

Potential bias in the NOAA manometric measurement system

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Offsets between CO₂ datasets from different measurement locations can lead to mis-appropriation of carbon sources and sinks. To avoid such offsets, CO₂ measurements should be calibrated on a common scale such as the WMO CO₂ X2007 scale, which is recommended by the WMO (World Meteorological Organization). NOAA maintains the WMO CO₂ calibration scale using 15 aluminum high-pressure cylinders (primary standards), which are measured regularly with a manometric system. One advantage of the manometric method is that it provides traceability to the SI while also allowing for periodic measurement over time to assess drift. To measure CO₂ with the manometric system, an aliquot of gas from a primary standard is introduced into a precisely known large volume and together with the measured pressure and temperature the number of moles in the large volume can be calculated. Then the gas is pumped through a cold trap, where the CO₂ of the sample is frozen out and the other constituents are evacuated. The trapped CO₂ is transferred to a smaller volume by using liquid nitrogen. After thawing, temperature and pressure of the small volume are measured. The pressure and temperature measurements of the two volumes in combination with the known ratio of the small to the large volume can be used to calculate the CO₂ mole fraction of the gas sample. However, there is the possibility of small CO₂ losses in the manometric system due to e.g. adsorption by the glass and steel walls, diffusion through O-rings of the valves, which adds to the uncertainty of the CO₂ measurement of the primary standards. By identifying and quantifying potential losses, improvements in manometric CO₂ measurement might be achieved, which could reduce uncertainties and improve drift detection.