A Study of Diurnal and Seasonal Variations of Carbon Dioxide and Methane in the Eastern Highland Rim Region of Tennessee

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Introduction

Located on the eastern side of the geographically diverse Highland Rim in Tennessee, the city of Cookeville (36.1628° N, 85.5016° W) has a slightly higher elevation than the surrounding major towns of Nashville and Knoxville, presenting an ideal location for ground-based atmospheric measurements of carbon dioxide (CO_2) and methane (CH_4). In this study measurements of CO_2 and CH_4 are made using a Picarro Cavity ring-down spectrometer to understand the local and regional methane and carbon cycle within the Eastern Highland Rim region, using Cookeville as a an example. Beginning the summer of 2016 through May 2017, measurements of CO_2 and CH_4 revealed a remarkable seasonal and diurnal variation. In a period of one week during the summer of 2016, the respective atmospheric dry molar fractions of CO_2 and CH_4 as measured by the CRDS analyzer were: 400.85 ± 1.67 ppm and 1.908 ± 0.030 ppb. An increase in the dry mole fractions of the two greenhouse gases was observed during the winter of 2017 where 414.29 ± 1.68 ppm and 2.049 ± 0.026 ppm of CO_2 and CH_4 were recorded in January 2017, respectively.

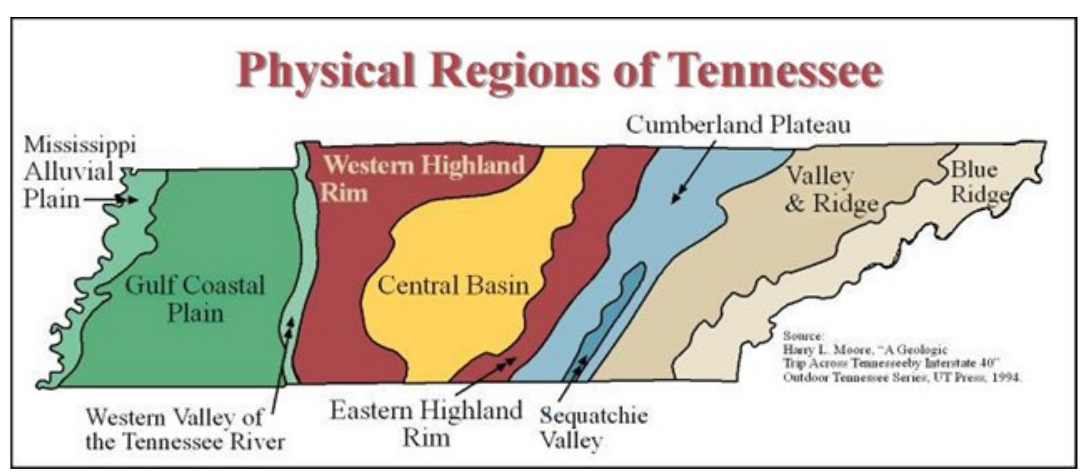

Figure 1: Physical Regions of the state of Tennessee, showing the location of the Eastern Highland Rim where Cookeville lies.

