Laboratory And Mountaintop Inter-comparisons Of CCGG Trace Gas Sampling Systems:
Identifying, Understanding, And Quantifying Measurement Uncertainties For Programmable Flask Package (PFP) Air Samples

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1. Abstract

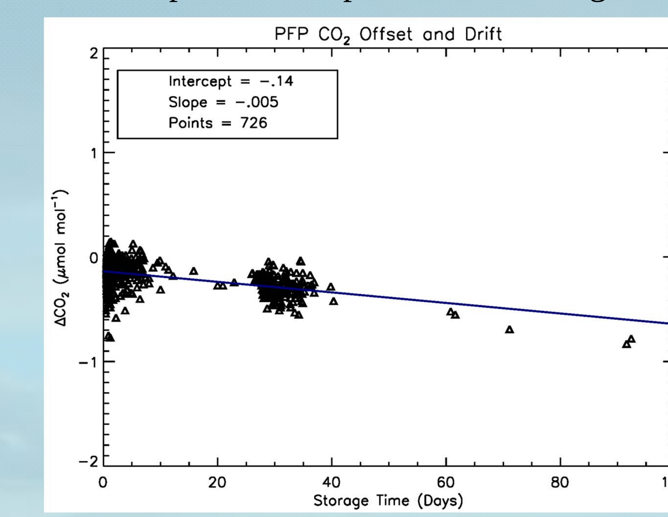
The Global Monitoring Division (GMD) Carbon Cycle Greenhouse Gases group (CCGG) carries out extensive quality control testing and verification related to its various measurement programs, with the goal that the atmospheric measurements obtained meet the uncertainty guidelines outlined by the World Meteorological Organization Global Atmosphere Watch (e.g. inter-laboratory comparability of ± 0.1 ppm for CO_2, ± 2 ppb for CH_4 and CO, ± 0.1 ppb for N_2O). CCGG carries out routine testing and inter-comparisons in the laboratory and in the field. This poster shows representative examples of tests and experiments carried out to investigate sampling issues related to the use of the CCGG Programmable Flask Package (PFP) system (See Panel 2).

In addition to ongoing laboratory tests and experiments, we have carried out several field campaigns atop nearby Mt. Evans to investigate the numerous atmospheric trace gases measured in PFP air samples for possible measurement biases related to the sampling equipment. From this location we could sample real atmospheric air, with relatively low variability, while using our sampling systems as they are normally used in our network sampling programs (See Panel 3). Investigating the equipment, the sampling techniques, and the storage of sample air in the flasks is critical to obtaining accurate analytical measurements representing the actual ambient atmospheric conditions at the time an air sample was collected.

2. PFP-V3 Flask Sampling Equipment (a) and routine laboratory PFP storage tests (b)

a) The PFP-V3 and programmable compressor package (PCP): Each PFP holds twelve 0.75L glass flasks (filled to 40 psia) connected by a stainless steel welded manifold, a pressure sensor, and control electronics. The PCP contains the system's power, pumps, and flow meter. These two units are deployed on small aircraft for altitude-based sampling and for time- or event-based sampling at tall towers and other surface sites. In the future these units may also be used on board ships.

b) PFPs and standard 2.5L flasks (used as controls) are filled from high pressure cylinders of dry whole air and are subsequently measured on the CCGG analysis system (MAGICC). PFP CO_2 mixing ratios show a small but significant time-independent negative bias with respect to the control flasks and also an approximately linear depletion of CO_2 with increasing storage time. The time-dependent depletion of CO_2 is consistent with preferential permeation through the teflon o-rings in the flask valves.



