

**Title:** Readme for NOAA-Picarro on ATom-1,2,3,4

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### **1.0 Data Set Overview:**

This dataset contains atmospheric measurements of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and carbon monoxide (CO) mixing ratios made with the NOAA Picarro instrument onboard the NASA DC8 aircraft during the four ATom campaigns in 2016-2018.

### **2.0 Instrument Description:**

The Picarro Cavity Ring Down Spectrometer (Crosson 2008) is a commercial instrument (Picarro, Santa Clara, CA, USA) measuring atmospheric concentrations of CO<sub>2</sub>, CH<sub>4</sub>, CO, and H<sub>2</sub>O (model G2401m). The instrument was modified in our lab 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. The instrument was also modified to have a shorter measurement interval (~1.2 seconds for ATom-1&2 and ~2.0 seconds for ATom-3&4 instead of ~2.4 seconds from the original configuration) by reducing the number of scans of the CO spectroscopic peak and therefore yielding a less-precise CO measurement (1 $\sigma$  of the raw 1-2 second measurements was ~9 ppb for ATom-1&2 and ~4.5 ppb for ATom-3&4 instead of ~4 ppb from the original configuration).

### **3.0 Data Collection and Processing:**

On ATom-1, the instrument was located on a rack shared with the PANTHER instrument with an inlet mounted on window #10 on the port side of the NASA DC8. The inlet consisted of an 1/4 inch inner-diameter stainless steel tube, with a 45-degree forward-facing beveled end, mounted on a pylon with three other inlets for the PANTHER, UCATS, and PFP instruments. On ATom-2 through ATom-4, the instrument was located on a rack shared with the DLH instrument with an inlet mounted on window #5 on the port side of the aircraft. The inlet consisted of an 1/8 inch inner-diameter stainless steel tube flush-mounted inside of a straight-through anodized aluminum shroud with an electro-polished 3/4 inch stainless steel sleeve.

Sample air was collected via a pump located downstream of the analyzer. Mass flow through the analyzer was constant, but volume flow varied with temperature and pressure. Measurement times were corrected for a lag time in the sample line of ~5-15 seconds for ATom-1, ~2-10 seconds for ATom-2 and ~2-8 seconds for ATom-3&4, using ambient pressure and temperature measurements from the DC8, and then bin-averaged into 1-second intervals.

