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

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The growth rate of the mole fraction of atmospheric methane (CH_4) 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 CH_4 will advance our understanding of its variable growth rate and its effect on global climate change. Stable isotopes of CH_4 are a useful means to delineate sources and sinks of atmospheric CH_4. The Stable Isotope Laboratory at CU-INSTAAR has measured carbon isotopes of CH_4 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 $d^{13}C$ of atmospheric CH_4 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 CH_4 standards inter-compared among different laboratories. At INSTAAR, our $d^{13}C$ of CH_4 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 CH_4 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 ^{14}C of CH_4 at INSTAAR, but which also allows for higher precision Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) measurements of $d^{13}C$ of CH_4-derived CO_2. INSTAAR's calibration for $d^{13}C$ of CO_2 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.

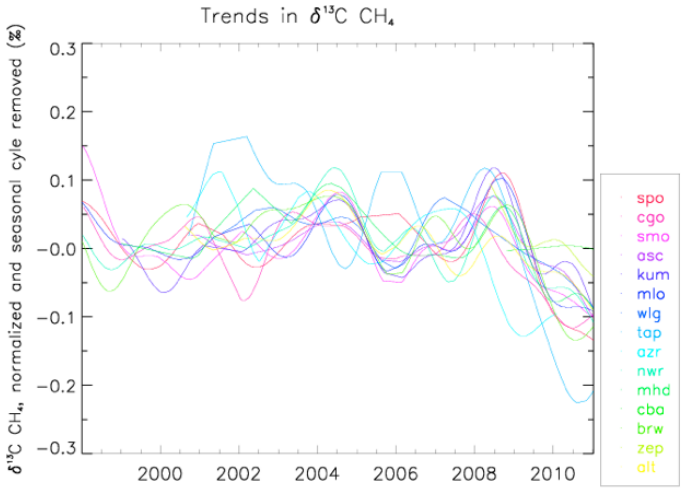

Figure 1. Atmospheric observations (1998—2011) of $\delta^{13}C$ of CH_4 from a 15-site subset of the NOAA/ESRL Global Monitoring Division Cooperative Air Sampling Network show oscillations in growth over the last decade and more negative trending over the last 4 years.