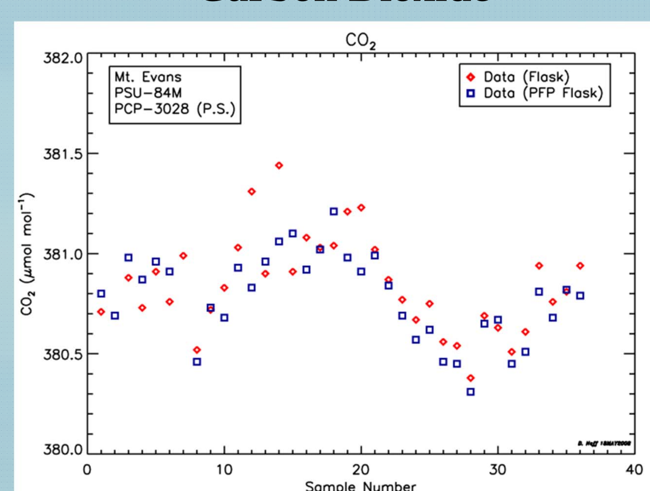
3. Mountaintop Inter-comparisons and Experiments (Panels 4-9)

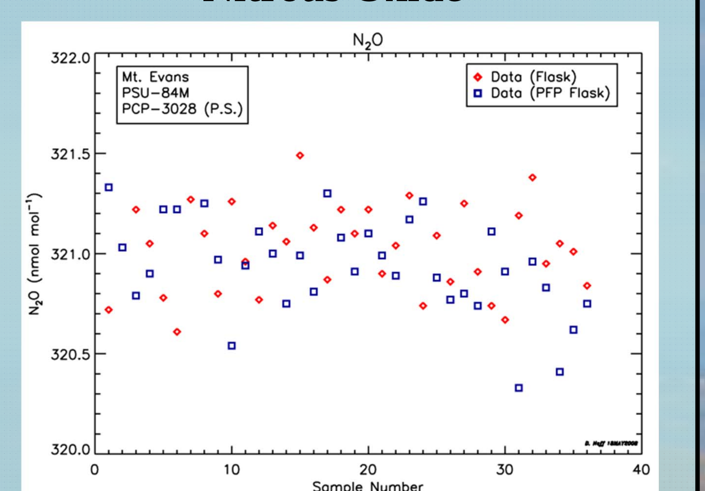
We obtained near-simultaneous real air samples near the summit of Mt. Evans (elevation ~ 4350 m; located ~ 50 miles west of Denver, Colorado) in September 2007 and 2008, using both the CCGG PFP sampling system and the manual 2.5L flask unit (PSU). This general PSU design has been in use for more than 10 years in the CCGG Cooperative Global Air Sampling Network, and network measurements from PSU samples are well characterized. The PFP-V3 system is currently in use in the CCGG North American aircraft and tower networks. We obtained concurrent CO_2 measurements from continuous analyzer systems as well. We carried out further field work atop Mt. Evans in 2009 and 2010 to obtain similar real atmosphere inter-comparisons for several halocarbons and other atmospheric trace species and to investigate particular sampling effects related to sample inlet lines.

The field inter-comparison samples were collected in the same manner as samples are collected in the GMD Global and North American networks. The dry air mole fractions of six atmospheric trace species (CO_2, CH_4, CO, H_2, N_2O, SF_6) were measured in the 2007 and 2008 samples, and ~20 other species were measured and investigated for the 2009 field inter-comparison. This mountaintop location was chosen in order to sample atmospheric air largely free of influence from nearby sources or sinks and with low variability over the sampling timescale, in order to provide for optimum real air sample inter-comparisons.

