An Acetylene Tracer-Based Approach to Quantifying Methane Emissions from Distributed Sources Using Cavity Ring-Down Spectroscopy

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Abstract

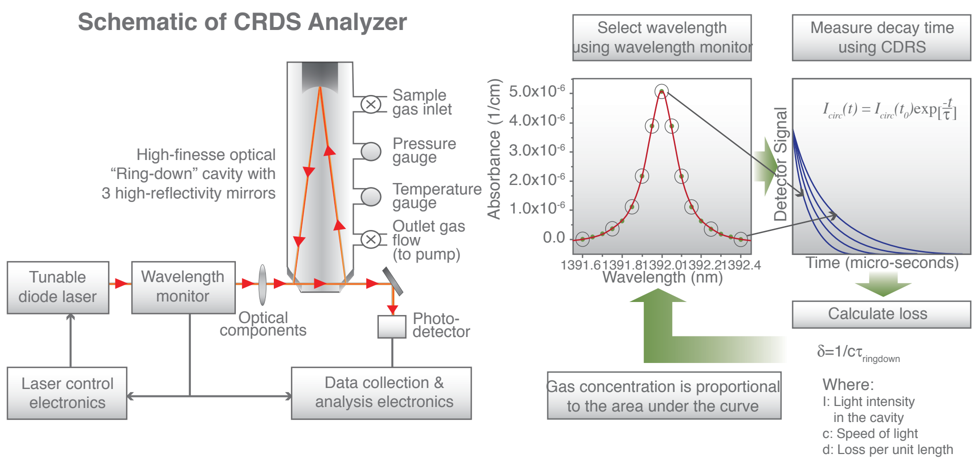
The quantification of fugitive methane emissions from extended sources such as landfills is problematic due to the high temporal variability and spatial heterogeneity of the emission. Additionally, the relationship between the emission rate and the gas concentration at a given location is dependent on the meteorological conditions and local topography, preventing accurate quantification of the emission rate.

When the total source emission is of interest, tracer methods allow quantitative measurements to be made using a single, mobile gas analyzer located in the far field of the source (i.e., at a distance that is large compared with the size of the extended source). Making measurements in the far field enables both the extended source and the tracer to be approximated as point sources. By releasing a tracer gas at a known rate at or near the center of the extended area source, the far-field measurement of the ratio of concentrations yields the ratio of emission rates, since the effects of atmospheric dispersion are the same for both species.

An ultra-sensitive, dual species gas analyzer based on cavity ring-down spectroscopy has been developed to measure the concentrations of methane and acetylene with the required sensitivity and speed. Acetylene has been selected as a tracer gas due to its low concentration in the environment and the high detection sensitivity that can be achieved.

We present field measurements of landfill methane plumes and overlapped acetylene plumes using this new instrument. Both mobile and fixed-point field data obtained with this analyzer are presented that demonstrate simplicity and robustness of the method. Both the strengths and the limitations of the acetylene tracer-based method are discussed.