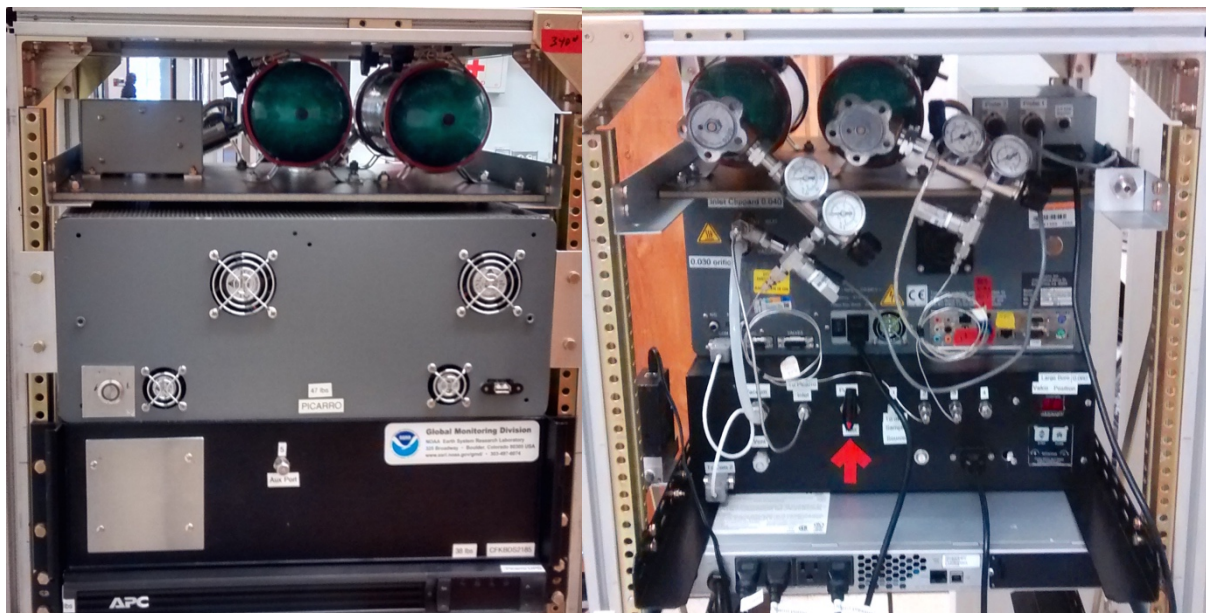


Figure 1. The rear-facing (left) and forward-facing (right) sides of the NOAA Picarro system in preparation for ATom-2 with the following modules from top to bottom: calibration tanks, analyzer, valve and pump box.

The sample stream was not dried; dry mole fractions were computed using analyzer-specific empirical corrections, derived from laboratory tests performed before and after each 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 each campaign against six tanks with values assigned by the Central Calibration Laboratory at NOAA GMD ([www.esrl.noaa.gov/gmd/ccl](http://www.esrl.noaa.gov/gmd/ccl)) traceable to World Meteorological Organization (WMO) scales that span the following concentration ranges: 388 – 460 ppm CO<sub>2</sub> (scale: X2007), 1775 – 3061 ppb CH<sub>4</sub> (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 CO<sub>2</sub> and CH<sub>4</sub> 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  $\pm 0.2$  torr. No such relationship was demonstrated for CO within the precision of the measurement.

