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Evaluation of the Airborne Quantum Cascade Laser Spectrometer (QCLS)
Measurements of the Carbon and Greenhouse Gas Suite—CO₂, CH₄, N₂O, and CO—During the CalNex and HIPPO campaigns

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Abstract

We present an evaluation of aircraft observations of the carbon and greenhouse gases (CO₂, CH₄, N₂O, and CO) using a direct-absorption pulsed quantum cascade laser spectrometer (QCLS) operated during the HIPPO and CalNex airborne experiments. The QCLS made continuous 1 Hz measurements with 1-sigma Allan precisions of 20, 0.5, 0.09, and 0.15 ppb for CO₂, CH₄, N₂O, and CO, respectively, over >500 flight hours on 79 research flights. The QCLS measurements are compared to two vacuum ultraviolet (VUV) CO instruments (CalNex and HIPPO), a cavity ring-down spectrometer (CRDS) measuring CO₂ and CH₄ (CalNex), two broadband non-dispersive infrared spectrometers (NDIR) measuring CO₂ (HIPPO), two onboard gas chromatographs measuring a variety of chemical species including CH₄, N₂O, and CO (HIPPO), and various flask-based measurements of all four species. QCLS measurements are tied to NOAA and WMO standards using an in-flight calibration system and mean differences when compared to NOAA CCG flask data over the 59 HIPPO research flights were 100, 1, 1, and 2 ppb for CO₂, CH₄, N₂O, and CO, respectively. The details of the end-to-end calibration procedures and the data quality-assurance and quality-control (QA/QC) are presented. Specifically, we discuss our practices for the traceability of standards given uncertainties in calibration cylinders, isotopic and surface effects for the long-lived greenhouse gas tracers, interpolation techniques for in-flight calibrations, and the effects of instrument linearity on retrieved mole fractions.
1. Introduction

Growing interest in understanding the drivers of climate change has sparked innovation in instrumentation to measure long-lived greenhouse gases and associated chemical tracers (Chen et al., 2010; Fried et al., 2009; Nelson et al., 2004; O’Shea et al., 2013; Xiang et al., 2013; Zare et al., 2009). The improvements in measurement precision and ease-of-use must be matched with a corresponding increase in calibration efforts to achieve comparable gains in compatibility. Many sensors rely on the accuracy of spectroscopic parameters (e.g. linestrengths and their pressure and temperature dependencies) to derive in situ ‘spectroscopically-calibrated’ mixing ratios from raw spectra (Rothman et al., 2009; Zahniser et al., 1995). The use of this raw data is often appropriate, particularly if: 1) a sensor is linear with respect to the range of observed concentrations, and 2) the quantity of interest is the relative enhancement of one chemical tracer versus another or versus background values measured on the same sensor. More and more studies, however, are incorporating data from different sensors (Gerbig et al., 2003, Zhao et al., 2009, Xiang et al., 2012, Miller et al., 2008). It is in this context that spectroscopically-calibrated mixing ratios are insufficient, as small differences in sensor accuracies can have large effects, e.g., on inversion studies.

Here we discuss the traceability of airborne in situ spectrometer measurements. We present an overview of the quantum cascade laser spectrometer (QCLS) sensor used on two airborne campaigns—the HIAPER Pole-to-Pole Observations (HIPPO: Wofsy et al., 2011) campaign on the NCAR HIAPER-GV and the California Research at the Nexus of Air Quality and Climate Change experiment (CalNex; Ryerson et al., 2012) on the NOAA P-3—and present measurement comparisons with other onboard sensors and flask samplers. We describe operations of the QCLS and the calibrations of the carbon and greenhouse-gas measurements of CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, and CO. We evaluate the traceability of calibration standards from the World Meteorological Organization (WMO) and National Oceanic and Atmospheric Administration (NOAA) calibrated values to the in-flight standards as well as long-term sensor stability. We then characterize the in-flight drift through interpolations to periodic sample replacements with calibrated air and discuss how this affects our overall accuracy. In the context of traceability and sensor accuracy, we discuss sample conditioning, surface equilibration effects, and isotopic effects on calibration standards.

2. Quantum Cascade Laser Spectrometer

2.1 QCLS Hardware

This work focuses on data collected using the Harvard/NCAR/Aerodyne Research Inc. quantum cascade laser spectrometer (QCLS). To the extent they are needed in explaining the traceability of our measurements, we briefly describe the instrument characteristics, noting that more details of the spectrometer are available in Jimenez et al. (2005) and Jimenez et al. (2006). The QCLS uses three pulsed quantum cascade lasers to measure CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, and CO by absorption spectroscopy. One laser (QCL1, ~2319 cm\textsuperscript{-1}) is used as a light source for a differential absorption measurement of CO\textsubscript{2} by recording the difference between a sample absorption spectrum and the absorption spectrum of a calibrated standard flowing through a separate reference cell. The remaining two lasers, housed in a second optical compartment, are tuned across absorption lines for CH\textsubscript{4} and N\textsubscript{2}O in one scan (QCL2, ~1275 cm\textsuperscript{-1}), and CO in another (QCL3, ~2169 cm\textsuperscript{-1}), making use of a multi-pass astigmatic sample cell to increase the
effective optical path length (McManus et al., 1995). Laser beams from QCL2 and QCL3 are co-aligned through an anchor point before being directed into the sample multi-pass cell. The light pulses from the 3 QCLs are detected using photovoltaic detectors housed and cooled in two liquid nitrogen (LN$_2$) dewars: one for CO$_2$/QCL1, and the other for both CH$_4$/N$_2$O/QCL2 and CO/QCL3. The CO$_2$ optical table, QCL1, two 10-cm path length sampling cells, and a dewar housing InSb detectors for the CO$_2$ portion of the QCLS are enclosed in a temperature-controlled pressure vessel flushed with ultra-high-purity nitrogen to remove the effects of absorption external to the sampling cells. QCL2 and QCL3, an astigmatic multi-pass sampling cell with an effective 76 m path length, and a dewar housing the HgCdTe detectors are mounted on a second optical table surrounded by a temperature-regulated enclosure. The pulses from QCL2 and QCL3 are temporally multiplexed on the same pair of detectors.

The spectra acquired from the two optical tables are controlled and analyzed by the same computer. TDL Wintel® software controls the laser temperature and overall output frequency, the tuning ramp rate (the wavelength frequency range and rate over which the laser is tuned) and the detector multiplexing for QCL2 and QCL3 which share a pair of common detectors. The temperature regulation of the QCLS is achieved by means of Peltier modules coupled to a closed-circuit recirculating fluid kept at fixed temperature within 288.0 ± 0.1 K. With the exception of the chiller fluid, electronics and computer, the CO$_2$ measurement (QCLS-CO2) can be considered independent from the CH$_4$, N$_2$O, and CO measurements (QCLS-DUAL) and we refer to those two sensors as such.

