Estimation of Urban Biospheric and Anthropogenic CO_2 Atmospheric Signals Using CO Tracer Technique.

Wilson K. Gichuhi and Lahiru P. Gamage
Tennessee Technological University
1 William L Jones Dr, Cookeville, TN 38505
Cookeville, Tennessee, USA

The 3rd International Electronic Conference on Atmospheric Sciences
16/11/2020 - 30/11/2020

Corresponding author email: wgichuhi@tntech.edu

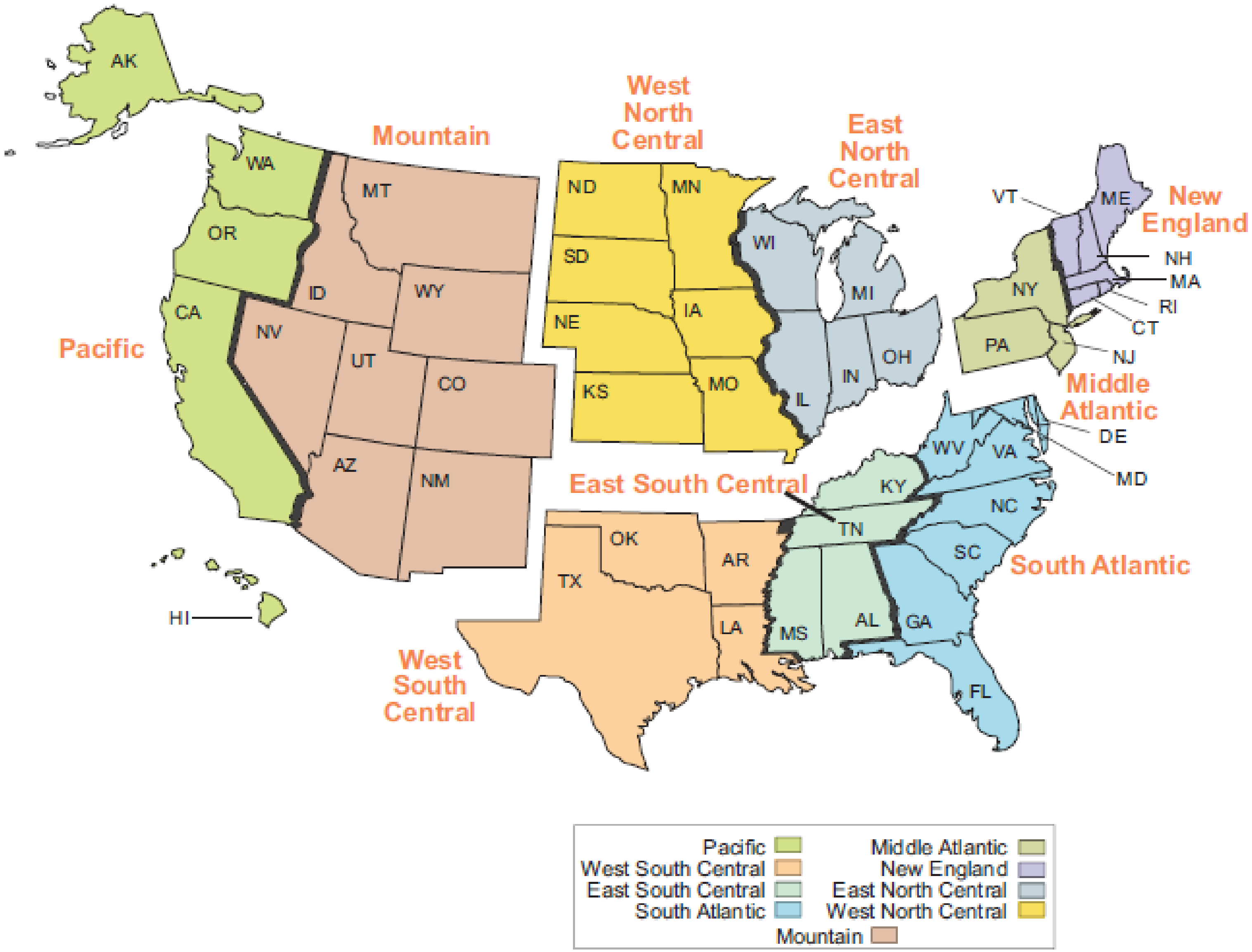
$CO:CO_2$ Ratio Technique: Brief Review and Comparison with other Tracer Techniques

- Oxygen isotope ratio ($\delta^{18}O$): Can distinguish between biogenic and anthropogenic CO_2 based on the fact that evaporative enrichment of $H_2{}^{18}O$ in plants and soils imparts a unique signature to evolved CO_2 in respiration. This require intensive modelling of evaporative enrichment and CO_2 equilibration

- Radiocarbon (^{14}C) isotopic tracer technique: Based on the fact that fossil fuel combustion releases CO_2 with no ^{14}C since the half-life of ^{14}C is much shorter than the age of fossil fuels. The technique is expensive

- In addition to cost effectiveness, the CO tracer technique is based on the fact that local excess biogenic sources of CO are negligible in the urban environment. The technique provides continuous diurnal and seasonal Information on urban CO_2 sources that are useful in deciphering seasonal patterns of energy use and respiratory fluxes

