Laboratory And Mountaintop Identification And Testing Of Sources Of Bias In Carbon Dioxide Measurements Of Atmospheric Air Collected And Stored In Glass Flasks

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1. Abstract

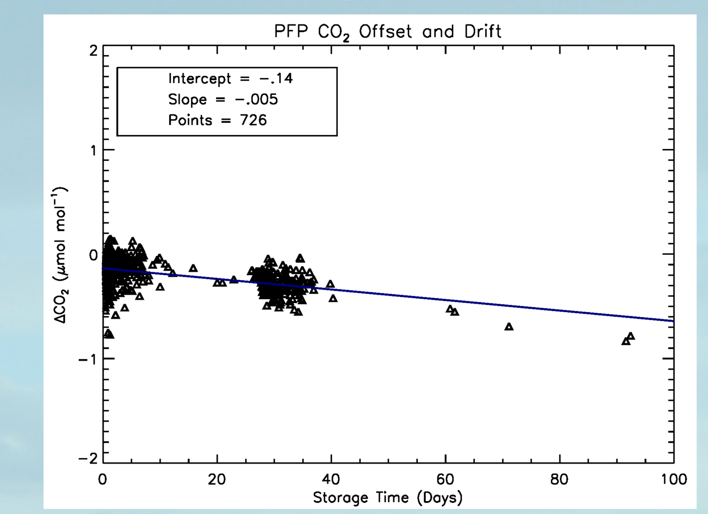
The Global Monitoring Division (GMD) Carbon Cycle Greenhouse Gases group (CCGG) carries out extensive quality control testing and experimentation related to its Global Greenhouse Gas Reference Network, with the goal that the atmospheric measurements obtained meet the uncertainty guidelines outlined by 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).

Laboratory tests have revealed that the presence of ordinary levels of water vapor in atmospheric air samples (even after sample drying) collected in glass flasks, in conjunction with contaminates on the flask surface, can significantly bias measurements of carbon dioxide in these samples. This poster shows representative tests results investigating this bias and other sampling biases related to the use of the CCGG PFP system (see Panel 2). 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 borosilicate 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 might 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.



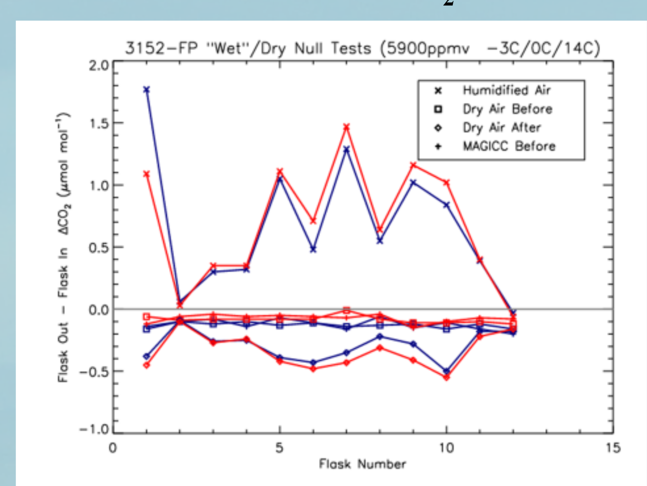
3. Summary Of Laboratory Testing Of H_2O Adsorption CO_2 Bias (Panels 4-6)

Laboratory experiments have revealed that the presence of relatively low amounts of water vapor in atmospheric air samples collected in glass flasks, in conjunction with contaminates on the flask surface, can significantly bias measurements of carbon dioxide in these samples. This bias appears to be related to a process involving the surface adsorption characteristics of water vapor and carbon dioxide in these samples. This process can bias the measured dry-air mole fraction of carbon dioxide, ranging from a 0.1 ppm to more than a 1.0 ppm increase to the measured dry-air mole fraction in the sample relative to the ambient air initially collected.