The instrument is fully autonomous and sampling, calibration, temperature regulation, and pressure regulation are controlled by a data-logger (CR10X, Campbell Scientific). It logs control variables and periodically dumps them via a serial connection to the computer running TDL Wintel® for storage on a solid state hard drive. Because the sampling and control strategy is controlled by the data-logger and the spectral analysis is performed by the TDL Wintel® software running on the computer, in-flight spectra are acquired using a fixed nominal cell pressure and cell temperature. Raw spectra are later reanalyzed with the logged CR10 cell pressure and cell temperature measurements to generate spectroscopically-calibrated mixing ratios. Figure 1 shows the raw spectra and the Levenberg-Marquardt fits to the absorption lines within the scan according to the HITRAN database (Rothman et al., 2007) for the three QCLS. The CO$_2$ spectrum appears inverted because this particular air sample has less CO$_2$ than the calibration air flowing through the reference cell.

Optical-based measurements are particularly sensitive to fluctuations in temperature and pressure (Zahniser et al., 1995) and careful controls must be implemented, particularly during flight where large dynamic ranges in both variables are observed (Fried et al., 2008). In-flight calibrations at regular intervals from gas cylinders are used to track sensor drift. As long as the inter-calibration time interval is shorter than the long-term drift, standard additions can offset inaccuracies due to pressure and temperature fluctuations. The Allan variance, a measure of the precision of a sensor as a function of averaging time (Werle et al., 1993), can be used to quantify both the short-term (e.g. electronic noise) and long-term precision of a sensor as well as the drift. Figure 2 shows the in-flight Allan variance for the CO$_2$, CH$_4$, N$_2$O, and CO measurements from the QCLS with 1-second RMS precisions (Allan standard deviations) of 20, 0.5, 0.09, and 0.15 ppb, respectively. The measurements shown in Figure 2 were taken during a section of HIPPO that sampled a relatively constant air mass above the remote Pacific Ocean. This is the same section of data presented in the supplementary material section of Kort et al. (2011). Table 1 summarizes the Allan precisions at 1, 10, and 100 seconds for the 4 species. During flight
sampling, the Allan precision between 1 and 10 seconds improves for all species, but only continues to improve between 10 and 100 seconds for N$_2$O. This is largely because atmospheric variability in CO$_2$, CH$_4$, and CO is larger relative to N$_2$O as the atmospheric lifetime of N$_2$O is ~118 years (Hsu and Prather, 2010) and the sources are more spatially uniform than for the other species. Because of this, Table 1 also includes the Allan precision from laboratory tests that sampled air continuously flowing from calibration cylinders with near-ambient atmospheric concentrations.

The flow schematics for QCLS-CO$_2$ are shown in Figure 3. The two schematics are very similar. QCLS-CO$_2$ and QCLS-DUAL have independent inlets. On the HIAPER-GV, both inlets extend out from the QCLS rack to a dedicated NCAR HIAPER Modular Inlet (HIMIL) mounted to the edge of the aircraft. The HIMIL extends the inlet 28 cm from the body of the aircraft (NCAR, 2005) and the two QCLS inlets, both 316 stainless steel 0.25” OD sample from within the center flow path, oriented away from the direction of flow (i.e. rear-facing). This orientation minimizes large particle entrainment and protects the sampling system from liquid water and ice. For the NOAA P-3 aircraft, the inlets both consist of stainless steel 3/8” OD tubing bent at 90 degrees to be parallel to the aircraft and oriented at -135 degrees relative to the horizontal direction of flight. Once the sample enters the body of both aircraft, the two sample lines consist of ~1.5 m of Synflex type 1300 tubing (6.35 mm = 1/4” OD for QCLS-CO$_2$ and 9.525 mm = 3/8” OD for QCLS-DUAL) and each sample stream reaches a 2 μm filter (47 mm OD Pall Zefluor membrane) mounted in an aluminum filter holder (Gelman Sciences, Inc., Rossdorf, Germany). Calibration gases are added downstream of the filter using a combination of 2-way and 3-way solenoid valves. When activated, the solenoid valves allow air from two sets of calibration gas decks which each include 3 cylinders (1.1 L for QCLS-CO$_2$ and 2.0 L for QCLS-DUAL) to ‘over-blow’ the inlet, with the excess flow exiting the aircraft through the HIMIL. The regulators for the calibration cylinders are set on the ground to achieve an excess flow >100 sccm (QCLS-CO$_2$) or >200 sccm (QCLS-DUAL) which flows via the filters and inlets out the aircraft. From this point, the sample (or calibration) air travels through a 1-tube (QCLS-CO$_2$, see Daube et al., 2002 for an explanation of this choice) or 50-tube (QCLS-DUAL) Nafion membrane dryer to remove the bulk of the water vapor. Then the air passes through a Teflon dry-ice trap to further reduce the dewpoint to below -70 °C. A stainless steel filter (Swagelok, SS-4FW-2, 2 μm stainless steel mesh) at the outlet of the dry-ice trap ensures that particles cannot exit the trap, thaw, evaporate, and contaminate the measurement cell mirrors. From the dry ice trap, air enters the sample cells, the pressures of which are controlled both upstream and downstream of the cell using a pressure controller and valve (MKS 722, 100 torr range). For QCLS-CO$_2$, the 9.7 cm$^3$ sample cell is controlled to 70 ± 0.1 hPa using another MKS 722 and the reference cell pressure is matched using a differential pressure controller and valve (MKS 223B, 100 torr absolute, 10 torr differential range). For QCLS-DUAL, the 0.5 L cell is controlled to 77 ± 0.1 hPa. After the pressure control element downstream of the sample cells, the flows are routed back through the outer tube enclosing the Nafion membrane tubes to create the necessary H$_2$O gradient across the membrane. The flows are then combined into a 4-stage diaphragm pump (KNF Neuberger, Inc. UN726) fitted with Teflon-lined diaphragms. Two of the heads are connected in parallel and the remaining two downstream pumps are connected in series to compensate throughput and power. For the HIAPER-GV, the exhaust is then dumped to a dedicated exhaust manifold in the aircraft. For CalNex, the exhaust is dumped through a third stainless steel port downstream of the inlet.

Overall instrument response time is largely controlled by the sample cell pressure and volume, the flow rate, and the inlet pressure and volume. Additional lags associated with mixing
within the different sampling volumes are second order effects, but are minimized by using 6.35
mm OD and 9.525 mm OD Synflex for QCLS-CO2 and QCLS-DUAL respectively. The larger
diameter tubing is needed for QCLS-DUAL because of the larger sample cell volume. The flow
rates through QCLS-CO2 and QCLS-DUAL are 0.1 and 1.0 slpm, respectively, which
correspond to cell flushing times on the order of 1 sec for both sensors, assuming plug flow.

