Application of Cavity-Ring-Down-Spectroscopy to Measure Local and Regional Methane Fugitive Emissions

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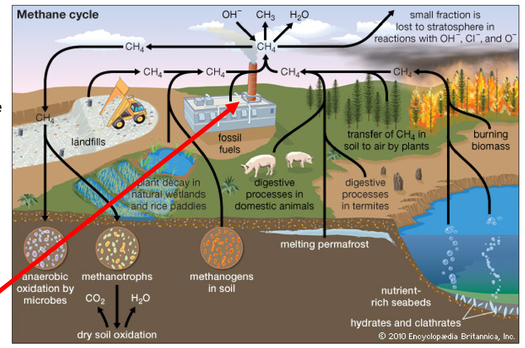
Introduction

Abstract

Rising concerns about the direct and indirect role of fugitive emissions on Earth's climate and their contributions to Carbon/Methane cycles has led to the need for improved and expanded measurement capabilities of critical greenhouse gases in the atmosphere. In this work, a high precision Cavity-Ring-Down Spectroscopic Technique (CRDS) is used to simultaneously and continuous measure carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), and water vapor (H_2O) in ambient air. High accuracy of the measurements is established by reference to calibration using standard reference gases. The precision and accuracy of the analyzer meet and exceed the compatibility targets set by the World Meteorological Organization–Global Atmosphere Watch for baseline measurements in the unpolluted troposphere for CO_2, CO, and CH_4 in the Northern Hemisphere. Preliminary results of indoor and outside ambient air measurements at Tennessee Tech University are presented as a testbed for deploying the CRDS analyzer in the field to detect and measure CH_4 fugitive emissions in various locations within Putnam County.

Methane cycle

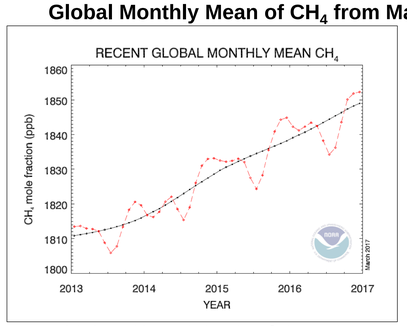
- The methane cycle is the biogeochemical cycles where methane is exchanged among the biosphere, geosphere, hydrosphere, and atmosphere of the Earth.



Fugitive emissions

Figure 1: Methane Cycle[1], showing the various type of sources and sinks of Methane. The red arrow shows where the fugitive emissions are expected

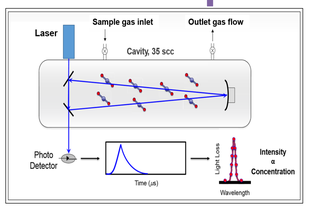
Global Monthly Mean of CH_4 from Mauna Loa Site, Hawaii



- Rising Methane levels in the past two years, with
- The red line and diamonds are globally averaged monthly mean values centered on the middle of each month.
- The black line and squares show the long-term trend.

Figure 2: Global monthly trend of Methane[2], time-series starting in 2013. These monthly mean atmospheric methane abundance determined from different marine surface sites.

Experimental set-up



- Laser based technique that can measure different gases in atmosphere.
- Very small amount of sample size is needed for the analysis.
- Three mirror cavity with a long path length of approximately 20 km, increases the sensitivity of the instrument.

Figure 3: Instrumentation and basic technique of CRDS. Intensity of the light loss of the laser proportional to the concentration of the gaseous species

- In CRDS, the beam from a single frequency laser enters a cavity defined by three high reflectivity mirrors.
- Since the mirrors have slightly less than 100% reflectivity (99.999%), the light intensity inside the cavity steadily leaks out and decays to zero.

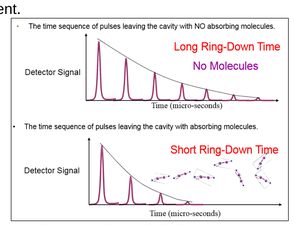


Figure 4: Ring-down profiles of CRDS[3]. Ring-down profile shows the time which is taken to decay the laser inside the cavity. When there is a laser absorbing species inside the cavity, the ring down time decreases.