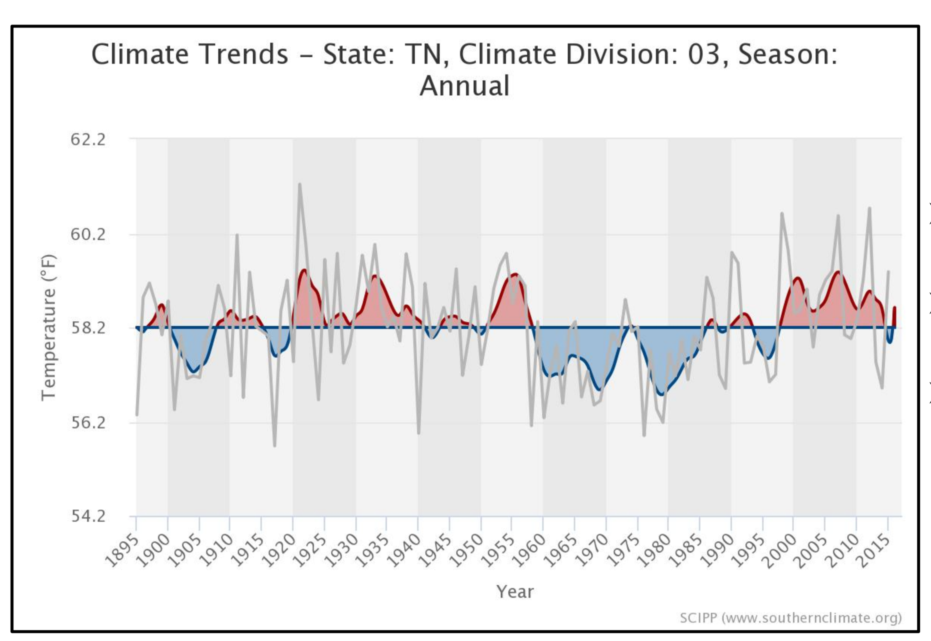

Figure 2: Historical Climate Trends showing annual rainfall and temperature trends in middle Tennessee.[3]

- Red curve indicates a warmer period than the historical average.
- Blue curve is a period that is cooler than the historical average.
- Future temperature rise depends partly on the amount of greenhouse gasses added to the atmosphere. Global temperatures are expected to increase another 3-12 degrees Fahrenheit by 2100 (IPCC).

Experimental Setup and Methods

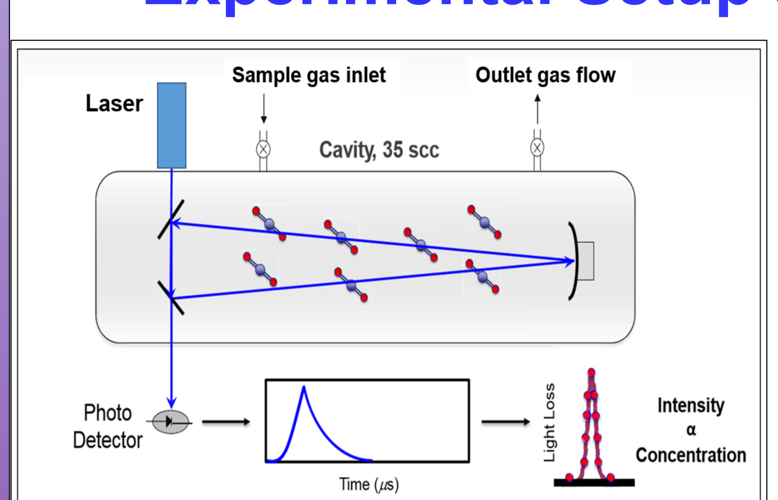

Figure 3: Schematic of CRDS Analyzer

- Light from a tunable distributed feedback laser (DFL) is directed into a 35 cc optical cavity containing the analyte gas of interest.
- IR laser light circulates in the cavity many times, resulting in a pathlength of 20 km or more.
- A photodetector positioned behind this mirror measures the light intensity at each pass, resulting in exponential energy decays from the cavity.
- This energy decay is measured, as a function of time, on the photodetector and is known as a "ringdown."

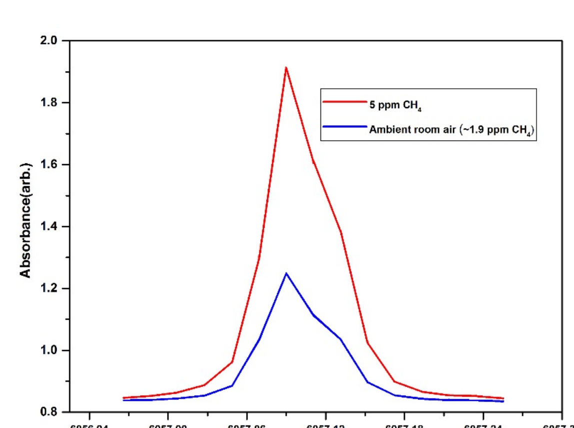

Figure 4: Cavity ringdown line shapes of ambient room air and $^{12}CH_4$ in the overtone region where the IR line intensities are very weak.