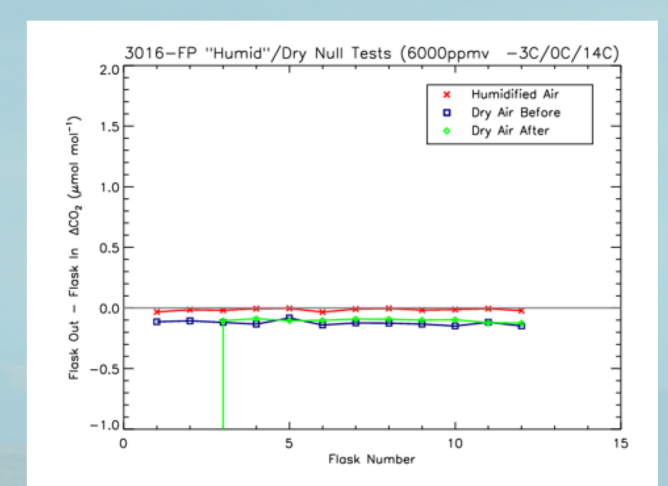
This bias can be eliminated by cleaning the flask surface, however at present this requires complete disassembly of the PFP and involves baking each flask at near the annealing temperature of the borosilicate glass. This process is expensive in terms of money and time, and the flask contaminations appear to return relatively quickly. Fortunately, there appears to be a method of mitigating this bias simply by exposing the flask to humid air (at pressure and with sufficient storage time) prior to collecting the actual field air sample. There are several ways to carry this out, and we are investigating these methods in the lab and in the field (see for example the poster by Kofler, et al.). In the laboratory, the adsorption related bias outlined above can be eliminated by these "Prefill" techniques. We are investigating the development of contaminations and will be testing for more convenient cleaning techniques.

4. Positive CO_2 Bias Induced By Water Vapor/Contamination Combination

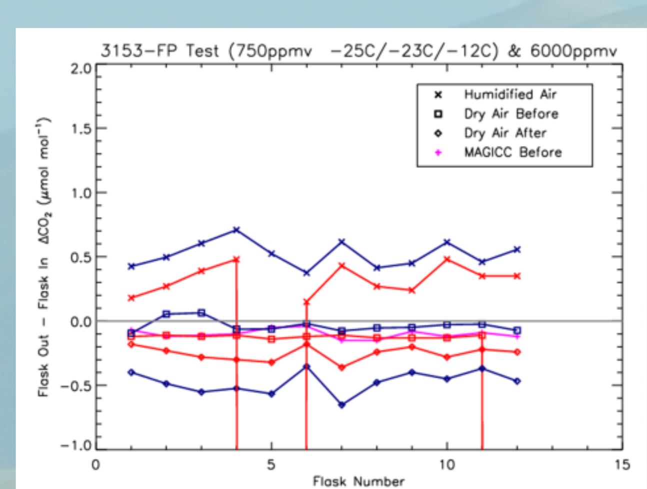
Existence And Repeatability Of Bias In Sample Flasks



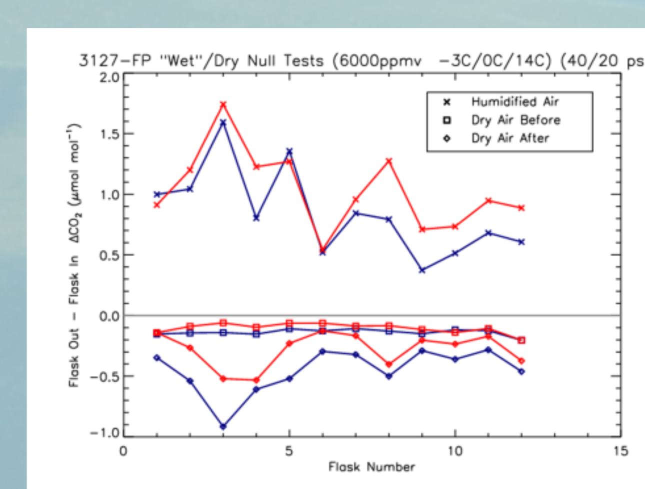
Clean/New Flasks



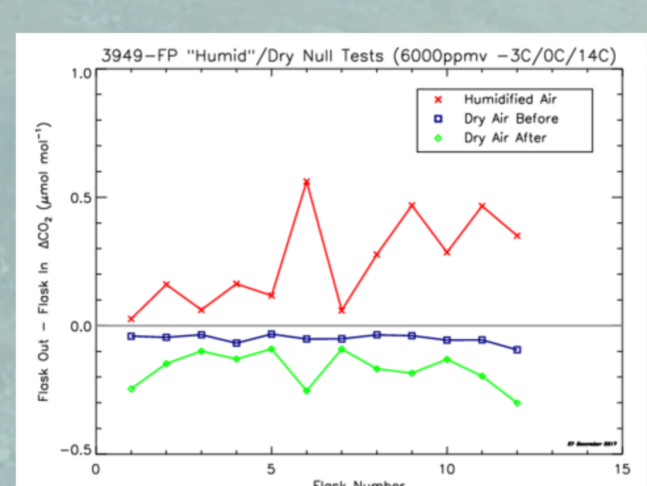
Sensitivity To Water Vapor In Sample Air