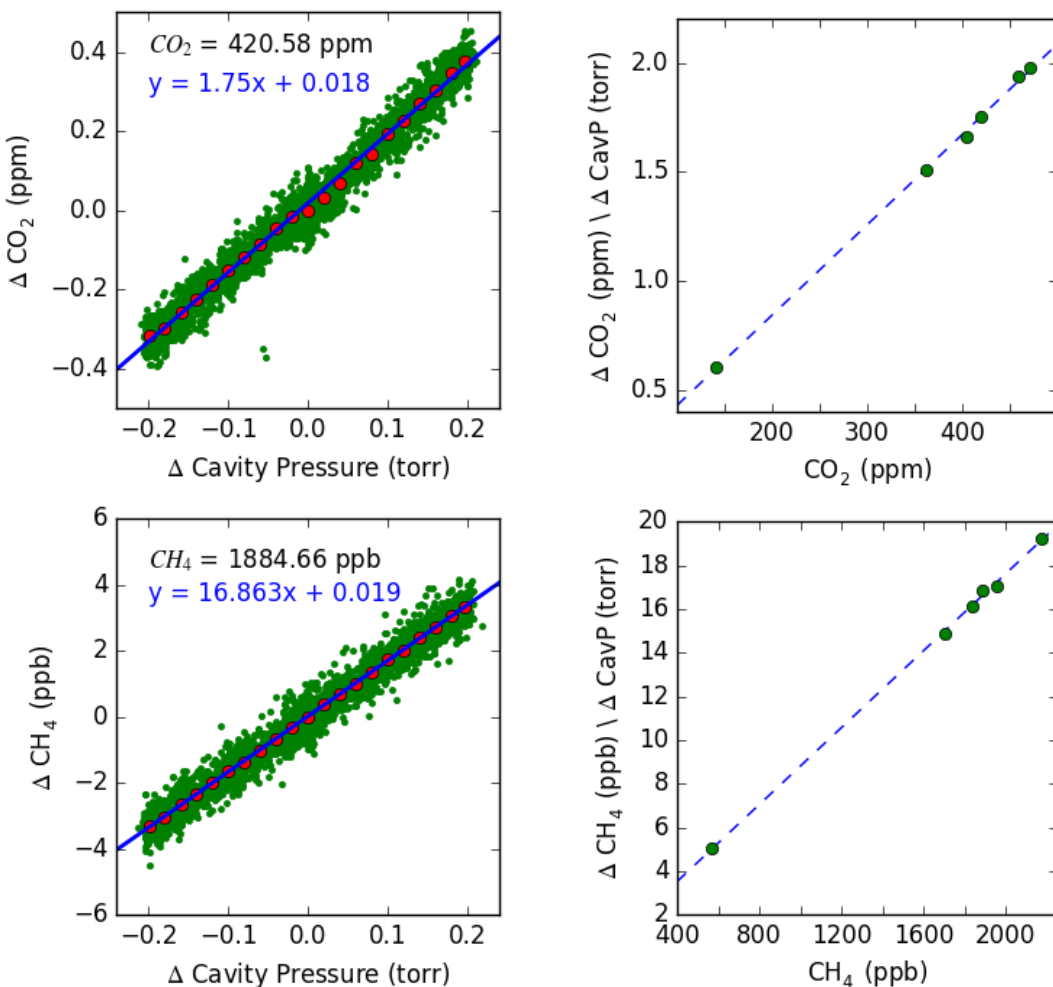


Figure 2. Demonstration of the empirical cell pressure correction to the analyzer-reported values for CO<sub>2</sub> (upper panels) and CH<sub>4</sub> (lower panels). The left panels show the linear dependence of the reported concentration to cell pressure excursions at fixed concentrations. The right panels show the concentration dependence of the slope magnitude.

Two 2-L high-pressure reference cylinders with the following concentration ranges were flown with the Picarro system: ~388-405 ppm CO<sub>2</sub> on ATom-1&2, ~393-411 ppm CO<sub>2</sub> on ATom-3, ~399-414 ppm CO<sub>2</sub> on ATom-4, ~1818-1918 ppb CH<sub>4</sub> on ATom-1&2, ~1851-1920 ppb CH<sub>4</sub> on ATom-3, ~1864-1951 ppb CH<sub>4</sub> on ATom-4, ~128-135 ppb CO on ATom-1&2, ~121-129 ppb CO on ATom-3, ~130-132 ppb CO on ATom-3&4. Each of the cylinders was measured immediately before and after each flight, and during flight for 3 minutes every other hour on ATom-1&2 and for 1.5 minutes every 1.5 hours on ATom-3&4 (Figure 3). These in-situ calibration measurements were used to apply a single offset correction to the measurements for each flight. The assigned values of these tanks are from measurements by the NOAA GMD Central Calibration Laboratory prior to and after each ATom deployment. These measurements demonstrated that the tanks' assigned CO values drifted by up to ~4 ppb over ~9 months between initial and final calibrations. We assumed this drift was linear to approximate their assigned CO values during each flight.