- The ringdown time measurements are repeated continuously at well-controlled wavelength points as the laser is tuned across the molecular signature of the analyte gas generating ringdown profiles.
- The ringdown profiles are transformed into an absorption curve with a well defined line-shape.

Results and Discussion

G2401 CRDS only measures $^{12}C_{CO2}$ and $^{12}C_{CH4}$ peaks

Table I: CRDS Calibration Data

Gas	Actual concentration by the Air gas (ppm)	Average concentrations by CRDS over a period of 9 months
CH_4	5.034 ± 1%	4.956 ± 0.003
	9.887 ± 1%	9.748 ± 0.002
	14.74 ± 1%	14.560 ±0.007
CO_2	257.5 ± 1%	246.900 ± 0.007
	406.5 ± 1%	395.300 ± 0.010
	500.1 ± 1%	488.900 ± 0.010
CO	1.807 ± 1%	1.971 ± 0.001
	9.898 ± 1%	9.710 ± 0.002
	20.00 ± 1%	19.320 ± 0.007

Table 2: Percentage composition of the main CO_2 isotopes from HITRAN[2]

Isotope	Abundance
$^{12}C^{16}O_2$	0.984204
$^{13}C^{16}O_2$	0.011057
$^{16}O^{12}C^{18}O$	0.003947

Table 3: Percentage composition of the main CH_4 isotopes from HITRAN

isotope	Abundance
$^{12}CH_4$	0.988274
$^{13}CH_4$	0.011103
$^{12}CH_3D$	0.000616

- The G2401 Picarro CRDS measures the main $^{12}C^{16}O_2$ and $^{12}CH_4$ isotope, which is consistent with the calibration data. No significant drift has been observed in the last 10 months.

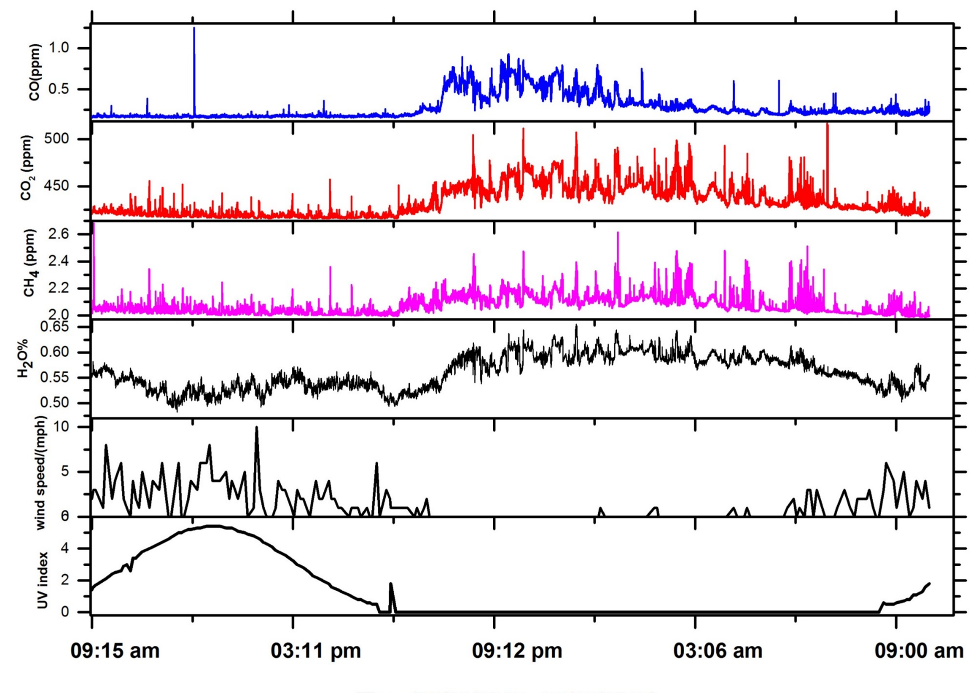

Figure 5: Typical diurnal variations of hourly mixing ratios for CO, CO_2, CH_4, and H_2O observed on the 19th and 20th days of March 2017. The corresponding wind speed variation[3] and solar index[3] are also shown in the lower panels.

