Characterization of Cavity Ring-Down Spectrometers for Methane Stable Isotopes

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Introduction

Fugitive emissions of atmospheric methane (CH_4) from natural gas drilling, production, processing and distribution activities from the Marcellus Shale geologic formation have the potential to impact the current state of the climate. Thus, it is useful to quantify these emissions from natural gas as well as other sources both biogenic and anthropogenic (e.g. wetlands, cattle, landfills). Regional emissions can be quantified using an atmospheric transport model with a Bayesian inversion to minimize differences between simulated and observed atmospheric CH_4 concentrations. Measurements of CH_4 concentrations and its stable isotope ($^{13}CH_4$) from commercial towers, between 46-61 m AGL, in northeast PA, are ongoing since May 2015.

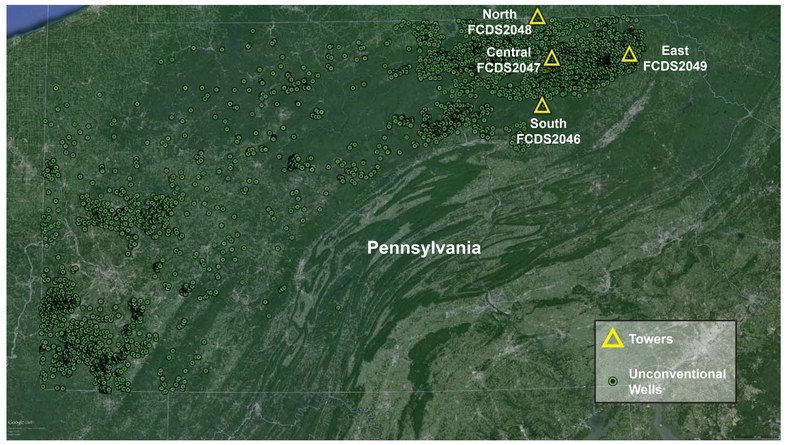

Fig 1. Map of Pennsylvania with permitted unconventional natural gas wells (green circles) and network of towers with methane concentration and stable isotope measurements.

Objective

Establish a network of precise and accurate measurements of methane and its stable isotope to estimate and attribute regional emissions from anthropogenic and biogenic sources using an atmospheric inversion technique.

Needs and Hypotheses

Regional enhancements based on preliminary simulations are expected to be 30-100 ppbv. Observations from the tower measurements to-date show CH_4 background mixing ratios near 1900 ppbv and peaks typically 2500 ppbv, and sometimes as large as 5000 ppbv. Differences in isotope ratios between biogenic and thermogenic sources are nominally 10 ‰. Thus, the needed precision in the isotope measurement is 0.16-0.5 ‰. The cavity ring-down spectrometers (CRDS, Picarro G2132-i) used in this study have a specified 0.5 ‰ precision over a 15 min average. The isotope measurement is expected to drift and so frequent calibration may be needed. It is expected that the response of $^{13}CH_4$ is a function of the $^{12}CH_4$ mixing ratio.

