Uncertainties of NOAA GHG measurements from discrete air samples and zonal means

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Measurements of atmospheric greenhouse gases (GHG) can not be effectively compared nor properly analysed unless they include estimates of uncertainty. At NOAA, our earliest measurements of CO_2 from discrete samples began in the 1960s when few accompanying quality assurance (QA) data were collected, hampering efforts to estimate uncertainties.

I will describe a method to calculate uncertainties for discrete samples that includes a common framework of multiple terms combined in quadrature. We estimate uncertainty in each measurement from the following: $\sigma_u^2 = \sigma_{st}^2 + \sigma_{lt}^2 + \sigma_{sp}^2$. σ_{st} is short-term measurement noise (i.e., repeatability). We can assess it from the variance in measurements of test flasks filled simultaneously, from the mean difference between pairs of air samples collected simultaneously at sites with low natural variability (e.g., South Pole), and from the variance in measurements of air from a cylinder. σ_{lt} is the long-term variability of the analytical system (reproducibility); it is an assessment of how compatible measurements are over times scales of months to years. This is difficult to assess. Neither "test" flasks nor target cylinder measurements reveal significant long-term biases, but in both there may be periods when measurements are significantly different from assigned values. We use the mean difference between measurements of a target cylinder and its assigned value as a proxy for this parameter. σ_{sp} is a measure of our ability to propagate the WMO standard scales (reproducibility of standard scale propagation), and it is based on repeat calibrations, more than one year apart, on an independent analytical system dedicated to propagating the standard scales. Additional uncertainty terms are added when necessary. For example, early measurements of CO_2 were made against standards of CO_2 in N_2, and these were later corrected to account for pressure broadening effects. In this case, we include a term for the uncertainty in this correction.

We've historically assessed uncertainty in zonal averages from our network distribution with a "bootstrap" method. To account for potential intermittent bias lasting over variable periods, we've developed a Monte Carlo (MC) approach to compliment our bootstrap method. The MC method is designed to realistically account for periods of bias by modifying actual data based on bias randomly selected from a Gaussian distribution and applying it to a randomly selected analysis period from 3 to 24 months. One hundred sets of time series are produced, each with a unique, randomly-selected bias and time-period. As with the network bootstrap method, the 100 time-series are smoothed temporally and spatially to produce zonal means, and each of those are averaged to produce the statistics of interest. As an example, the uncertainty on the annual increase for N_2O is about a factor of 10 larger when determined with the MC method compared to the bootstrap. Because N_2O is very well mixed in the background atmosphere, there is little spatial variability to exploit in the network bootstrap analysis, and uncertainties are unreasonably small, so this new method produces more believable uncertainties.