Partitioning of Biogenic and Anthropogenic CO_2 Signals using CO Tracer Technique

Lahiru P. Gamage[1,2], Ha H. Nguyen[3] and Wilson K. Gichuhi[1*]

[1]Department of Chemistry, [2]School of Environmental Studies and [3]Department of Chemical Engineering, Tennessee Tech University, 1 William L. Jones Dr., Cookeville, TN 38505.

Abstract

The poster reports a CO:CO_2 ratio technique in the estimation and quantification of biogenic CO_2 ($CO_{2\ bio}$) and anthropogenic CO_2 ($CO_{2\ anth}$) signals in an urban setting following continuous dry mixing ratio measurements of carbon dioxide (CO_2) and carbon monoxide (CO) using a wavelength-scanned cavity Ring-Down spectroscopic (CRDS) technology. The measurements were carried out in different days during the spring, summer and winter of 2017 and 2018 at a height 15 m above the ground. The CO:CO_2 correlation ratios (β values) were evaluated using regression analysis after subtracting the region's background concentration based on a 5th percentile background subtraction technique. For the year 2017, β values (ppb:ppm^{-1}) of 9.7 ± 0.4, 5.3 ± 0.4, and 2.0 ± 0.2 were obtained for the winter, spring and summer seasons, respectively. In 2018, a similar trend in the β values was observed where values of 8.7 ± 0.5, 7.4 ± 0.7, and 2.6 ± 0.5 measured in winter, spring, and summer seasons, respectively. Correlation values (r^2) of 0.9, 0.8 and 0.6 were obtained for winter, spring and summer seasons respectively, indicating the strong biospheric CO_2 exchange during summertime. This strong biospheric signal is brought about by the strong photosynthetic activity in the summertime as opposed to the dominant respiratory carbon fluxes that dominates the winter season.

Introduction

- The three contributors to the overall atmospheric CO_2 signal ($CO_{2(Tot)}$) are, background CO_2(CO_{2Bg}), anthropogenic CO_2(CO_{2An}), and the biospheric CO_2(CO_{2Bio}).

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

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

- It can be assumed that the greatest source of CO in Cookeville region is fossil fuel burning and therefore anthropogenic CO (CO_{An}) ca be calculated as,

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

- Assuming that CO_2 and CO are co-emitted by anthropogenic sources at a given ratio, β, then the CO_{2An} can be derived from CO_{An} as follows,

$$CO_{2An} = \beta . CO_{An} \quad \ldots\ldots\ldots\ldots \quad 4$$

- By combining equation 1-4,

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

Techniques and Methods

Study site and Cavity Ring-Down Spectroscopic Technique:-

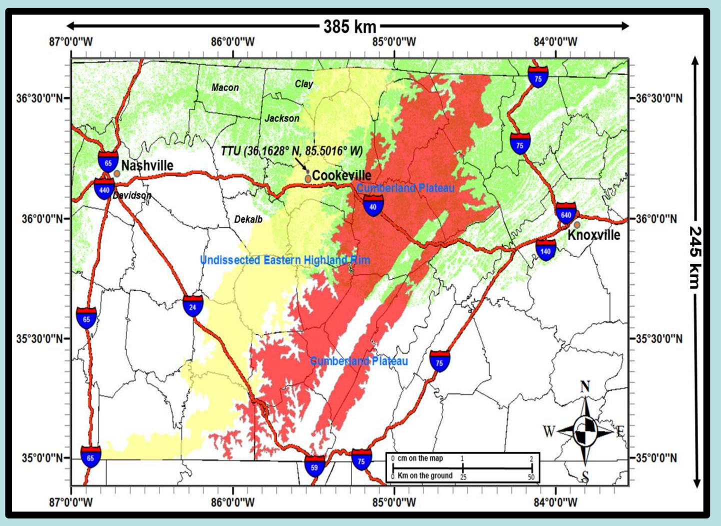

Figure 1: Map of the location and surroundings of the study site (36.1628° N, 85.5016° W).

