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Long-term greenhouse gas measurements from aircraft

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Abstract

In March 2009 the NOAA/ESRL/GMD Carbon Cycle and Greenhouse Gases Group collaborated with the US Coast Guard (USCG) to establish the Alaska Coast Guard (ACG) sampling site, a unique addition to NOAA's atmospheric monitoring network. This collaboration takes advantage of USCG bi-weekly Arctic Domain Awareness (ADA) flights, conducted with Hercules C-130 aircraft from March to November each year. NOAA has installed window-replacement inlet plates on two USCG C-130 aircraft and deploys a pallet with NOAA instrumentation on each ADA flight. Flights typically last 8 h and cover a very large area, traveling from Kodiak, AK in the south up to Barrow, AK in the north, and making altitude profiles near the coast as well as in the interior. NOAA instrumentation on each flight includes: a flask sampling system, a continuous $CO_2/CH_4/CO/H_2O$ analyzer, a continuous ozone analyzer, and an ambient temperature and humidity sensor. GPS time and location from the aircraft's navigation system are also collected. Air samples collected in flight are analyzed at NOAA/ESRL for the major greenhouse gases and a variety of halocarbons and hydrocarbons that influence climate, stratospheric ozone, and air quality. Instruments on this aircraft are designed and deployed to be able to collect air samples and data autonomously, so that NOAA personnel visit the site only for installation at the beginning of each season. We present an assessment of the cavity ring-down spectroscopy (CRDS) $CO_2/CH_4/CO/H_2O$ analyzer performance operating on an aircraft over a three-year period. We describe the overall system for making accurate greenhouse gas measurements using a CRDS analyzer on an aircraft with minimal operator interaction. Short and long-term stability of the CRDS analyzer over a seven-month deployment period is better than 0.15 ppm, 2 ppb, and 5 ppb for CO_2, CH_4, CO respectively, considering differences of on-board reference tank measurements from a laboratory calibration performed prior to deployment. This stability is not affected by variation in pressure or temperature during flight. Biases and standard deviations of comparisons with flask samples suggest that atmospheric

variability, flask-to-flask variability, and possible flask sampling biases may be driving biases in the comparison between flasks and in-situ CRDS measurements.

1 Introduction

Quantifying greenhouse gas (GHG) emissions in the Arctic is crucial for understanding changes in the carbon cycle, because of their large potential impact on the Earth's warming. As organic carbon stored in thawing Arctic permafrost resurfaces, a portion of it will be emitted as either methane (CH_4) or carbon dioxide (CO_2). Because methane's global warming potential is more than 25 times greater than that of CO_2 for a 100-yr time horizon (Forster, 2007), and because Arctic stores of organic carbon are estimated to be larger than the total carbon from anthropogenic emissions since the beginning of the industrial era, Arctic CH_4 emissions will potentially create an important feedback mechanism for climate change (McGuire et al., 2009; Jorgenson et al., 2001; Keyser et al., 2000; O'Connor et al., 2010). An understanding of how the permafrost thaw evolves is of paramount importance.

In response to the need to better understand the cycling of CO_2 and CH_4 in the Arctic, the NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) aircraft program collaborated with the USCG to establish the ACG site, complementing existing Alaskan NOAA ground stations at Barrow (BRW) and Cold Bay (CBA), and a flask-only aircraft site near Fairbanks (PFA). ACG's high-resolution GHG dry mole fraction (moles of a trace gas per mole of dry air) measurements, which include several altitude profiles from the ground to 8 km on each bi-weekly flight, are a valuable addition to the NOAA global network and to the existing suite of Arctic measurements. In contrast with past aircraft campaigns that focused on Arctic GHG measurements (Harriss et al., 1992, 1994; Conway et al., 1993; Kort et al., 2012; Jacob et al., 2010; Vay et al., 2011), ongoing measurements over multiple years at ACG will enable investigation of both seasonal and inter-annual variability.

The USCG Air Station Kodiak regularly conducts Arctic Domain Awareness (ADA) flights, using their fleet of C-130 Hercules aircraft for routine monitoring of the melting sea ice and changing conditions around Alaska. The NOAA aircraft group collaborated with the USCG to install an atmospheric sampling payload aboard the aircraft slated for these survey missions. Flights depart the USCG Air Station on Kodiak Island, Alaska, then typically transect at high altitude over the Alaskan interior to Barrow, where the aircraft either lands or descends to low altitude. The aircraft conducts a low-altitude survey of the coastline west toward Kivalina and then continues back to Kodiak (Fig. 1), with flights typically lasting approximately eight hours. From March to November for three seasons so far (2009–2011), the NOAA aircraft group has deployed its observation system on these USCG flights, measuring greenhouse gases and ozone nearly every two weeks, totaling 38 successful data flights. The program is currently into its fourth season.

This paper outlines our methodology for making high-quality GHG measurements in the field in a monitoring mode, in which the instrumentation must run semi-autonomously for long periods of time, in contrast to campaign-mode deployments in which a scientist is in the field and available at all times to oversee the operation of the various instruments. We detail the advantages and disadvantages of the system and show results, including comparisons between the continuous analyzer and flask measurements.

2 Methods

The system, designed for easy installation on the C-130 aircraft, is strapped to a pallet that is loaded and unloaded from the aircraft for each flight (Fig. 2, left panel). The inlets delivering external air to the instrumentation are mounted through an aluminum plate that replaces a circular window on the fuselage of the aircraft forward of the propellers (Fig. 2, right panel). There are three separate inlet lines, one for each of three systems (1 through 3 below). Although there have been slight changes made to

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the system over the years, the basic measurement components of the system are: (1) a continuous in-situ CO_2, CH_4, CO, and H_2O analyzer, (2) a continuous ozone monitor, (3) a flask package system, (4) a temperature and relative humidity sensor, and (5) GPS measurements of location and time for measurement synchronization. Details of each instrument (excepting the ozone monitor) and its measurements are described below; this paper focuses primarily on the operation and performance of the in-situ continuous GHG analyzer.

2.1 Continuous CO_2/CH_4/CO/H_2O

The relatively recent introduction of cavity ring-down spectroscopy (CRDS) instruments for measuring trace gas mole fractions (Crosson, 2008) has led to a rapid incorporation of these systems at various GHG measurement sites around the world. The measurements are calibrated and expressed as dry mole fractions. In comparison to non-dispersive infrared (NDIR) instruments, CRDS instruments have been shown to be more stable over short and long time scales, requiring less frequent calibration. CRDS instruments are also very linear in their response, requiring fewer standard gases for calibration. One reason for the measurement stability is that the instrument maintains tight control of temperature and pressure in the measurement cell, allowing simple deployment in the field without additional environmental controls. Numerous scientific studies that used CRDS analyzers to make CO_2 and CH_4 measurements at stationary ground and tower sites have demonstrated these advantages (Miles et al., 2012; Winderlich et al., 2010; Richardson et al., 2012). Chen et al. (2010) describe the use of a CRDS analyzer aboard an aircraft during the Balanco Atmosferico Regional de Carbono na Amazonia (BARCA) campaign, and show that their results compare favorably with an NDIR analyzer deployed on the same aircraft. CRDS analyzers have been used in light aircraft to investigate urban CO_2 and CH_4 emissions as well (Turnbull et al., 2011; Mays et al., 2009; Cambaliza et al., 2011). Other non-NDIR and modified NDIR techniques for CO_2 and CH_4 measurement have been used extensively in aircraft as well, usually in the framework of a campaign in which a scientist or engineer monitors instrument performance either in flight or pre- and post-flight, (Daube et al., 2002; Martins et al., 2009; Miller et al., 2007; Xueref-Remy et al., 2011; Paris et al., 2008; Wofsy et al., 2011). Machida et al. (2008) have successfully deployed an NDIR analyzer on Japan Airlines commercial aircraft for continuous measurements of CO_2 with no operator present, and Chen et al. (2012b) and Biraud et al. (2012) have done so on light aircraft making regular profiles with NDIR CO_2 analyzers over long periods of time.