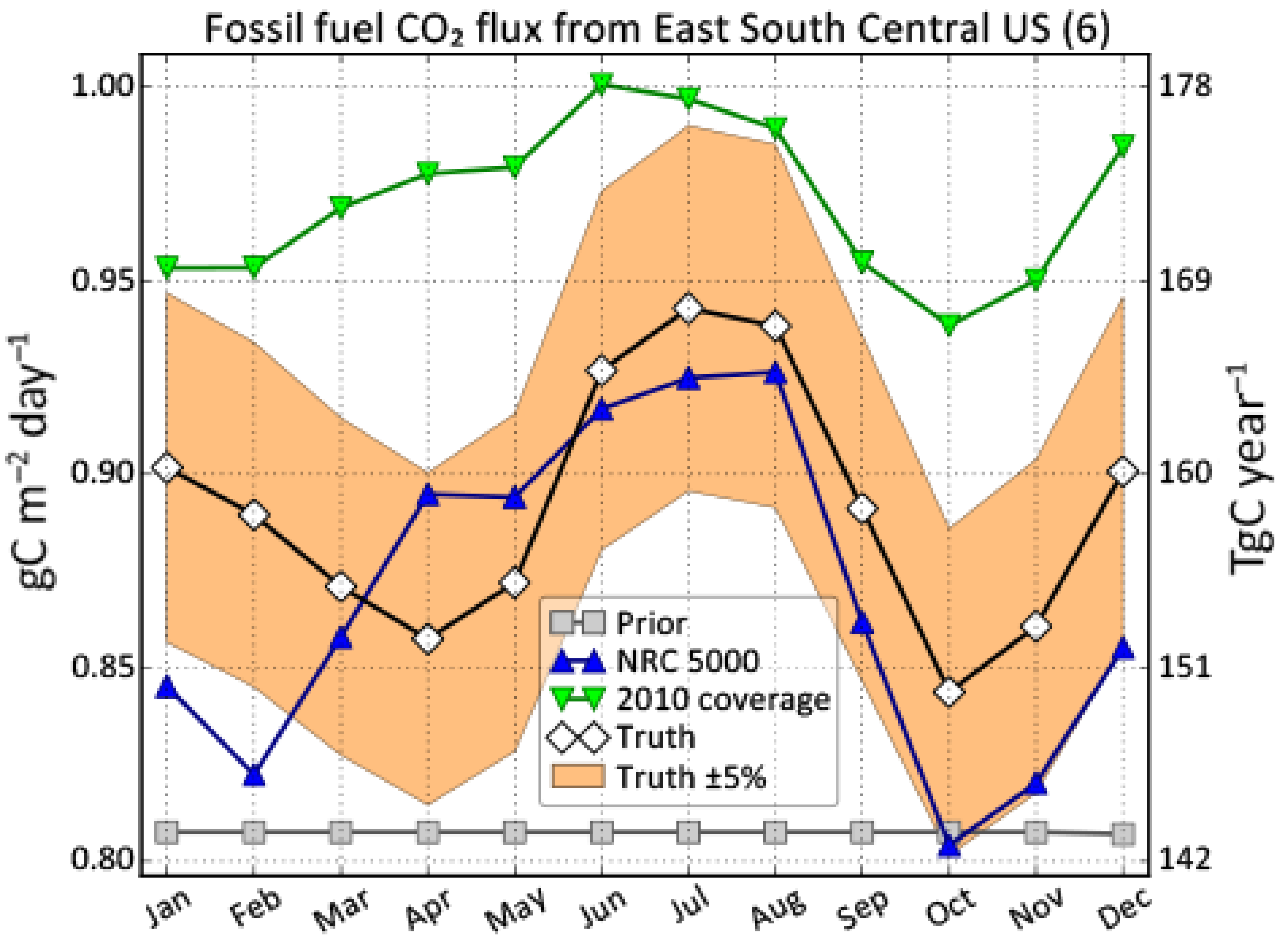
Review Fossil Fuel CO_2 Flux Estimates in the United States



- Nine regions defined by the US Census Division, over which fossil fuel CO_2 flux estimates are aggravated
- We focus son East South Central Region where our measurements are made

Basu et al., Atmos. Chem. Phys., 16, 5665–5683, 2016

East South Central USA Region Fossil Fuel Fluxes: Previous Work



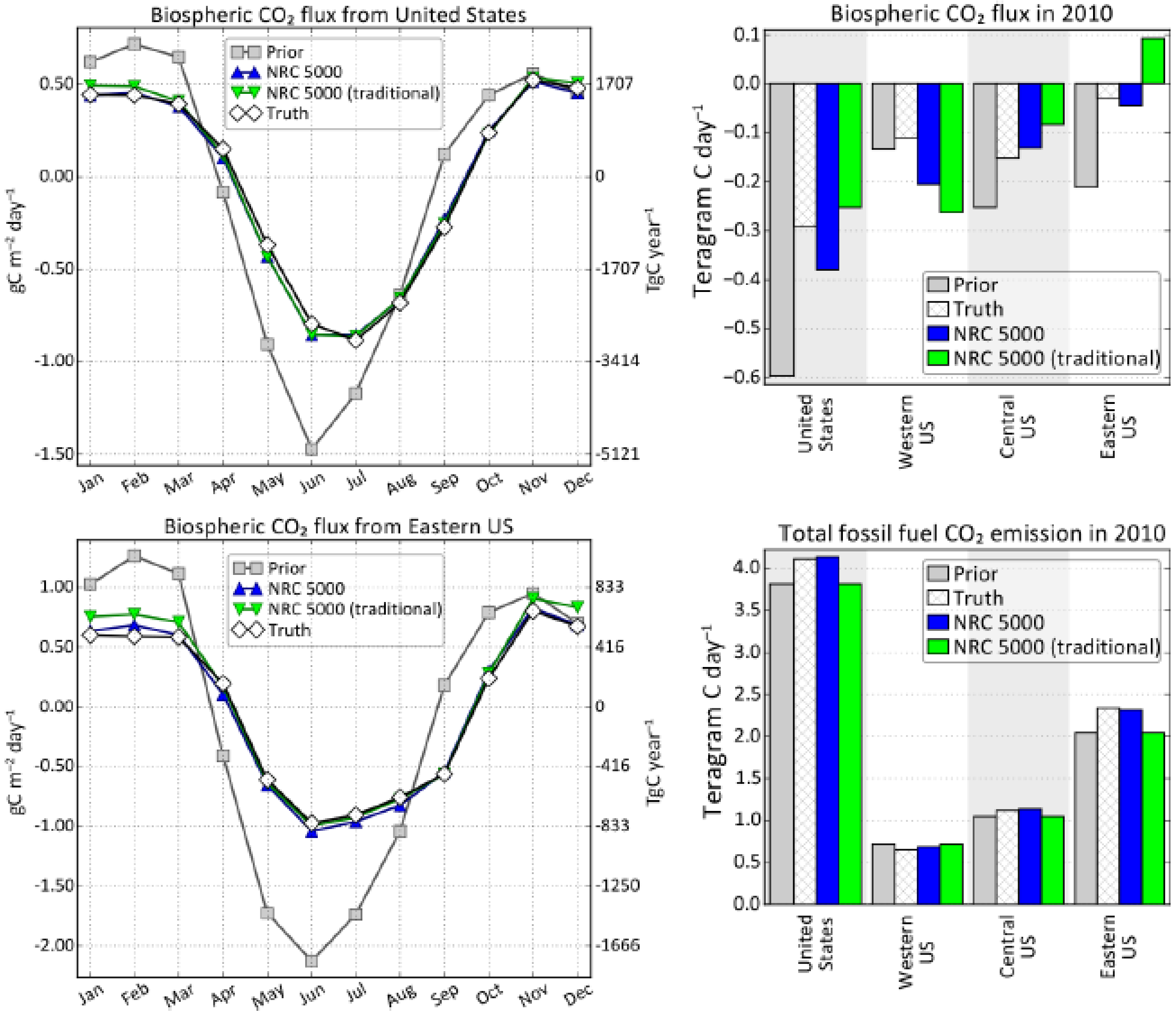
- Observation System Simulation Experiments (OSSEs)
- Evaluated the ability of the dual tracer inversion framework to separately estimate fluxes over the conterminous US using synthetic observations corresponding in space and time to:

(a) actual observations in the NOAA ESRL Global Greenhouse Gas Reference Network

(b) An enhanced observational network with $^{14}CO_2$ measurements

Basu et al., Atmos. Chem. Phys., 16, 5665–5683, 2016

Biospheric Fluxes over the USA and the Eastern Region: Previous Work

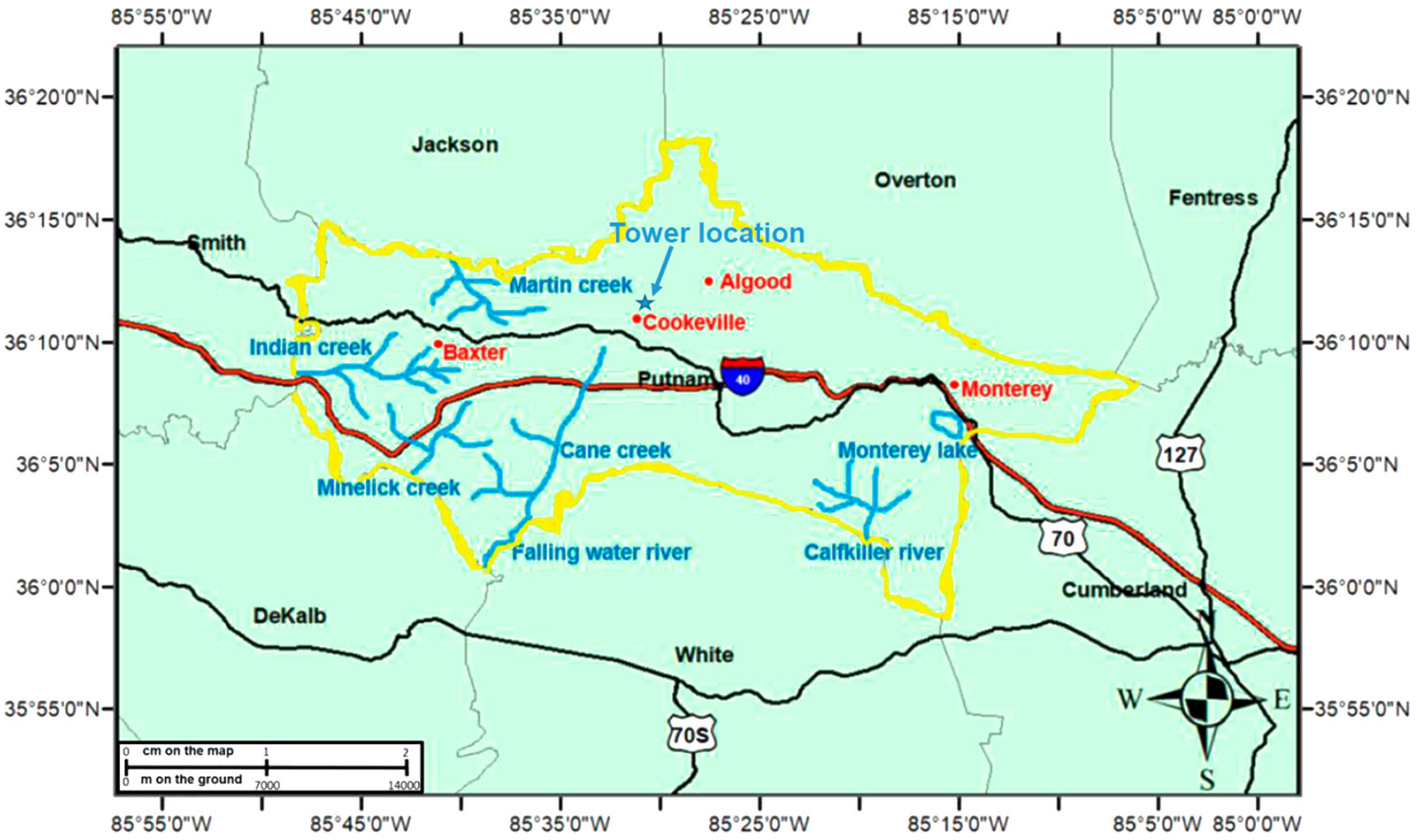


Monthly net biospheric CO_2 flux estimates for the NRC 5000 network scenario with and without $^{14}CO_2$ observations along with prior and true fluxes aggregated for the conterminous and eastern US

- NRC 5000 (traditional) inversion model: does not optimize fossil fuel fluxes and does not assimilate $^{14}CO_2$ observations.
- For both the inversions above, large numbers of CO_2 observations in the NRC 5000 scenario drive the biosphere flux estimates toward true fluxes
- Adding $^{14}CO_2$ helps to address carry-over bias arising from erroneous specification of the fossil fuel prior.

Basu et al., Atmos. Chem. Phys., 16, 5665–5683, 2016

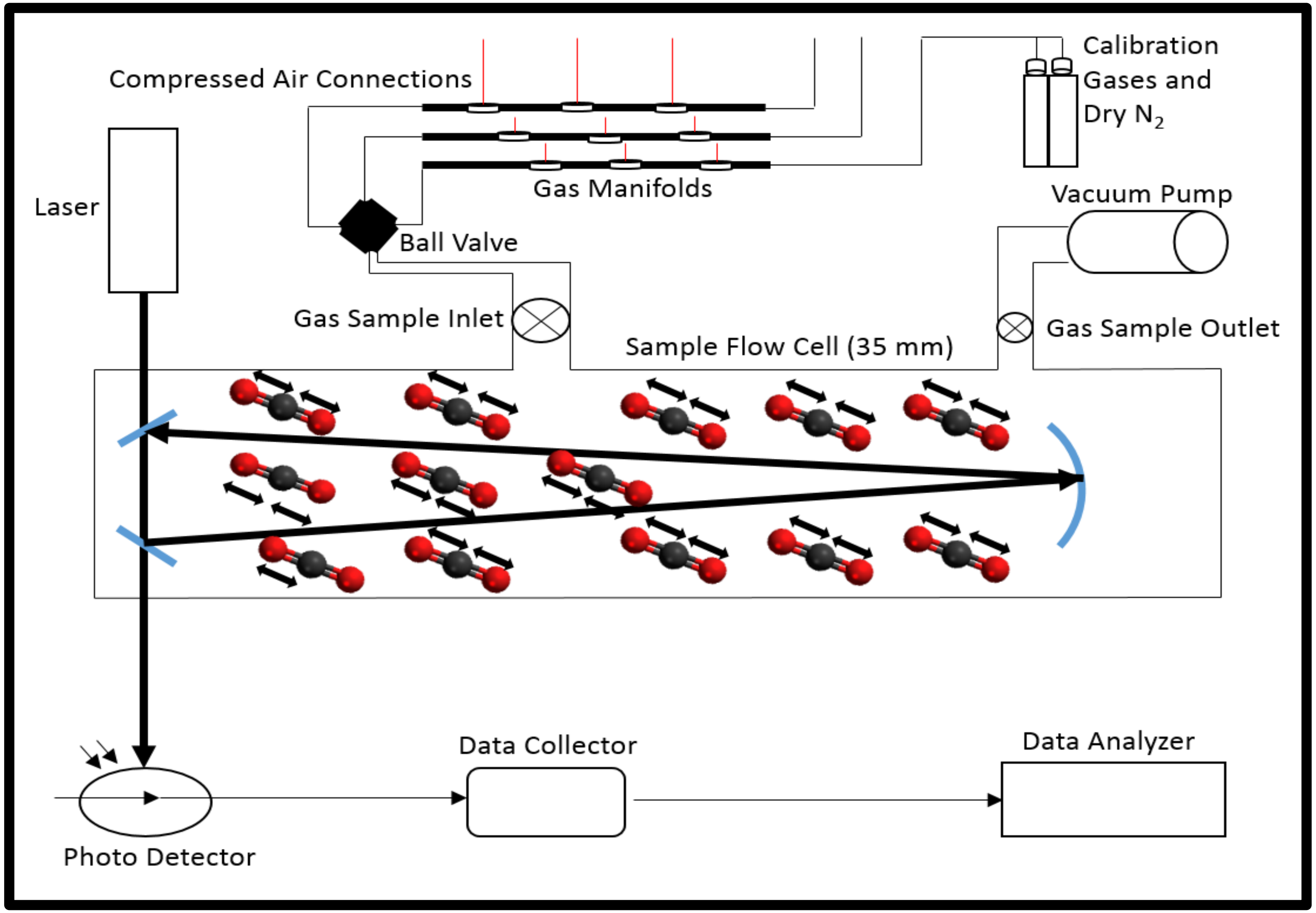
Study Site: Eastern Highland Rim region of the United States