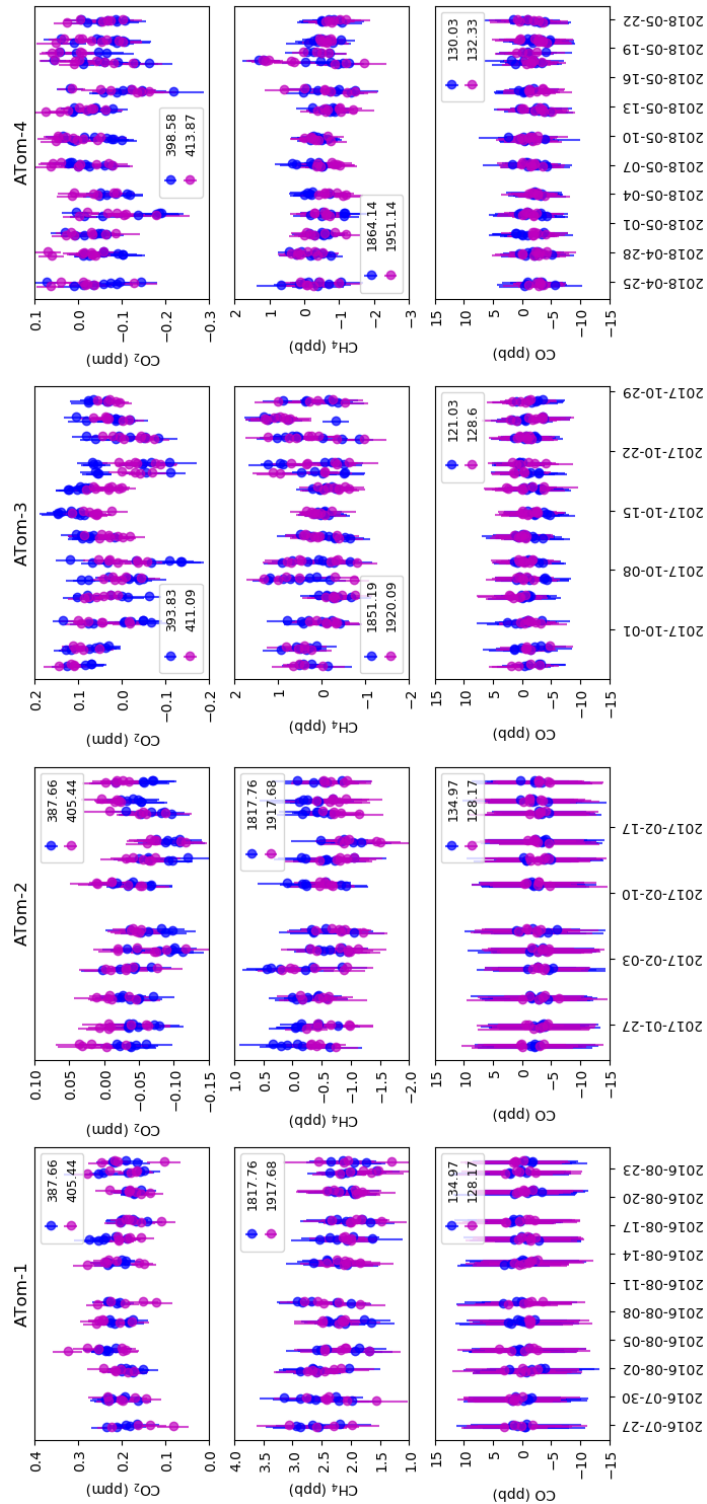


Figure 3. Measurements of the two in-situ calibration tanks during each campaign. The two tanks are distinguished by color and the legends give their assigned values. Error bars represent one standard deviation of the measurements at the native time resolution (~1.2-2.0 seconds). A final correction to the data was applied as the mean offset between measured and assigned tank values for each flight.

#### 4.0 Data Format:

Data are given in comma-delimited ICARTT files, with one file per flight. Dry-air mixing ratios are reported in parts per million for CO<sub>2</sub> and parts per billion for CH<sub>4</sub> and CO on the following WMO scales: CO<sub>2</sub>-X2007, CH<sub>4</sub>-X2004A, CO-X2014A. The 'UTC\_Start' 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:

Average total analytical uncertainty ( $1\sigma$ ) is approximated as the square-root of the sum of squares of the following independent components for CO<sub>2</sub> in ppm, CH<sub>4</sub> 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/](http://www.esrl.noaa.gov/gmd/ccl/)):  
0.04, 0.24, 2.18
- ii. Uncertainty in the water correction, approximated as the difference in final measurements resulting from either of the two sets of water correction coefficients, derived in the lab before and after each campaign. This quantity captures both uncertainty inherent in the test and changes in the analyzer response:  
0.02, 0.16, 0.34
- iii. Uncertainty in the lab calibration, approximated as the difference in final measurements resulting from either of the two sets of calibration coefficients, derived in the lab before and after each campaign. This quantity captures both uncertainty inherent in the test and changes in the analyzer response:  
0.01, 0.05, 0.17
- 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:  
0.06, 0.53, 1.63
- v. During a 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). For the CO measurement on ATom-3&4, this estimate was derived from measurement of a single tank in the lab over several hours.  
0.04, 0.44, 8.68 (ATom-1&2), 4.21 (ATom-3&4) (1-second time bins)  
0.02, 0.25, 3.05 (ATom-1&2), 2.07 (ATom-3&4) (10-second averages)