2.2 QCLS Traceability

In-flight calibrations are done by replacing air in the sample cell with air from
compressed gas cylinders in two gas decks mounted on the QCLS flight rack (see Figure 3). The
QCLS-CO2 gas deck contains three 1.1 L carbon-fiber wrapped aluminum compressed air
cylinders (SCI ALT-765) and the QCLS-DUAL gas deck has three 2.0 L cylinders (SCI ALT-764). The QCLS-CO2 gas deck is filled with three whole-air standards containing CO2 dry-air
mole fractions in the ~370-410 ppm range, two of which are used as spans: a low-span at ~375
ppm, a high-span at ~405 ppm, and the other as the reference at roughly ambient mole fractions
of ~390 ppm. The QCLS-DUAL gas deck also contains two spans and a zero, which is ultra-pure
whole air. The gas decks are filled using air from size AL (29.5 L) compressed air cylinders
ordered from Scott-Marrin (Riverside, CA). The AL cylinders used to fill the QCLS-CO2 gas
deck are calibrated on the historic Harvard Licor-based ground calibration unit discussed in
Daube et al. (2002) by comparison to a set of 4 primary cylinders obtained from NOAA with
CO2 values on the WMO scale (X2007). The AL cylinders used to fill the QCLS-DUAL gas
deck are calibrated using the QCLS itself and a set of ‘primary’ size ALM cylinders (48.1 L)
filled at Niwot Ridge and calibrated by NOAA. We refer to the AL cylinders used to fill gas-
decks as ‘secondary’ calibration cylinders. Secondary cylinders are typically initially pressurized
to ~ 2100 psi and the flight cylinders in the gas decks are filled to as high a pressure as possible,
usually >1800 psi. Gas-deck cylinders are filled directly from the AL secondary cylinders using
1/8” stainless-steel tubing after 3 rounds of flushing and purging the regulator and the fill line.
The gas-deck cylinders are themselves conditioned by being purged, then filled and flushed
twice (to 300 psig then 500 psig) before being filled to maximum pressure. Gas decks are
sampled until the pressure drops to 500 psi, well before drifts in concentration become apparent
(Daube et al., 2002). Table 2a summarizes the two calibrations of the primary cylinders used in
HIPPO and CalNex and Table 2b summarizes the calibration obtained for the secondary
cylinders used to fill the QCLS-DUAL gas deck.

Figure 4 shows the calibration procedure used to calibrate a secondary cylinder for
QCLS-DUAL in the lab. We turn on the QCLS and allow it to equilibrate while it is sampling
zero-air from an AL cylinder for at least 2 hours. Three primary tanks and a secondary ‘target’
tank are plumbed into an external bank of solenoid valves connected to the QCLS-DUAL via an
external port on the gas deck. The QCLS is operated in exactly the same mode as during in-flight
sample additions of calibrated air, where the calibration solenoid is actuated and excess
calibration air (>200 sccm for QCLS-DUAL) flows out through the QCLS inlet. The primary
and secondary tanks are plumbed into the external solenoid bank and the QCLS via 1/8” OD
stainless steel tubing. After equilibration, we sample zero-air for 5 minutes, then sequentially
flow air from three primaries in order of lowest to highest concentration for 3 minutes each.
After this sequence, we sample the target secondary tank, also for three minutes. We then repeat
this cycle an additional 3 times, as shown in Figure 4, not sampling the target secondary on the
last iteration. Figure 5 shows the data corresponding to the 270 pink points in Figure 4,
concatenated together for each of the QCLS-DUAL species during three independent sets of calibrations in 2010-2012 for the same tank, CC89589 (Table 2b). We calculate linearly interpolated (using the two closest) and quadratically interpolated (using all three) values that correspond to the mean of the three 90-second sampling segments. The average of those values is reported as the calibrated secondary values (Table 2b), where values more than 2σ from the mean, if they exist, are excluded in the calculation.

We test for filling errors by filling the gas decks with secondary tanks and then performing a similar calibration of the gas deck itself. For gas deck calibration, we sample the low-span and high-span ‘targets’ one after the other and use all four primary cylinders. Because use of the primary cylinders with QCLS required the instrument to be in a laboratory setting, we were able to perform gas-deck calibrations only before or after a given deployment. When the small cylinders in the gas decks reached 500 psi, they were flushed (3X) and filled with calibration air from AL secondary cylinders. For HIPPO, the refills would take place in Christchurch, NZ, using a different set of secondary cylinders than the secondary cylinders used to fill the gas decks on the first half (southbound) set of the HIPPO flight circuit. We would therefore calibrate the gas deck after filling it but before using in on the southbound flights, and after both filling it and using it on the second half northbound set of the HIPPO flight circuit. Because of these logistics, the calibration values calculated during gas-deck calibrations were only used as a check against filling error, ensuring that the gas-deck values fell within 3σ of the uncertainty attributed to the secondary tank calibration (Figure 5) from the NOAA primary cylinders. For consistency, and because calibrations of the gas decks themselves required the use of the primary cylinders, the calibration values assigned to the air in the gas decks were always the values from the secondary cylinder calibrations shown in Figure 5. Figure 5 also shows that, within uncertainty, there is no evidence of drift in the secondary cylinders from 2010 to 2012.

In-flight data are then tied to the NOAA scale by periodic sample replacement with air from the gas decks. The sampling structure is shown in Figure 6. Within a given 60 minutes, the calibration sequences is as follows: minutes 7-9, 22-24, 37-39, 52-54 sampled zero/reference, minutes 9-10 and 39-40 sampled low-span, minutes 10-11 and 40-41 sampled high-span, and minutes 41-42 sampled a check-span. Because of the different equilibration times for the different species, we changed the order of the LS and HS additions to occur before the zero-air additions (see below). The zero was sampled most frequently at 15-minute intervals to track QCLS drift. The low and high-spans were sampled at 30-minute intervals, and the reference-span was sampled every hour for one minute. For a given hour of flight, the effective sampling duty cycle was therefore ~78% (47 minutes of sampling per hour). The calibrations for QCLS-DUAL and QCLS-CO2 occur on the same interval. Instead of sampling zero-air like QCLS-DUAL, however, the QCLS-CO2 samples the reference gas in both the sample and reference cell in order to obtain a relatively flat spectrum. The zero/reference is sampled for 2 minutes for two main reasons: 1) the zero/reference is the most frequently sampled calibration standard and therefore tracks the environmental temperature and pressure variability which cause drift, and 2) the equilibration of the N₂O trace is slower than the other species. Because the gas deck reference/zero-air additions are used to track drift and to interpolate the measurement to standard values, equilibration of the gas-deck standard additions is essential.

