

Title: Readme for NOAA-Picarro ORCAS data

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1.0 Data Set Overview:

This dataset contains atmospheric measurements of carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO), and water vapor (H₂O) mixing ratios made with the NOAA Picarro instrument onboard the NCAR Gulfstream V aircraft during the ORCAS campaign in January-February, 2016.

2.0 Instrument Description:

The Picarro Cavity Ring Down Spectrometer (Crosson 2008) is a commercially-available instrument (Picarro, Santa Clara, CA, USA) measuring atmospheric concentrations of CO₂, CH₄, CO, and H₂O (model G2401m). The instrument was modified in our lab to have a shorter measurement interval (~1.2 seconds instead of ~2.4 seconds) by reducing the number of scans of the CO spectroscopic peak and therefore yielding a less-precise CO measurement (1 σ on 1-2 second measurements is ~9 ppb instead of ~4 ppb). The instrument was also modified to have a lower cell pressure set point (80 torr instead of 140 torr) to allow it to operate across the full pressure altitude range of the campaign without requiring upstream pressurization of the sample stream.

3.0 Data Collection and Processing:

Sample air was collected through a rear-facing 1/8 inch inner-diameter stainless steel tube mounted inside the HIAPER modular inlet (HIMIL, www.eol.ucar.edu/homes/dcrogers/Instruments/Inlets/) via a pump located downstream of the analyzer. Mass flow through the analyzer is constant, but volume flow varies with temperature and pressure. Measurement times were corrected for a ~3-12 second lag in the sample line using ambient pressure and temperature measurements from the GV and bin-averaged into 1-second intervals.



Figure 1. The NOAA Picarro system onboard the GV for the ORCAS campaign with the following modules from top to bottom: calibration tanks, valve box, analyzer, pump box.

The sample stream was not dried; dry mole fractions were computed using analyzer-specific empirical corrections, derived from laboratory tests performed before and after the campaign, that account for dilution and pressure-broadening effects (Rella et al. 2013, Chen et al. 2013). The analyzer response was calibrated in the lab before and after the campaign against six tanks with known concentrations traceable to World Meteorological Organization (WMO) scales with the following concentration ranges: 388 – 460 ppm CO₂ (scale: X2007), 1775 – 3061 ppb CH₄ (scale: X2004A), 82 – 409 ppb CO (scale: X2014A).

Lab tests were performed to characterize the dependence of reported measurements to small excursions in cell pressure away from its set point of 80 torr (similar to section 3.3 in Filges et al. 2015), induced by changes in sample pressure at the analyzer inlet due to rapid changes in altitude. We found that CO₂ and CH₄ values vary linearly with cell pressure for excursions of $\pm \sim 1$ torr and that the slope is dependent on concentration (Figure 2). We use this lab-derived empirical relationship to correct raw campaign data for cell pressure variability to within ± 0.2 torr. No such relationship was demonstrated for CO within the precision of the measurement.

