# On Reconciling Competing Atmospheric Concentration Estimates from an In Situ ECD GC

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In situ sampling of atmospheric trace gases by electron capture detector (ECD) gas chromatography has been performed by the ESRL GMD HATS group since the mid-1980s. Calibration is accomplished by reference to a series of compressed gas standards prepared by our standards lab in Boulder then shipped to remote field sites. The in situ systems alternate sampling between the atmosphere and a pair of calibration tanks. One tank typically contains concentrations of trace gases similar to those found in the remote troposphere. The other is diluted by ~10% with ultra-pure air. The two tanks are used to provide a local, 2-point, linear approximation with nonzero intercept of the ECD response curve. Since, either tank on its own can provide a 1-point, linear approximation with zero intercept, this setup allows for three competing estimates of the atmospheric concentration (e.g. see the green, red, and blue series in the figure below). Disagreements between the three estimates arise from three primary sources: 1) a nonlinear in situ system ECD response curve (or a linear response with nonzero intercept) that is poorly-approximated by the 1-point estimates; 2) uncertainties encompassing the cal-gas concentrations determined independently by our standards lab; 3) hidden or otherwise unquantifiable in situ system measurement biases. Ratios of cal-gas concentrations and in situ system responses were used to derive an "ECD response factor" and a set of cal-gas concentration offsets by the singular value decomposition of an overdetermined linear system. The results were used to bring all three estimates into agreement using modifications of the original equations (e.g. see the black series in the figure below). This poster will focus on the details of this method using examples taken from its application to the Radiatively Important Trace Species (RITS) data.
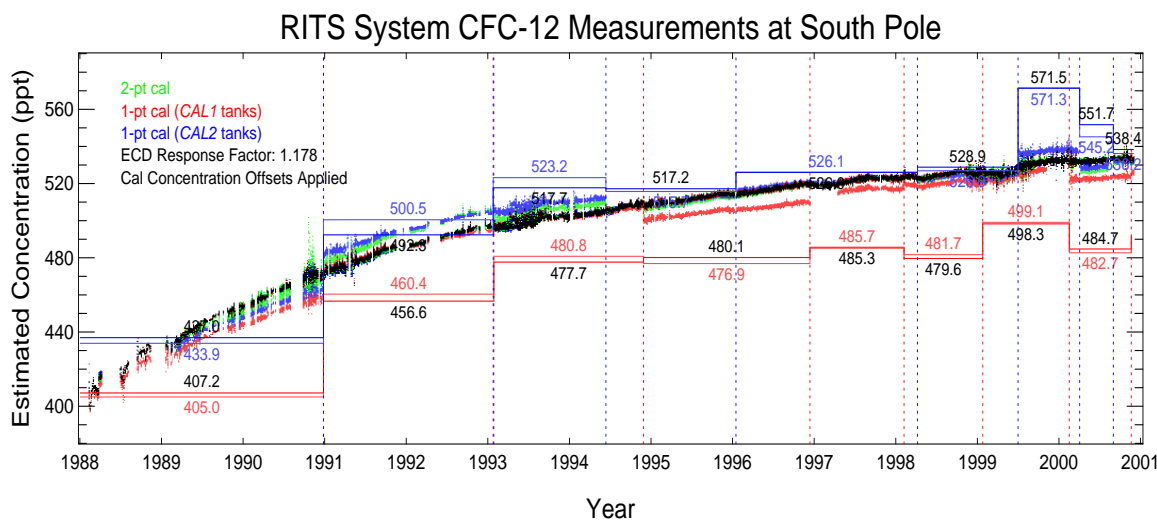


**Figure 1.** Time series plot of four air concentration estimates of CFC-12 measured by the RITS system at South Pole. A 1-point calibration computed with reference to measurements from the *CAL1* (~10% diluted) inlet stream is shown in red. A 1-point calibration computed with reference to measurements from the *CAL2* (undiluted) inlet stream is shown in blue. A 2-point (*CAL1*, *CAL2*) calibration is shown in green. A weighted average of the two 1-point calibrations after modification by an ECD response factor and a set of derived cal-gas concentration offsets is shown in black. Numerically-labeled, solid, pale-red and pale-blue step functions indicate the CFC-12 concentrations in the tanks as determined by our standards lab. These cal-gas concentrations were used to compute the red, blue, and green series. Solid, bright-red and bright-blue step functions with black labels indicate the modified tank concentrations that were used to compute the black series.