A CRDS analyzer (Picarro, Inc.) is the central component of the measurements aboard the ACG flights. In the 2009 and 2010 seasons, a G1301-m series 3-species flight analyzer was used to measure CO_2, CH_4, and water vapor (two different units, serial numbers CFADS08 and CFADS09, respectively). Since the beginning of the 2011 season, a newer G2401-m series 4-species analyzer (CFKBDS2007) has been flown, adding continuous CO measurements.

2.1.1 Plumbing schematic

A vacuum pump downstream of the CRDS analyzer installed on the C-130 pulls external air through the aircraft inlet and through the analyzer (Fig. 3). Upstream of the analyzer, care is taken not to interfere with the main sample airstream with pumps, valves, or metering that might lead to contamination. A rack-mounted control box contains a sample-selection rotary valve (Vici Valco multiport valve (MPV)) controlled by a Campbell Scientific CR1000 data logger. The sample enters the aircraft through a 1/4″ OD Kynar line into the control box, flowing past a pressure sensor (P_i) into one of the ports on the MPV. Three calibration tanks are connected via 1/16″ stainless steel tubing to other ports on the MPV. The 1/16″ tubing ensures that there is some pressure drop between the outlet of the tank regulators, set to approximately 2–3 psig, and the inlet of the analyzer, when the tank gas is flowing through the line, maintaining pressure close to 1000 millibar (mb) at the analyzer inlet during calibration periods. Picarro CRDS analyzers are designed to accept inlet air at close to or below ambient pressure. Exceeding one atmosphere of pressure by a significant amount (this is unit-dependent) causes instability in the pressure of the analyzer cell (also called the cavity). The C-130 has a pressurized cabin so regulator delivery pressure does not vary significantly in flight, while sample pressure varies with altitude. There is a brief spike in the cavity pressure when switching between a standard gas and the sample stream, due to the difference in their pressures.

Once a stream is selected by the MPV, the air flows through a short length of 1/8″ OD stainless steel tubing past a second pressure sensor (P_a) into the analyzer. Inside the analyzer, a proportional valve controls the flow of air into the analyzer cell, maintaining constant pressure in the cell at 140 ± 0.02 torr (186.7 ± 0.03 mb) (standard deviation given for G2401 model in the laboratory). Temperature in the cell is also tightly controlled at 45 ± 0.008 °C. As directed by the manufacturer, the vacuum pump is connected downstream of the analyzer, and the mass flow rate through the analyzer is determined by the diameter of a critical orifice between the cell and the vacuum pump. The critical orifice maintains a constant mass flow rate through the analyzer that is independent of ambient pressure (either in the cabin or outside the plane), provided the vacuum pressure downstream of the orifice (between the cavity and the pump) is at least half of the cell pressure. Picarro provides a critical orifice with analyzers designed for flight, but different diameter orifices can be used to further reduce the flow rate if needed. At the ACG site, the mass flow rate has been between 250 standard cubic centimeters per minute (sccm) (in 2009) and 350 sccm (in 2010 and 2011), depending on the analyzer. High flow rates increase the pressure drop upstream of the cavity, reducing the altitude ceiling at which the analyzer can perform. For this reason, in 2010 a custom wide-bore MPV was used to accommodate the higher flow rate, because it was found that the pressure drop through the valve with the standard size ports was unacceptable for altitudes close to 8 km, where the C-130 spends much of its flight time.

The plumbing for the deployment of the CRDS analyzers was designed to be as simple as possible, given that they are to be run autonomously with minimal user interference. The design, however, introduces several trade-offs. First, the standard tank gas is delivered to the analyzer at higher pressure (just over 1000 mb) compared with the sample stream pressure, which can be as low as 340 mb at altitude. Fortunately, the analyzers can stabilize cavity pressure in response to such a pressure change within 10 s. Second, the ~6 m sample inlet line is not flushed continuously while the analyzer samples from a standard tank. Thus, after every calibration, typically approximately 60 s of data are discarded (corresponding to three flush volumes of the line), to flush any effects due to pressure changes in the inlet line from the stopped flow as well as the stagnant sample air. Third, the standard gas is delivered to the analyzer dry while the sample air stream is not dried, so measurement uncertainty depends on the uncertainty of the water vapor correction (the water vapor correction is addressed in later section). We note here that if the sample stream were dried or the standards wetted, the measurement uncertainty would similarly depend upon the uncertainty of the drying or wetting system.

The transition from wet to dry air leads to long equilibration times between the sample and the reference gas for both CO_2 and CH_4. In flight, calibration standards are run through the analyzer for three minutes, with the first minute discarded prior to averaging because of the ~60 s equilibration time needed to arrive to the within 0.1 ppm of CO_2 and 1 ppb of CH_4 of the final value. 60 s of data is discarded after every switch (both from standard to ambient and from ambient to standard). In the laboratory with the same model G2401 m analyzer (SN CFKBDS2059), it was found that transitioning from 1.4 % to essentially 0 % water vapor resulted in a significantly slower CO_2 and CH_4 response than when transitioning between two dry tanks or two wet tanks containing different CO_2 and CH_4 mole fractions (Fig. 4). This slow transition from wet to dry air requires a longer flushing time to reach a steady reading of the standard gas. The additional flush time results in a higher consumption of standards than would be necessary if all incoming air were dried. We note that after 60 s, the bias in the measurement is under 0.1 ppm for CO_2 and 1 ppb for CH_4. The actual average of 120 more seconds after that is biased by a negligible amount however.

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A system software parameter change was made to the laboratory instrument, reducing the averaging time for the response of the measurement baseline for CO_2 and CH_4, and led to a marked improvement in the analyzer's response to a fast change in water vapor. To test the new parameter, an experiment was conducted in the laboratory alternating between two streams of the same standard gas: one wet to approximately 1.7 % H_2O, the other dry (0.0006 % H_2O). The parameter adjustment decreased the response time needed to achieve the final value within 0.1 ppm for CO_2 and 2 ppb for CH_4 decreased by a factor of two, from 40 s to 20 s (Fig. 5). The short-term precision of the laboratory analyzer was slightly degraded (the standard deviation increased by ~ 10 %) with this change. This software parameter will be adjusted on the flight instrument as well to allow for shorter calibration times and to better capture rapid gradients in water vapor and CO_2, CH_4, and CO that often exist in profiles between the boundary layer and the free troposphere or the free troposphere and the stratosphere.