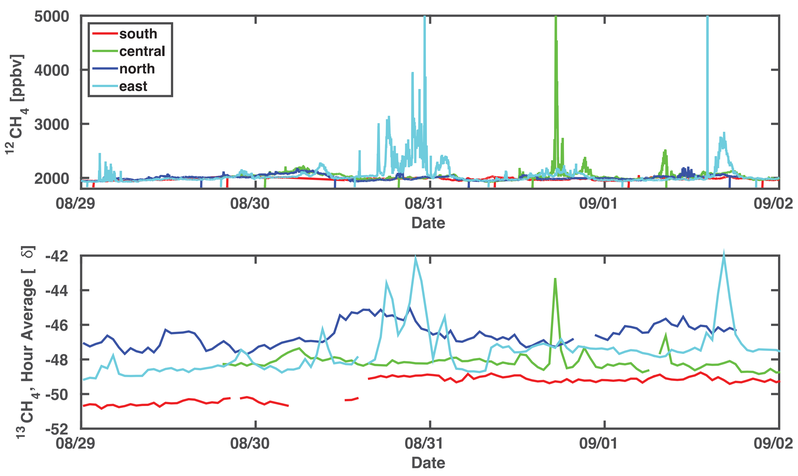

Fig 2. (Top) Timeseries of atmospheric $^{12}CH_4$ mixing ratios from the 4 towers for an example 5 day period. (Bottom) Timeseries of hourly-averaged methane stable isotope ratios expressed in delta notation over the same period. A calibration on the $^{13}CH_4$ HAS NOT been applied.

Methods

1. Calibrate 4 analyzers in the laboratory for CH_4 mixing ratio using primary standards (NOAA).
2. Determine the CH_4 mixing ratios of isotopic standards.
3. Challenge analyzers with four CH_4 mixing ratios and four isotopic standards by diluting isometric instrument isotope standards (~2500 ppm) with zero air.

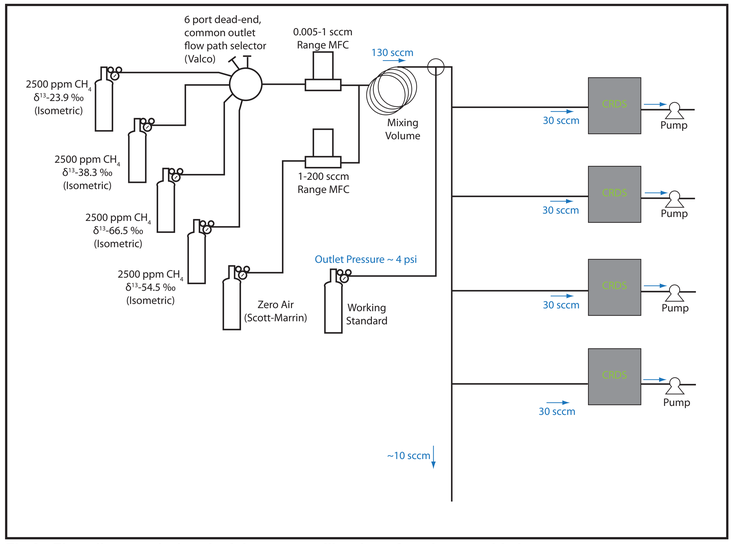

Fig 3. Flow diagram during the laboratory calibration of methane stable isotopes.

Method Evaluation

Each isotopic standard was sampled using 4 dilution flows that targeted CH_4 mixing ratios between 1.8 ppmv (~ambient) and 10 ppmv and repeated. Four calibrations were conducted between January-April 2015 to evaluate short-term and long-term drift. Isotope ratios of -23.9, -38.3, -54.5, -66.5 ‰ were sampled. The heavy isotope ratios (e.g. -23.9 ‰) represent thermogenic CH_4 sources and the light isotope ratios (e.g. -66.5 ‰) represent biogenic sources.

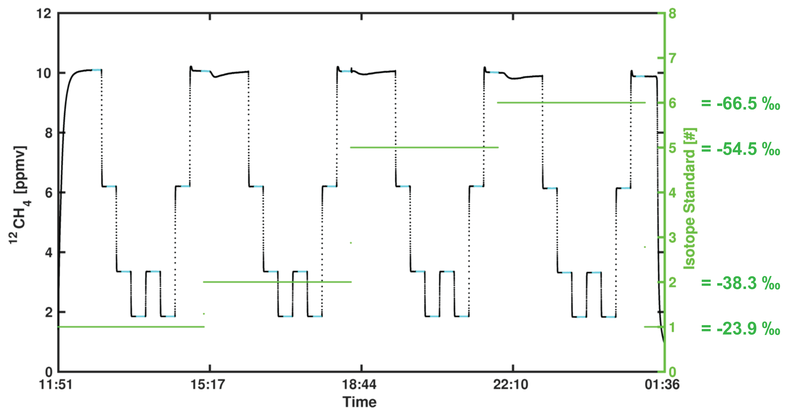

Fig 4. Timeseries of the $^{12}CH_4$ mixing ratio response to changes in dilution flow and changes in isotope ratio standards (black dots). A flag showing which isotope standard is being sampled is shown (green line). The isotope standards 1, 2, 5, 6 have isotope ratios of -23.9, -38.3, -54.5, -66.5 ‰, respectively. Subsets of the timeseries used for the calibration averages are shown (cyan).