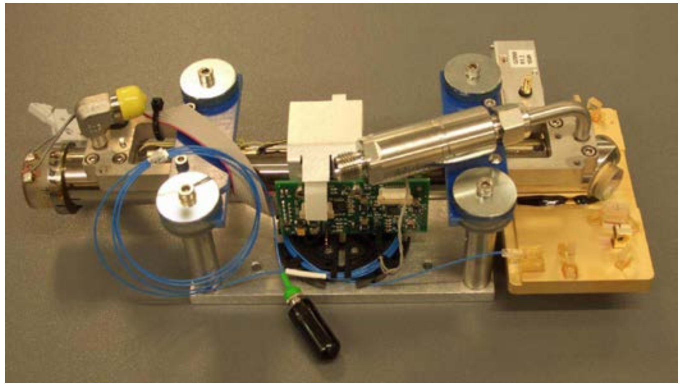


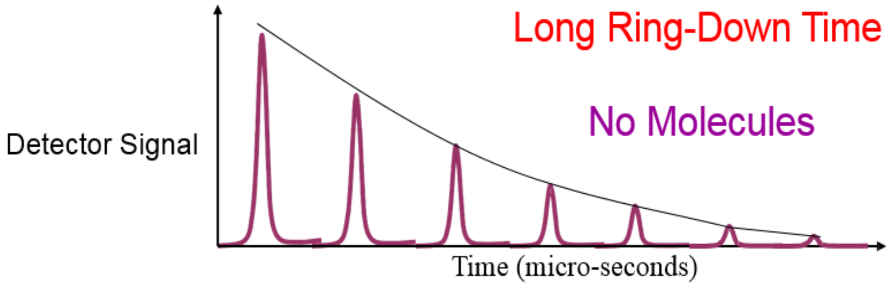
Map of the location and surroundings of the city of Cookeville and the study site (36.1628° N, 85.5016° W).

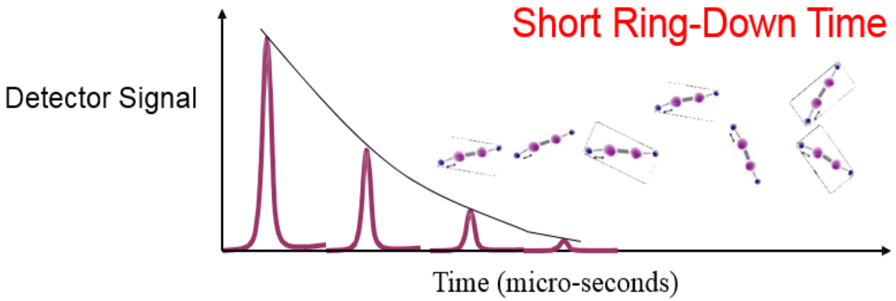
- The study site is surrounded by broadleaf and deciduous trees and shrubs, hence accurate quantification of surface sources, atmospheric sources resulting from the oxidation of hydrocarbons like isoprene is important
- Comprehensive quantitative understanding of the sources and sinks that contribute to the observed CO mole fractions and the associated seasonal trends have been carried out to see the effect of isoprene. No major effect on CO mole fractions by isoprene oxidation were found.

Experimental Methods: Cavity Ring-Down Spectroscopy (CRDS)