- Diurnal pattern for CO_2, CH_4, and CO mixing ratios shows a similar trend.
- Gradual increase at night as compared to day time.
- Local polluting emissions associated with heating of homes during winter and vehicle emissions during traffic.

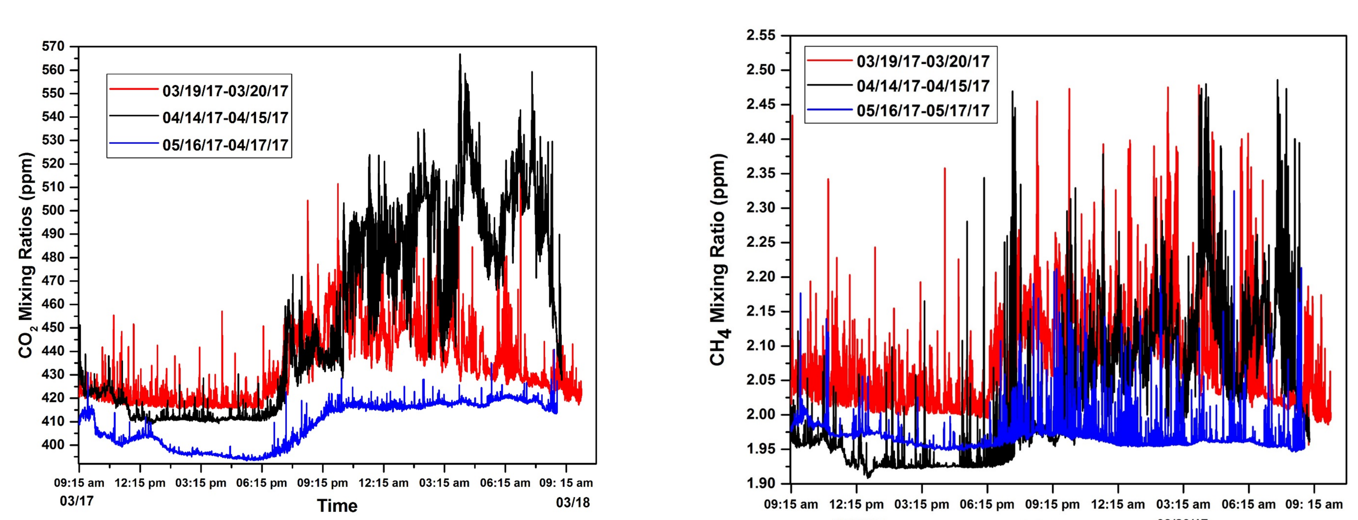

Figure 6: Typical diurnal variations of hourly mixing ratios for CO_2 and CH_4 as observed on March, April, and May 2017. Although a similar trend in elevated levels during the night time is observed, there is a reduction in the atmospheric mixing ratios of the two gases from March to May 2017.

- Diurnal variation similar for the month of March through May.
- Mixing ratios more representative of local ground background levels in the Cookeville region.
- Decrease in CO_2 levels due to the large uptake of CO_2 by the forests as the winter period ends.