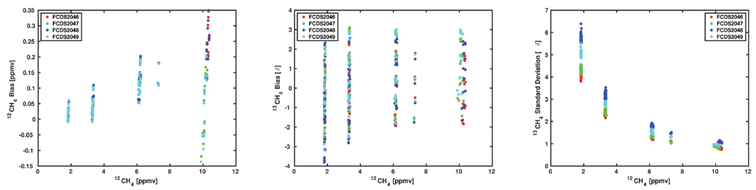

Fig 5. (*Left*) Bias of $^{12}CH_4$ response (response-target) as a function of $^{12}CH_4$ mixing ratio for all calibration points. $^{12}CH_4$ biases are ~3%. (*Center*) Bias of $^{13}CH_4$ response (response-target) as a function of $^{12}CH_4$ mixing ratio. (*Right*) $^{13}CH_4$ response noise (1σ) as a function of $^{12}CH_4$ mixing ratio. Each analyzer is shown as a different color.

Results

The response of $^{13}CH_4$, averaged over 10 minutes to changes in the target isotope ratio is linear, with slopes (for each analyzer) of 1.077 ± 0.002. There are no clear changes in the slope with changes in $^{12}CH_4$ mixing ratios. The offset of the $^{13}CH_4$ response to changes in target isotope ratios is 3.7 ± 0.3 ‰. The variability at a particular target $^{13}CH_4$ is ±2.7 ‰ over a range of $^{12}CH_4$ of 1.8-10 ppmv and 4 different analyzers.

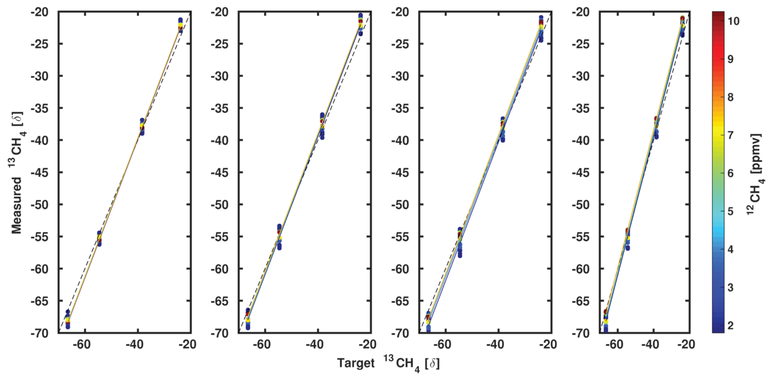

Fig 6. Response of $^{13}CH_4$ to changes in the target $^{13}CH_4$ for analyzers (*left to right*) FCDS-2046, -2047, -2048, and -2049 (dots). The measured $^{12}CH_4$ for each calibration point is indicated by its color. A linear regression was calculated for the four $^{12}CH_4$ mixing ratios sampled (colored lines). A 1:1 line is shown (dashed).