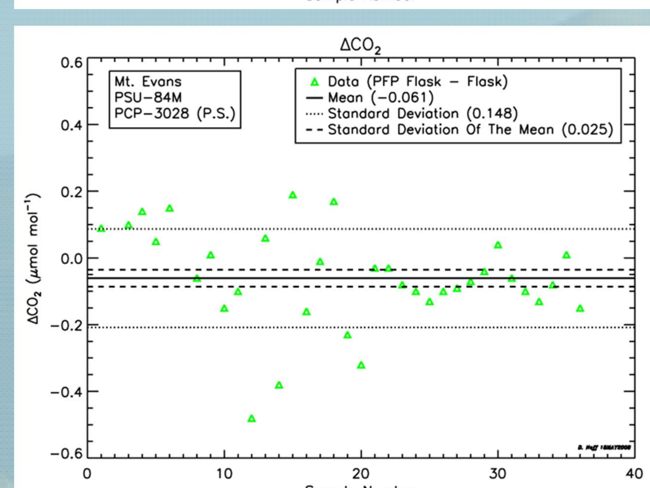
Carbon Dioxide | **Nitrous Oxide**

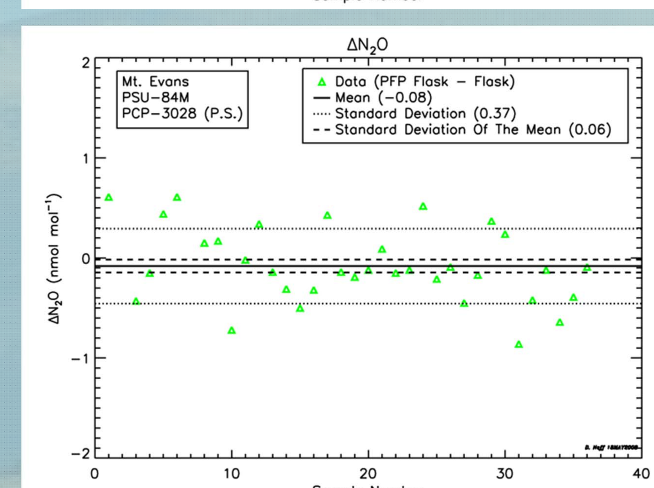
4. "Time Series" of Measured Dry-Air Mole Fraction, Mt. Evans 2007



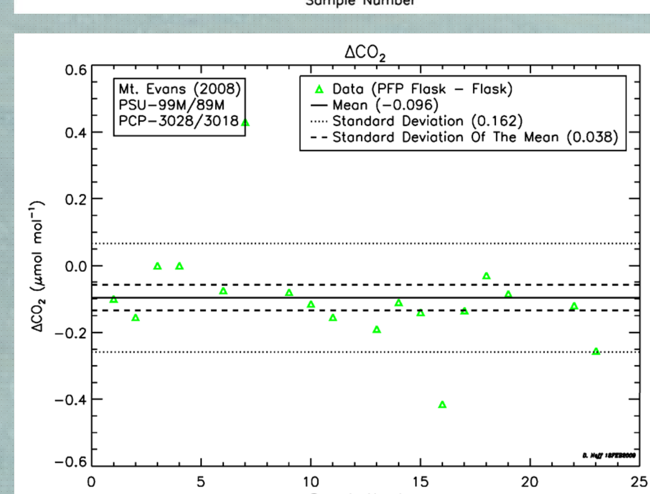


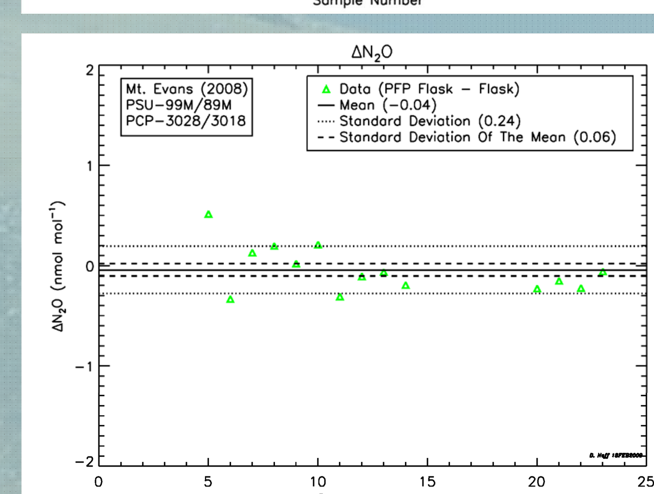
5. (PFP Flask - Network Flask), Mt. Evans 2007