Results and Discussion

Calibration : Precise and accurate calibrations with factory calibration standards reveals the correct isotopic composition of the mixtures.

Table 1: Main Isotopes and their abundance of CO_2, CH_4 and CO

Species	Isotopes	Composition	Precise mole fraction reported by CRDS(ppm)	As gas Concentration(ppm)
CH_4	$^{12}CH_4$	0.988274	4.9500 ± 0.0003	5.0340 ± 0.0003
	$^{13}CH_4$	0.011103		
	$^{12}CH_3D$	6.157510×10^{-4}		
CO_2	$^{12}C^{16}O_2$	0.984204	246.85 ± 0.01	257.50 ± 0.01
	$^{13}C^{16}O_2$	0.011057		
	$^{16}O^{12}C^{18}O$	0.003947		
CO	$^{12}C^{16}O$	0.986544	14.740 ± 0.001	14.560 ± 0.001
	$^{13}C^{16}O$	0.011084		
	$^{12}C^{18}O$	0.001978		

Reference: Hitran database

Table 2: Concentrations of CH_4 standards given by the CRDS analyzer and factory(after subtracting isotopes)

Concentrations CRDS (ppm) given by CRDS (ppm)					Concentrations given by factory (ppm)	Comments
09/12/2016	09/21/2016	01/11/2017	02/08/2017	02/11/2017		
4.9500	4.9500	4.9600	4.9500	4.9500	4.9414	CRDS measures only $^{12}CH_4$ isotope
9.7500	9.7500	9.7500	9.7500	9.7500	9.7740	CRDS measures only $12CH_4$ isotope
14.5500	14.5600	14.5600	14.5600	14.5600	14.5671	CRDS measures only $12CH_4$ isotope
0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	CRDS measures only $^{12}CH_4$ isotope

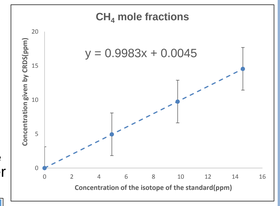


Figure 5: Concentrations of the main isotope of the standard vs concentrations given by CRDS. CRDS analyzer measures the $^{12}CH_4$ line at 6057.1 cm^{-1}.

Main Isotopes of CH_4 ($^{12}CH_4$ and $^{13}CH_4$)

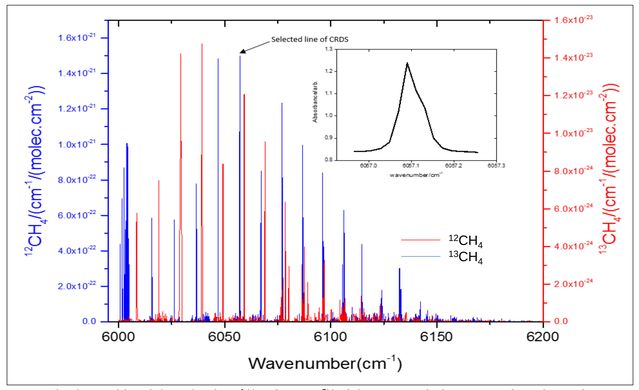


Figure 6: The intensities (given by (cm^{-1}/(molec.cm^{-2}))of the two main isotopes of Methane from 6000 cm^{-1} to 6400 cm^{-1}. Inset of the figure shows the line profile showing a single line of the second overtone spectra observed by CRDS analyzer for 1.9000 ppm CH_4.