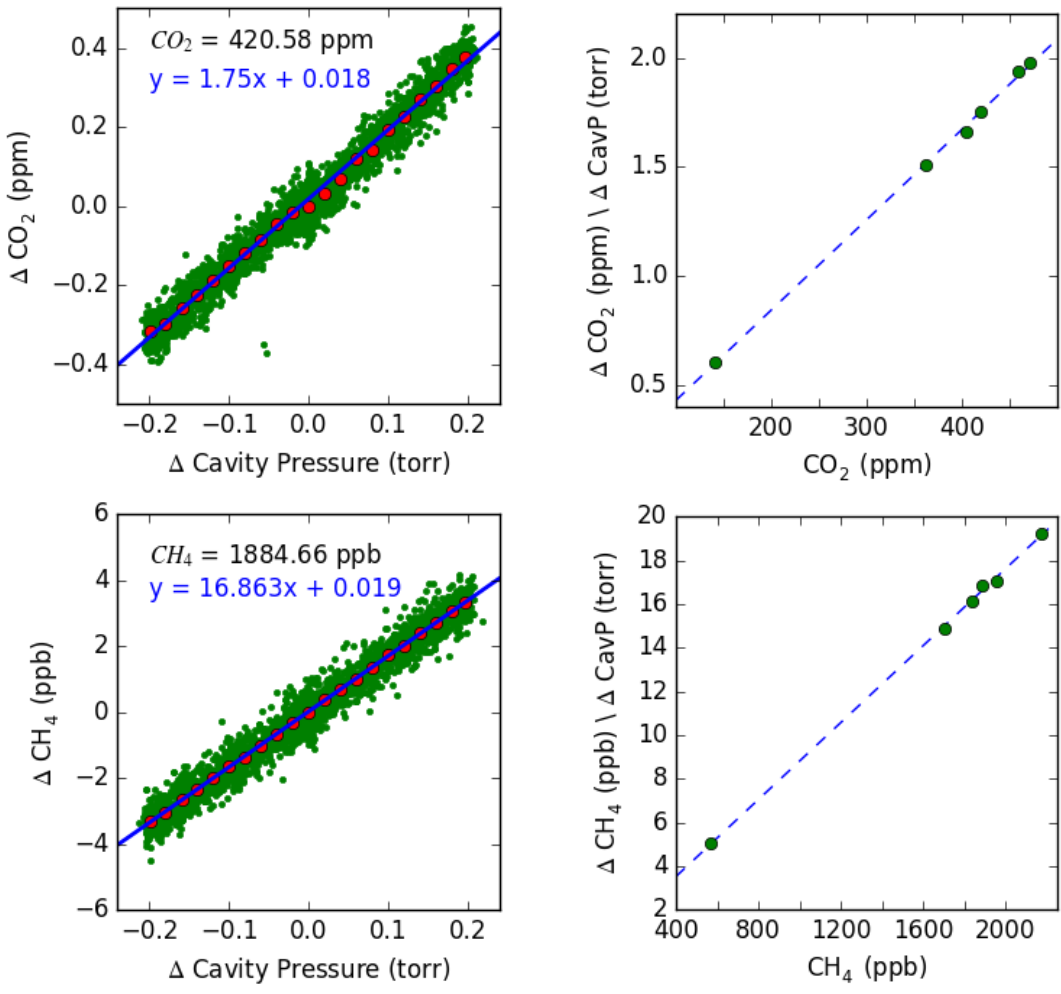


Figure 2. Demonstration of the empirical cell pressure correction to the analyzer reported values for CO₂ (upper panels) and CH₄ (lower panels). The left panels show the linear dependence of the reported concentration to cell pressure excursions at fixed concentrations. The right panels show the concentration dependence of the slope magnitude.

Two 2-L high-pressure reference cylinders with the following concentration range were flown with the Picarro system: ~393-406 ppm CO₂, ~1892-914 ppb CH₄, ~127-150 ppb CO. Each of the cylinders was measured for 3.5 minutes every other hour during the flight, and immediately before and after each flight (Figure 3). These in-situ calibration measurements were used to apply a time-dependent offset correction to the measurements from each flight.

