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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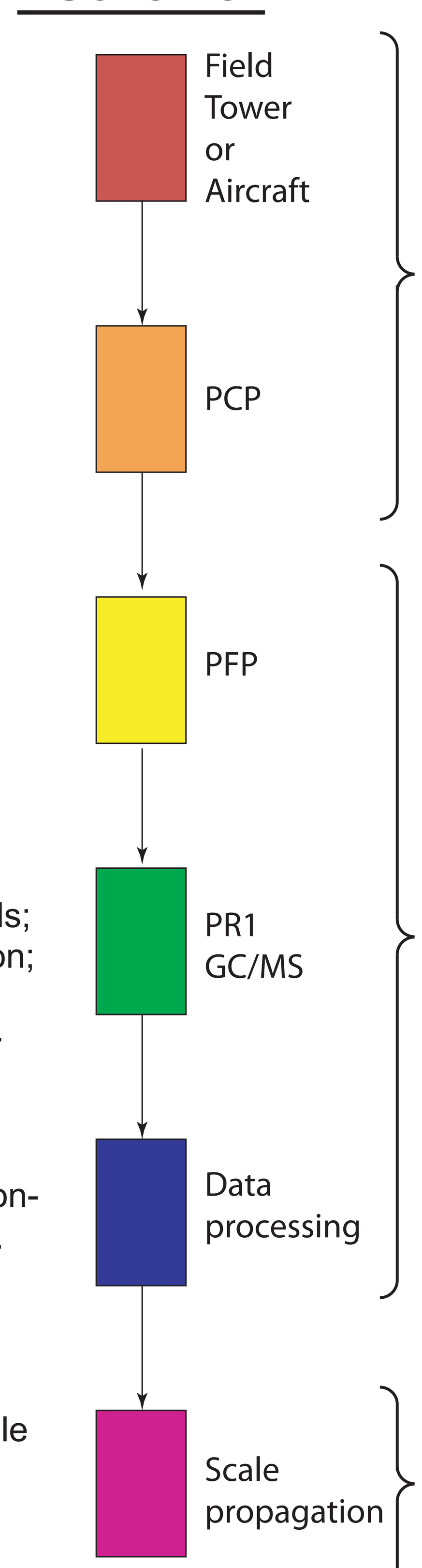
OVERVIEW

Program	Ambient whole air samples collected throughout North America analyzed by the PERSEUS GC/MS ('PR1') for 60 halocarbons, hydrocarbons and sulfur-containing compounds, typically present at part-per-quadrillion (ppq) to part-per-billion (ppb) mole fractions, quantitated with relative precisions of 0.1% to several percent.
Platforms	Small aircraft, Tall towers, Mobile lab
Sampling equipment	Programmable Packages (PFP) – Twelve 0.7-L glass flasks with automated valves. Programmable Compressor Packages (PCP) – Two diaphragm pumps in series to flush and pressurize flasks to ~40 psia.
Throughput	6,000 to 8,000 flasks collected per year (2015-present).
Goals of This Study	Estimation of Relative Uncertainties, μ_R, which are relevant to interpretation when all data are all from the same network, same instrument, same calibration scale, etc. Estimation of Total Combined Uncertainties, μ_T, which are relevant to interpretation of combined datasets from different networks, different instruments or scales, etc. These uncertainties play an important role in discerning spatial and/or temporal gradients, or in evaluating the weighting of observations relative to model predictions.
The Problem	From sampling to analysis, many aspects introduce potential random errors, and any systematic bias corrections applied introduce further uncertainties. The complexity of interaction of these aspects generally precludes individual component isolation and evaluation.
Our Solution	An assembly of experimental evaluations serves as a 'proxy' for representing the most significant uncertainty elements.