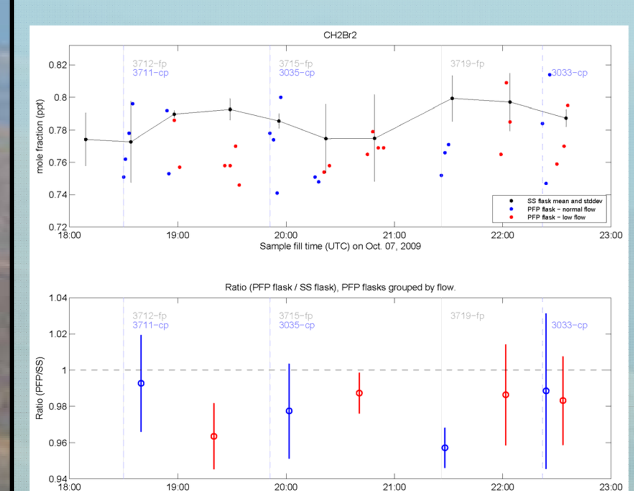
6. (PFP Flask - Network Flask), Mt. Evans 2008

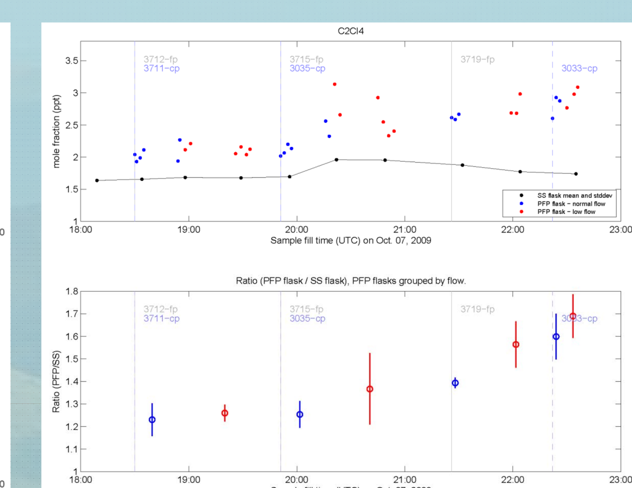


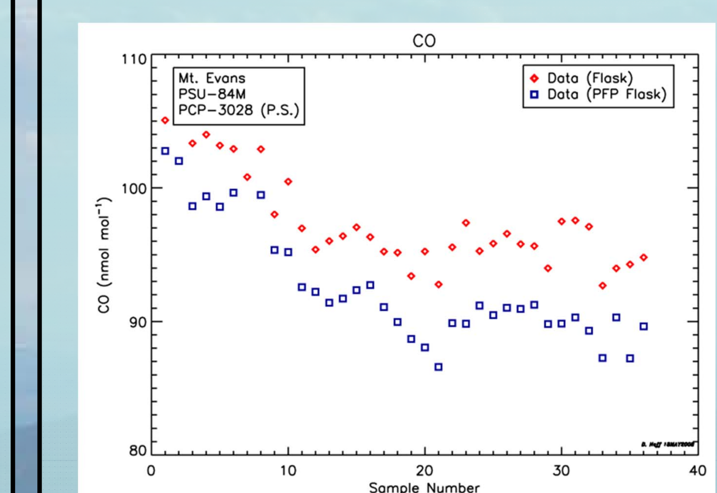


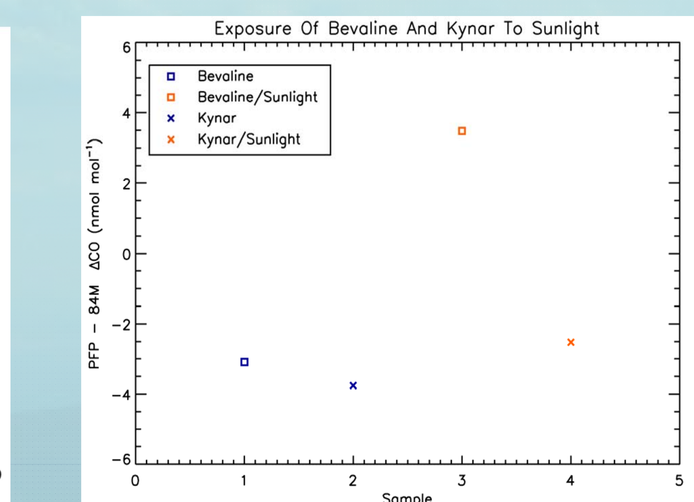
7. Halocarbons and other Atmospheric Trace Species Inter-comparisons, Mt. Evans 2009