2.1.2 Short-term precision

The short-term precision of each analyzer, indicated by the value of one standard deviation (1-σ) of measurements of dry gas from a reference tank at the reported frequency, typically ~ 0.5 Hz, is indicated in Table 1, both for laboratory and flight conditions. Pressure noise in the analyzer cavity due to aircraft motion is the cause of the significantly larger noise in the flight measurements. It should be noted that the values given in Table 1 are for flight at low altitudes (500–2000 m) with presumably higher turbulence. At high cruising altitudes, the short-term precision is significantly improved, indicating that the cavity pressure noise is not caused by high-frequency vibration of the aircraft propellers, but rather aircraft motion due to atmospheric turbulence in flight. During the 2012 season, a new proportional valve for controlling flow at the measurement cavity inlet was installed in CFKBDS2007, replacing the original valve. This valve (Clippard Part No. EV-PM-10-6025-V) was chosen by the manufacturer to reduce the pressure noise in the cavity during flight conditions. Flights with the new valve indicate a significant improvement in cavity pressure noise during turbulent flight conditions (the one standard deviation of 2.2-s pressure measurements improved from 0.3 torr to 0.06 torr), and consequently the short-term precision of the analyzer for CO_2 and CH_4 is dramatically improved. The precision of the CO measurement in the G2401 series analyzer is not reduced by flight conditions or the introduction of a new proportional valve and remains the same throughout.

2.1.3 Calibrations: long-term stability and in-situ corrections

The analyzers were calibrated in the laboratory each year prior to and after each season's deployment, with a series of four or five standard reference tanks calibrated on the World Meteorological Organization (WMO) scale at NOAA/ESRL. Drift in each analyzer between laboratory calibrations in March and December of the same year was found to be ≤ 0.05 ppm CO_2, < 2 ppb CH_4, and < 3 ppb for CO in the ambient range of mole fractions. Similar results have been shown for CO_2 in other Picarro CRDS analyzers (Richardson et al., 2012).

NOAA-calibrated reference tanks are also deployed aboard the aircraft and sampled periodically during flight, typically sampling a single tank every 30 min for three minutes, alternating between three different tanks for different calibration cycles. One set of tanks was used for the entire 2009 and 2010 seasons, with a new set of three tanks deployed for the entire 2011 season and used currently in 2012. When the initial set of tanks was returned to NOAA/ESRL they underwent a final calibration to quantify any degradation or drift in the tanks, and none was found within the uncertainty of the laboratory calibration for either CO_2 or CH_4. The tanks deployed in March 2011 have not yet been returned for an intermediate calibration.

Analysis of in-flight tank measurements is described below for the 2011 season, for the model G2401-m analyzer. Unless specifically noted in the text, the observations in previous seasons using the G1301-m series analyzers were similar. In-flight tank measurements, obtained by averaging the data from the last two minutes of a standard run, show little overall measurement drift over the 8 flight hours, with peak-to-peak changes typically < 0.1 ppm in CO_2, 1 ppb in CH_4, and 5 ppb in CO. However, there is some scatter to the residuals of the standard tank measurements, defined as the differences between the measured values (averaged over the last two minutes of a calibration run and corrected using a pre-deployment laboratory calibration) and the actual value of the tank (Fig. 6). We note that the CRDS analyzer requires approximately 30 min to warm up. During this time instrument precision and stability should be monitored, or measurements made during this time should be discarded. In Fig. 6 for CO_2 (left panel), the first standard measurement is approximately 0.1 ppm higher than subsequent measurements, which is an indication of this warm-up period. Variability in the individual standard tank measurements usually exceeds the overall drift over the time of the flight, and does not seem to be captured at the frequency that the calibrations are run (every 30 min for the data shown in Fig. 6). One standard deviation of the residuals over the course of a single flight is 0.04 ppm CO_2, 0.3 ppb CH_4, and 1.5 ppb CO on average. We note that these statistics are reported for analyzer performance prior to the inlet proportional valve change mentioned in the previous section, which occurred too late in the 2012 season to compile performance statistics over time.

To avoid introducing artificial noise into the sample data by correcting for shorter-term temporal changes in the standard measurements, the flight measurements are corrected only for the mean temporal drift that occurs in the standard measurements over the time of the entire flight. To perform this correction, a linear fit to the average of the residuals of all the available tanks with time is calculated (black dashed line in Fig. 6) and subtracted from the mole fraction of the sample stream. As a check on this technique, corrections to the measured mole fractions using other methods (such as using a time-varying average of the tanks or a time-varying first-order fit to the tank concentrations) are compared with the first method to ensure that the chosen correction technique is appropriate. If the final calibrated mole fractions are dependent on the technique choice by an amount greater than our target uncertainties (0.1 ppm CO_2, 1 ppb CH_4, 5 ppb CO), the data will be examined more thoroughly and a different calibration method could be used; this has not occurred so far at this site.

In addition to their low variability within each flight, tank measurements on board the aircraft throughout each season show little overall drift. Because the same tanks are used throughout the season, we can quantify the drift of the measurement of the same tanks over the entire season. The one-sigma variability of one flight tank measurement over the season is similar to that seen over the course of one flight (0.04 ppm CO_2, 1 ppb CH_4, and 1 ppb CO) (Fig. 7). In 2011, the G2401-m analyzer's CH_4 calibration drifted upwards by approximately 2 ppb; the other two tanks showed the same trend. Post-deployment instrument calibration in the laboratory in January 2012 showed only a 1.4 ppb change from the initial calibration in March 2011, however. If it were linear over time, the drift during the 7 months of the 2011 season should only have been approximately 1 ppb, rather than 2. We do not suspect degradation of the reference tanks themselves, because all three tanks show the same trends. Based on this information, we recommend that for measurements of CO_2, CH_4 and CO using 1000 or 2000-series Picarro CRDS analyzers in the absence of in-situ standards, a calibration should be performed at least every 6 months, depending on the uncertainty required for the measurement – annual calibrations may be sufficient to satisfy the 2 ppb inter-site comparison goal of the WMO. CO_2 shows a very slight drift of approximately 0.15 ppm over the season (with no measurable drift in the laboratory calibrations). CO was stable, showing no long-term drift. In 2009 and 2010, the G1301-m analyzers deployed at the site showed no measurable drift in either CH_4 or CO_2; we conclude that this type of long-term drift is analyzer-specific, and that periodic calibration is necessary to track long term analyzer drift.

The measured values of the standard tanks shown in Fig. 7 have also been examined as functions of aircraft cabin temperature and pressure, and outside altitude. No correlation has been found with any of these variables (shown for CO_2 in Fig. 8, with similar results for both CH_4 and CO, and for the 2009 and 2010 seasons, not shown).

2.1.4 Water vapor correction

An important advantage to the CRDS units used for the ACG flights is that dry air mole fractions of CO_2, CH_4, and CO can be calculated using empirical water vapor corrections that compensate for dilution, pressure broadening, and line interferences due to water vapor (Richardson et al., 2012; Rella et al., 2012; Chen et al., 2012a). Laboratory tests were performed on each unit prior to and after deployment in the field to determine and assess the stability of these empirical water vapor corrections. Empirical water vapor correction tests were performed using two different methods to add water vapor to dry standard gases from tanks. One method used standard gas flowing through either a wetted stainless steel filter housing or through the same filter housing filled with silica gel that had been wetted with acidified (pH ∼ 5) distilled water. Using wetted silica gel to deliver the water vapor to the gas stream resulted in a smoother water vapor transition across a range of about 2.5 % to fully dry. The second method similarly wetted the standard gas using a hydrophobic membrane (Celguard, "micro-module") loaded with a small amount (∼ 2 ml) of acidified distilled water. No significant drifts in these water vapor correction functions have been observed. Methodology for performing these water vapor tests is described in detail elsewhere for CO_2 and CH_4 (Chen et al., 2010; Winderlich et al., 2010; Rella et al., 2012), and for CO (Chen et al., 2012a).