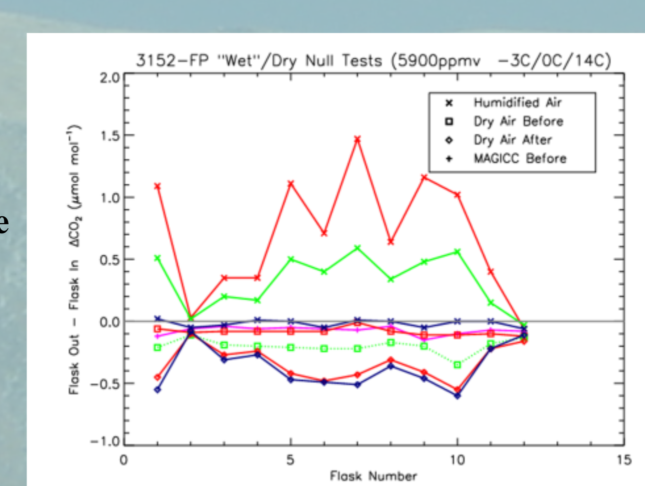
Sensitivity To Flask Air Pressure



Flask Biases Developing In "RECON" PFP

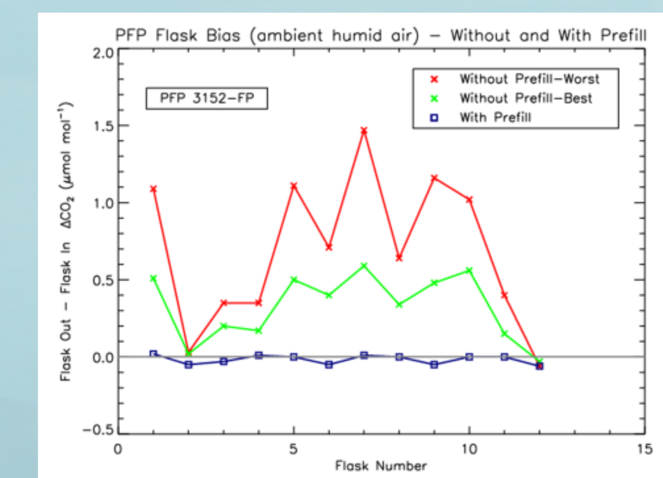


Effects Of Partial Surface Drying And "Prefill"

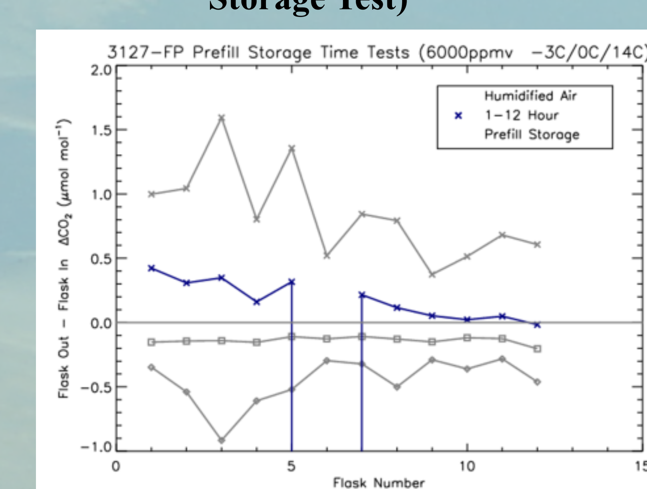


5. Mitigating Bias With "Prefill"

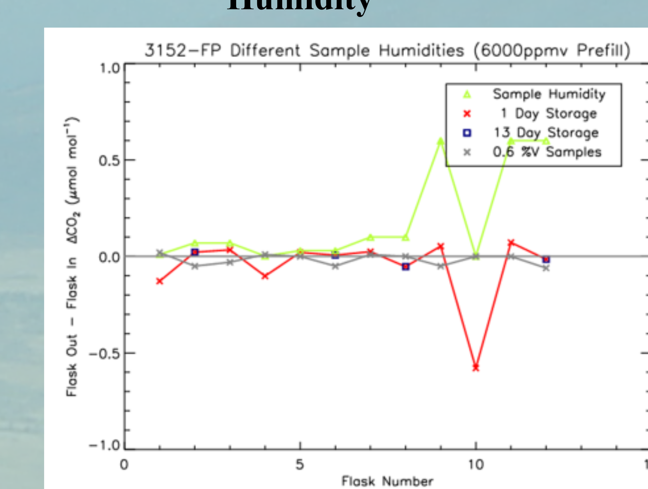
Summary Example Of Laboratory Prefill Efficacy



