Quantifying Methane Fluxes Simply and Accurately: The Tracer Dilution Method

Abstract

Methane is an important atmospheric constituent with a wide variety of sources, both natural and anthropogenic, including wetlands and other water bodies, permafrost, forests, landfills, and areas with significant petrochemical-extraction, drilling, transport, or processing, or refining occur. Methane is important in the carbon cycle, has significant impact as a greenhouse gas, and is ubiquitous in modern life as a source of energy. Its sources and sinks in marine and terrestrial ecosystems are only poorly understood. This is largely because high-quality, quantitative measurements of methane fluxes in these different environments have not been available, due to the lack of robust field-deployable instrumentation. In addition, most significant sources of methane extend over large areas (from 10^4 to 1,000,000 square meters) and are heterogeneous emitters – i.e., the methane is not emitted evenly over the area in question. Quantifying the total methane emissions from such a source is a tremendous challenge, compounded by the fact that atmospheric transport from emission point to detection point can be highly variable.

In this presentation we describe a robust, accurate, and easy-to-deploy technique called the tracer dilution method, in which a known gas (such as acetylene, nitrous oxide, or sulfur hexafluoride) is released in the same vicinity of the methane emissions. Measurements of methane and the tracer gas are then made downstream of the release point. This so-called far-field, where the area of methane emissions cannot be distinguished from a point source (i.e., the two gas plumes are well-mixed). In this regime, the methane emissions are given by the ratio of the two measured concentrations, multiplied by the known tracer emission rate. The challenges associated with atmospheric variability and heterogeneous methane emissions are handled automatically by the transport and deposition.

We present detailed methane flux results from four different landfills in the United States, using a commercially available Cavity Ringdown Spectroscopy (CRDS) dual-species (methane–acetylene) analyzer. This instrument, because of its high precision, mobility, and assay-time, enables quantification of the methane flux from a variety of extended area sources. The landfills studied varied widely in their size, location, topography, and physical access. Data were collected using two versions of the method: the Mobile Tracer Method, in which the tracer is released by a high flammability gas source and the methane emissions are measured downstream of the release point; and a new method called the Mid-Field Stationary Method, in which the instrument is located at a fixed location at a closer distance than the far-field, where the plume overlap is not ideal. In addition, we describe how these methods can be used to quantify methane emissions from other natural and anthropogenic extended area sources, such as wetlands.

Cavity Ring Down Spectroscopy (CRDS) – How it Works

- Light from a tunable semiconductor diode laser is directed into a small (35 cm) optical resonator cavity containing the analyte gas
- Light circulates in the cavity ~100,000 times, traveling ~30 cm or more, providing parts-per-trillion detection levels for some gases.
- The ring down time measurement is continuously repeated (~100 times per second) at several different wall-corrected points in wavelength as the laser is tuned across the molecular signature of the analyte gas.
- The ring down profiles are transformed into an absorption curve with a well defined line shape.
- The gas concentrations or isotope ratios are determined by a multi-parameter fit to this line shape and are proportional to the area under the curve.
- Picarro’s patented Wavelength Monitor controls the laser position with incredible accuracy, ensuring the measurement is independent of potentially interfering gas species.
- CRDS is a measurement of line-of-sight abundance and so offers unmatched precision and sensitivity.
- CRDS has complete immunity to laser noise since the laser is actually off during the measurement.

Picarro’s New Methane / Acetylene Analyzer (G1203)

- Acetylene has been used as a tracer for validation of the EPA OTM-10 for extended source emission measurements.
- Molecular mass 20, close to air.
- Naturally occurring concentrations rather low (~1 ppbv).
- Decomposes in atmosphere with half-life of ~13 days.
- Easily available and inexpensive.
- High-flammability.
- Other possible tracers, sulfur hexafluoride and nitrous oxide, are powerful greenhouse gases.

The Solution – The Tracer Dilution Method2,3

- Release a tracer gas (e.g., acetylene) near the extended source.
- Measuring points can be either on the far-field or on the extended source.
- The tracer location can be at the far-field (called the far-field the extended source and the tracer have identical plumes.
- Dual analyzer (methane & acetylene) monitors the target and tracer gases simultaneously.
- The relative plume profiles can be used to quantify emissions.

Fast Measurements – Simple Analysis

- Field studies were performed at three landfills in the United States (Danville, Indiana; Altamont, California; Redwood, California).

Stationary Measurements – Let the Plume Come to You

- Fixed location 130 m downstream of landfill.
- Natural variation in wind direction & wind speed causes variability in the signal as the plumes sweep across the detection point.
- High correlation between acetylene and methane indicates good overlap between plumes.

“Mid-field” analysis for when the far-field is too far

- Measurement location is closer than the far-field – the size of the methane emitter is significant compared to the distance to the measurement location.
- Correlation between methane and acetylene plumes is not perfect.
- Model first-order differences between Gaussian plumes, relative shift of plume centroid and plume width.
- Methodology allows for simple substitution of other plume shapes.