Sampling, analysis and data processing - Sources of uncertainty

Example Influences	Idealized Scheme	Proxies used in this study
Losses to and/or contamination from the tubing of the inlet; leaks.	Field Tower or Aircraft	**No proxy currently available.** Losses/contaminations due to contact with inlet tubing, pump polymers and other 'wetted' materials not explicitly accounted for in this study.
Losses to and/or contamination from the 'wetted surfaces'; leaky connections; outgassing of polymer materials (e.g., pump diaphragms, flow meter, filters).	PCP	
Losses to and/or contamination from the 'wetted surfaces'; leaky connections; outgassing of polymer materials (e.g., Viton o-rings).	PFP	**PFP long-term storage tests** These tests include variance influences that span the processes of: - Loss/contamination from filling and storing samples in PFP flasks. - Analyte perturbation from sample drying, preconcentration, desorption, and chromatography and MSD noise. - Peak integration. - Blank correction (if applicable). - Sensitivity drift correction. - Nonlinearity correction (within range). - Scale propagation to the 'S1' secondary standard. **Figure 1** shows an example of the data dispersion induced by these processes.
Losses to and/or contamination from the 'wetted surfaces'; leaky connections; outgassing of polymer materials; losses during drying, preconcentration; errors in temperature and pressure transducers; chromatographic coelutions; MS detector noise.	PR1 GC/MS	
Peak integration errors; blank and nonlinearity corrections; drift corrections.	Data processing	
Analyte drift correction in tanks; scale propagation errors; gravimetric preparation errors.	Scale propagation	**Secondary-Primary comparisons.** Chromatographic responses of secondary standards are assigned absolute calibration values based on comparison with gravimetrically-prepared Primary standards. **Figure 2** shows an example.



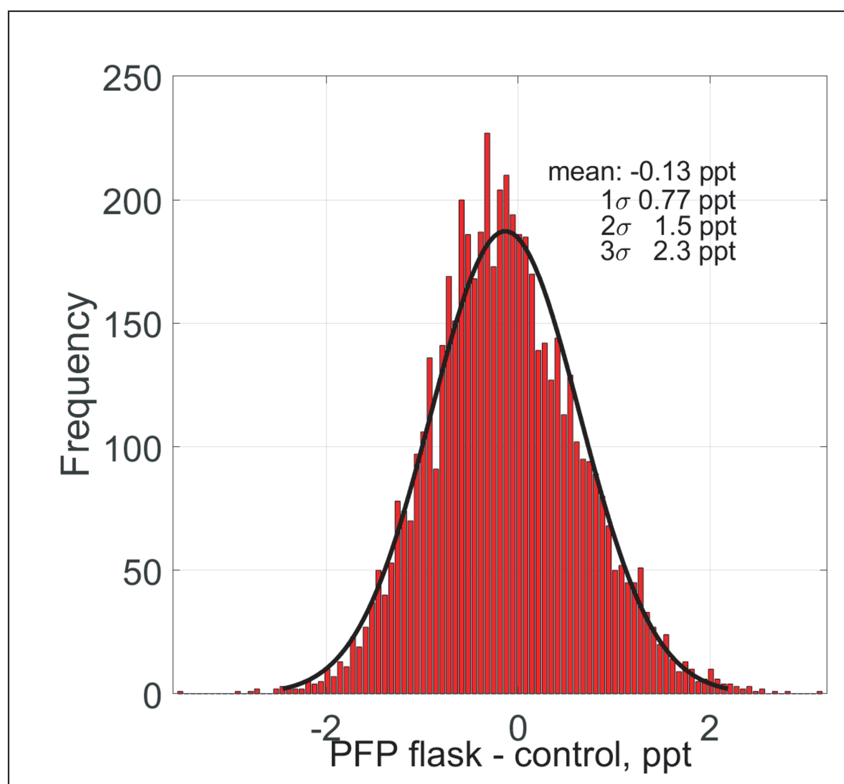


Figure 1: Example results for CFC-12 (CCl_2F_2) from PFP long-term storage of air samples. Whole dry air is filled into PFP flasks and stored ~30 days before analysis to characterize data dispersions caused by this process. In this histogram, the differences between each PFP flask and the same air in the control (i.e., the tank from which the PFP was filled) are plotted as red bars. A Gaussian fit is used to estimate the standard deviation. Although an on-going process, to date, 132 unique PFPs have been tested, with many replicated over time for a total of 274 PFP analyses (3,288 flasks). The 1-σ standard deviation of these CFC-12 results is μ_{LT} = 0.77 ppt.