The water vapor correction for CO_2 and CH_4 takes the form of

$$\frac{X_{G,\mathrm{wet}}}{X_{G,\mathrm{dry}}} = 1 + a \times \mathrm{H_2O_{reported}} + b \times \mathrm{H_2O^2_{reported}}$$

where X_G is either CO_2 or CH_4, H_2O_{reported} is the variable "h2o_reported" in the Picarro output file (this is an uncalibrated water vapor measurement), and the coefficients *a* and *b* are determined in laboratory testing. We found the water vapor corrections did not change by more than 0.1 ppm for CO_2 or 1 ppb for CH_4 at the highest H_2O values used in laboratory tests, approximately 2.5 %. In typical flights, H_2O values were lower than this level, usually below 1.5 %.

The water vapor correction for CO takes a different form because there is significant absorption interference from CO_2 and water with the CO absorption line (details in Chen et al., 2012a). For this dataset the correction used is

$$\mathrm{CO}_{\mathrm{corrected}} = \frac{\mathrm{CO}_{\mathrm{wet}} - (A \times \mathrm{H_2O}_{\mathrm{pct}} + B \times \mathrm{H_2O}^2_{\mathrm{pct}} + C \times \mathrm{H_2O}^3_{\mathrm{pct}} + D \times \mathrm{H_2O}^4_{\mathrm{pct}})}{1 + a' \times \mathrm{H_2O}_{\mathrm{pct}} + b' \times \mathrm{H_2O}^2_{\mathrm{pct}}}$$

where $\mathrm{CO}_{\mathrm{wet}} = \mathrm{peak84raw} \cdot 0.427 \cdot 1000$ (C. Rella, Picarro, personal communication, 2011), and “peak84raw” is the reported value for the raw CO measurement in the analyzer data stream. The parameters A, B, C, D, a', and b' are empirically determined from laboratory water experiments.

The water vapor variable reported by Picarro “h2o_pct” is determined from the water vapor absorbance line that overlaps with the CO absorbance line used in the G2401, and is different from the water vapor measurement used for the CO_2 and CH_4 correction (“h2o_reported”). Incidentally, the actual water vapor measurement that Picarro reports is the variable “H2O”, and is related to “h2o_reported” (Winderlich et al., 2010). The uncertainty of the CO water vapor correction is within 2 ppb up to 4 % water vapor (Chen et al., 2012a). As discussed later, this uncertainty in the CO correction is one of the main contributors in the uncertainty of continuous CO measurements at ACG. Although it is smaller than the short-term precision (4 ppb) of the same analyzer, it may introduce a bias in the result rather than random noise.

2.2 Flask packages

Programmable Flask Packages (PFPs) are used to collect discrete air samples on the C-130 flights. These air-sampling devices are used routinely on aircraft as part of the NOAA/ESRL Global Monitoring Division’s Carbon Cycle and Greenhouse Gases network (Sweeney et al., 2012, and http://www.esrl.noaa.gov/gmd/ccgg/aircraft/index.html). The PFP is composed of twelve 0.7 l borosilicate glass flasks with glass valves sealed with Teflon O-rings at each end, a stainless steel manifold, and a data logging

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and control system. The 7.5 cm diameter cylindrical flasks are stacked in two rows of six. The flexible manifold connects all of the flasks in parallel on the inlet side of the flasks. The data logger records actual sample flush volumes and fill pressures during sampling, along with system status, GPS position, ambient (outside the aircraft) temperature, pressure, and relative humidity. One or two PFPs are sampled on each flight (12 or 24 flasks) through a 3/8″ OD Kynar inlet line. A rack-mounted Programmable Compressor Package (PCP) that contains two air pumps (KNF-Neuberger MPU1906-N828-9.06 and PU1721-N811-3.05) with aluminum heads and Viton diaphragms plumbed in series is used to flush and pressurize the flasks.

Samples collected in PFPs are analyzed at NOAA/ESRL for CO_2, CH_4, H_2, SF_6, CO, and N_2O 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 and pass it through a trap for drying maintained at $\sim -80\,^{\circ}$C, before sending the sample to an analyzer. All measurements are reported as dry air mole fractions relative to standard scales maintained at NOAA/ESRL (Novelli, 2003; Dlugokencky, 2005; Hall et al., 2007; Novelli et al., 1991; Zhao and Tans, 2006).

The same flask samples are also analyzed for a suite of halocarbons and hydrocarbons, as well as stable isotopes of CO_2 (both ^{13}C and ^{18}O, at INSTAAR, University of Colorado) using methods documented online (http://www.esrl.noaa.gov/gmd/ccgg/aircraft/index.html), and by Montzka et al. (1993) and Vaughn et al. (2004). Uncertainties for species measured in flasks are documented in the references above.

2.3 Temperature and relative humidity

A Vaisala HMP-50 temperature and relative humidity probe is mounted on the exterior of the inlet plate. It has been fitted with a custom housing that allows airflow to reach the sensor without allowing solar radiation to affect measurements. It was calibrated by the manufacturer prior to purchase to a typical uncertainty of ±3 % of relative humidity and 0.6 °C for temperature.

2.4 Global Positioning System (GPS) and timing

GPS location and time from the aircraft navigation system is logged both by the CR1000 data logger and the flask system at 10-s intervals during flight. The data is interpolated onto a one-second time scale. Data from the CRDS analyzer are corrected for the lag time in the inlet system; the lag time is measured on the ground and corrected based on outside air pressure.

2.5 Data collection and system control

Deploying a trace gas sampling and measurement system without a scientist on-board requires having a robust method for controlling and recording system parameters and collecting data post-flight. An additional unit in the instrument rack at ACG is a control box that contains a Campbell Scientific CR1000 data logger, the MPV, pressure sensors and the plumbing connections. The data logger plays a central role in the system and serves a variety of functions: (1) records the outputs of the CRDS analyzer, ozone analyzer, temperature and humidity sensor, and GPS system via serial communications, (2) controls the MPV to deliver the sample and reference gases to the CRDS analyzer, (3) triggers the PFP package to sample at pre-programmed time intervals if no operator is available to trigger them manually, (4) logs the output of ancillary sensors that are needed to monitor the function of the overall system. The ancillary sensors include several pressure sensors to measure cabin pressure, inlet line pressure, and the analyzer inlet pressure. The inlet line pressure, once it is corrected for the pressure drop due to flow through the inlet line (which is also dependent on the external pressure), is effectively the ambient pressure outside the aircraft. The analyzer inlet pressure is either equal to the inlet line pressure or it is equal to the delivery pressure of the standards, depending on the MPV position. This pressure measurement is needed to determine if the calibration tank regulators require adjustment.

Prior to the flight, a technician installs the flask packages, powers up the system, inserts a flash card into the CR1000 card reader, and then flushes gas through the

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standard tank regulators. A regulator-flushing protocol that did not require a technician was designed and implemented in 2009, but the long time interval between flights and the fact that a technician was available made it more efficient to purge the regulators manually. Once powered, the continuous system requires no operator. Although the control box can trigger the flask samples, the on-board operator communicates with the Coast Guard crew to arrange for better-targeted flask sampling and triggers each flask at pre-determined locations. Upon landing, the operator removes the CR1000 flash card, downloads data from the CRDS analyzer via a USB flash drive, and ships the samples and data cards back to NOAA/ESRL in Boulder, Colorado.