Two representative examples are shown here. Laboratory tests suggested enhancements of both of these compounds in PFPs. The field inter-comparison showed the CH_2Br_2 enhancement to be an artifact of the laboratory test setup (likely an issue related to the gas cylinder regulator used). The C_2Cl_4 enhancement was confirmed.





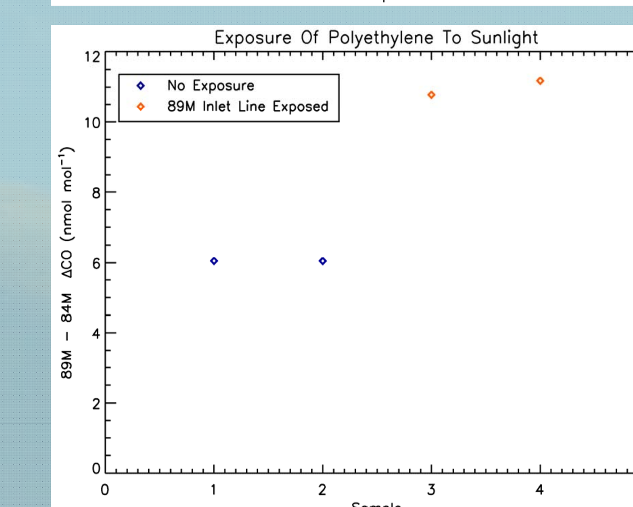


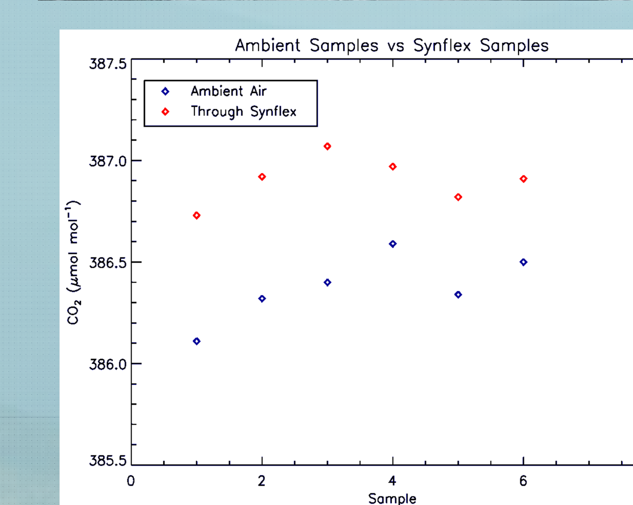


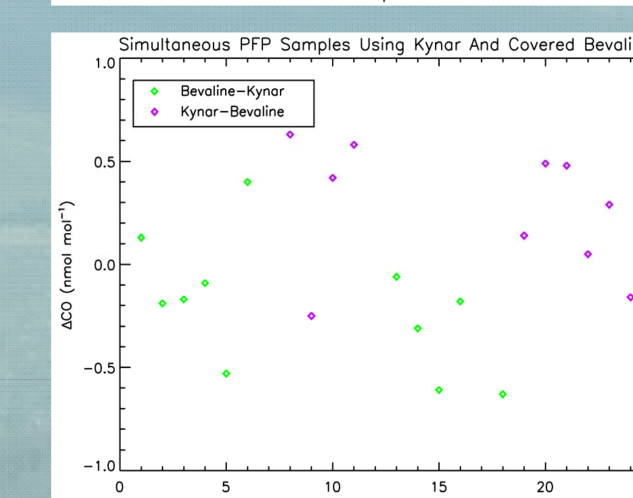
8. Sampling Biases/Inlet Line Effects, Mt. Evans 2010