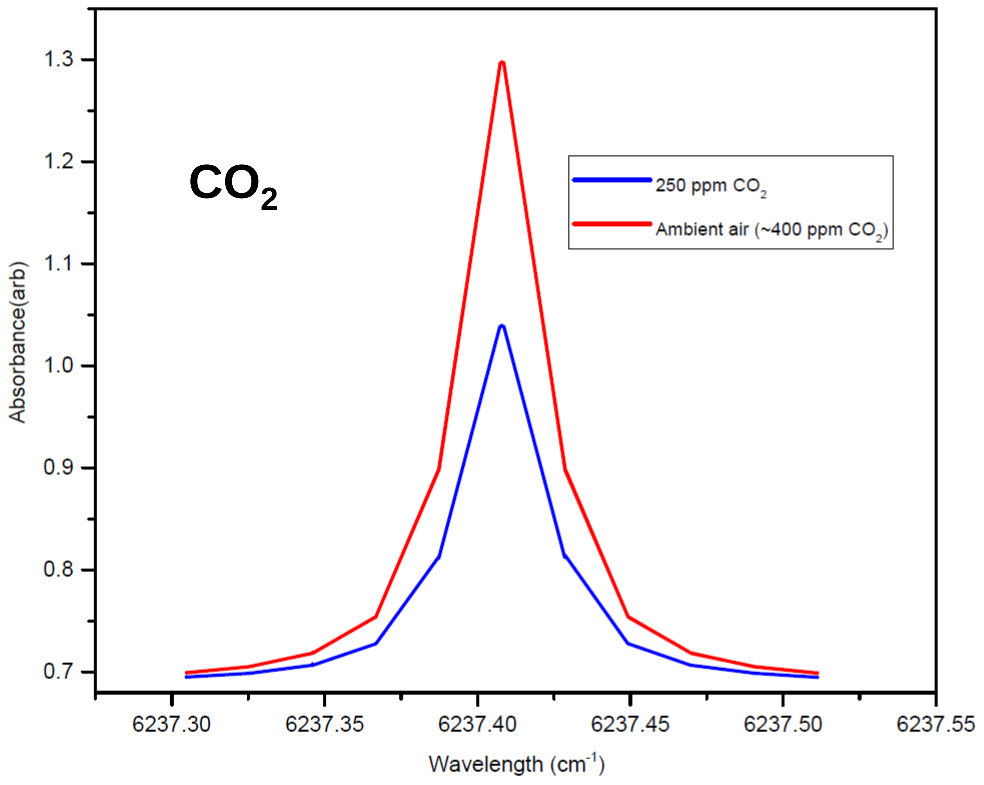


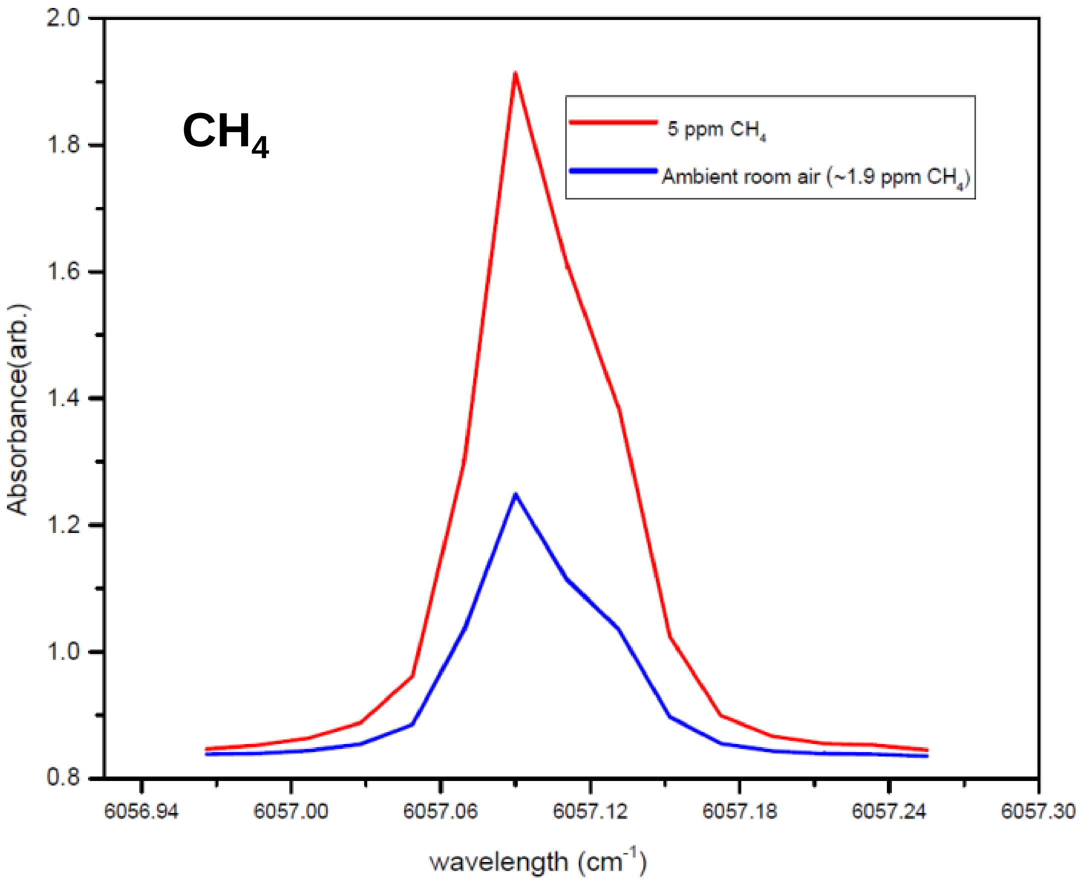




Ref: User manual of Picarro. G2401 CRDS analyzer

CRDS Measurement in the Overtone Region





High precision mode, uses the 6057.0795 cm^{-1} line while the high dynamic range mode uses the lines at 6056.8134 and 6056.840 cm^{-1} lines.

Precision and Drift Tests

Gaseous species and gas concentrations (ppm)		Drift analysis (24 hrs.)		Precision tests (29 hours)					
		Required (ppb)	Observed (ppb)	5 sec (σ)		5 min (σ)		1 hour (σ)	
				Required (ppb)	Observed (ppb)	Required (ppb)	Observed (ppb)	Required (ppb)	Observed (ppb)
CO_2	250	< 100	42.330	< 50	9.943	< 20	15.740	< 10	16.100
	400		28.557		13.361		20.861		21.327
	500		53.160		17.494		25.679		26.928
CH_4	1	< 1	0.069	< 1	0.090	< 0.5	0.135	< 0.3	0.136
	2		0.115		0.159		0.232		0.233
	5		0.567		0.387		0.568		0.573
	10		0.658		0.703		1.045		1.056
	15		0.637		1.022		1.431		1.441
CO	2	< 10	1.506	< 15	2.478	< 1.5	3.580	< 1	3.600
	10		1.286		2.681		3.880		3.905

$CO:CO_2$ Ratio Technique

(Gamage et al., *ACS Earth Space Chem.* 2020, 4, 4, 558–571):

$$CO_{2(Tot)} = CO_{2(Bg)} + CO_{2An} + CO_{2Bio} \quad \text{......(1)}$$

$$CO_{2Bio} = CO_{2(Tot)} - (CO_{2Bg} + CO_{2An}) \quad \text{......(2)}$$

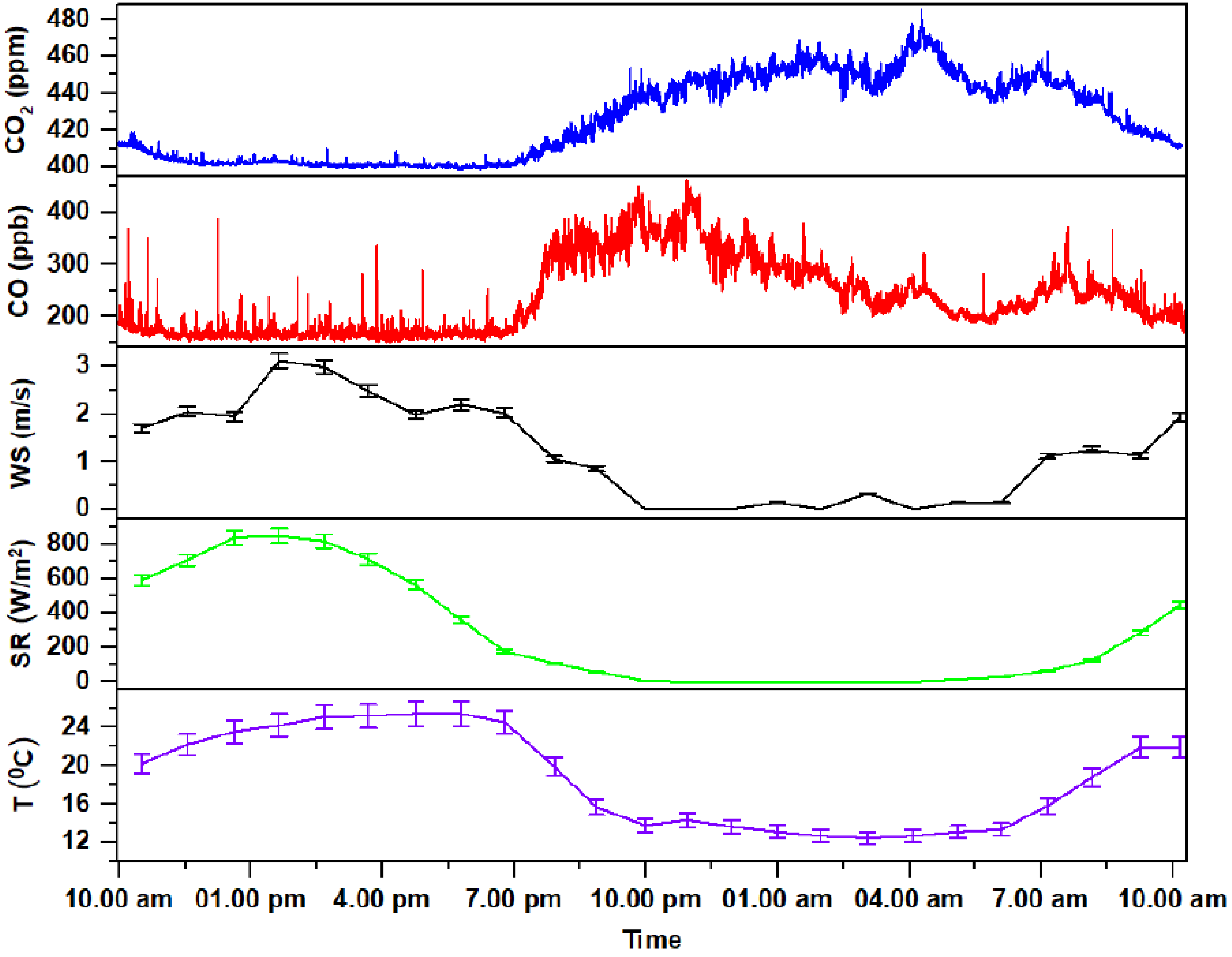
$$CO_{An} = CO_{(Tot)} - CO_{Bg} \quad \text{......(3)}$$