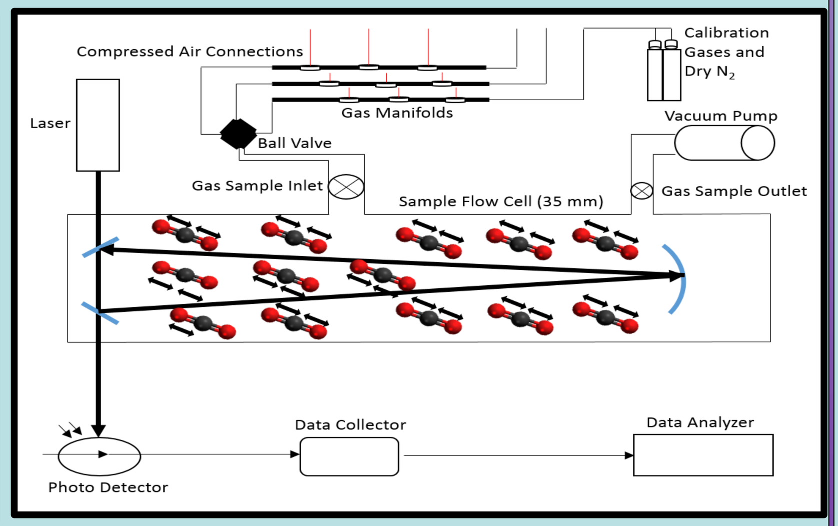

Figure 2: The schematic diagram of Cavity ring-down spectroscopy set-up and the associated components in the laboratory.

- The basic instrumentation of CRDS consists a laser, a high optical cavity consisting of three highly reflecting mirrors, and a photodiode detector.
- CRDS measures gases simultaneously at their overtone regions: CO_2 at 6237.4 cm^{-1} and CO at 6380.4 cm^{-1}.

Results and Discussion

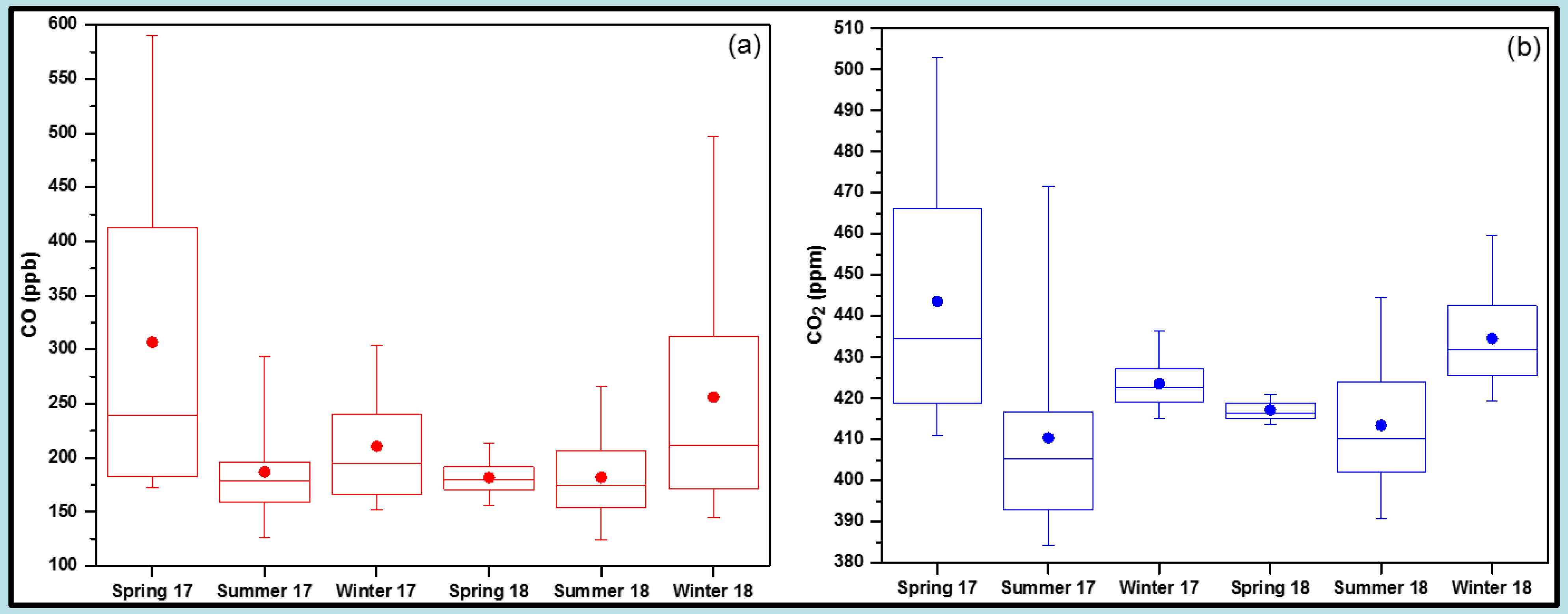

Figure 3: Box plots of CO (left) and CO_2 (right) seasonal mixing ratios for the air masses observed at ~ 15 m above ground in Cookeville in 2017 and 2018