We ran a number of tests to characterize the slow equilibration in N₂O observed in the zero-air additions. Figure 7 shows a concatenated time series of various sampling intervals in which we repeatedly switched between a zero-air cylinder and a span cylinder for 3-minute intervals. The different colors indicate different combinations of elements upstream of the
sensing cell that came into contact with the sample. The tests included instances in which the
air went straight from the cylinders to the sampling cell (through a nominal 0.5 m of Synflex that
was unavoidable). Various other upstream elements were added between the cylinder and the
sampling cell, including different lengths of Synflex, stainless steel tubing, PFA, and Nafion™
tubing. Figure 7 shows this data superimposed upon one another (with the zero-air value
assigned from the mean value of 145-165 seconds of the 180 second sampling window) and the
y-axis range normalized by the secondary cylinder calibrated value (N₂O = 319.3 ppb, CH₄ =
1919.6 ppb, CO = 223.4 ppb) and multiplied by an arbitrary constant (here 500) to zoom in on
the transition to the zero-air sampling. Both CH₄ and CO are largely unaffected by the different
sampling materials, likely because of their lower boiling points (-164°C and -192°C,
respectively) relative to N₂O (-88°C). Stainless steel was the only sampling material that was not
affected by absorption/desorption for N₂O. The importance of this effect scaled with the surface
area of the Synflex or PFA encountered. Using stainless steel is impractical in many instances, so
this effect is often unavoidable, but is important to consider in the context of measurement
traceability. We reached a compromise by sampling the zero-air for 2 minutes, sampling the LS
and HS before sampling the zero-air, and using a smaller sampling window to calculate the zero-
air spectroscopically-calibrated mixing ratios of N₂O, as seen in Figure 6.

Using a reference calibration cylinder (one with near-ambient atmospheric
concentrations, e.g. CC56519 in Table 2b) instead of a zero to track instrument stability would
minimize the effect of this problem. Because this tank is used so frequently to track drift,
however, it would have been impractical to use, particularly on HIPPO where opportunities to
ship calibration tanks and refill the gas decks are limited. We tested this assumption on one flight
during HIPPO V (RF14; Sept 9, 2011) and showed that using a 1-minute equilibration time for a
reference tank at ambient concentrations gave nearly equivalent results as using a 2-minute zero-
air tank.

It should be noted that the boiling point of CO₂ (-57°C) is even higher than that of N₂O,
so this effect is equally important for CO₂ and can be observed in Figure 6. However, it matters
to a much smaller extent as the Synflex is always in contact with air that is very close to ambient.

To distinguish sampling intervals from calibration intervals, we use an empirical
relationship that is a function of ambient pressure and tubing length. These differ for HIPPO and
CalNex because of the hardware configurations, notably the use of the HIMIL on HIPPO. For
HIPPO and QCLS-DUAL, we calculate experimental delay times from the HIMIL to the
calibration-addition point just downstream of the inlet filter (Figure 3) as a linear function of
ambient pressure in the HIMIL. We also calculate a time delay corresponding to the equilibration
time from that point to the measurement cell as a quadratic function of ambient pressure in the
HIMIL. These have the functional form:

\[ t_{\text{delay}} = 1.6201 \cdot P_{\text{amb}} \]  
\[ t_{\text{equil}} = 0.02763 \cdot P_{\text{amb}}^2 + 0.14993 \cdot P_{\text{amb}} + 3.75488 \]

where time and pressure have units of sec and mbar. The dynamic range of ambient pressure is
much smaller in CalNex and does not include a HIMIL, which affects the pressure at the inlet, so
the equilibration time for CalNex is treated as a constant value derived from plume comparisons
between QCLS and a fast-response black-carbon measurement (Schwarz et al., 2010) that was
available for both HIPPO and CalNex. Equations for QCLS-CO₂ have different coefficients but
the same form. The equations were calculated empirically during several test flights on each
campaign and then held constant throughout each campaign.
The HIMIL port, designed to slow air-flow, complicated the instrument equilibration time but dampened the input pressure variability of the sample. For CalNex, however, the variability in the sample pressure was occasionally not adequately controlled by the pressure control elements. Certain fluctuations in pressure were able to propagate to the QCLS-DUAL sample cell and affect the measurements. The effect of this cell ‘ringing’ was most apparent in the N₂O measurement which occasionally showed high-frequency (1 Hz) positive and negative excursions of >1-2 ppb for N₂O, a trace that should only see negative excursions in stratospheric air. We apply a filter which removed measurements in which the 1Hz rate change of pressure is greater than 3 standard deviations of the mean (σ = 0.16 hPa/sec). This resulted in an effective duty cycle that was 3% lower than without the pressure filter, but removed spurious spikes in the data.

Calibration time intervals were determined using these functions and the solenoid valve actuation time, and a mean mixing ratio for each sample addition was calculated in a given window. The zero-air values measured every 15 minutes were then fit using a penalized Akima spline interpolation technique (Akima, 1970) to evaluate the drift of the instrumentation. Other filters, such as loess, splines, interpolators occasionally cause severe curvature in the interpolation, particularly near the beginning of flight where sensors may not be fully equilibrated. This zero-air Akima-spline is evaluated at all the 1 Hz sampling times and subtracted from the entire dataset. Using the zero-air Akima-spline-subtracted data for the QCLS-DUAL species (for example, CH₄,raw), the mean values of each low-span and high-span window are interpolated using the same Akima-spline to the measurement times. CH₄,raw is then linearly interpolated to the low-span Akima-spline and high-span Akima-spline (CH₄,ALS and CH₄,AHS, respectively) according to:

\[ CH₄,cal = \left( \frac{CH₄,raw - CH₄,ALS}{CH₄,AHS - CH₄,ALS} \right) \cdot (CH₄,HSV,AL - CH₄,LSV,AL) + CH₄,LSV,AL \] (3)

where CH₄,LSV,AL and CH₄,HSV,AL are the two constant values of the low-span and high-span secondary AL calibration cylinders used to fill the gas-deck (Table 2b). The equations for N₂O and CO are equivalent and generate the calibrated sample dry-air mole-fractions (CH₄,cal in Equation 3). Figure 8 shows the different Akima-splines for an arbitrary flight during HIPPO 5, along with the ambient pressure. The axes are all scaled such that the different tracers – zero-air, low-span, high-span, and reference air – from the gas decks have equivalent ordinate ranges. The CO₂ trace in Figure 8 is in units of ppb relative to the reference, meaning that a value of -17500 corresponds to the low-span that is 17.5 ppm lower than the near-ambient reference. Figure 8 is a standard output product of the batch processing and is purposely scaled to emphasize the fluctuations of calibration standards over the course of a given flight. Because of the linear interpolation between the zero-subtracted low-span and high-span, the relative fluctuation of those two standards has the largest effect on the effective calibrated measurements.