$$CO_{2An} = CO_{An} / \beta \quad \text{...... (4)}$$

$$CO_{2Bio} = CO_{2(Tot)} - CO_{2Bg} - (CO_{(Tot)} - CO_{Bg}) / \beta \quad \text{...... .(5)}$$

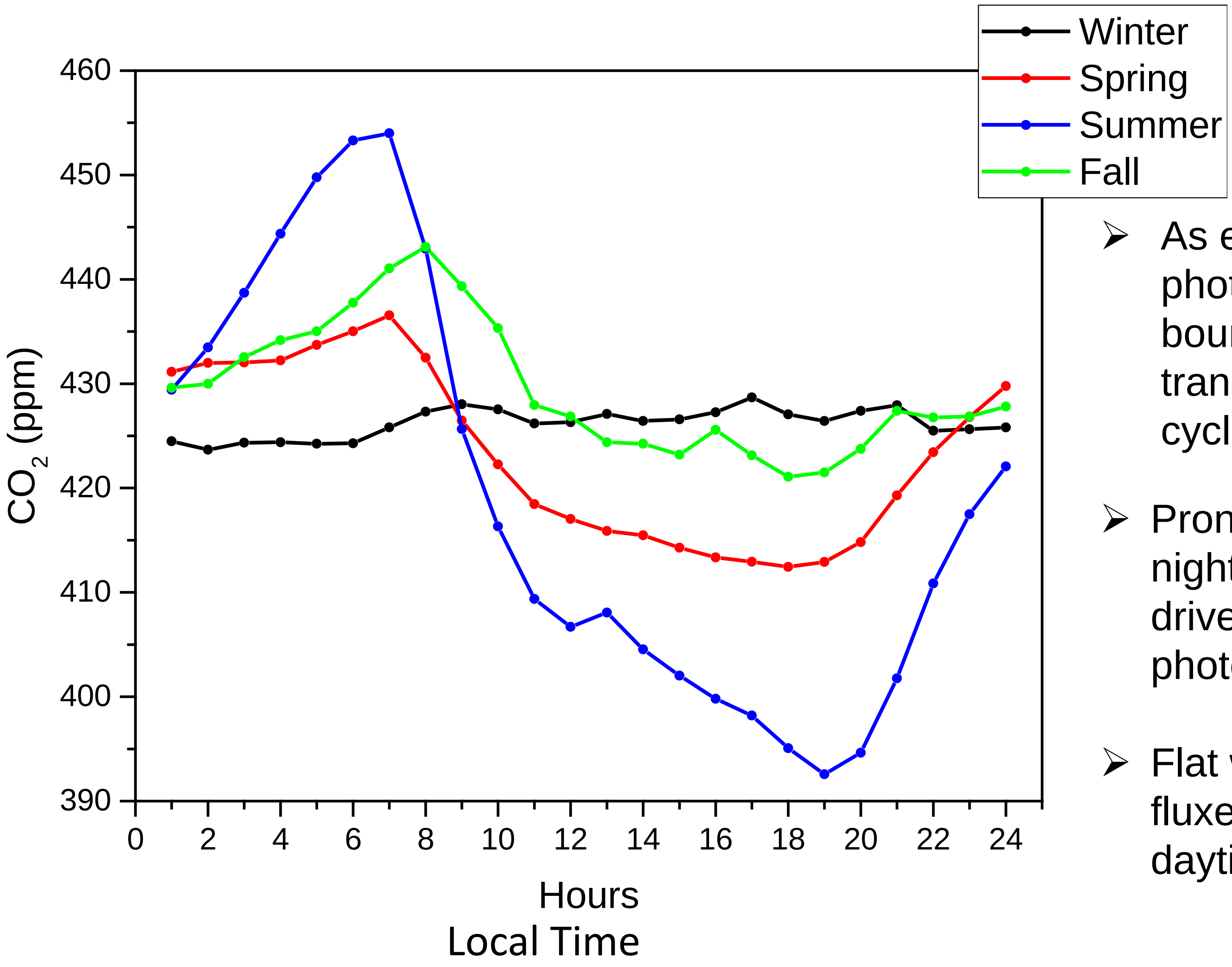
CO_{An}:CO_{2An} ratios (β ratios) were determined using the total weighted least squares regression method, taking into account the uncertainties in both the measured CO_2 and CO mixing ratios

Typical Diurnal Cycle of CO and CO_2 Mixing Ratios (5-day average)