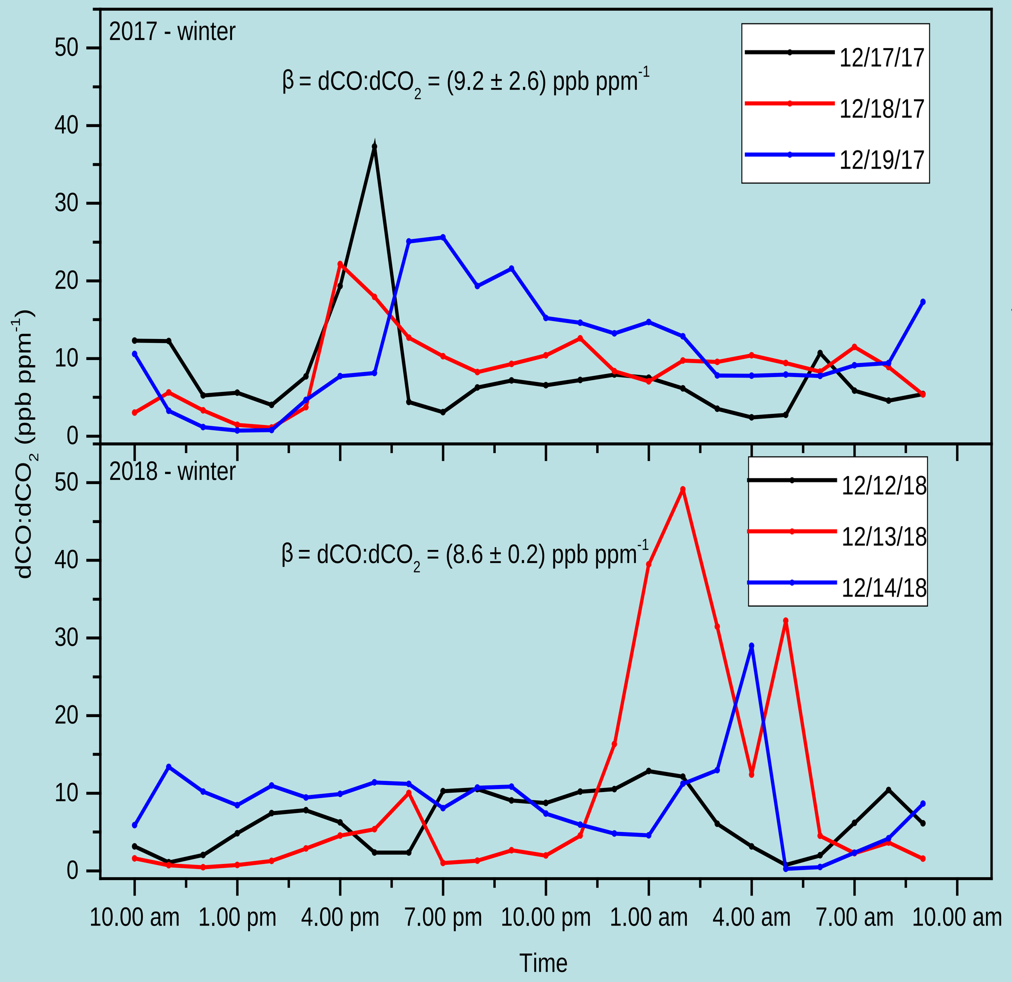

Figure 4 (a): Variations of hourly averaged dCO:dCO_2 ratios for the different days in winter for both 2017 and 2018.

