Laboratory Identification and Testing of Sources of Bias in Carbon Dioxide Measurements of Atmospheric Air Collected and Stored in Glass Flasks

D. Neff[1,2]

[1]Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309; 303-497-4271, E-mail: don.neff@noaa.gov
[2]NOAA Earth System Research Laboratory, Global Monitoring Division (GMD), Boulder, CO 80305

The Global Monitoring Division's Carbon Cycle Greenhouse Gases research group carries out extensive quality control activities 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. For measurements of the dry-air mole fraction of carbon dioxide this guideline is for an interlaboratory comparability of ± 0.1 ppm.

Laboratory tests have revealed that the presence of ordinary levels of water vapor in atmospheric air samples (with or without drying) collected and stored 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 inside the flasks. 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 relative to the ambient air initially collected. Results of these laboratory tests and related tests are presented, including flask preparation and sampling techniques that can greatly reduce or eliminate these biases in field samples. In the laboratory, the adsorption related bias outlined above can be eliminated simply by "prefilling" the glass flask with air that includes a small amount of water vapor (e.g. ~0.6% by volume) prior to collecting the air sample to be measured. The figure below shows examples of this bias and how it is eliminated by using an appropriate "prefill".
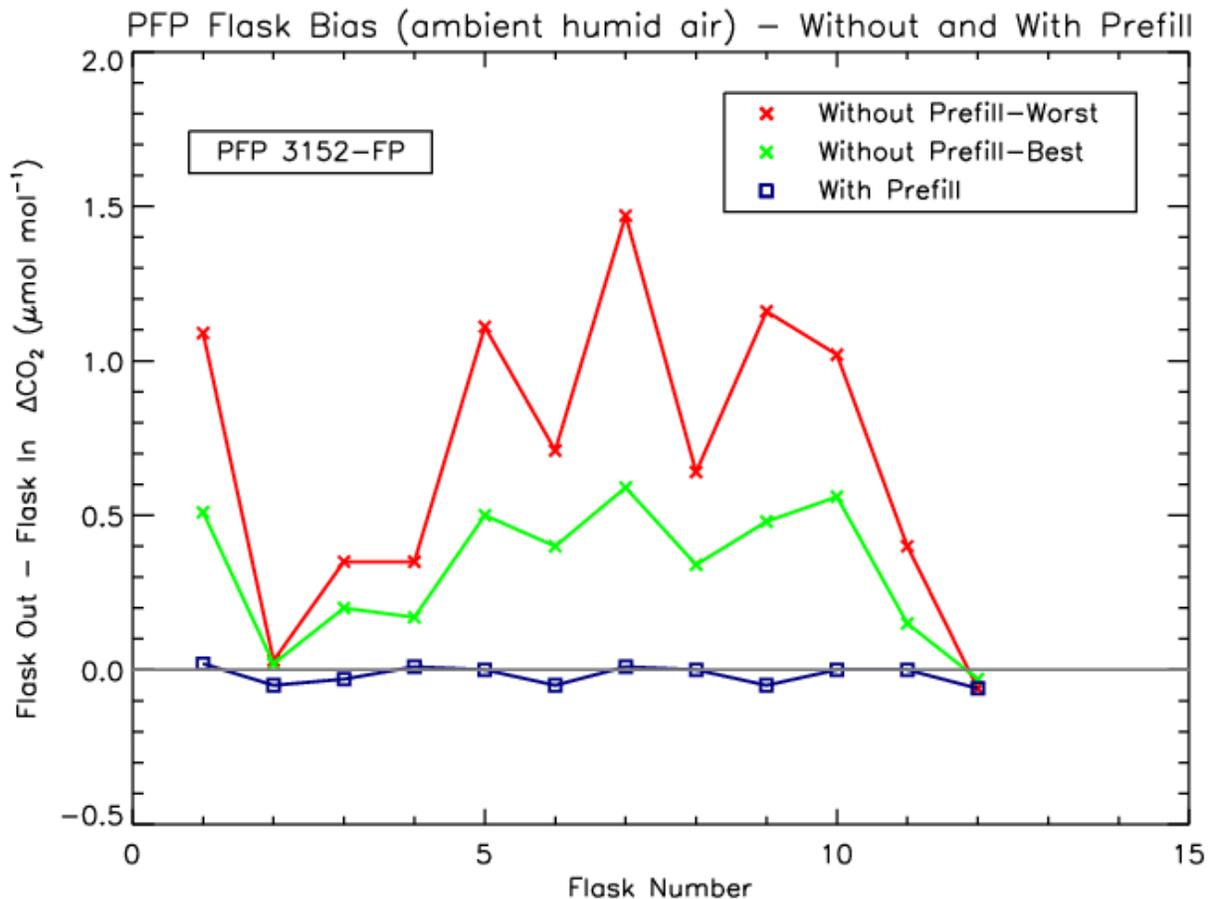
Figure 1. Example of adsorption related bias and its elimination through "prefilling".