Measurement and Calibration Uncertainty in the CSIRO atmospheric CO2 Stable Isotope Program

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The CSIRO atmospheric CO_2 stable isotope measurement program has been running for nearly 40 years. Early measurements focused on samples collected at Cape Grim, Tasmania, but the program expanded during the 1980s to a global flask collection program with numerous international partners. Two independent programs were run by CSIRO at Cape Grim for almost 30 years that provided a unique opportunity to assess sample collection, measurement and calibration procedures and test new procedures.

Initial measurements were calibrated using a high purity CO_2 gas calibrated against NBS19 carbonate. As the measurement program developed a series of high-purity CO_2 gases were intercalibrated to provide a calibration strategy for the measurements. With the acquisition of a new mass spectrometer in 1990 a new strategy was developed around whole air standards that were integrated with the CO_2 gases and the carbonate calibrations. The result of this measurement and calibration strategy is a high quality 35 year record of the stable isotopic composition of atmospheric CO_2.

An integral component of the calibration strategy was the establishment of a Quality Assurance system that enables any required corrections to be applied retrospectively to any measurement. Every step in the strategy has been assigned an uncertainty or a method for calculating the associated uncertainty. Some components of the final uncertainty assigned to a measurement come from values "assigned" to standards, while other components are calculated from measurements performed on a daily basis. Two recent developments to the system are (1) an automated recalibration procedure that assesses current and past calibrations and revises, when necessary, all measurements and determines an uncertainty for every measurement, and (2) a link to the WMO-CCL for the stable isotopes of CO_2. As almost all whole air and pure CO_2 standards are still available for analysis, the revised calibration procedure allows us to demonstrate consistency of the long-term trends observed in the atmosphere.

This talk will present the “production” version of this procedure and the newly developed, and soon to be implemented, revised procedure. Topics to be covered include:

Determination of instrumental effects
Development of ion correction procedures
The long-term atmospheric $\delta^{13}C$ record
Flask same-air comparisons with NOAA(INSTAAR) & ECCC
Round-robin exchanges, such as the IAEA funded CLASSIC program
Implications for carbon cycle modelling