The CO₂ calibration additions shown in Figure 8 are treated in a slightly different fashion than the QCLS-DUAL species. Because QCLS-CO2 is a differential measurement and the range of observations is the largest of any species (in terms of concentration changes measured over the course of a flight), the CO₂ interpolation is not calculated linearly. Instead, we take the median of the low-span, reference, and high-span values calculated over the course of any particular flight and fit a quadratic function to those median values for that flight. The reference-subtracted measurements are then quadratically interpolated using this fixed function. We
368 experimented with different methods to calibrate the CO₂ measurements and found that using a
369 method similar to QCLS-DUAL resulted in spurious wave generation in the measurements that
370 was not physical. Because the reference/zero calibration is sampled at 2X the frequency of the
371 spans, the reference trace is able to best compensate for the measurement drift. Physically, we
372 expect that the response of QCLS-CO₂ over the range of concentrations sampled should not
373 change dramatically, and this is confirmed in the flight-to-flight variability of the quadratic
374 interpolation function (see below). For this reason, we fix the quadratic function and make it
375 follow the more frequent reference calibration trace.
376
377 Figure 9 shows the variability of the quadratic function for QCLS-CO₂ (during CalNex)
378 and the linearity of QCLS-DUAL (in lab using data from a secondary tank calibration). The 4
379 sets of panels show the 1:1 plot of the raw spectroscopically-calibrated QCLS mixing ratios
380 versus the NOAA-calibrated primary cylinder values. The linear fits to QCLS-DUAL are
381 calculated using a type II regression with prescribed errors in the abscissa and ordinate (York,
382 2004). For the x-axis, the uncertainties are prescribed by the NOAA calibrations and for the y-
383 axis, errors are given by the standard deviation of the mean spectroscopically-calibrated QCLS
384 measurements. The bottom panel shows the residual values for the different tanks. For CO₂, the
385 fit is not linear, as described above, and the residuals shown are flight-to-flight differences in the
386 quadratic fit function over the course of the CalNex mission, which showed greater variance in
387 the quadratic fit coefficients compared to HIPPO. The residual values shown for CO₂ correspond
388 to the standard deviation of the quadratic fit function over the mission, and can be considered an
389 estimate of the sensor accuracy as a function of concentration. To put these estimates of errors in
390 context, the histogram distributions of the HIPPO and CalNex CO₂ measurements are shown
391 along with their 10-90% quantile ranges (solid blue and red lines) to show that this is a very
392 minor error effect for the majority of the measurements.
393
394 The accuracy of the QCLS-CO₂ measurements are determined by secondary cylinders
395 calibrated against NOAA standards using the Harvard Ground Support Equipment (GSE),
396 described in detail in Daube et al. (2002). The GSE is a Licor model 6251 NDIR analyzer, which
397 measures molecular absorption of CO₂ in a sample stream relative to a reference stream of air.
398 Because it is a nondispersive analyzer, the measurement is sensitive to different parts of the
399 molecular absorption band of CO₂. Tohjima et al. (2009) characterized the sensitivity of 3 Licors
400 (two 6252 and one 6262) to each of the isotopologues of CO₂. They use a Relative Molar
401 Response (RMR) value for each isotopologue to calculate the effective change in concentration
402 determined for each isotopologue (see their Table 4). Given a hypothetical CO₂ mixing ratio of
403 400 ppm, the isotopic abundances in HITRAN (Rothman et al., 2007) can be used to approximate
404 the individual mixing ratios of the three dominant isotopologue – \(^{16}\text{O}^{12}\text{C}^{16}\text{O}, ^{16}\text{O}^{13}\text{C}^{16}\text{O}, and
405 ^{18}\text{O}^{12}\text{C}^{18}\text{O} – as 393.68160, 4.42296 and 1.57883 ppm, respectively. The sum of these three
406 concentrations is less than 400 (399.68339) as other minor isotopes contribute to the total
407 concentration. Atmospheric CO₂ has an approximate isotopic composition of \(\delta^{13}\text{C} = -10 \%\) and
408 \(\delta^{18}\text{O} = 40 \%\), where these quantities are calculated according to:
409
410 \[
411 \delta^{13}\text{C}_{\text{CO}_2} = \left(\frac{R_{13}}{R_{13}^{\text{vpdb}}} - 1\right) \cdot 1000
412 \]
413
414 \[
415 \delta^{18}\text{O}_{\text{CO}_2} = \left(\frac{R_{18}}{R_{18}^{\text{smow}}} - 1\right) \cdot 1000
416 \]
417
418 where R13 represents the ratio of \(^{13}\text{C}\) to \(^{12}\text{C}\) in a sample of CO₂ or in the standard Vienna Pee
419 Dee Belemnite (vpdb = 0.011180) and R18 represents the ratio of \(^{18}\text{O}\) to \(^{16}\text{O}\) in CO₂ or in
Standard Mean Ocean Water (smow = 0.0020052). Using these equations, we can calculate atmospheric values for R13 and R18 of 0.0110682 and 0.002085408, respectively. The abundance of the dominant isotopologue ($^{12}\text{C}^{16}\text{O}^{16}\text{O}$) must therefore be 1 minus the R13 and twice the R18 abundances, or 0.984761, which corresponds to a concentration of 393.592606.

Because QCLS-CO2 only scans across one absorption line for the dominant isotopologue (mass 44), calibration additions using cylinders with non-atmospheric isotopic composition can therefore result in biases in the measurements. A hypothetical tank that has a total CO$_2$ concentration of 400 ppm and isotopic composition of $\delta^{13}\text{C} = -35$‰ and $\delta^{18}\text{O} = 10$‰ (typical of a Scott Marrin cylinder) will have dominant isotopologue $^{16}\text{O}^{12}\text{C}^{16}\text{O}$, $^{16}\text{O}^{13}\text{C}^{16}\text{O}$, and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ concentrations of 393.752405, 4.312064 and 1.618919 ppm, the sum of which is still 399.68339. But the concentration of the $^{12}\text{C}^{16}\text{O}_2$ isotopologue is higher by 0.1598 ppm compared to the concentration with near-atmospheric isotopic composition. This must be accounted for in relating calibration cylinder values to sample concentrations.

The mean RMR corrections for the three dominant isotopologues from the two Licor-6252 are 1) the mean of 1.0073 and 1.0040, 2) the mean of 0.21 and 0.45, and 3) the mean of 1.26 and 1.43, which are multiplied by the difference in isotopologue concentrations between the 400 ppm cylinder and the 400 ppm atmospheric sample. When summed, the mean value is -0.059 ppm with a range over the two instruments of -0.041 to -0.077 ppm. Chen et al. (2010) calculated a similar value using specific isotopic composition of the tanks of -0.09 ppm.

To account for the combined effect on the QCLS-CO2 calibration, the -0.059 ppm and the 0.1598 values must be added to the retrieved sample mixing ratio. The -0.059 ppm puts the calibration cylinder values calculated using the GSE onto the same isotopic scale as the NOAA primaries (i.e. atmospheric isotopic composition). The 0.1598 value accounts for the fact that QCLS-CO2 derives a total mixing ratio using the absorption spectrum of the dominant $^{12}\text{C}^{16}\text{O}_2$ isotopologue and the HITRAN abundance, which differs from the atmospheric abundance as shown above. These effects partially offset, but result in a ~0.1 ppm bias term, which is important considering that atmospheric concentration gradients are often not much larger than this. The particular isotopic values of the calibration cylinders (Table 2b) were measured by the Stable Isotope Ratio Facility for Environmental Research (SIRFER) and were used to calculate the exact corrections for the tanks. The NOAA primary tanks had near-atmospheric $^{13}\text{C}$ isotopic composition of around -10 to -15‰, Scott Specialty tanks usually fell in the -45 to -50‰ range, and Scott-Marrin usually fell in the -30 to -40‰ range.