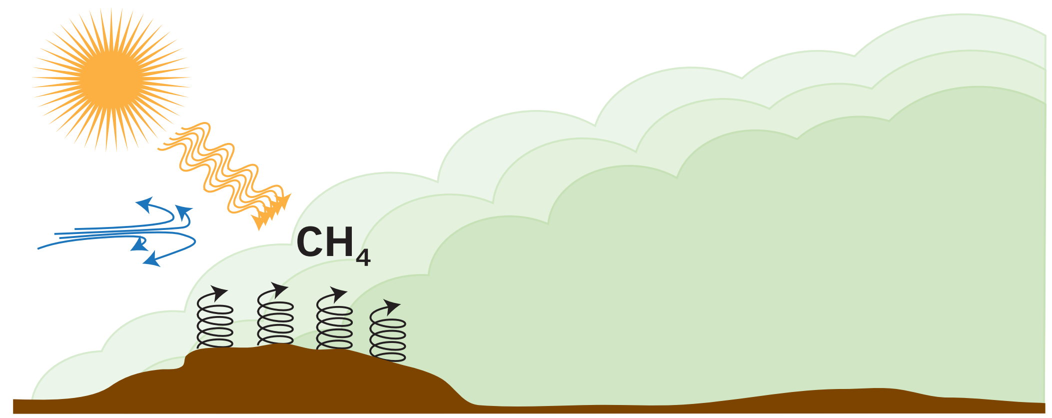
Schematic of CRDS Analyzer



Cavity Ring Down Spectroscopy (CRDS) – How it Works

- Light from a tunable semiconductor diode laser is directed into a small (35 cc) optical resonator cavity containing the analyte gas
- When the build-up is complete, the laser is shut off
- Light circulates in the cavity ~100,000 times, traveling ~20 km or more. The high precision of CRDS comes from this incredibly long pathlength providing parts-per-trillion detection levels for some gases.
- There are three partially reflective mirrors on the cavity; a small amount of light leaks out from the third mirror. A photodetector is positioned behind this mirror, measuring the light intensity
- The energy decays from the cavity, through loss mechanisms, exponentially in time. This energy decay is measured, as a function of time, on the photodetector – and is known as a "ringdown"
- In an empty cavity, the only loss mechanisms are the mirrors and the ring-down time (the exponential decay time) is long
- When gas is present, the rotational vibrational modes provide additional loss mechanisms and the ring-down times get shorter, in proportion to gas concentration
- The ring down time measurement is continuously repeated (~100 times per second) at several different well-controlled 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 lineshape
- The gas concentrations or isotope ratios are determined by a multi-parameter fit to this lineshape (red curve) 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 time not of absorbance and so offers unmatched precision
- CRDS has complete immunity to laser noise since the laser is actually off during the measurement, thereby offering significantly better sensitivity than other laser techniques

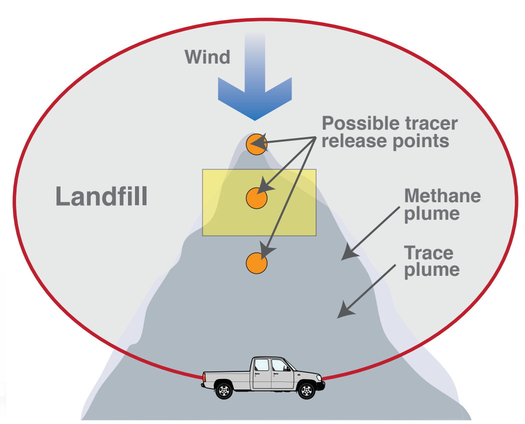
The Challenge – Quantifying Emissions from Extended Area Sources



Extended area sources present a major challenge for emissions quantification. Consider, for example, the challenge of measuring methane emissions from landfills. Landfills account for a substantial fraction (~30%) of anthropogenic methane emissions in the United States. Landfills are large (~ 1 sq. km) areas with variable emissions over the area.

While it is straightforward to measure the methane concentration on or around the landfill, calculating the total emissions is incredibly difficult, due to both the high variability in emissions from point-to-point on the landfill and the large uncertainty in atmospheric transport from the emissions points to the measurement points.

The Solution – The Tracer Dilution Method[1,2,3]



Experimental Recipe

- Release a tracer gas (e.g., acetylene) "near" the extended source
- Tracer locations can be outside the fence line
- At km distance (called the far field), the extended source and the tracer gas have identical plumes
- Dual analyzer (methane & acetylene) monitors the target and tracer gases simultaneously
- The relative plume profiles can be used to quantify emissions

$$\frac{Q_{target}}{Q_{tracer}} = \frac{C_{target} - C_{target,\ background}}{C_{tracer} - C_{tracer,\ background}}$$

Acetylene as a tracer

Acetylene has been used as a tracer for validation of the EPA OTM-10 for extended source emission measurements.

- ☑ Molecular mass 26, close to air.
- ☑ Naturally-occurring concentrations rather low (~1 ppbv).
- ☑ Decomposes in atmosphere with half-life of ~13 days.
- ☑ Readily available and inexpensive.
- ☑ Strong absorption bands in near infrared band
- ☒ High flammability

Other possible tracers, sulfur hexafluoride and nitrous oxide, are powerful greenhouse gases!

[1]Scheutz, C., Samuelsson, J., Fredenslund, A.M., Kjeldsen, P., *Methane emission quantification from landfills using a double tracer approach*, Proceedings Sardinia 2007, Eleventh International Waste Management and Landfill Symposium, CISA publisher, Cagliari, 2007.

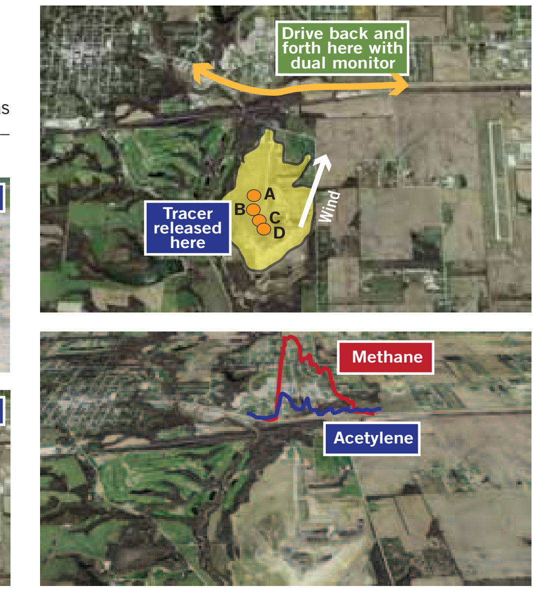
[2]Borjesson, G., Samuelsson, J., Chanton, J., Adolfsson, R., Galle, B., and Svensson, B., *A national landfill methane budget for Sweden based on field measurements, and an evaluation of IPCC models*, Tellus, 61B, 424-435 (2009).

