Maintaining quality with quantity: lessons learned in the corrections and calibrations of INSTAARs large isotopic dataset

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The Stable Isotope Laboratory at CU-INSTAAR works with NOAA Global Monitoring Division's Global Greenhouse Gas Reference Network to measure stable isotopes of carbon dioxide and methane. We have 27 years of isotopic measurements of $\delta^{13}C$ and $\delta^{18}O$ of CO_2 and 19 years of measurements of $\delta^{13}C$ of CH_4. Here we highlight ongoing challenges to maintaining the world's longest continuous monitoring program for stable isotopes of these greenhouse gases.

Recently, krypton (Kr) has been shown to interfere with measurement of atmospheric $\delta^{13}CCH_4$, assumed to result from tailing of doubly charged $86Kr^{2+}$ and scattering of singly charged Kr ions (Schmidt et al. 2013). One method of removing this interference is by installation of a post-combustion column (PoraBond Q, 12 m) in-line with the GC-IRMS sample stream to separate Kr from CH_4-derived CO_2. Measurement of a suite of standards of different methane mixing ratios shows the effect to be between 0.017 and 0.03 permil per 100 ppb increase in CH_4. Interpolation over the last 19 years of INSTAAR measurements, when globally-averaged atmospheric methane increased from 1772-1840 ppm, indicates that the effect of the Kr interference on $\delta^{13}CCH_4$ is likely no more than -0.03 ‰, compared with the global long term decline in globally-averaged $\delta^{13}CCH_4$ of 0.25 ‰. We are working to better quantify this effect and correct the $\delta^{13}CCH_4$ time-series record accordingly.

We have also seen new challenges in recent years maintaining our INSTAAR isotopic CO2 scale (our independently established tie to VPDB) within our lab, as we now measure samples on four different instruments. A standard cylinder measured periodically on all instruments and with different working references between 1996 and 2015 has a reproducibility (1 σ standard deviation) of 0.023 permil for $\delta^{13}CCO_2$ and 0.123 for $\delta^{18}OCO_2$; since 2005 it is 0.019 and 0.042 permil respectively. Considering the long time frame, the magnitude of this variance is respectable; however, our past strategy of "bootstrapping" our scale between working references is inadequate to stay within our targeted precision of 0.015 and 0.03 permil. We are in the process of switching to the JENA-06 scale (established by MPI-BGC, the Central Calibration Laboratory for CO_2 isotopes), and establishing standard operating procedures to propagate the scale to multiple working references. The resulting change in our dataset will be modest: INSTAAR data are too positive by about 0.02 permil for $\delta^{13}C$ and 0.06 permil for $\delta^{18}O$. We are assessing our agreement at more negative isotopic values, where INSTAAR measurements are less precise both within and between instruments, possibly due to instrument-specific scale contraction or expansion. We will discuss our efforts to resolve these issues, our timeline and methods for reprocessing our large data set to the JENA-06 scale, our estimation of uncertainties, and our adoption of best practices going forward.