The error for CH$_4$ due to differing isotopic composition between the atmosphere ($^{13}\text{C} \approx -47$‰) and calibration cylinders ($^{13}\text{C} \approx -30$‰) was calculated to be a ~0.3 ppb effect, smaller than the 1 Hz precision. The effects for N$_2$O and CO were proportionally smaller and these effects are therefore ignored for QCLS-DUAL.

3. Missions and Other Instrumentation

The QCLS was operated in the same configuration in both CalNex and HIPPO with only minor changes due to the aircraft-specific issues already discussed. We now present comparisons with other coincident instruments, synchronized in time using the STRATUM-1 aircraft data system.

For HIPPO, two additional fast-response (>1 Hz) CO$_2$ sensors were available for comparison: the OMS sensor (Daube et al., 2002), and the NCAR Airborne Oxygen Instrument (AO2), which includes a single-cell Licor-820 sensor. Figure 10 shows the 1 Hz measurement difference distribution for QCLS against OMS and AO2 for all HIPPO flights. QCLS-CO2 and
OMS agree to better than 0.05 ppm, with a standard deviation of the difference of 0.37, owing in part to the slower cell response time of OMS. Assuming the sensors have no covariance, the 1Hz OMS precision of 0.1 ppm and the 1 Hz QCLS precision of 0.02 ppm would sum in quadrature for an expected precision of 0.1 ppm. The actual distribution is 0.37 ppm, roughly a factor of 4 higher. The AO2 instrument has a 1-sigma, 1-second precision of ~0.6 ppm. QCLS-CO2 and AO2 agree to within 0.15 ppm and have an even larger variance on the distribution of the measurement differences. It is important to note that many unresolved biases spanning one hour or an entire flight exist among the CO2 sensors on HIPPO and tend to average out as presented in Figure 10. The Research Aviation Facility (RAF) vacuum ultraviolet (VUV) CO sensor is the only other fast-response instrument measuring one of the QCLS species (Gerbig et al, 1999).

That comparison, also shown in Figure 10, shows a bias of 1.8 ppb over the HIPPO mission.

Two onboard gas chromatographs—the Unmanned Aircraft Systems (UAS) Chromatograph for Atmospheric Trace Species (UCATS, Moore et al., 2003; Fahey et al., 2006; Wofsy et al., 2011) and the PAN and other Trace Hydrohalocarbon ExpeRiment (PANTHER; Elkins et al., 2002; Wofsy et al., 2011)—measured a variety of chemical species including CH4, N2O, and CO. Figure 11 shows the one-to-one comparison of the QCLS to PANTHER (top) and UCATS (bottom) after applying the averaging kernel of each GC to the 1 Hz QCLS data. In addition to the in situ data, sparser flask measurements from the NOAA Whole Air Sampler (NWAS) are compared in Figure 12. The axis ranges on Figures 11 and 12 are the same, with the exception of N2O, which has large variability from the GC-based measurements. Table 4 summarizes the median differences with NOAA for each of the QCLS species at the mean concentration measured on each of the 5 HIPPO transects. Mean biases calculated over the course of HIPPO are -112, 0.85, 1.07, and -1.94 ppb for the 4 species. Only N2O falls outside of the estimated uncertainties in the measurements. This is in part due to the recalibration of primary cylinder 4 (Table 2a) that deviated from the original value by more than 4 times the 1σ NOAA calibration uncertainty. This cylinder falls on the high range of the NOAA N2O calibration standards and is only bracketed by one NOAA standard with higher concentration (Hall et al., 2007). Additional CO2 flask data was available from the NCAR/Scripps Medusa flask sampler which collected air in 1.5 L glass flasks for analysis in the Scripps Oxygen Laboratory. Table 5 presents the corresponding median differences between QCLS and Medusa at the mean concentration measured on each of the 5 HIPPO transects. Although the CO2 offsets for individual missions to Scripps are not correlated with the offsets to NOAA, the 5-mission average is very similar at -10 ppb.

For CalNex, the payload of the NOAA P-3 aircraft included simultaneous 1 Hz measurements of CO using the NOAA VUV spectrometer (Holloway et al., 2000) and CO2 and CH4 using the NOAA/Picarro Cavity Ring-Down Spectrometer (CRDS). The comparisons for all three species are shown in Figure 13. No additional sensors measured N2O during CalNex. The CRDS made 1-Hz measurements of CO2 and CH4 with 1-second RMS precisions of 100 and 1.5 ppb, respectively (Peischl et al., 2012). Both sets of measurements were independently calibrated to NOAA standards during flight, accounting for roughly 20% of the sampling duty cycle for each instrument. The QCLS and CRDS CO2 data agreed well with one another, with a mean difference of 0.05 ppm and standard deviation of 0.51 over 130 flight hours of sampling, similar to the QCLS and OMS comparison on HIPPO. The mean difference in CH4 was 4.5 ppb, more than our estimated uncertainty, with a standard deviation of 5.1 ppb. The cause of the CH4 measurement discrepancy has remained a mystery despite extensive efforts to explain the difference. These biases correspond to errors of 0.01% and 0.25 % for CO2 and CH4.
respectively, using background concentrations of 390 ppm and 1800 ppb. The bias between the
independent CO sensors was 1.1 ppb during CalNex. It should be noted that the NOAA VUV
CO sensor did not dry the ambient air during measurement and reported wet mole fractions.
Dilution therefore accounts for some of the bias. The in-flight NOAA VUV CO measurements
were calibrated by means of standard additions traceable to NIST with backgrounds determined
by catalytically scrubbing CO from the ambient air sample.

To minimize data gaps in the 1 Hz flight data over the missions, we fit a loess curve with
a 1000 second span window to calculate the time-evolution of the QCLS minus
OMS/CRDS/VUV concentration bias. The QCLS data is used as the primary data, and
calibration gaps are filled using the sum of the OMS/CRDS/VUV data and the loess bias curve
(CO2.X in HIPPO, CO2.X and CH4.X in CalNex, and CO.X in both HIPPO and CalNex). This
resulted in an overall mission data retrieval duty cycle of over 95% for HIPPO and 97% for
CalNex, a significant improvement over the ~78% duty cycle from QCLS alone. These merge
products are denoted CO2.X, CH4.X, and CO.X. A merge product for N2O was not created
because no other fast-response N2O sensors were available for either mission.