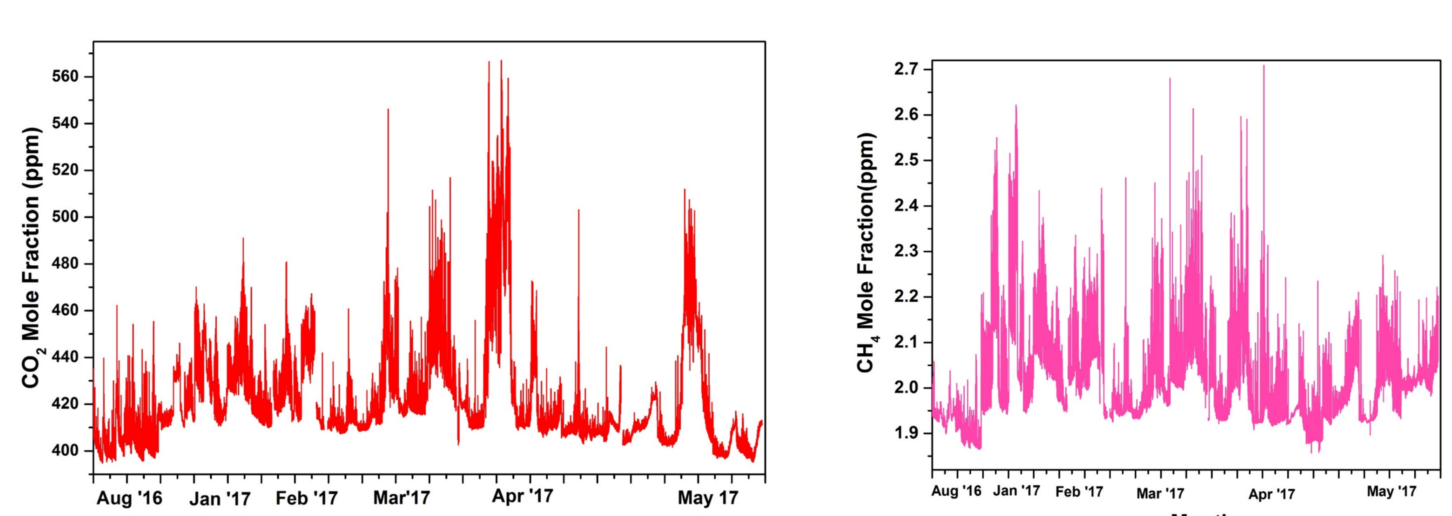

Figure 7: Monthly variations of CO_2 (left) and CH_4 (right) and mixing ratios from Summer 2016 to May 2017.

- Analyzer directly records data after every 5 seconds from the top of a football field, which is ~ 45 m above ground.
- Lowest observed value for CO_2 is 394.83 ppm in Aug '16.
- For CH_4, the minimum value of 1865.2 ppb was measured in May 2017.

Table 4: Summary of monthly average CO_2 mixing ratios observed in Cookeville, Tennessee

Month, Year	Mean (ppm)	Min. (ppm)	Max. (ppm)
Aug. '16	403.02 ± 5.31	394.83	462.21
Jan. '17	425.46 ± 12.37	409.000	491.00
Feb. '17	432.56 ± 12.93	412.45	480.82
Mar. '17	423.05 ± 15.33	407.33	546.15
Apr '17	424.38 ± 28.85	402.53	566.94
May '17	411.64 ± 18.31	393.32	511.85

- Monthly average mixing ratios of CO_2 higher than the levels observed at Observatory sites like Mauna Loa.
- Major CO_2 and CH_4 sources expected to be from vehicle, industries and residential emissions.
- Decreased vegetation during winter reduces major CO_2 sink.
- Spikes and maximum levels are usually associated with vehicle emissions due to the nature of the monitoring site.

Table 5: Summary of monthly average CH_4 mixing ratios observed in Cookeville, Tennessee

Month, Year	Mean (ppb)	Minimum (ppb)	Maximum (ppb)
Aug. '16	1917.3 ± 30.6	1865.2	2073.2
Jan. '17	2074.8 ± 11.8	1941.1	2621.8
Feb. '17	2076.02 ± 57.3	1976.2	2335.5
Mar. '17	2012.79 ± 74.5	1925.2	2680.2
Apr. '17	1966.08 ± 75.9	1857.4	2709.1
May '17	1987.11 ± 46.85	1880.4	2324.9

- Monthly average mixing ratios of CH_4 higher than the levels observed at Observatory sites like Mauna Loa.
- CH_4 concentrations rising faster than at any time in the past two decades since 2014.
- A likely major driver of the recent rapid rise in global CH_4 concentrations is increased biogenic emissions mostly from agriculture.
- Ground based measurements at the local-scale needed to understand uncertainties in CH_4 fluxes.