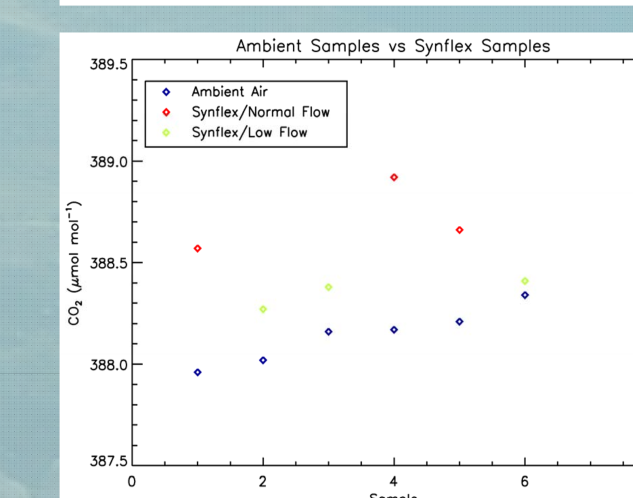
CO offsets observed in both the 2007 and 2008 inter-comparisons were investigated and found to be caused by the generation of significant quantities of CO in two of the three common inlet line materials used, when those relatively short inlet lines were exposed to intense sunlight for a sufficient time.

In another set of experiments pairs of PFP flask samples of the same air parcels were taken: one sample of the pair was taken from a short inlet line, and the other of the pair was sampled through a long (~500 meters) Synflex inlet line. CO_2 is enhanced, and correlated with the pump-induced pressure transient, in samples taken through the long Synflex inlet line.