4. Conclusions

During the HIPPO and CalNex flight measurement campaigns, we have achieved
measurement compatibilities with respect to WMO/NOAA scales of 0.03%, 0.05%, 0.3%, and
2% for CO2, CH4, N2O, and CO relative to background concentrations of 390 ppm, 1850 ppb,
325 ppb, and 100 ppb, respectively, by adequately regulating pressure and temperature and by
using a robust in-flight calibration procedure that improves upon spectroscopically-calibrated
measurements. We report long-term compatibility for CO2, CH4, N2O, and CO from nearly 450
flight hours of 100, 1, 1.1, and 2 ppb, respectively. The datasets generated using the QCLS for
HIPPO and CalNex have provided extensive global (HIPPO) and regional (CalNex) coverage
and have been useful in many studies to date (Graven et al., 2013; Wunch et al., 2010; Kort et al.,
2011; Wecht et al., 2012; Kort et al., 2012; Xiang et al., 2012; Peischl et al., 2012). We
emphasize the importance of in-flight calibrations traceable to WMO/NOAA standards, essential
in studies that combine measurements from independent sensors, and present our practices for
their implementation.
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$P = 50.7$ torr; $L = 10$ cm;  
$T = 296.15K; lw = 0.0085 cm^{-1}$
**Figure 1:** Absorption spectra for the 3 quantum cascade lasers. QCL1 (a) is a differential measurement of $^{12}$CO$_2$ and therefore appears inverted because this sample has a lower concentration of CO$_2$ than the reference gas. QCL2 (b) shows the spectrum for CH$_4$ and N$_2$O and QCL3 (c) shows the spectrum for CO.
Figure 2: Time series for the 4 QCLS species during 20 minutes of in-flight sampling over the Pacific during HIPPO II (top) and the Allan variance as a function of averaging time for the data shown (bottom). Table 1 summarizes these data and also provides corresponding values for sampling from a calibration cylinder in the laboratory. All concentrations are reported in units of ppb, including CO₂, which is the concentration relative to the reference concentration. In this plot, the CO₂ concentration is ~1.5 ppm above the reference gas concentrations of ~390 ppm.
Figure 3: Schematic of the QCLS-CO2 (top) and QCLS-DUAL (bottom) sampling system. The QCLS-CO2 pressure-vessel that contains the spectrometer is hermetically sealed and purges with UHP N₂ prior to each flight.
Figure 4: The sampling sequence used to calibrate a secondary cylinder for QCLS-DUAL (Table 2b) using 3 primary cylinders (Table 2a). Zero air (light blue) is sampled for 5 minutes, the primary cylinders are then each sampled for 3 minutes (light green) in order of increasing concentration and then the target secondary cylinder (pink) is sampled for 3 minutes. We use the last 90 seconds of a given 5-minute zero-air sample (light blue) to calculate 5 zero-air values (blue squares). These 5 values are linearly interpolated (Interp.) to the sampling times and that time series (blue trace) is then subtracted from to the raw mixing ratios (gray trace) to yield the black trace (which appears nearly indistinguishable from the gray trace except in the case of CO). The last 90 seconds (light green) of the ‘zero-subtracted’ data (black trace = gray trace – blue trace) are then averaged to generate a value for each of the 4 primary sampling intervals (dark green squares). For each primary, the primary value at the QCLS sampling times is linearly interpolated to those 4 values (green lines). The last 90 seconds of the target sampling window (pink) are then interpolated (both linearly and quadratically) to the green lines (either the 2 closest for linear interpolation or the closest 3 for quadratic interpolation) which bracket the secondary concentration of interest, as shown in Figure 5.
**Figure 5:** The concatenated target secondary cylinder interpolated values (i.e., the pink points in Figure 4) which were linearly interpolated to the bracketing primaries (green) or quadratically interpolated to the three closest primaries (blue). The three columns present the calibration of the secondary cylinder QCLS-DUAL gases CH$_4$ (top row), N$_2$O (middle row), and CO (bottom row) for the secondary cylinder CC89589 on 29 Jan 2010, 14 Jan 2011, and 10 Feb 2012, that was used to fill the gas deck for HIPPO III, IV, and V, illustrating the stability of the tank over time. The values printed on the figure represent the mean of the 270 linearly interpolated values. The standard deviations of these values are roughly 0.4, 0.05, and 0.03 ppb for CH$_4$, N$_2$O, and CO, respectively.
Figure 6: Calibration sequence of in-flight measurements. The reference gas (QCLS-CO2) and zero gas (QCLS-DUAL) are sampled every 15 minutes, a low-span and a high-span every 30 minutes, and a check-span every two hours. The sample data (green) are then calibrated to the WMO/NOAA scale using the mean values of each group of the calibration spans (red).
**Figure 7:** A series of square-wave tests, alternatively sampling from a reference secondary tank with near-ambient concentrations of the QCLS-DUAL species and a zero-air tank every 5 minutes, superimposed upon one another to illustrate the slow sample equilibration time for N$_2$O. The y-axis range is defined as the difference between the dry-air mole-fractions of the secondary tank (N$_2$O = 319.3 ppb, CH$_4$ = 1919.6 ppb, CO = 223.4 ppb) and zero (the zero-air mole-fractions), each divided by an arbitrary constant (here = 500) to focus the plot on the transition region. A decrease in the surface area of PFA or Synflex results in a faster equilibration time. Both CH$_4$ and CO do not exhibit this behavior.
Figure 8: The gas-deck in-flight calibration addition stability over the course of RF09 on HIPPO V. Each point represents the average of the group of red points in Figure 6 and the axes for each QCLS species are equivalent in range. The lines represent the Akima spline interpolations to the different spans (red = low-span, blue = high-span, black = zero) and are used to relate the spectroscopically-calibrated mixing ratios to the NOAA scale. QCLS-CO2 and QCLS-DUAL use different interpolation techniques as discussed in the text. The HIMIL inlet pressure is also shown in gray.
Figure 9: An estimate of the calibration linearity (A-D) and uncertainty (E-H) for the 4 QCLS species. For QCLS-CO2(A), the quadratic interpolation function for each research flight in CalNex (which was more variable than in HIPPO; colored dates range from 27 Apr 2010 to 22 Jun 2010) is shown. The standard deviation across the 21 flights as a function of calibrated mixing ratio reaches a minimum at the value of the reference gas deck calibration cylinder as shown in the bottom panel (E) where the black lines converge at ~392 ppm. The histograms (E) of the CalNex (blue) and HIPPO (red) are shown and the 10% and 90% quantiles are plotted as vertical lines for each, indicating that the variability in the quadratic interpolation function typically contributes no more than 0.1 ppm (i.e. black line intersects blue and red lines within 0.1 ppm). For QCLS-DUAL (B,C,D), the 1:1 correspondence of the spectroscopically-calibrated QCLS mixing ratio is plotted against 4 known primary cylinders and regressions are calculated using the error uncertainties from the primary cylinders shown in Table 2a. Panels F,G, and H show the standard deviation of the residual uncertainty, where we exclude the very low CH4 primary (~500 ppb, panels B and F) and the very high CO (~1000 ppb, panels D and H) from the uncertainty estimate.
Figure 10: The 1 Hz HIPPO I-V data comparison for QCLS-CO2 with OMS (left) and AO2 (middle) as well as the QCLS-DUAL CO comparison with the RAF VUV-CO.
Figure 11: QCLS-DUAL comparisons to the onboard gas chromatographs PANTHER (A,B,C) and UCATS (D,E,F) for CH$_4$ (A,D), N$_2$O (B,E), and CO (C,F). The UCATS instrument had issues with the chromatography during HIPPO 2 and is not shown. The HIPPO 4 measurements of N$_2$O from UCATS were also excluded because of non-linear instrument response during several flights.
Figure 12: QCLS comparisons to NOAA flask data during HIPPO I-V for CO$_2$ (A), CH$_4$ (B), N$_2$O (C), and CO (D). With the exception of N$_2$O which has a much tighter correlation with the flask measurements, the axes are all scaled to the same ranges as Figure 11. The biases for each fit are reported in Table 4. The type II regressions (York, 2004) in these figures use uncertainty values of 200, 2, 0.2, and 1 ppb for the QCLS measurements of CO$_2$, CH$_4$, N$_2$O, and CO, respectively, corresponding to the calibration uncertainties shown in Table 2a, and half of those values for the NOAA CCG flask values (Zhao and Tans 2006, Dlugokencky et al., 2005, Hall et al., 2007, Novelli et al., 1994).
Figure 13: The 1 Hz CalNex data comparison for QCLS with the NOAA/Picarro CRDS for CO$_2$ (left) and CH$_4$ (middle) as well as the comparison with the NOAA VUV sensor for CO (right).
Table 1: Allan precision as a function of averaging time for the 4 QCLS species measured during the in-flight sampling of a relatively constant air mass on HIPPO II, October 22nd, 2009 (‘flight’) and during laboratory testing sampling continuously from a secondary calibration cylinder (‘lab’). Accuracy estimates are based on the accuracy of the NOAA primary cylinders, where accuracy in this context is an estimate of how well the scale can be transferred to different instruments or laboratories at near-ambient mole fractions.