2.6 Comparison of CRDS and flask measurements

Because flask air samples are collected through a separate inlet line and measured by different analyzers at NOAA/ESRL, which are in turn calibrated with a different set of reference gas standards on the same scale as the in-situ system's reference gas standards for CO, CO_2 and CH_4, the flask air samples are independent of the continuous measurements and provide a necessary reference to other NOAA global sites. An ongoing comparison thus provides a realistic measure of the overall uncertainty of the entire measurement process. Flask sample measurements are compared with the continuous in-situ measurements by averaging the continuous data over the flushing and filling time of the flasks, using a weighting function similar to that described in Chen et al. (2012b). The flask system records the times (from the GPS antenna) at which the flask sample is triggered and at which it is complete, so that the timing between the flasks and the continuous systems is coordinated, as long as the difference in line lag time is considered.

Histograms of the seasonal ACG flight differences between continuous (CRDS) and flask measurements of CO_2 (Fig. 9), CH_4 (Fig. 10) and CO (Fig. 11) show little bias but significant scatter around the mean. Some of the scatter can be attributed to uncertainties in timing; because there is no pressure measurement in the flasks, the flask flushing and filling sequence is modeled based on laboratory measurements (Neff et al., 2012). Some of the scatter, however, cannot be attributed to timing issues. For example, when flasks filled during periods of high variability are omitted from the calculation, the standard deviation of offsets is still relatively large compared to the mean. In 2011, the offsets for CO_2 (Fig. 9, right panel) are −0.16 (mean) ±0.42 (1-σ) ppm. Considering only flasks filled during periods of low atmospheric variability (1-σ variability in the continuous analyzer over the flask flush and fill time < 0.2 ppm), the offsets are −0.20 (mean) ± 0.27 (1-σ) ppm for CO_2. For CH_4, the offsets in 2011 change from 0.4 ± 1.8 ppb to 0.4 ± 1.3 ppb when considering flasks filled during variability < 3 ppb, and for CO there is no measurable improvement (from -0.6 ± 2.8 ppb to -0.6 ± 2.6) when considering variability < 5 ppb.

The absolute bias (mean) of the CO_2, CH_4, and CO in-situ to flask comparisons is smaller than the variability (1-σ standard deviation) but larger than the standard error ($\sigma/\sqrt{N}$) (in all cases except for CH_4 in 2009), indicating that the bias, although smaller than our target uncertainty in most cases, is statistically significant. In all three years for CH_4 and in 2010 and 2011 for CO_2, the median offsets are smaller than WMO-recommended limits (i.e. 0.1 ppm for CO_2 and 2 ppb for CH_4). The means for CO_2 reflect several flask outliers, where the flasks are biased high. High CO_2 flask measurements have been recently observed in flask to in-situ comparisons at NOAA ground sites as well, and seem to have become more prevalent since 2011 (Andrews, 2012). CO measurements show a mean bias smaller than the WMO inter-laboratory compatibility goal (2 ppb) in 2011, and the offsets between the CRDS measurements and the flask measurements have been shown to have no dependence on day of year, water vapor, ambient pressure, CO_2, CH_4, or CO (Chen et al., 2012a).

In 2009, although the scatter of the offsets is small, the median CO_2 offset is significantly greater than WMO recommendations (+0.22 ppm). Subsequent re-analysis of the continuous data using only a laboratory calibration from December 2009 (i.e. not using the correction of the on-board tanks) reduces the bias to 0.04 ppm. Although we have no reason to reject the in-situ calibrations outright, this fact does suggest the possibility of a problem in the standard delivery (the tanks were calibrated at NOAA post-mission and were within 0.1 ppm of CO_2 from their initial calibration, so tank drift is not likely to be a factor). It is possible that the reference tank regulators were not adequately flushed. The two tanks that were not run as frequently (high and low targets that ran once every 3 h) showed clear evidence of lack of flushing, with very low measured values; they were not used in the calibration at all in 2009 for this reason. The ambient-level main tank, which was run every 30 min, was the only tank used for in-situ calibration and may possibly also have been inadequately flushed. It was during this 2009 season that rather than being manually flushed by the on-board technician, the regulators underwent an automated flushing sequence in which the tanks ran more frequently at the start of the flight. In 2010, the on-board technician began to do a more rigorous flushing of the regulators by hand prior to departure, flushing the entire regulator volume at least three times, and results improved. Whatever the cause, the data from subsequent years do not show this bias in CO_2.

The in-situ to flask comparison for CO_2 for all years does not meet the WMO interlaboratory compatibility goal (mean of 0.1 ppm for CO_2) even when periods of high variability have been filtered out. In trying to understand the cause of this poor repeatability between continuous and flask measurements of CO_2, it is important to consider Figs. 6, 7, and 8, which not only demonstrate the stability of the standard measurements over a season but also for each flight (standard deviations for both under 0.04 ppm in CO_2). Separate water vapor correction tests suggest that in 1 % water vapor there is an additional uncertainty due to possible drift in the correction of less than 0.1 ppm (Rella et al., 2012). Taken together ($\sim$0.14 ppm when summed in quadrature) these errors are significantly smaller than the observed repeatability suggesting that there are errors in gas handling upstream of the standard tank introduction or, that there are errors in the flask measurements contributing to poor reproducibility.

To test the integrity of the in-situ gas handling, thorough leak checks on all inlet lines are performed whenever possible (prior to each season at the minimum). Two additional tests are performed annually on the aircraft system: (1) a standard gas is run through a portion of the inlet line at ambient external pressure during flight (by utilizing a T-fitting for excess flow outside the aircraft), and (2) on the ground, a standard gas is run through the complete inlet line from the exterior of the aircraft. These tests are performed at least once per year to evaluate the effects of both low pressure and of any kind of contamination in the inlet line, and have proven valuable in confirming that the in-situ analyzer stream has not been contaminated prior to entering the MPV.

Testing of the PFP sampling system is also routinely performed. Laboratory tests done with PFP flasks filled sequentially with a single tank and compared with single glass flasks (typically used in the NOAA ground network) show measurement offsets of -0.09 ± 0.05 ppm for CO_2 (http://www.esrl.noaa.gov/gmd/ccgg/aircraft/qc.html). Recent analysis of wet samples in the laboratory and comparisons with in-situ CO_2 measurement systems on towers (Andrews, 2012) suggest that the PFP flasks may have uncertainties as high as 0.3 ppm for CO_2 due to possible surface-water interactions when sampling wet air (as is done on the C-130) or due to residual water vapor in PFP flasks from insufficient drying prior to sampling. Unlike low-pressure network flasks, the PFP flasks store air samples at 40 psia (2700 mb); effects of off-gassing from any surface area exposed to the sample will therefore be amplified. These tests on the PFP flasks and sampling system are on-going at NOAA and are targeted towards both resolving the discrepancy between the in-situ and flask measurements and determining a more accurate uncertainty on the flask measurements of CO, CH_4, and CO_2.

The higher than desired uncertainty for CO_2 on both systems is a critical reminder that accurate GHG measurements must be validated whenever possible, and that frequent sampling of standards during flight may not be an adequate assessment of the true uncertainty of a system. When measurements are performed autonomously, especially when independent validation is not routine (e.g. flask vs. in-situ comparisons are not possible), we recommend periodic confirmation of measurements by either independent validation or rigorous tests such as those described above.