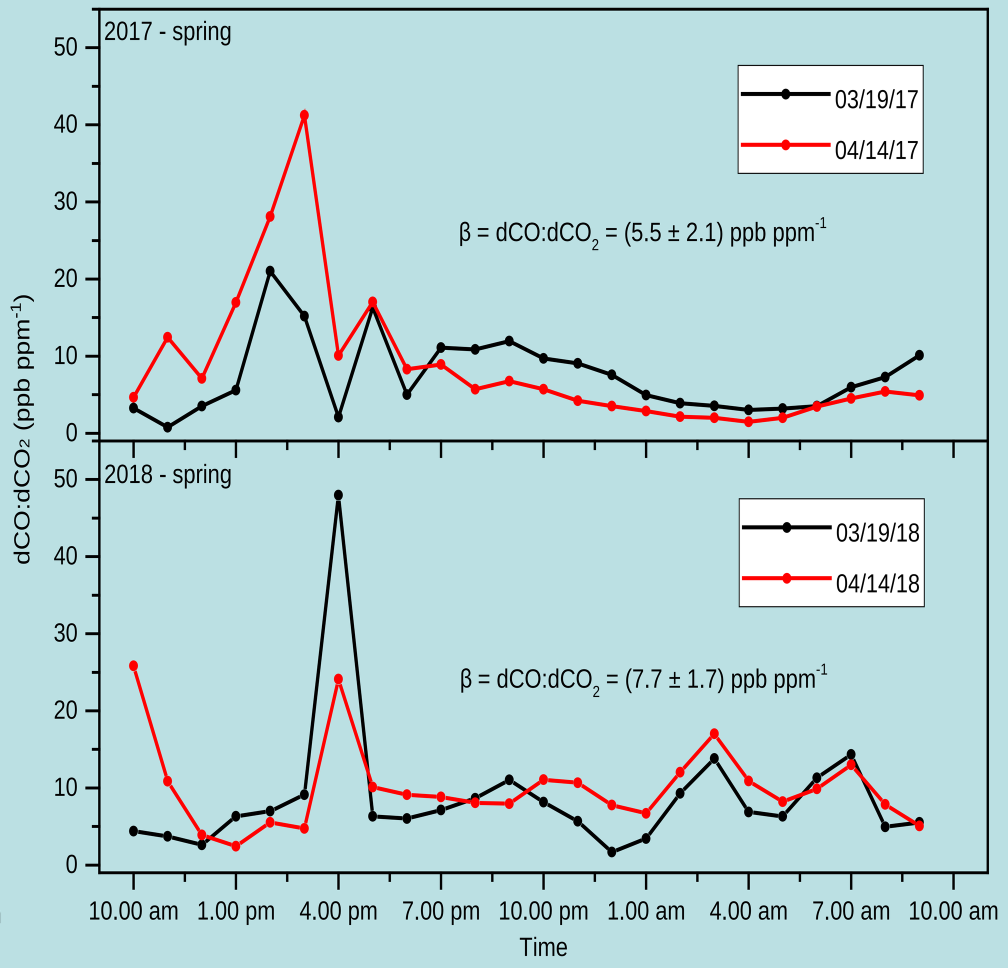

Figure 4 (b): Variations of hourly averaged dCO:dCO_2 ratios for the different days in spring for both 2017 and 2018.