<table>
<thead>
<tr>
<th>Species</th>
<th>1 sec flight</th>
<th>10 sec flight</th>
<th>100 sec flight</th>
<th>1 sec lab</th>
<th>10 sec lab</th>
<th>100 sec lab</th>
<th>Accuracy (ppb)</th>
</tr>
</thead>
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<td>CO₂</td>
<td>20.</td>
<td>20.</td>
<td>27</td>
<td>13</td>
<td>2.3</td>
<td>1.7</td>
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<td>0.47</td>
<td>0.50</td>
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<tr>
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<td>0.021</td>
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<td>0.018</td>
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<td>Name</td>
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<td>Cal Date</td>
<td>CH(_4) (ppb)</td>
<td>N(_2)O (ppb)</td>
<td>CO (ppb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
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<td></td>
<td></td>
<td></td>
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<td>1(\sigma)</td>
<td>M.R.</td>
<td>1(\sigma)</td>
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<td>0.2</td>
<td>45.1</td>
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<td>6/30/2011</td>
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<td>0.2</td>
<td>50.4</td>
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<td>1801.1</td>
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<td>339.2</td>
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<td>2.4</td>
<td>248.12</td>
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<td>Primary 5</td>
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<td>0.2</td>
<td>247.85</td>
<td>0.11</td>
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|          | Δ = -3.4    | Δ = -0.4 | Δ = -5.3 |
|          | Δ = -2.1    | Δ = 0    | Δ = -1.3 |
|          | Δ = 0       | Δ = -0.23 | Δ = -0.3 |
|          | Δ = 4.4     | Δ = -0.64 | Δ = -2.3 |
|          | Δ = 3.7     | Δ = 0.27 | Δ = -1.2 |

Table 2a: Summary of the primary calibration cylinders used during the CalNex and HIPPO campaigns for QCLS-DUAL. The primary cylinders were filled and calibrated at NOAA in 2005, then recalibrated again after CalNex and before HIPPO IV in 2011. The difference between the two calibrations is shown for each tank and each species.
<table>
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<tr>
<th>Name</th>
<th>Cylinder ID</th>
<th>Date</th>
<th>CH$_4$ (ppb)</th>
<th>N$_2$O (ppb)</th>
<th>CO (ppb)</th>
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<td>01/29/2010</td>
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<td>01/29/2010</td>
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Table 2b: Summary of the secondary calibration cylinders used to fill the gas deck during the CalNex and HIPPO campaigns for QCLS-DUAL. Tanks that were used for multiple deployments were recalibrated prior to each use. The naming corresponds to the usage of each cylinder as follows: H1, HIPPO-I; H2, HIPPO-II; H3, HIPPO-III; etc.; CN, CalNex; LS, Low Span; HS, High Span; REF, Reference.
Table 3: Summary of the HIPPO and CalNex flight dates, duration, and locations.

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<th>Location</th>
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<th>Location</th>
<th>HIPPO II YYMMDD</th>
<th>Location</th>
<th>HIPPO II Hours</th>
<th>Location</th>
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<th>HIPPO III Hours</th>
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<th>Location</th>
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<th>Location</th>
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<th>Location</th>
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<td>CO&lt;&gt;OK</td>
<td>100316</td>
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<td>around CO</td>
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**Total Flight Hours**: 81.1  87.6  81.6  93.9  99.2  122.2

**Total Flights**: 14  13  13  14  14  19
Table 4: Biases between QCLS and NOAA flask measurements at the reported mean concentrations of each species for the five HIPPO campaigns.

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<th>CO₂ (ppm)</th>
<th>CH₄ bias (ppb)</th>
<th>CH₄ (ppb)</th>
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<td>1813.7</td>
<td>1.07</td>
<td>322.4</td>
<td>-1.94</td>
<td></td>
</tr>
</tbody>
</table>

Mean concentrations of each species for the five HIPPO campaigns.
Table 5: Biases between QCLS and MEDUSA flask measurements at the reported mean concentrations of CO$_2$ for the five HIPPO campaigns.

<table>
<thead>
<tr>
<th>HIPPO</th>
<th>CO$_2$ bias (ppm)</th>
<th>CO$_2$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIPPO 1</td>
<td>-0.28</td>
<td>386.16</td>
</tr>
<tr>
<td>HIPPO 2</td>
<td>0.03</td>
<td>386.54</td>
</tr>
<tr>
<td>HIPPO 3</td>
<td>0.03</td>
<td>389.48</td>
</tr>
<tr>
<td>HIPPO 4</td>
<td>-0.14</td>
<td>390.30</td>
</tr>
<tr>
<td>HIPPO 5</td>
<td>-0.18</td>
<td>387.70</td>
</tr>
<tr>
<td>Mean</td>
<td>-0.11</td>
<td></td>
</tr>
</tbody>
</table>