Time Scale Of Prefill H_2O Adsorption (1-12 hour Prefill Storage Test)



Sensitivity To Difference Of Prefill And Sample Humidity

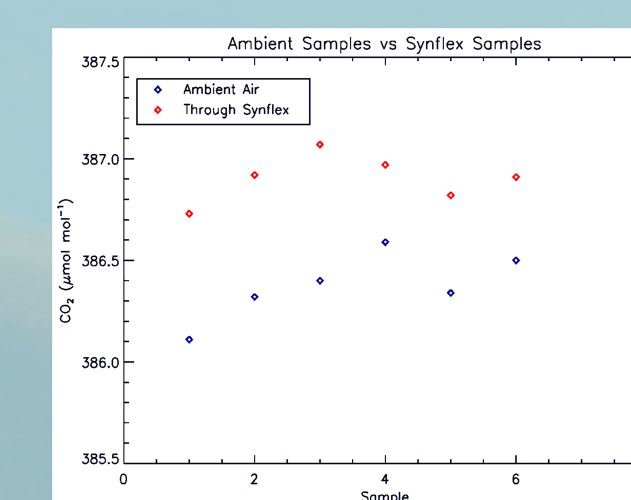


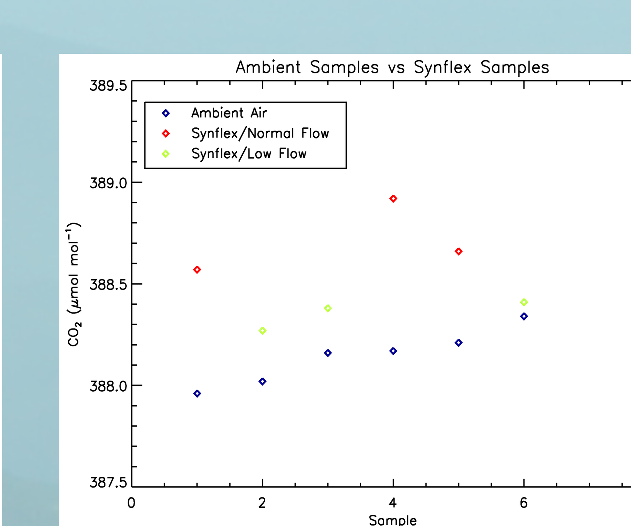
Sensitivity To Difference Of Prefill And Sample CO_2 Mole Fraction

Several tests with varying CO_2 in prefill air (more than 300ppm differences from ambient background) have showed little or no effect on the efficacy of prefills.

7. Sampling Biases/Inlet Line Effects, Mt. Evans

As part of a set of mountaintop experiments (taking advantage of stable free tropospheric air) 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.