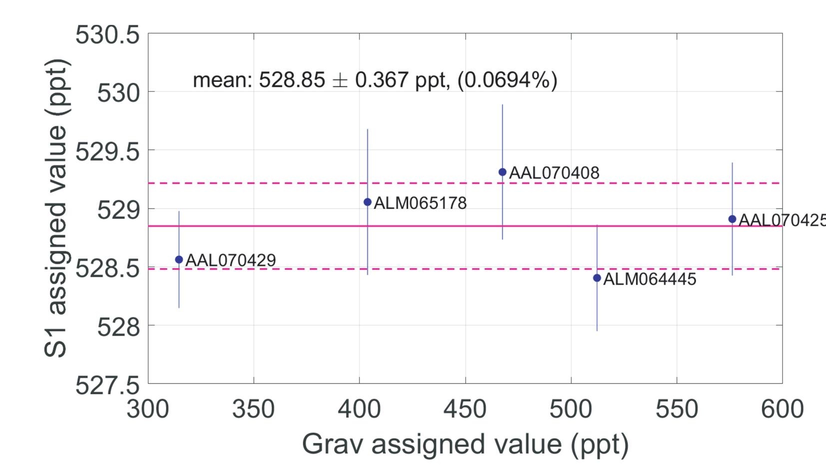


Figure 2: Example of absolute calibration scale propagation from GC/MS comparison of gravimetrically-prepared Primary standards ('gravs') to our whole air secondary standard 'S1' (tank SX-3577). We used data from five gravs spanning a mole fraction range of 315 to 576 ppt to assign a mean CFC-12 calibration to S1 of 528.85 ppt (solid magenta line), with uncertainty μ_{Sec} = ± 0.367 ppt (dashed magenta lines).

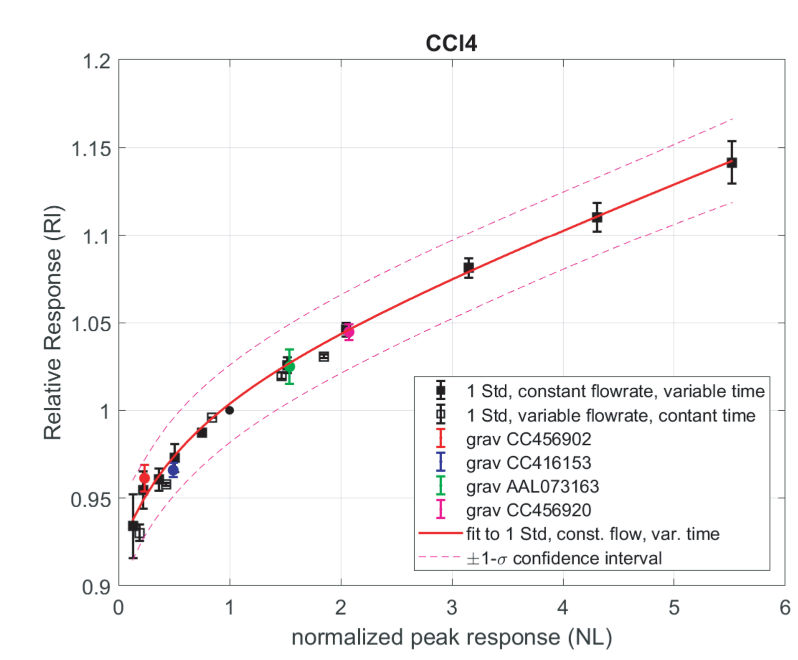


Figure 3: Example of a nonlinearity curve for carbon tetrachloride (CCl_4). We have the capabilty to map nonlinearity over a range of about 10% to 500% of the working standard mole fraction. This is accomplished by injecting different volumes of the same working standard gas so as to vary the number of mole reaching the detector, i.e., the "1 std, constant flowrate, variable time" method.

The 1-σ confidence interval, denoted μ_{NL}, of the fitted line (red) is shown as dashed magenta lines. For CCl_4, this μ_{NL} is about 0.99 ppt, provided that the normalized peak response is within the mapped nonlinearity range. For data outside these limits, we increase μ_{NL} to account for the increased uncertainty.

Primary standard uncertainty, μ_{Gr}. Gravimetric preparations of primary standards involves errors from a variety of sources, which are listed in Table 1. See Table 2 for some example μ_{Gr} values.

Table 1: Typcial relative contributions of gravimetric preparations from various sources:

Source	Contribution	Comment
mass determination (weighing)	60%	masses of capillaries, shot volumes, tanks, etc.
transfer efficiency	1%	losses on walls of transfer lines.
analyte purity	3%	typical reagent purity 98 to 99.9%.
diluent gas (air) analyte contamination	30%	assessed by GC analysis.
diluent gas (air) molecular weight	5%	driven primarily by measured oxygen content.
analyte molecular weight	<1%	includes isotopic differences.