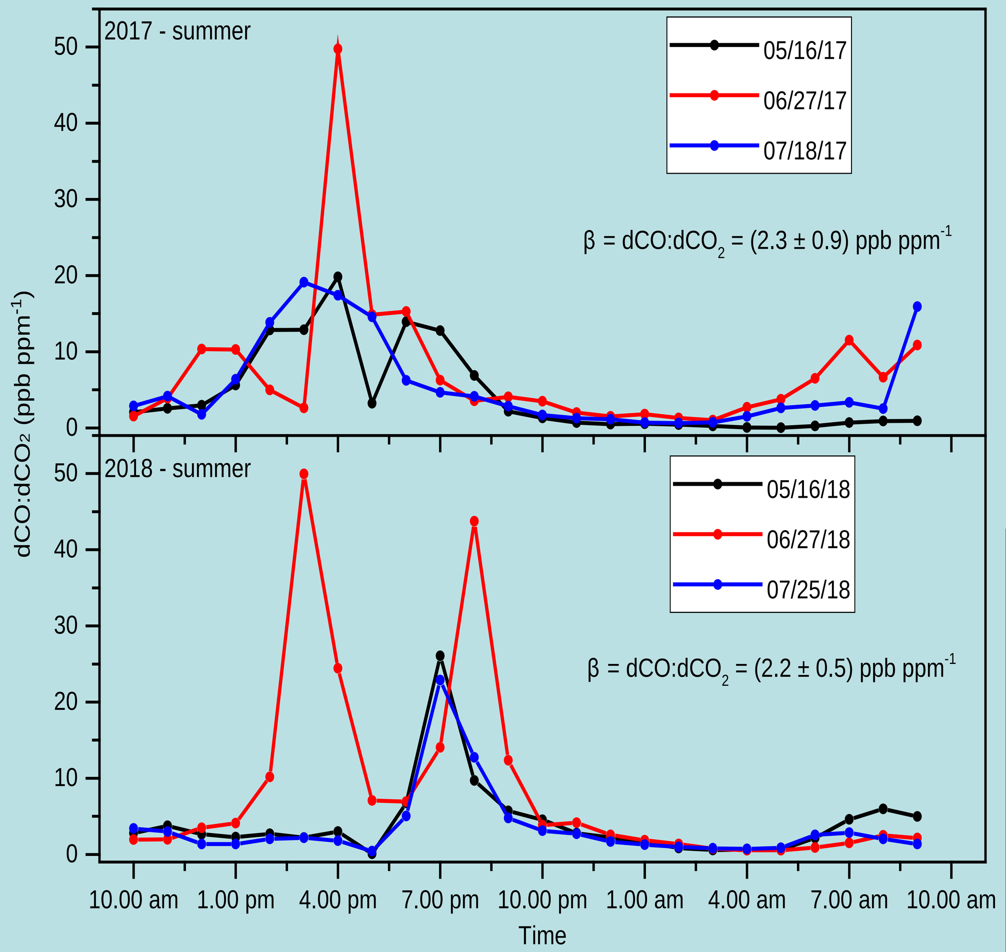

Figure 4 (c): Variations of hourly averaged dCO:dCO_2 ratios for the different days in summer for both 2017 and 2018.

- The highest β values were generally associated with afternoon hours between 4 p.m. and 7 p.m.
- Correlations between CO_2 and CO were higher during the evenings irrespective of the season.
- This is an indication of vehicle emissions during the afternoon rush-hour traffic.
- Night time β values were comparatively lower than other time slots except for winter.

Table 1: Observed β values and their r^2 values.

Season	Period	Observed β value (R^2)	
		2017	2018
Spring	Morning (7:00 a.m. – 10:00 a.m.)	5.1 ± 0.4 (0.9)	7.5 ± 1.6 (0.8)
	Evening (4:00 p.m. – 7:00 p.m.)	10.2 ± 1.0 (0.9)	7.9 ± 0.6 (0.9)
	Night (12:00 a.m. – 5:00 a.m.)	3.1 ± 0.7 (0.7)	8.0 ± 0.9 (0.9)
	Spring, Overall	5.3 ± 0.4 (0.8)	7.4 ± 0.7 (0.7)
Summer	Morning (7:00 a.m. – 10:00 a.m.)	1.8 ± 0.5 (0.6)	4.8 ± 1.9 (0.3)
	Evening (4:00 p.m. – 7:00 p.m.)	8.2 ± 0.6 (0.9)	5.4 ± 1.6 (0.7)
	Night (12:00 a.m. – 5:00 a.m.)	1.1 ± 0.1 (0.8)	0.3 ± 0.2 (0.2)
	Summer Overall	2.0 ± 0.2 (0.6)	2.6 ± 0.5 (0.3)
Winter	Morning (7:00 a.m. – 10:00 a.m.)	9.6 ± 0.7 (0.9)	8.5 ± 1.2 (0.8)
	Evening (4:00 p.m. – 7:00 p.m.)	7.8 ± 1.7 (0.7)	10.9 ± 3.1(0.8)
	Night (12:00 a.m. – 5:00 a.m.)	10.5 ± 0.6 (0.9)	6.9 ± 0.6 (0.9)
	Winter Overall	9.7 ± 0.4 (0.9)	8.7 ± 0.5 (0.8)