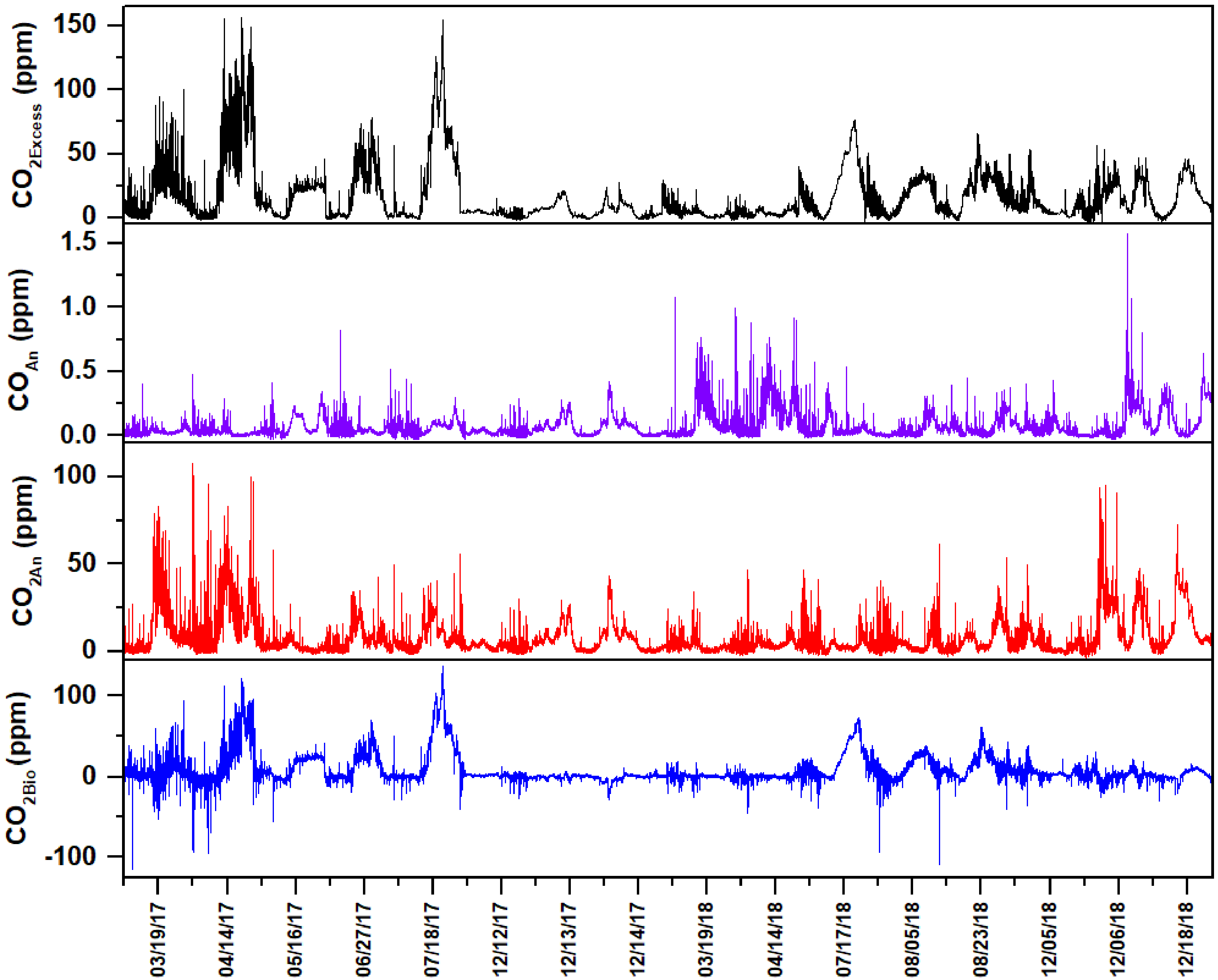
- Significant increases in CO_2 and CO mixing ratios during the nighttime, where the highest concentration is observed between 11 p.m. and 1 a.m.
- Mixing ratios for both gases can vary significantly with changes in local meteorological conditions.
- Relative contribution of anthropogenic and biogenic sources of CO_2 in urban regions can vary on relatively short diurnal and seasonal scales

Seasonal and Standardized Diel Patterns of CO_2



- Diel pattern standardized by subtracting 24- hr mean CO_2 from hourly CO_2.
- As expected the day/night alterations between photosynthesis and respiration, atmospheric boundary layer dynamics, and local/regional pollution transport processes all contribute to observed diel cycles in CO_2 mixing ratios.
- Pronounced diel cycles of CO_2 in summer, with night peaks and afternoon troughs that are mainly driven by nighttime respiration and daytime CO_2 photosynthesis drawdown
- Flat winter diel cycles are indicative of biological fluxes that are more constant throughout the daytime.

Partitioning Urban CO_2 signal into Bio and Anthropogenic signals



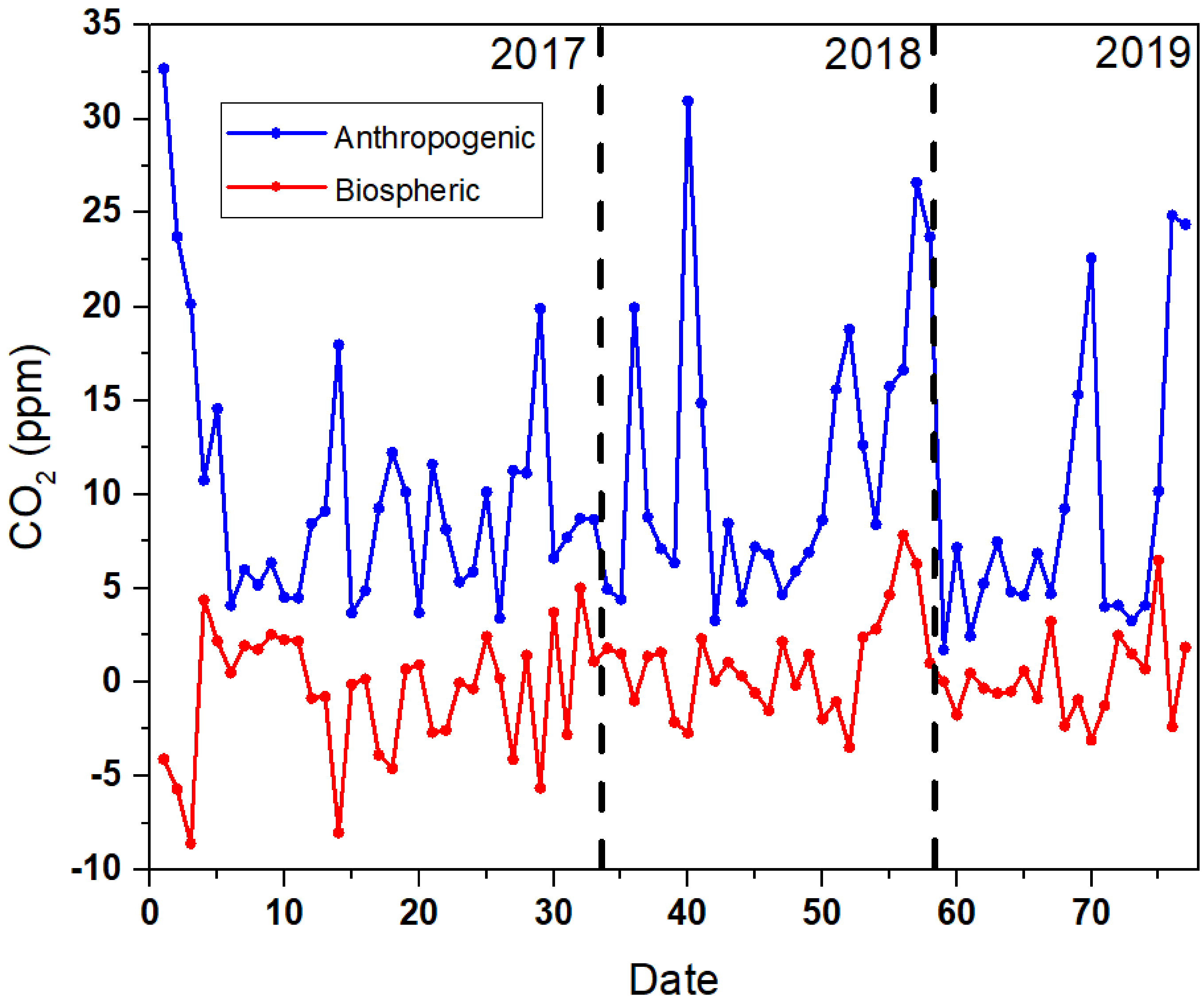
a) Daily mixing ratios of excess CO_2 over background levels ($CO_{2Excess}$) during the three seasons.