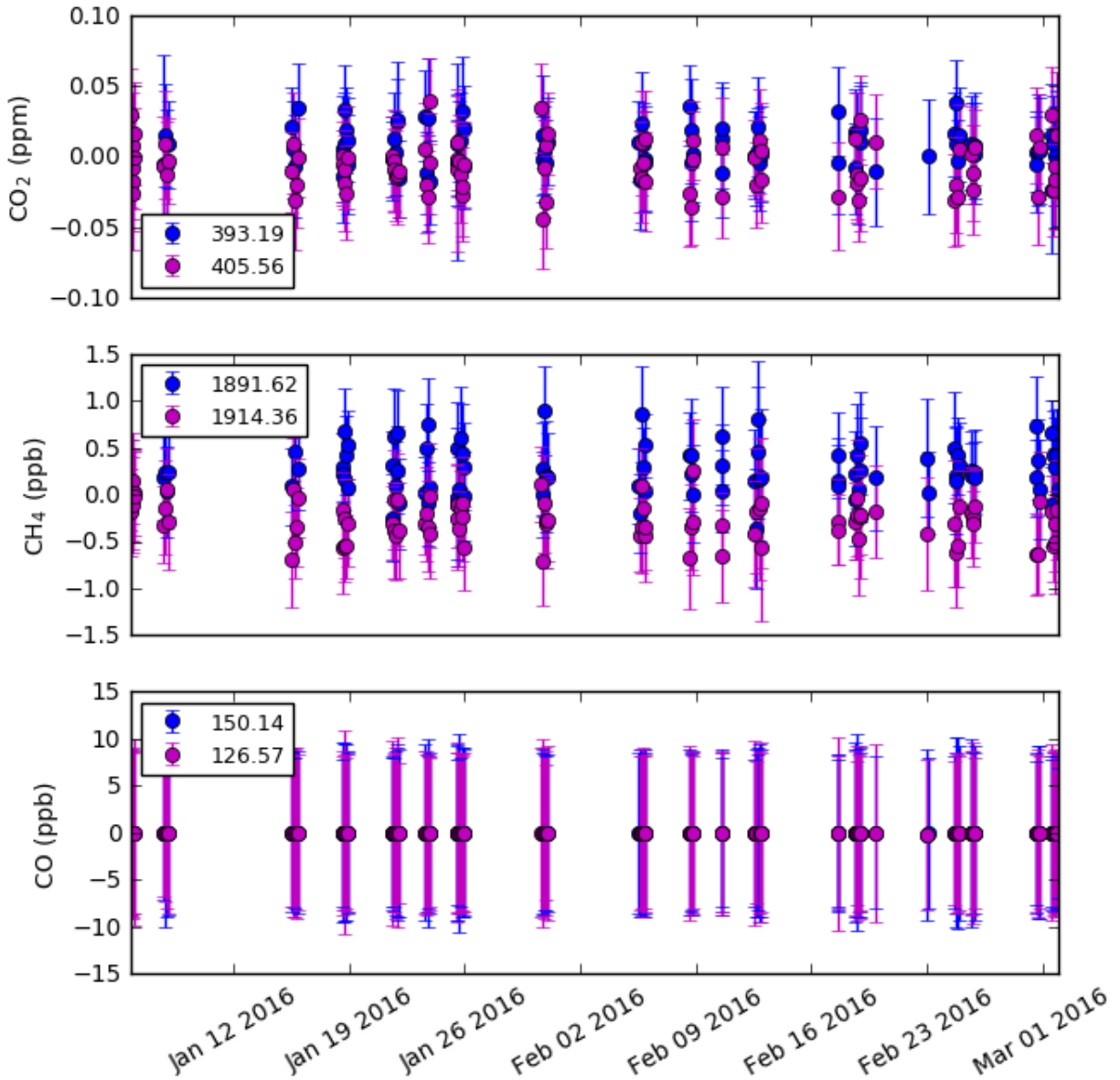


Figure 3. Residuals of the two in-situ calibration tank measurements for the whole campaign, including pre- and post-flight measurements, tests flights and the last ferry flight. The two tanks are distinguished by color and the legends give their assigned values. Error bars represent one standard deviation of the measurements at the native time resolution (~ 1.2 seconds).

4.0 Data Format:

Data are given in comma-delimited text files, with one file per flight. Mixing ratios are reported in parts per million for CO₂ and parts per billion for CH₄ and CO on the following WMO scales: CO₂-X2007, CH₄-X2004A, CO-X2014A. Water vapor measurements are reported in percent. The 'UTC' column gives the beginning of the 1-second time bins and represents the number of seconds since midnight on the day of takeoff.

5.0 Data Remarks:

Water vapor data are uncalibrated and are not intended for scientific use, other than evaluating the quality of the raw measurement itself.

Average total analytical uncertainty (1σ) is approximated as the square-root of the sum of squares of the following independent components for CO₂ in ppm, CH₄ in ppb, CO in ppb:

- i. Uncertainty in values assigned to tanks at the NOAA GMD Central Calibration Lab (www.esrl.noaa.gov/gmd/ccl/):
0.05, 0.25, 0.16*
- ii. Uncertainty in the water correction, approximated as the difference in final measurements for the campaign, from using either of the two sets of water correction coefficients, derived in the lab before and after the campaign. This captures both uncertainty inherent in the test and any possible drift in the analyzer response:
0.01, 0.16, 0.24
- iii. Uncertainty in the lab calibration, approximated as the difference in final measurements for the campaign, from using either of the two sets of calibration coefficients, derived in the lab before and after the campaign. This captures both uncertainty inherent in the test and any possible drift in the analyzer response:
0.00, 0.01, 0.25
- iv. Variability in mean in-situ calibration offsets for the campaign duration (Figure 3). This captures variability in the analyzer response and possible unaccounted-for drift in the tanks:
0.02, 0.36, 1.11
- v. For the duration of the first test flight, we measured tank air at ambient pressure and processed the data the same way as the rest of the campaign data. Variability in this dataset accounts for measurement precision and the impact of the cavity-pressure correction (Figure 4):
0.04, 0.49, 8.89 (1-second time bins)
0.02, 0.19, 3.26 (10-second averages)