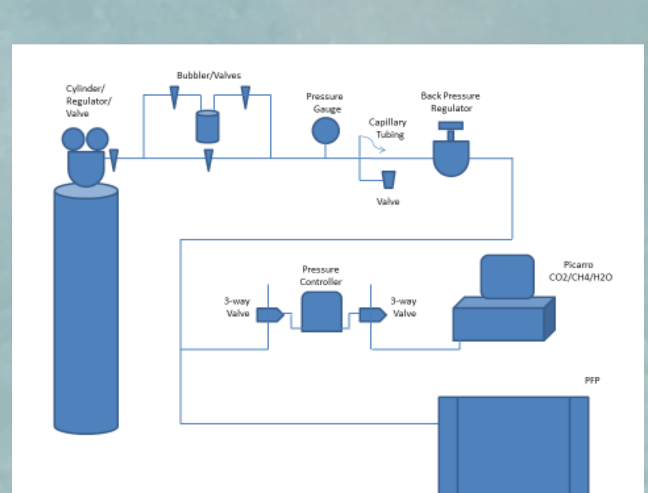




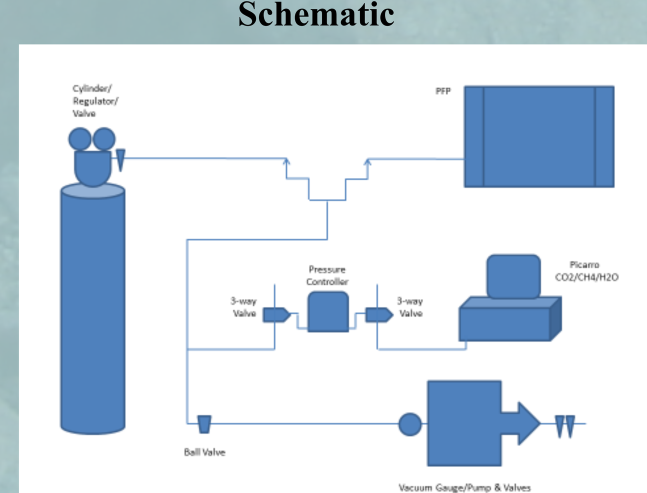
6. Experimental Setup And Example Of Measurements Of Air Into And Out Of Flasks

Laboratory testing of PFP flask storage effects use the setup shown below. Care is taken to ensure stable carbon dioxide and water vapor levels during flask filling. The sample air is measured during the flask flush and pressurization stages of filling, and then the sample air is measured on the same instrument after storage in the PFP flasks.

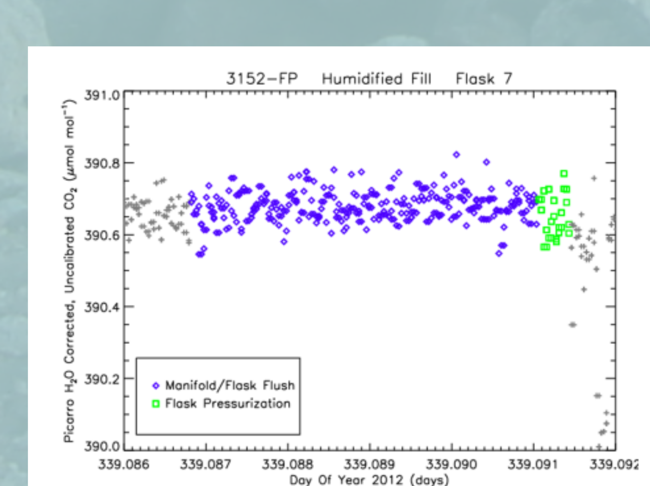
Flask Filling Schematic



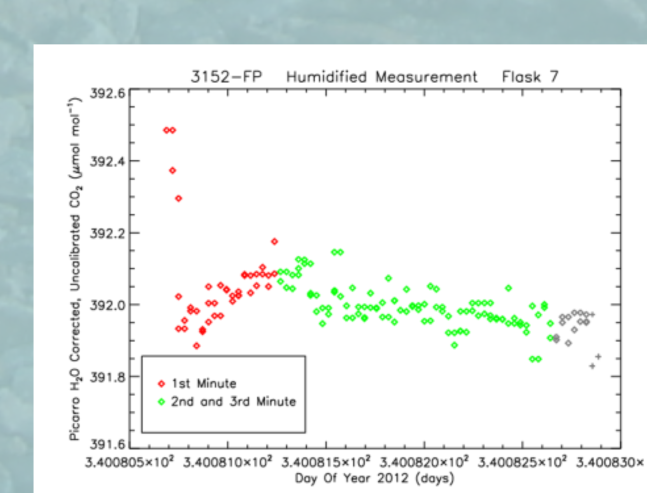
Flask Measurement Schematic



Example of Flask Fill



Example of Flask Measurement



8. Preliminary High Humidity/Condensation Experiments

Very high humidity air samples (with air samples collected and/or stored at temperatures below the dew point temperature) appear to have biases associated with the humidity of the air samples (see the poster by McKain, et al.). We have carried out several laboratory experiments to try to reproduce these results and identify a possible mechanism, with inconclusive results at present. Testing is ongoing.

The laboratory measurements so far have ranged from relatively small to no biases observed – however there have been a few exceptions to this with one negative bias (loss of CO_2) of nearly 1 ppm observed from a flask previously giving several null results. No clear correlations or repeated biases have yet been observed in these laboratory experiments. From conservative calculations, it is clear that simple dissolution of CO_2 into the condensed phase water present in these flasks is not a viable mechanism, alone, to explain the bias apparent in several sets of field data (see the poster by McKain, et al. for these field data). Even with condensation expected in the most humid samples, these conservative calculations suggest at most a -0.02 ppm CO_2 loss in a PFP flask due to dissolution alone.

9 Acknowledgements

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In addition, these experiments rely heavily on indirect, but critical efforts from other members of the NOAA/ESRL/GMD CCGG group.