[3]Czepiel, P., Mosher, B., Harriss, R., Shorter, J., McManus, J., Kolb, C., Allwine, E., and Lamb, B., *Landfill methane emissions measured by enclosure and atmospheric tracer methods*, J. Geophys. Rsch., V101, D11, 16,711 – 16719, 1996.

Remote Emission Detection and Quantification (REDAQ)
Area Source remote monitoring with Tracer Dilution Ratio
EPA Sponsored Project
In conjunction with Eastern Research Group and Waste Management

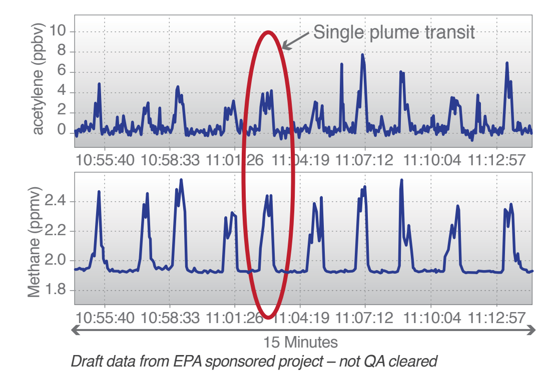
Field Study Using Picarro's New Methane / Acetylene Analyzer

A typical mid-western landfill in Danville, Indiana, was studied in summer, 2009. Transects of the dual methane – acetylene plumes were made on a nearby highway

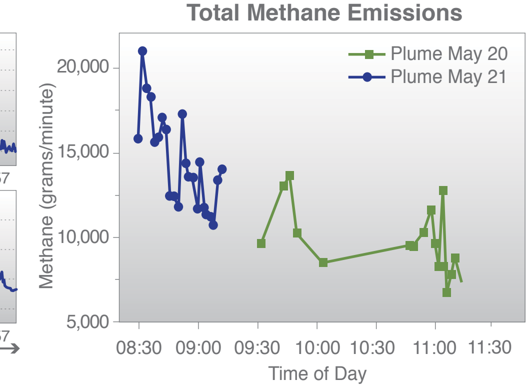


Fast Measurements – Simple Analysis

- Fast, quantitative, real-time emission data in just minutes
- Simple results: peak area ratio gives the landfill emission rate
- Repeated measurements allows measurements of landfill emissions over time

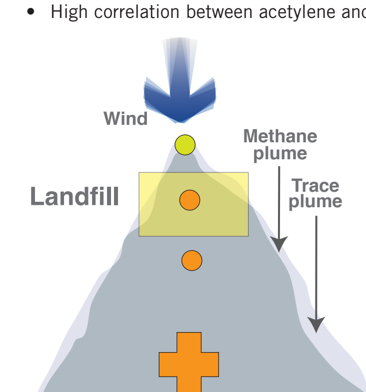


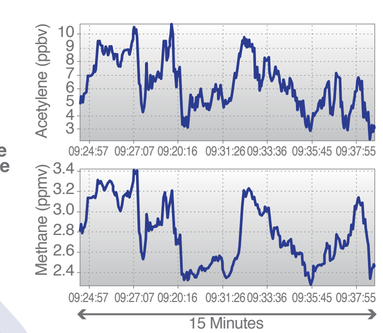
Total Methane Emissions

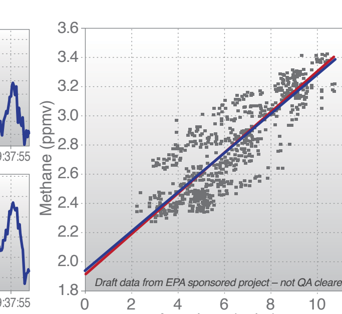


Stationary Measurements – Let the Plume Come to You

- Fixed location 1300 m downwind 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







Type of linear regression	Slope of the line	Total Methane Emissions
Constrained	0.138.1	7,207 g / min
Not constrained	134.9	7,040 g / min