2.7 Water vapor measurement

Not drying the sample stream to the CRDS allows us to measure water vapor in addition to CO_2, CH_4 and CO. Water vapor gradients are an important constraint on the boundary layer height, and the data can serve as an important way to evaluate vertical mixing in transport models. The water vapor measurement of the CRDS analyzers is based on a laboratory calibration done on a single instrument (Winderlich et al., 2010), reported at approximately 0.5-Hz in the 2000-series analyzers along with the three other species. We note that the response time of the H_2O measurement when switching from a wet to a dry gas is approximately 40 s to arrive within 0.01 % (or 100 ppm) of the final value in flight (Fig. 4, right panel, shows the same result from a laboratory experiment with the same model analyzer). Figure 12 (left panel) illustrates that during an altitude ascent and descent (on 28 June 2011 over Galena, AK), the CRDS water vapor measurements agree well and do not show significant lag due to this response time or due to the long inlet line. In the right panel of the same figure, the descending profile is compared to the H_2O calculated using the Vaisala temperature and relative humidity measurements, along with the external ambient pressure measurement, and equations from Goff (1957) and Buck (1981). Vertical gradients in H_2O are well resolved in both cases, although some difference in response time is apparent (the Vaisala probe has a response time that depends on various factors, including airspeed and the orientation of the protective shield).

Over the 2011 season, measurements from the CRDS analyzer and the T/RH sensor compare well considering the uncertainty in the Vaisala temperature and relative humidity measurements is reported to be 1 % of the reading, with a high correlation ($R^2 = 0.99$) and slope close to unity (Fig. 13). Further analysis, along with laboratory calibration, is required to evaluate the stability and the site to site comparability of the CRDS system for water vapor. However, the flight data show that the CRDS analyzer is capable of capturing gradients in H_2O that can be used to determine boundary layer height.

3 Conclusions

The GHG measurement system designed to operate on the USCG C-130 aircraft in Alaska is simple and robust. We recognize some trade-offs are necessary and have chosen a simple system despite the drawbacks (specifically, somewhat degraded response time, leading to a loss of some measurements surrounding calibration cycles). The decisions made in favor of a simpler system, such as not drying the sample stream, do not compromise the measurement error of the in-situ data within the stated uncertainties determined from flask comparisons, and allow for the measurement of water vapor. The large size of the aircraft used at this site allows for a relatively large payload, which has allowed NOAA to deploy flasks along with the CRDS system for measuring CO_2, CH_4, and CO, thus giving a real assessment of the uncertainties for each.

The C-130 payload capacity allows for the deployment of three large gas standard tanks for calibration of the CRDS analyzer, allowing us to evaluate the optimum methodology for running in-flight calibrations. We have found that a high frequency (every 30 min) of calibration runs may not be necessary because of the high stability of the CRDS analyzer. At ACG, the same low measurement error could be achieved by running a single standard tank at a frequency that allows for at least two calibration runs of each tank during a single flight (to confirm repeatability), for example at the start and end of each flight. In 2009, we found that a sampling problem (possibly inadequate regulator flushing) may have impacted the data quality and had better agreement with flasks when no in-situ tank calibrations were used at all. These findings suggest that when calibrations are run on an in-situ remote system, extreme care must be taken in the gas handling for both the standards and the sample. In the case of our ACG deployments it would have been possible to deploy our analysis system without standards given the low flight-to-flight variability of the laboratory calibration with respect to in-flight measurements. However, we would recommend that a target gas (ideally measured at the start and end of each flight) be used to track drift over the course of the flight and between flights. Periodic tests, as much as possible, of the entire system inlet are also recommended. Overall, three years of autonomous aircraft deployment of the CRDS system suggest that six-month deployments are possible without onboard calibrations, provided rigorous pre- and post-deployment laboratory tests are performed, including checking sample handling, water vapor testing, and quantifying drift from standards calibrated on the WMO scale. These results suggest that variations in pressure or temperature do not affect the CRDS measurements in anyway.

Data acquired at the Alaska Coast Guard site over three seasons have been shown to be of high quality and will be of high value to investigations of the Arctic carbon cycle. Data from ACG is available from the corresponding author until it becomes available online at the NOAA Carbon Cycle server (http://www.esrl.noaa.gov/gmd/dv/data/).

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Table 1. Typical short-term precision of Picarro CRDS analyzers at the fastest measurement frequency (∼ 0.5-Hz). Flight condition values occur during turbulent portions of flights (i.e. low altitudes and/or altitude changes).

Species	CFADS08 (2009)	CFADS09 (2010)	CFKBDS2007 (2011)	CFKBDS2007 (2012*)
CO_2 (laboratory)	0.05 ppm	0.05 ppm	0.03 ppm	0.03 ppm
CO_2 (flight)	0.2 ppm	0.2 ppm	0.1 ppm	0.04 ppm
CH_4 (laboratory)	0.4 ppb	0.4 ppb	0.2 ppb	0.2 ppb
CH_4 (flight)	2 ppb	2 ppb	1 ppb	0.3 ppb
CO (laboratory)	n/a	n/a	4 ppb	4 ppb
CO (flight)	n/a	n/a	4 ppb	4 ppb

* These data are for flights after the installation of a new inlet proportional valve.

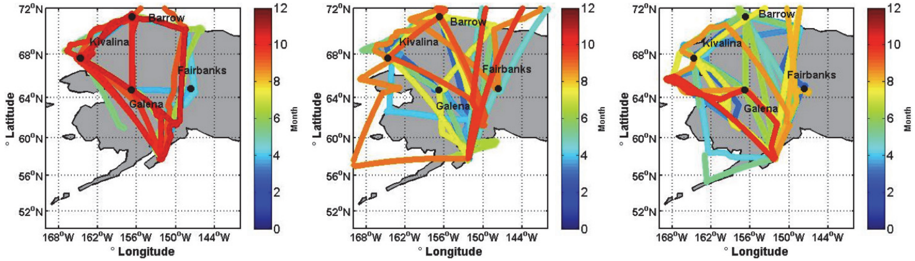

Fig. 1. Flight paths from the three complete seasons of GHG sampling: 2009 (left panel), 2010 (center panel), and 2011 (right panel). The 2012 season is currently underway. The color of the flight path corresponds to the month of the flight.

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Fig. 2. NOAA equipment pallet for USCG C-130: three reference gas cylinders, instrument rack, and two Programmable Flask Packages (PFPs) (left). Window replacement inlet plate (external view) (right).

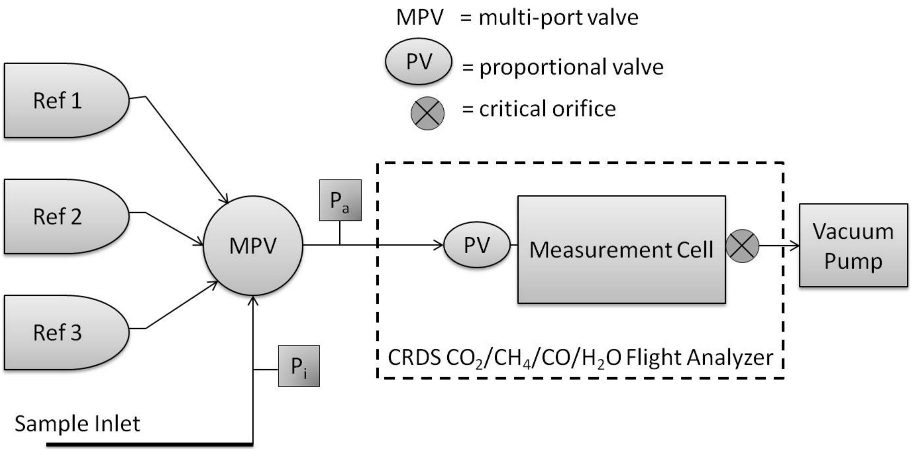

Fig. 3. Schematic diagram of $CO_2/CH_4/CO/H_2O$ sampling system on the C-130 aircraft.