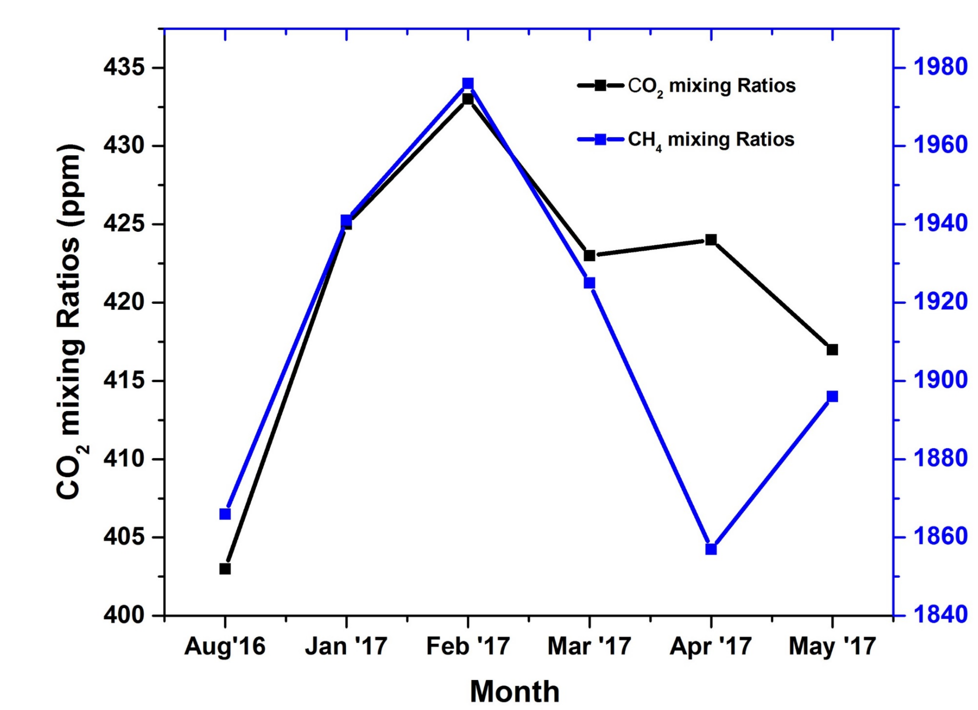

Figure 8: A plot of average monthly variations of CO_2 (left) and CH_4 (right) August 2016 to May 2017 observed in Cookeville, Tennessee

- Local emission sources more pronounced in the winter than in the summer months
- No obvious effect of wind speed and direction on the hourly, daily and monthly levels
- Generally, the day time averages are always lower than the night time for any given season
- Methane emissions from a local dairy farm suggests minimum contribution from dairy and beef farming in Cookeville region

Conclusions

- A Picarro G2401 cavity ring down spectrometer used to measure atmospheric concentrations of CO_2, CH_4, H_2O, and CO in a small urban site setting in Cookeville
- Measurements reveal a diurnal and seasonal pattern of CO_2 and CH_4
- Monthly averages higher than the concentrations at the background sites such as the Mauna Loa, USA, implying significant potential local emission sources in this region. Such sources include residential and vehicle emissions

References

1) http://www.southernclimate.org/pages/data-tools: Temperature trends for the period 1895 to Present retrieved from NOAA Southern Regional Climate Center (SRCC)

2) http://hitran.org/.High-resolution *tran*smission molecular absorption database

3) https://www.wunderground.com/personal-weather-tation/dashboard?ID=KTNCOOKE16 Tennessee Tech Millard Oakley STEM center weather station.

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