b) Calculated daily anthropogenic CO_2 using the respective winter β values and equation 2.

c) Biogenic CO_2

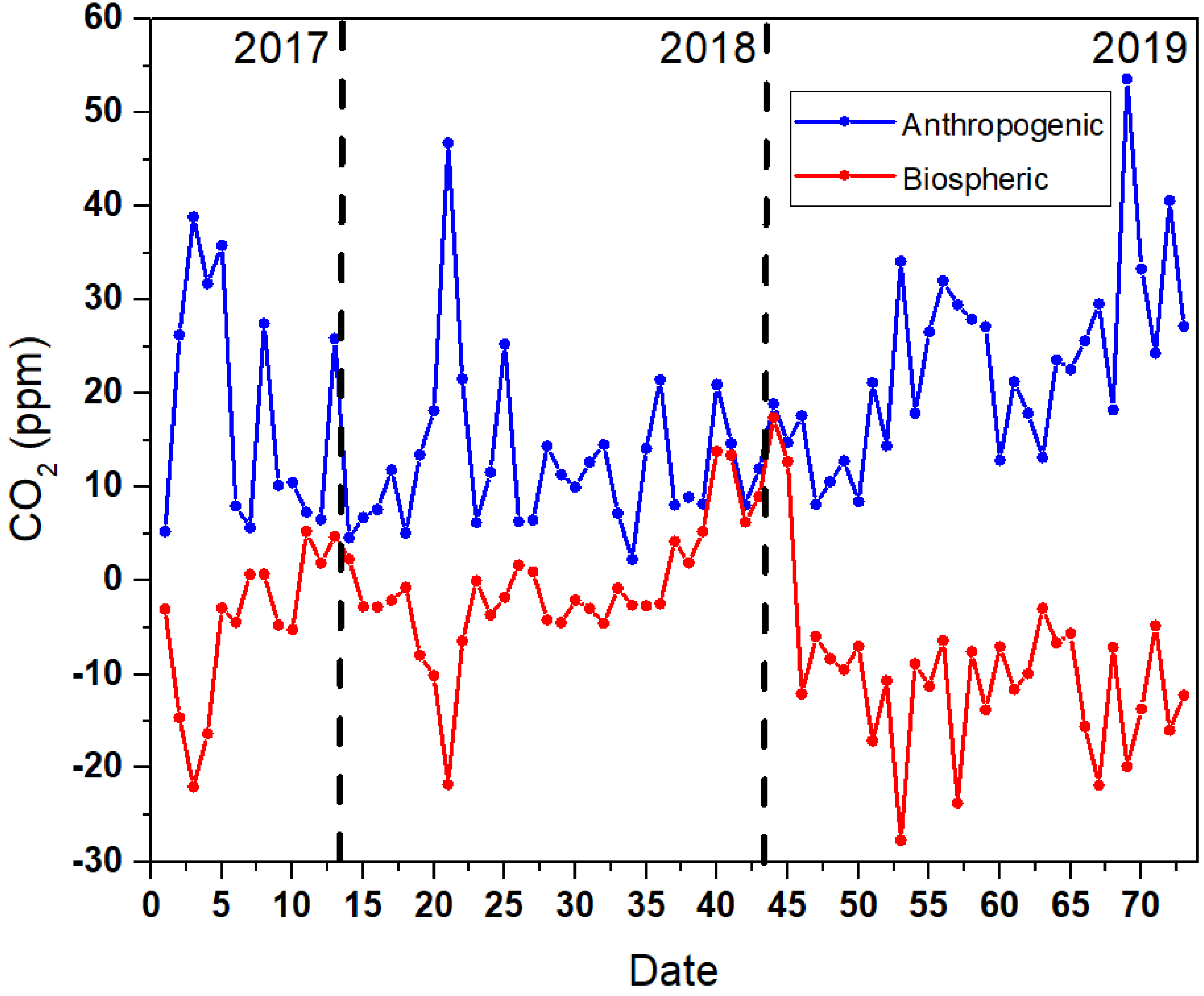
Winter Biospheric and Anthropogenic CO_2

Positive enhancement is expected in winter, when both CO_{2bio} and CO_{2ff} are sources to the atmosphere.



- CO_{2bio} signal varies seasonally and diurnally in both magnitude and in sign.
- Throughout the winter, the CO_{2ff} signal remains largely positive
- CO_{2bio} signal is also positive during the wintertime, albeit at far much lower mixing ratio magnitudes.
- The CO_{2bio} is mainly influenced by wintertime respiration and domestic biofuel burning.
- Although the CO_{2ff} is expected to remain positive during the summer, the daytime CO_{2bio} may be strongly negative due to photosynthetic drawdown

Springtime Biospheric and Anthropogenic CO_2 Signals



- Throughout the springtime, the CO_{2ff} signal remains largely positive
- In contrast with the winter months, we begin to see strong negative CO_{2bio} signals which are mainly due to strong photosynthetic drawdown
- During the spring, biological respiration can contribute more to CO_2
- Reduced wintertime domestic heating contributes to decreasing contributions of fossil fuels during spring.

Conclusions

- The CO tracer technique has been utilized in conjunction with continuous cavity ring down spectroscopic measurements to provide useful information about urban diurnal as well as seasonal anthropogenic and biospheric patterns in the Eastern Highland Rim region of the United States

- Continuous CRDS measurements have revealed that above-background biological respiration contributed increasingly more CO_2 than other sources during spring than during the wintertime.

- The winter CO_{2bio} values were all nearly zero or slightly positive, implying the active role of wintertime respiration fluxes.

- Overall, this study has demonstrated the potential of a CO-based technique method in quantifying CO_{2ff}, especially in the unavailability of the much more superior, though expensive techniques such as the $^{14}CO_2$

Acknowledgements

Funding

Chemistry Department

School of Environmental Sciences

Experiments: Dr. Lahiru Gamage.
Now a Research Associate at Tennessee State University