Estimating Uncertainties of GC/MS Analyses of Programmable Flask Package (PFP) Atmospheric Samples from the GGGRN North American Tower and Aircraft Programs

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Estimates of measurement uncertainty are one component often considered when interpreting atmospheric trace gas observations with the aim of estimating emissions. Uncertainty estimates are also critical in the evaluation of spatial and temporal trends from discrete measurements at different times, locations, and/or instruments.

The "Guide to the expression of uncertainty in measurement" (GUM 1995, 2008) defines uncertainty of a measurement as a "parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand." In general, uncertainty is comprised of many components, some of which may be evaluated as statistical distributions and characterized by standard deviations.

The Global Greenhouse Gas Reference Network (GGGRN) collects more than 8,000 flask samples of ambient air annually using Programmable Flask Packages (PFP) which are pressurized using Programmable Compressor Packages (PCP). Samples are acquired at a rate of approximately daily at 18 tower locations and approximately twice monthly aboard 15 small aircraft sites throughout North America. We have developed routine laboratory experiments that separate out the most relevant aspects of PFP/PCP sample collection and instrument processes so that their respective contributions to dispersion of the measurements or uncertainties may be elucidated.

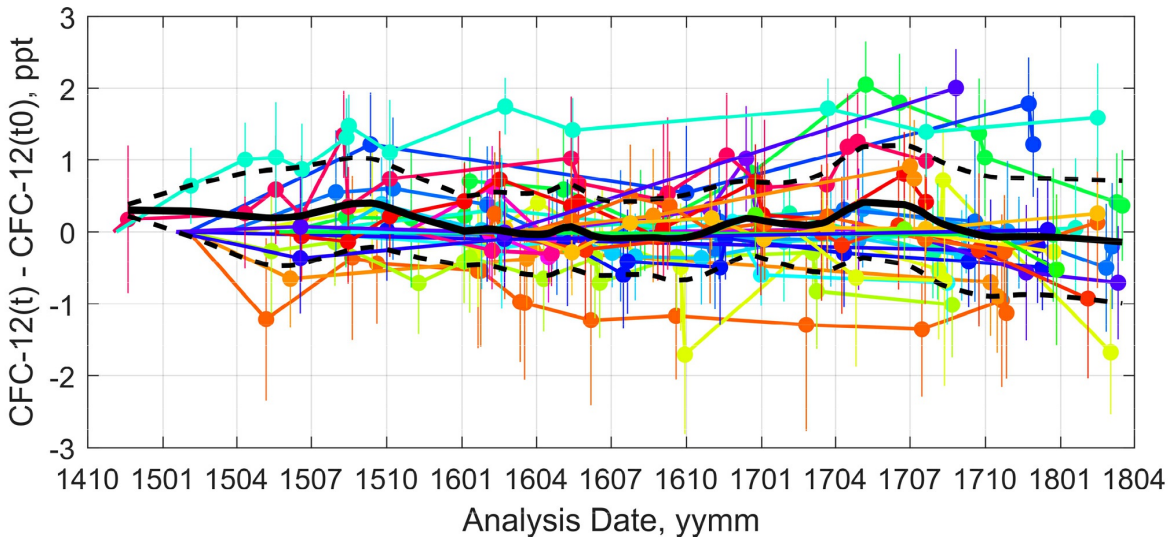

Figure 1. Long-term reproducibility of the PERSEUS GC/MS for CFC-12 (CCl_2F_2). More than 50 archived tanks of whole ambient air (Niwot Ridge, CO) were analyzed periodically over the past three years. Each color represents a different tank. Following the initial analysis of each tank, the change in assigned mole fraction over time can be calculated as the difference between the result at time *t* minus the initial (*t0*) result (dots, with 1-sigma errorbars). A running mean (Lowess smoothed) of all these differences is shown as a black solid line, with ±1-sigma standard deviation (black dashed line). The overall long-term reproducibility of CFC-12 is ±0.68 ppt, which represents the dispersion of the measurement from the combination of tank plus instrument.