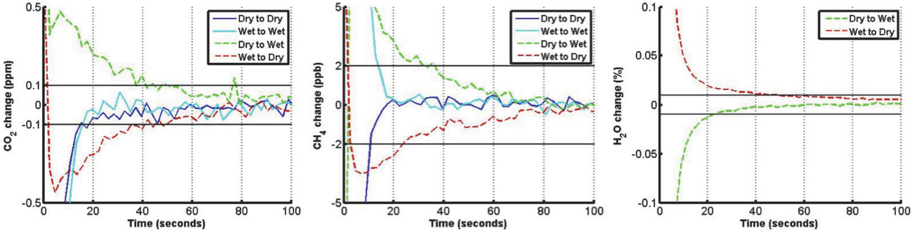

Fig. 4. Transition times between different standard gases for CO_2 (left), CH_4 (center), and water vapor (right), from a laboratory test, with parameters as they are at ACG. CO transition times were too short to be measureable within the instrument noise and are not shown. The WMO recommendations for site inter-comparability for CO_2 and for CH_4 are shown in solid black lines at 0.1 ppm and 2 ppb, respectively. The solid black lines on the right panel indicate 0.01 %, or 100 ppm H_2O.

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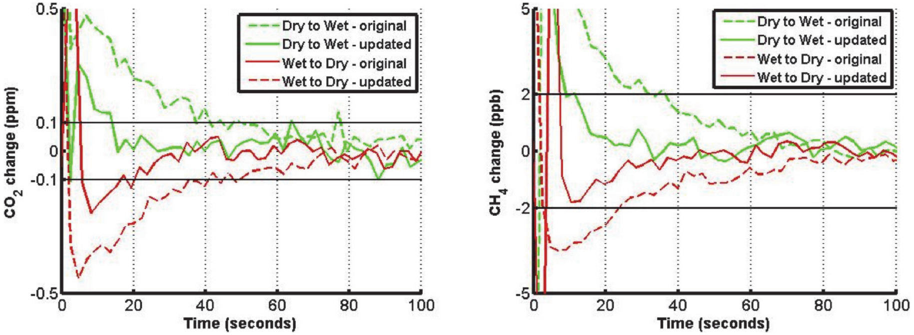

Fig. 5. Transition times from wet to dry gas (red) and from dry to wet (green) before (dashed lines) and after (solid lines) the analyzer software parameter change that controls the baseline response time. CO_2 is shown in the left panel and CH_4 on the right. The WMO recommendations for site inter-comparability are shown in solid black lines: 0.1 ppm for CO_2 and 2 ppb for CH_4.

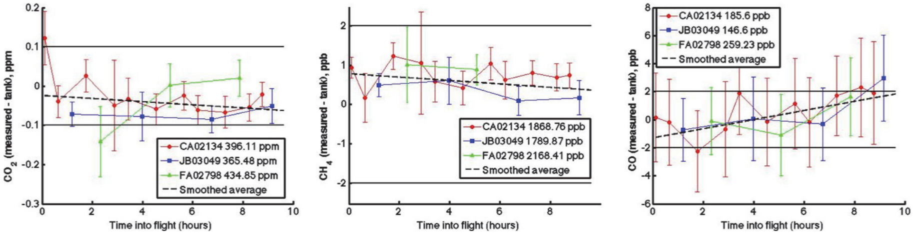

Fig. 6. Residuals of reference gas measurements for CO_2 (left), CH_4 (middle), and CO (right), during a flight on 4 April 2011. Different colors represent the different tanks, while the dashed black line is a linear fit with time to all the residuals. The dashed line is used to correct the sample mole fractions. Solid black lines represent the WMO goals for inter-site comparisons.

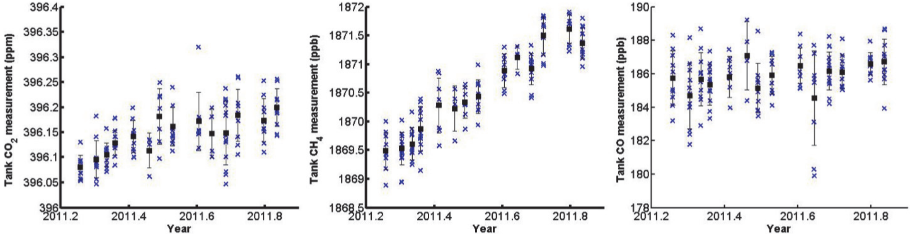

Fig. 7. Measurement of a reference gas tank on the aircraft during flight throughout the 2011 season for CO_2 (left panel), CH_4 (middle), and CO (right). Blue "×" symbols are the mean tank measurement during a single 3-min run; black squares are the average value during a single flight; error bars represent the standard deviation (1-σ) around that average.

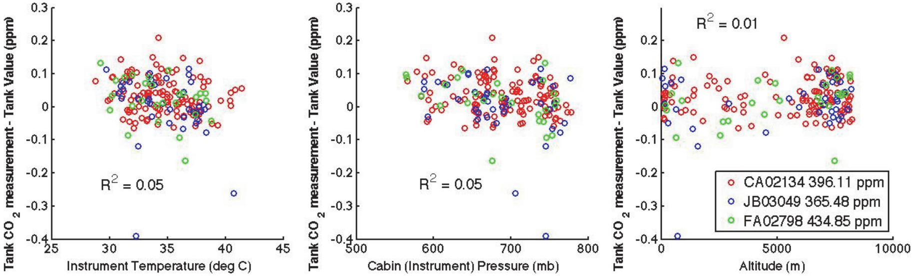

Fig. 8. Measurement of a reference gas tank in 2011, relative to the calibrated tank value, as a function of three environmental variables: instrument temperature (left), cabin pressure (middle), and aircraft altitude (right). Data from all three on-board tanks are shown in different colors, along with the correlation coefficient (R^2) for each. The measured value is determined using the pre-deployment laboratory calibration only.