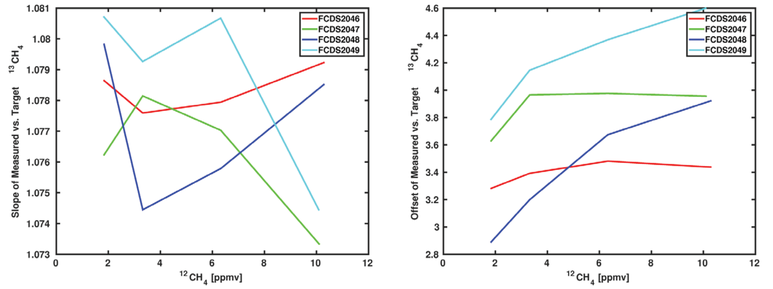

Fig 7. (*Left*) Slope of the measured $^{13}CH_4$ to the measured $^{12}CH_4$ mixing ratio for each analyzer (colors). There are no significant changes in slope with $^{12}CH_4$ mixing ratio. (*Right*) Offset of the measured $^{13}CH_4$ to the measured $^{12}CH_4$ mixing ratio for each analyzer (colors). Offsets increase with increasing $^{12}CH_4$ mixing ratio.

The calculated precision for the four CRDS analyzers range between 0.08-1.7 ‰ for 10-min averages. The precision is not a function of isotope ratio, but increases with increasing $^{12}CH_4$ mixing ratio. This calculation is conservative as it contains measurements over 3.5 months and does not account for instrument drift. If only calibrations over consecutive days are considered, the range of precision calculated is between 0.02-0.45 ‰. Instrumental drift was between -0.02 and 0.01 ‰ day^{-1}, requiring at least weekly, in-field calibrations of the instrument to achieve precisions of 0.1 ‰.

Table 1. Precision of CRDS $^{13}CH_4$ measurements for 10-min averages over 4 months.

FCDS 2046	Target Concentration [ppmv]				FCDS 2047	Target Concentration [ppmv]			
Isotope Ratio	1.83	3.31	6.13	10.22	Isotope Ratio	1.83	3.31	6.13	10.22
-23.9	0.7029	0.4304	0.1864	0.1217	-23.9	1.5232	0.8785	0.5676	0.394
-38.3	0.847	0.4008	0.1464	0.093	-38.3	1.5753	0.8798	0.6043	0.4607
-54.5	0.7533	0.4632	0.246	0.1112	-54.5	1.6603	0.902	0.5657	0.5043
-66.5	0.8774	0.4211	0.2149	0.0905	-66.5	1.3407	0.8731	0.5257	0.4975

FCDS 2048	Target Concentration [ppmv]				FCDS 2049	Target Concentration [ppmv]			
Isotope Ratio	1.83	3.31	6.13	10.22	Isotope Ratio	1.83	3.31	6.13	10.22
-23.9	1.4988	0.9887	0.5125	0.3526	-23.9	1.0635	0.7249	0.6036	0.0801
-38.3	1.4919	1.0131	0.5566	0.2897	-38.3	1.12	0.8641	0.5284	0.0615
-54.5	1.7063	1.0781	0.5803	0.4055	-54.5	1.0274	0.7252	0.6057	0.1379
-66.5	0.9552	1.1211	0.5563	0.3675	-66.5	0.9833	0.8604	0.6676	0.1118

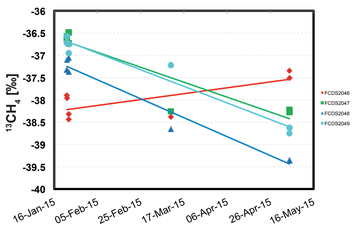

Fig 8. Example of instrumental drift while sampling the isotope ratio standard -38.3 ‰ at a target CH_4 mixing ratio of 3 ppmv for each analyzer.

Summary & Future Work

These results show that with vigilant in-field calibration of the CRDS CH_4 isotope and concentration measurements, an accuracy of 0.1 ‰ for the $^{13}CH_4$ over 10-15 minute average and ambient CH_4 concnetrations can be achieved. These methods will allow for the attribution of observed CH_4 to biogenic or thermogenic sources. These methods require the in-field calibration setup to have standards that span both high and low CH_4 mixing ratios as well as heavy and light isotope ratios. Because of this, we plan to deploy 4 such standard gases at each site. The standard tanks will be produced and characterized in-house using our compressed gas filling station and laboratory calibration setup.

Acknowledgements

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