How Useful Are Carbon Stable Isotopes of Methane? Improvements in Analysis and Quality Controls at the INSTAAR Stable Isotope Lab

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The INSTAAR Stable Isotope Lab has a twenty-year record of $d^{13}C$ measurements of methane from a subset of sample flasks in NOAA's Global Greenhouse Gas Reference Network. These data have been useful for testing hypotheses about the source of the increase in the atmospheric methane burden since 2007 (Schwietzke *et al.*, 2016, Schaeffer *et al.*, 2016, Nisbet *et al.*, 2016). However, the signals interpreted in these studies, with a range of ~0.3 permil, are small relative to our quoted measurement reproducibility of 0.07 permil, which is based on surveillance cylinders. As the growth rate of the atmospheric methane burden remains above 5 ppb yr^{-1}, and more scrutiny is given to both natural and anthropogenic emission sources, it will become increasingly more important not to over- or understate uncertainties in critical $d^{13}C\text{-}CH_4$ measurements.

Here we ask what we can do to improve our data quality, both by increasing measurement precision from our analytical system, and by strengthening our post-processing quality control. For example, we address the step in which we combust CH_4 to CO_2. The oxygen for this reaction comes from a laboratory cylinder, and the isotope ratio mass spectrometer measures the $d^{18}O\text{-}CO_2$ simultaneous with $d^{13}C\text{-}CO_2$, and these data may contain useful information regarding the efficiency of the combustion. We also consider new methods for oxygenating our reaction, such as dosing the combustion furnace with O_2 between every sample.

Furthermore, the uncertainty of global averages of atmospheric $d^{13}C\text{-}CH_4$ is dominated by analytical uncertainty – unlike for methane mole fraction, where uncertainty is dominated by variability in the atmosphere or by the choice of sites in the network. Here we use test flasks, flask pair differences, and surveillance cylinders to assess the uncertainty in our data over time. We also show how different metrics of analytical uncertainty affect our calculations of zonal and global means. We show that despite the large signal to noise ratio, our measurements are useful for understanding changes in the global methane budget.

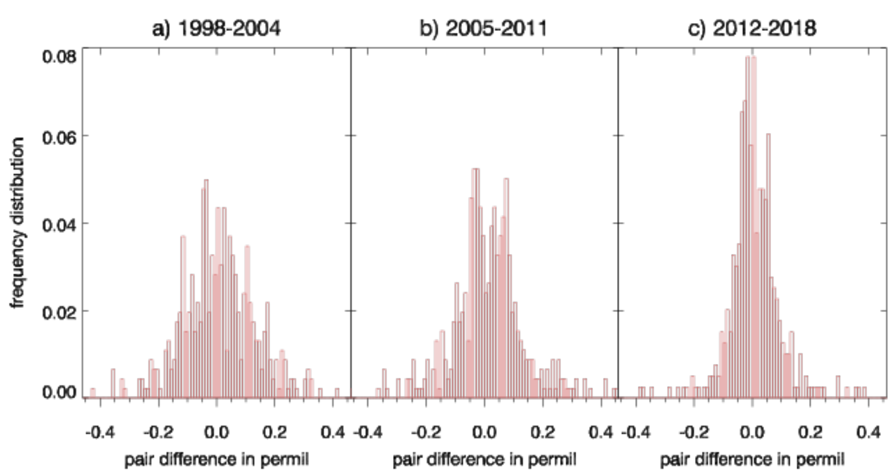

Figure 1. Flask pair agreement of $d^{13}C\text{-}CH_4$ data has improved since we began measurements in 1998. Data here are from the South Pole Station.