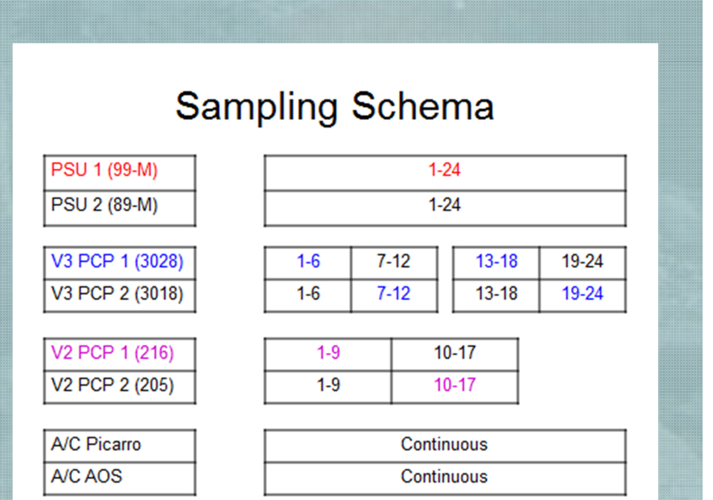




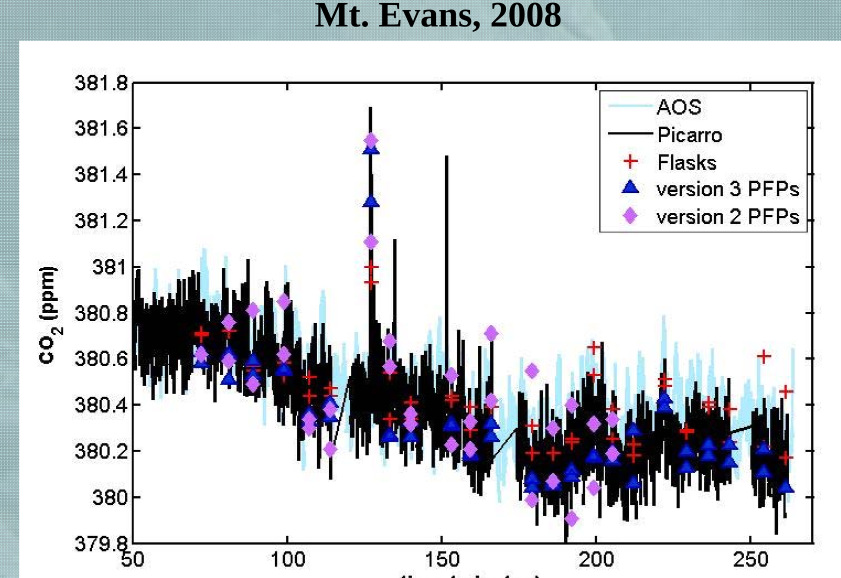


9. Summary of 2007/2008 Mt. Evans Inter-comparison Strategy

Near-simultaneous real air samples were obtained at regular intervals (approximately 10 minutes) – PFP flasks paired with PSU flasks filled through their respective pump systems. The samples were timed so that the two flasks reached their maximum fill pressure simultaneously. Individual inlet lines for the pump systems were collocated. Continuous CO_2 measurements were also obtained.

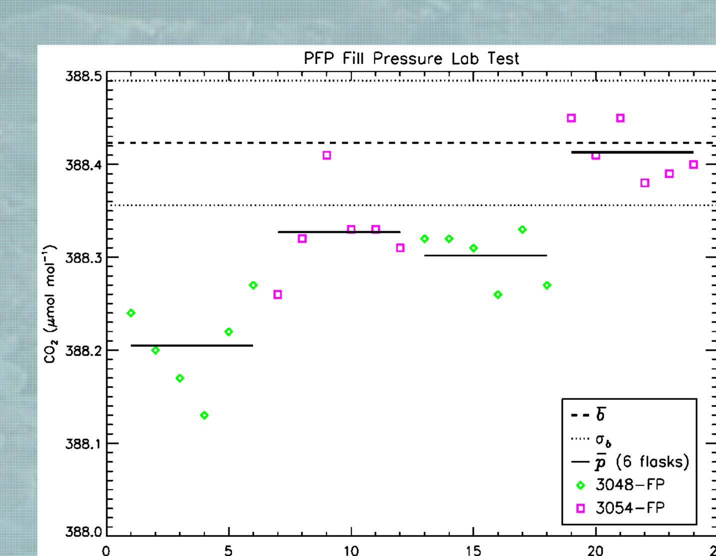


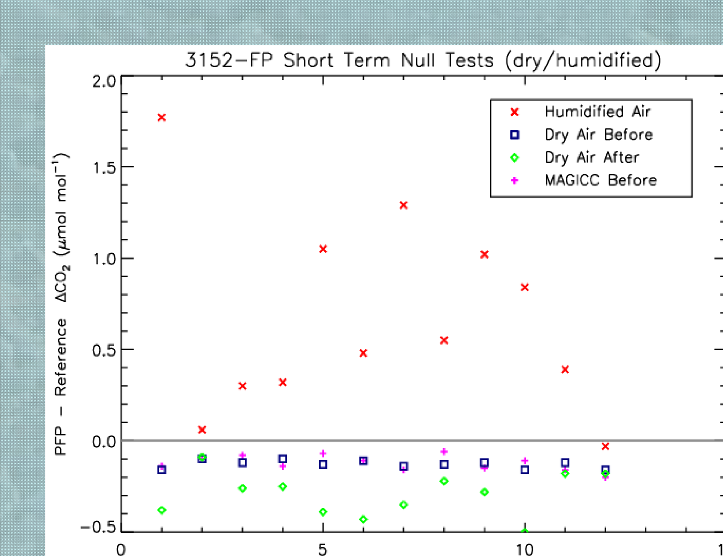
Time Series of Carbon Dioxide
Mt. Evans, 2008



10. Ongoing Laboratory Experiments

Several laboratory tests, and field tests, have been carried out to investigate the pressure dependence of the dry-air offset. A representative example is shown. Experiments are currently being carried out to investigate the effects that typical real sample water vapor can have on the CO_2 offset. A particularly egregious case is shown. The positive offsets seen in the humidified case, and the post-exposure negative dry-air offsets, appear to be related to an interaction of the water vapor with unknown contaminants in the PFP flasks.





11. Acknowledgements

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