Calibration and Field Testing of Cavity Ring-down Laser Spectrometers Measuring Methane Mole Fraction and the Isotopic Ratio of Methane, Deployed on Towers in the Marcellus Shale Region

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Four *in situ* cavity ring-down spectrometers (Picarro, Inc.) measuring methane (CH_4), carbon dioxide (CO_2) and the isotopic ratio of methane were deployed at towers with heights between 46 and 61 m a.g.l.. The study is focused on the Marcellus Shale natural gas extraction region of Pennsylvania. The leakage rate of methane determines whether natural gas is useful as a bridge fuel, in terms of greenhouse effects, compared to coal. Sources of methane can be distinguished via the isotopic signature: heavy isotope ratios are characteristic of thermogenic (e.g., oil and gas) CH_4 sources and light isotope ratios are characteristic of biogenic (e.g., landfills, agriculture) sources. The calibration of the isotopic methane instruments is challenging for several reasons, including the need for both a slope/intercept calibration and a mole fraction correction (Fig. 1), and cross-interference from ethane. We describe laboratory and field calibration of the analyzers for tower-based applications, and characterize their performance in the field from January 2016 – November 2016. Prior to deployment, each analyzer was calibrated using high mole fraction bottles with various isotopic ratios from biogenic to thermogenic source values, diluted in zero air. Furthermore, at each tower location, three field calibration tanks were employed, from ambient to high mole fractions, with various isotopic ratios. By testing various calibration schemes, we determined an optimized field calibration method.

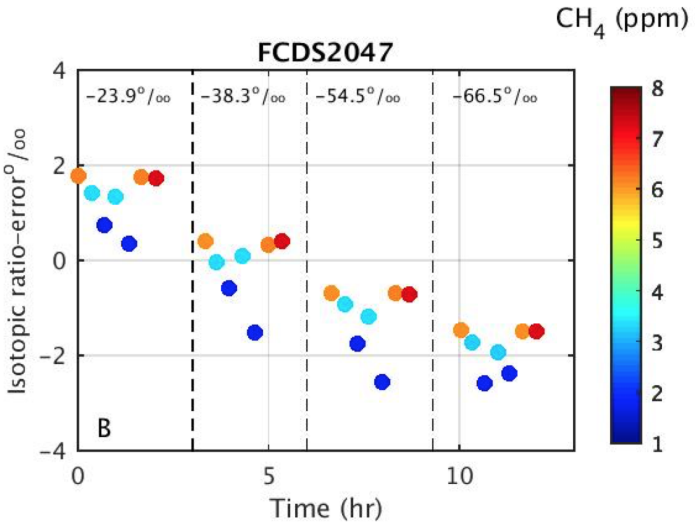

Figure 1. Isotopic ratio error (prior to calibration) as a function of measurement time during the laboratory calibration. For this test, commercially-available isotopic standard bottles (Isometric Instruments, Inc.) were diluted with zero air to produce mixtures with varying CH_4 mixing ratios and $\delta^{13}CH_4$. The dotted lines separate the four isotopic values tested. The colors indicate the CH_4 mole fraction. The isotopic ratios prior to calibration exhibit both a slope/intercept error and a mole fraction dependence.