By this methodology, total uncertainty is approximated for 1-second measurements as 0.08 ppm for CO<sub>2</sub>, 0.7 ppb for CH<sub>4</sub> and 8.9 ppb for CO, and for 10-second average measurements as 0.07 ppm for CO<sub>2</sub>, 0.7 ppb for CH<sub>4</sub>, and 3.6 ppb for CO. For the CO measurement on ATom-3&4, total uncertainty is estimated as 5.0 ppb at 1-second and 3.4 ppb at 10-seconds. As an independent check, a tank with an unknown value was measured during a test flight for ATom-2 and the data were processed the same way as ambient flight data. The resulting mean final values for the tank were different than the values assigned by the Calibration Laboratory by: 0.11 ppm CO<sub>2</sub>, 0.34 ppb CH<sub>4</sub>, and 0.96 ppb CO.

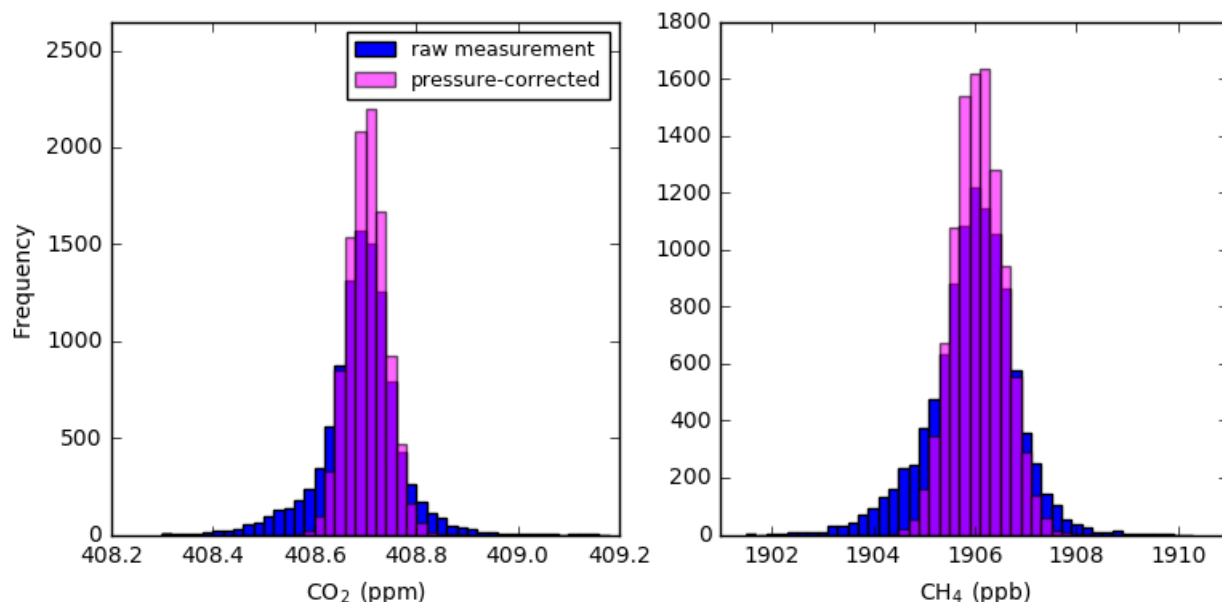


Figure 4. Distribution of raw 1-second and pressure-corrected measurements from a “null-test” conducted on test flight of a previous campaign, wherein a tank with an unknown value was measured at ambient pressure (~150-1000 hPa) for the duration of the flight. Carbon-monoxide is not shown because it is not sensitive to cell pressure variations within the detectable noise level of the measurement. The impact of the pressure correction on the final measurements for ATom is smaller than depicted here because of improved cell pressure control.

## 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 CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, 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.