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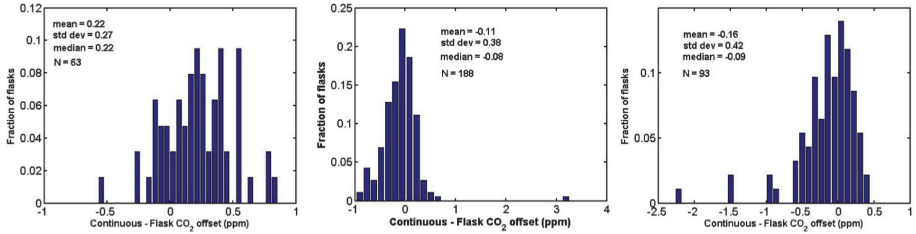
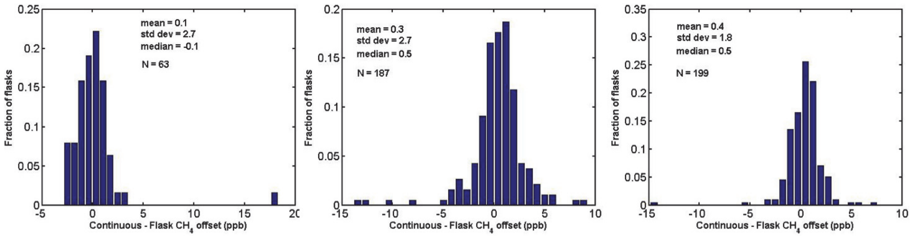


(a) (b) (c)

Fig. 9. (a–c) Differences between continuous (CRDS) CO$_2$ measurements and flask CO$_2$ measurements during flights over Alaska on the USCG C-130 for three seasons **(a)** 2009, **(b)** 2010, and **(c)** 2011. Negative offsets occur when the flask-measured mole fraction is higher than the continuous measurement. The mean for each season, one-sigma standard deviation, median, and number of flasks for comparison are indicated on each figure.



(a) (b) (c)

Fig. 10. (a–c) Differences between continuous (CRDS) CH_4 measurements and flask CH_4 measurements during flights over Alaska on the USCG C-130 for three seasons **(a)** 2009, **(b)** 2010, and **(c)** 2011. The mean for each season, one-sigma standard deviation, median, and number of flasks for comparison are indicated on each figure.

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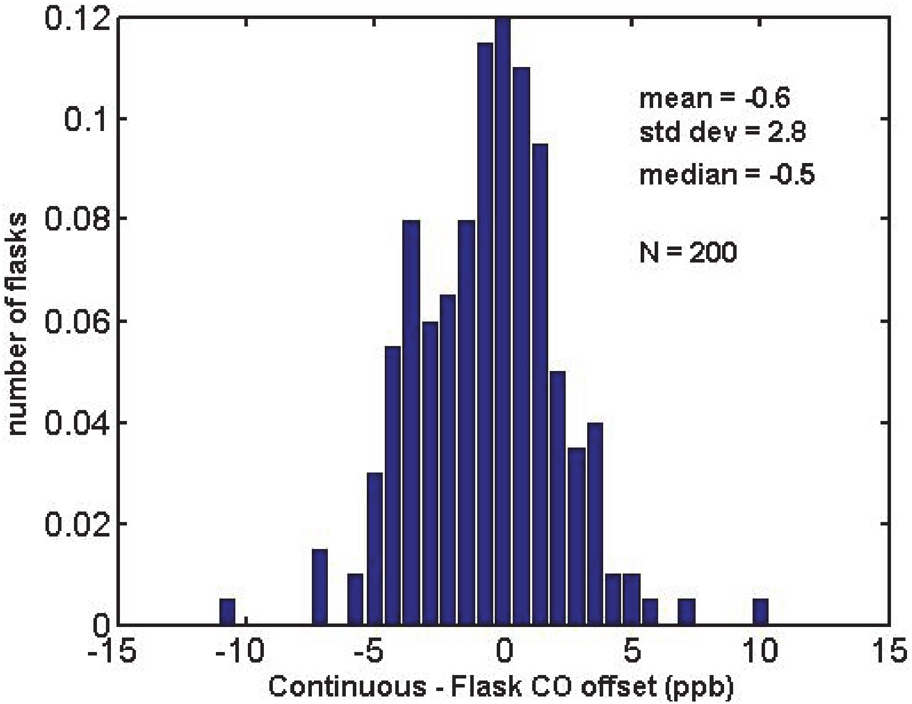

Fig. 11. Differences between continuous (CRDS) CO measurements and flask CO measurements during flights over Alaska on the USCG C-130 for 2011. The mean, one-sigma standard deviation, median, and number of flasks (*N*) are indicated on the figure.

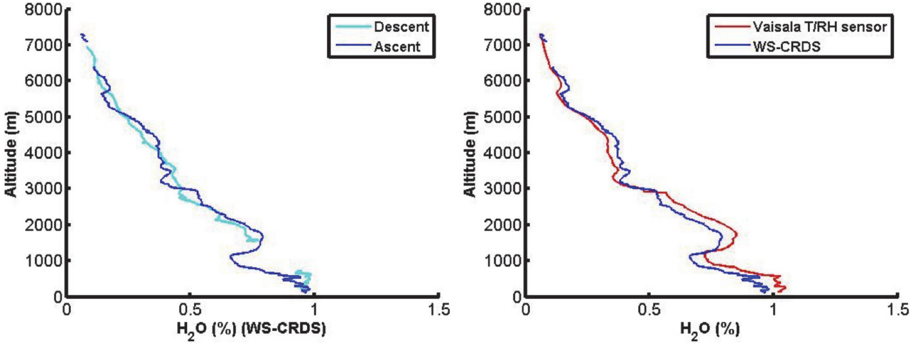

Fig. 12. Altitude profiles of water vapor (H_2O) measurements over Galena on 28 June 2012. Left panel: ascent and descent measurements from the CRDS analyzer (data gaps exist during calibration periods). Right panel: ascent measurements from both CRDS (blue) and calculated from in-situ temperature and RH measurements (red).

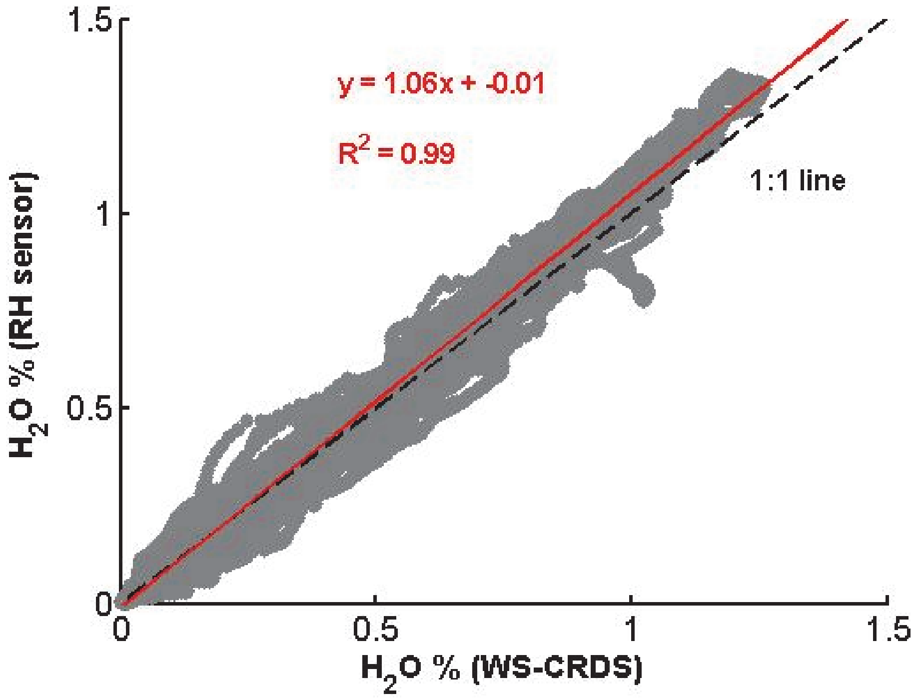

Fig. 13. Comparison of CRDS H_2O with values calculated from the temperature and relative humidity sensor over the entire 2011 season. Red line shows the linear fit to the data, while the black dashed line indicates the 1 : 1 relationship.