By this methodology, **total uncertainty is approximated for 1-second measurements as 0.07 ppm for CO₂, 0.68 ppb for CH₄ and 8.97 ppb for CO, and for 10-second average measurements as 0.06 ppm for CO₂, 0.50 ppb for CH₄, and 3.46 ppb for CO.**

*Post-campaign calibration of the in-situ tanks demonstrated that their assigned CO value had drifted by ~3-7 ppb over the ~1.5 years since the initial calibration. We assumed this drift was

linear to approximate their CO values during the campaign. If the rate of drift is assumed entirely unknown, uncertainty in the value assigned to tanks (term 1) would be 1.46-5.25 ppb for CO.

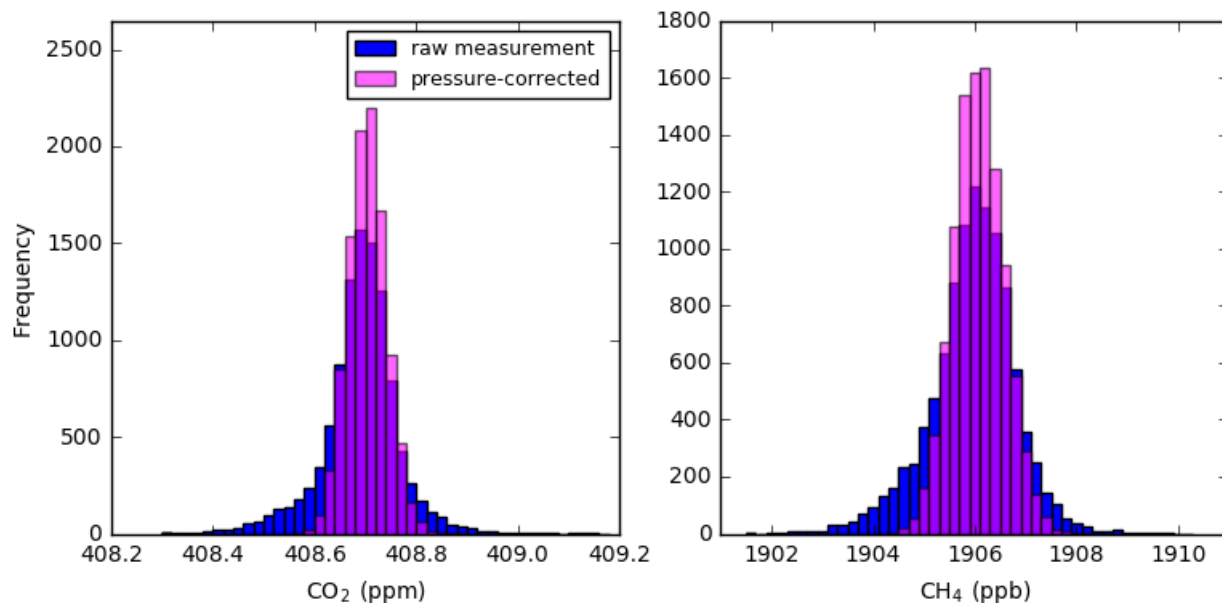


Figure 4. Distribution of raw 1-second and pressure-corrected measurements from the “null-test” on Test Flight 1, wherein a tank was measured at ambient pressure for the duration of the flight. Carbon-monoxide is not shown because it is not sensitive to cell pressure variations within the detectable noise level of the measurement.

6.0 References:

Chen H, et al. (2013) Accurate measurements of carbon monoxide in humid air using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech.* 6: 1031-1040, doi: 10.5194/amt-6-1031-2013.

Crosson ER (2008) A cavity ring-down analyser for measuring atmospheric levels of methane, carbon dioxide, and water vapour, *Appl. Phys. B*: 92, 403–408, doi:10.1007/s00340-008-3135-y.

Filges A, et al. (2015) The IAGOS-core greenhouse gas package: a measurement system for continuous airborne observations of CO₂, CH₄, H₂O, and CO, *Tellus B* 67 (27989).

Rella CW, et al. (2013) High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.* 6: 837-860, doi:10.5194/amt-6-837-2013.