 or CH_4.

The deployment and use of the AirCore in the field is simple and the technology involved is robust. When sampling a simple profile, the AirCore requires little instrumentation, depending on the level of desired personnel involvement. In previous deployments, a manual shut-off valve was used to seal the tubing upon retrieval, so that no powered instrumentation was needed to obtain a valid sample. The AirCore is highly configurable to a variety of shapes, sizes, lengths, and weights, depending on the carrier vehicle or science requirements (e.g.,

longer, thinner tubing could be used for higher-resolution measurements than those reported here). One could envision regular balloon flights with an AirCore returning on a maneuverable glider or return vehicle for easy recovery in the field, followed by shipment of the sample to an appropriate laboratory for analysis. Such a deployment scheme would result in greenhouse gas profiles to high altitudes across the region (or the globe) on a regular basis, depending only on the availability of infrastructure for shipping and analysis. Such profiles would prove invaluable to the carbon cycle community, allowing the investigation of regional carbon sources and sinks and providing information for inverse models and robust in situ validation of satellite and other remote sensing measurements at a lower cost than that of other methods.

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