Atmospheric simulations of CO, CO_2, CH_4 and H_2O at 140 torr, 20 km path length and 0.03 cm^{-1} instrumental resolution

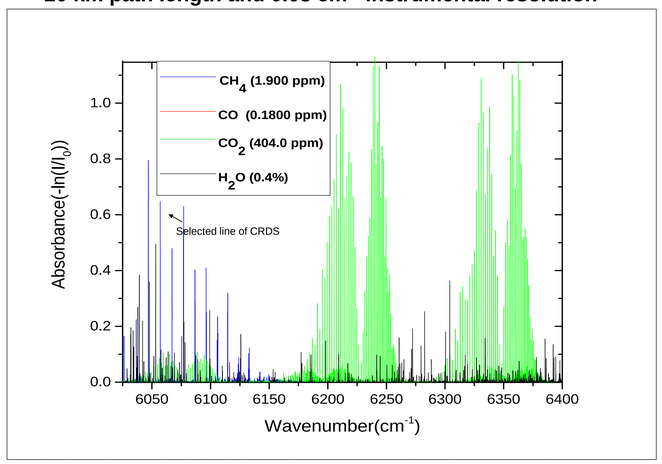


Figure 7: A horizontal Atmospheric simulations of CO, CO_2, CH_4 and H_2O from 6000 cm^{-1} to 6400 cm^{-1}. CO peaks are almost invisible in the graph due to lack of absorbance and the concentrations of CO in the air.

24 hours continuous measurements of ambient air using CRDS (Latitude: 36.1782, Longitude: -85.5069, football field at a height of 50 m)

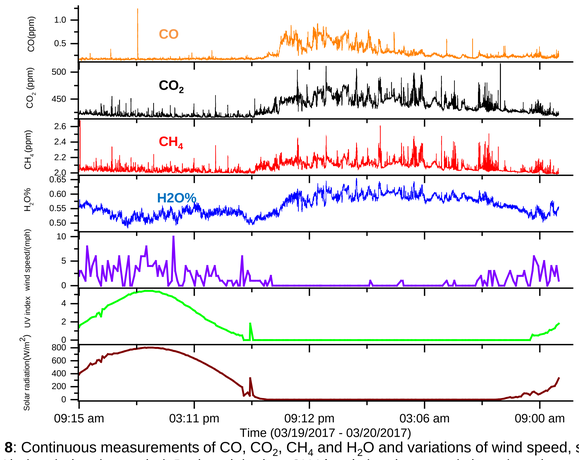
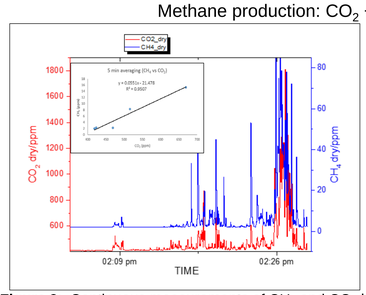


Figure 8: Continuous measurements of CO, CO_2, CH_4 and H_2O and variations of wind speed, solar radiation and UV index during that period. During night time CH4 levels has increased since there is no wind speed to mix the gases in the atmosphere.

Application1: Measurements of Methane emissions from enteric Fermentation in Ruminants

Methane production: $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$



- Information of methane emissions is rare due to difficulties associated with measurements.
- CRDS has moved a step further to measure this CH_4 emissions from livestock by using CH_4/CO_2 ratio at Hyder Burk farm pavilion.
- The ratio of CH_4/CO_2 is 0.0551 with the R^2 value of 0.9507 in 5 minutes sampling intervals.

Figure 9: Continuous measurements of CH_4 and CO_2 levels at Hyder Burk farm on 03/23/2017. Inset shows the 5 minutes averaging of CH_4 vs CO_2 concentrations.

Conclusion and future directions

Fugitive emissions

- Fugitive emissions are the sum of emissions from accidental discharges, equipment leaks, filling losses and etc.
- Solid fuels and oil/natural gas systems are the main sources of fugitive emissions.
- Poor quality and incomplete data about fugitive emissions on solid fuels
- Data on equipment leaks are often unavailable.
- CRDS technique can be applied to monitor fugitive emissions due to the very precise measurements.

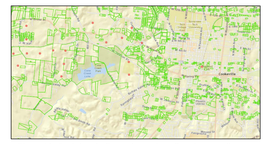


Figure10: Red dots indicate the active oil and gas wells near Cookeville as give by the Tennessee Department of Energy.

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