Relative uncertainty, μ_T, and total combined uncertainty calculation, μ_T, are estimated as:

$$\mu_R = (\mu_{LT}^2 + \mu_{NL}^2)^{1/2} \quad \text{Eq. 1}$$

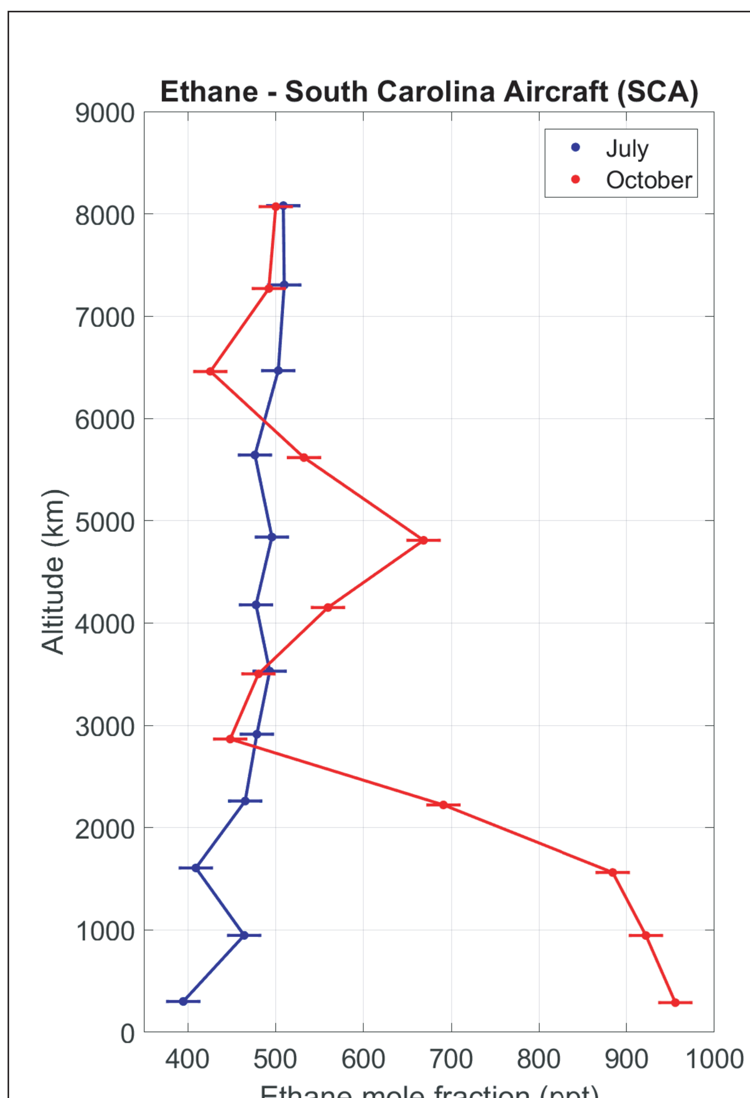
$$\mu_T = (\mu_{LT}^2 + \mu_{NL}^2 + \mu_{Sec}^2 + \mu_{Gr}^2)^{1/2} \quad \text{Eq. 2}$$

where:

μ_{LT} accounts for PFP long-term storage test variability, and includes instrument and data processing influences.
μ_{NL} accounts for nonlinearity correction, only in cases where the calibration range was exceeded. *
μ_{Sec} accounts for propagation of the relative scale to an absolute scale.
μ_{Gr} accounts for the variance of gravimetric preparations.

Table 2: Typcial uncertainty estimates. All units in ppt. A typical atmospheric mole fraction of each species is given as 'MF'. The last column illustrates the relative magnitude of the uncertainty to the atmospheric mole fraction. In this example, μ_{NL} is set to zero for data within the calibration range of nonlinearity mapping.

Analyte	MF	μ_{LT}	μ_{NL}*	μ_{Sec}	μ_{Gr}	μ_R	μ_T	$\mu_{T/MF}$
SF6	9	0.07	0.00	0.02	0.031	0.07	0.08	0.91%
HFC-125	22	0.23	0.00	0.27	0.054	0.23	0.36	1.62%
HCFC-141b	25	0.40	0.00	0.08	0.066	0.40	0.41	1.65%
HCFC-22	240	0.82	0.00	0.27	0.414	0.82	0.96	0.40%
CFC-12	550	0.77	0.00	0.37	1.615	0.77	1.83	0.33%
C2H6	2000	17.00	0.00	4.74	2.637	17.00	17.84	0.89%



Summary:
A method has been devised that allows calculation of a "first-pass" **relative and total combined uncertainties** based on experimental procedures. Future work will focus on including more variables. These uncertainties allow interpretation to confidently discern differences in altitude gradients, spatial gradients and to apply measurement uncertainties to modeling studies.

Example timeseries and aircraft profile with uncertainties
(left) Typical aircraft ethane profile from South Carolina showing Summer and Fall profiles with uncertainty errorbars (μ_T).
(below) Three typical months of HFC-125 data from San Francisco with uncertainty errorbars (μ_T).