Linking Carbon Isotopes of Methane to International Standards – Can We Close the Loop on Calibration?

J.P. Winokur1, S.E. Michel1, S. Morgan1, J.B. Miller2, S. Lehman1, B.H. Vaughn1 and J.W.C. White1

1Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO 80309; 303-492-5495, E-mail: winokuj@colorado.edu
2Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

The growth rate of the mole fraction of atmospheric methane (CH4) has varied substantially over time: the last three decades have seen a globally averaged increase of more than 200 ppb, followed by a period of relative stability, and in the last five years, an increase. Understanding the sources and sinks of atmospheric CH4 will advance our understanding of its variable growth rate and its effect on global climate change. Stable isotopes of CH4 are a useful means to delineate sources and sinks of atmospheric CH4. The Stable Isotope Laboratory at CU-INSTAAR has measured carbon isotopes of CH4 in the NOAA Earth System Research Laboratory, Global Monitoring Division’s Cooperative Air Sampling Network since 1998. These data—from a 15-site subset of the NOAA Network—show an overall decrease in δ13C of atmospheric CH4 in the last few years, with a maximum decrease of 0.3‰ amongst the sites. The significance of that observation, as well as the clear detection of trends, require well-calibrated CH4 standards inter-compared among different laboratories. At INSTAAR, our δ13C of CH4 scale is tied to that of UC-Irvine through multiple compressed, whole-air cylinders filled at Niwot Ridge, Colorado. While data show that our scale has remained stable over the last decade, calibration to the primary carbonate standards (NBS-19 and LSVEC) remains a challenge. Although linking whole air standards to primary reference materials has proven difficult, this has been a goal of the atmospheric CH4 isotope measurement community for some time, and was recently underscored by the International Atomic Energy Agency (IAEA)/World Meteorological Organization Scientific Advisory Group for Greenhouse Gases. Here we discuss the application of a new offline extraction system, developed to measure 14C of CH4 at INSTAAR, but which also allows for higher precision Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) measurements of δ13C of CH4-derived CO2. INSTAAR’s calibration for δ13C of CO2 is strongly tied to the VPDB scale; furthermore this will allow for direct comparison to IAEA carbonate standards. This is a significant step forward for methane isotope calibration at INSTAAR, and will contribute to efforts for worldwide inter-laboratory calibration.

Figure 1. Atmospheric observations (1998—2011) of δ13C of CH4 from a 15-site subset of the NOAA/ESRL Global Monitoring Division Cooperative Air Sampling Network show oscillations in growth over the last decade and more negative trending over the last 4 years.