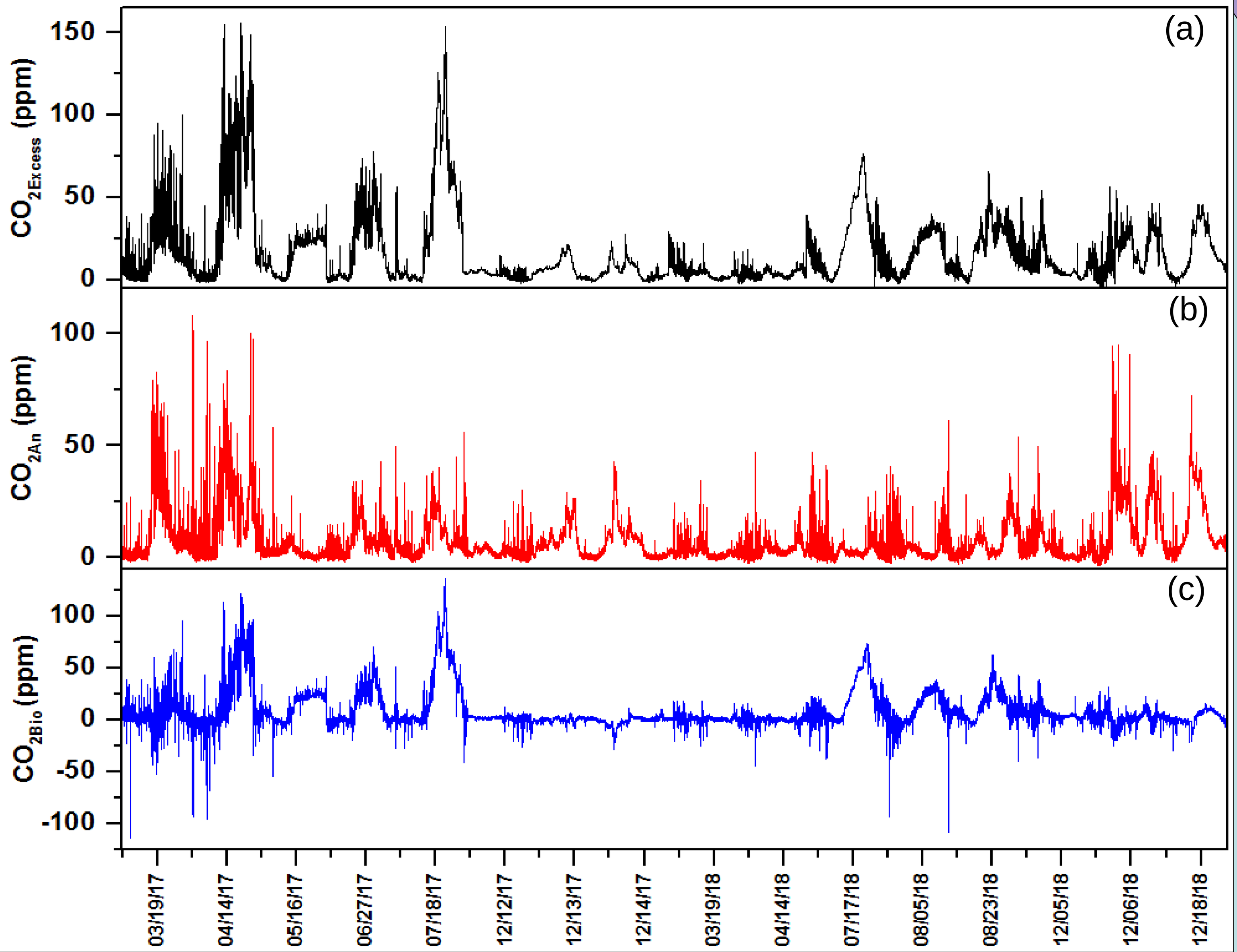

Figure 6: (a) Daily mixing ratios of excess CO_2 over background levels ($CO_{2Excess}$) during the three seasons. (b) Calculated daily anthropogenic CO_2 using the respective winter β values and equation 2. (c) Biogenic CO_2 calculated using equation 5.

- Winter time β values (9.7 ± 0.4 and 8.7 ± 0.5) were used in equation 4 and 5 to compute CO_{2An} and CO_{2Bio}.
- The average wintertime CO_{2Bio} values were 0.08 ± 3.31 ppm (2017) and 1.64 ± 8.50 (2018).
- The respective CO_{2An} values obtained in winter 2017 and 2018 are 5.44 and 11.76, respectively.

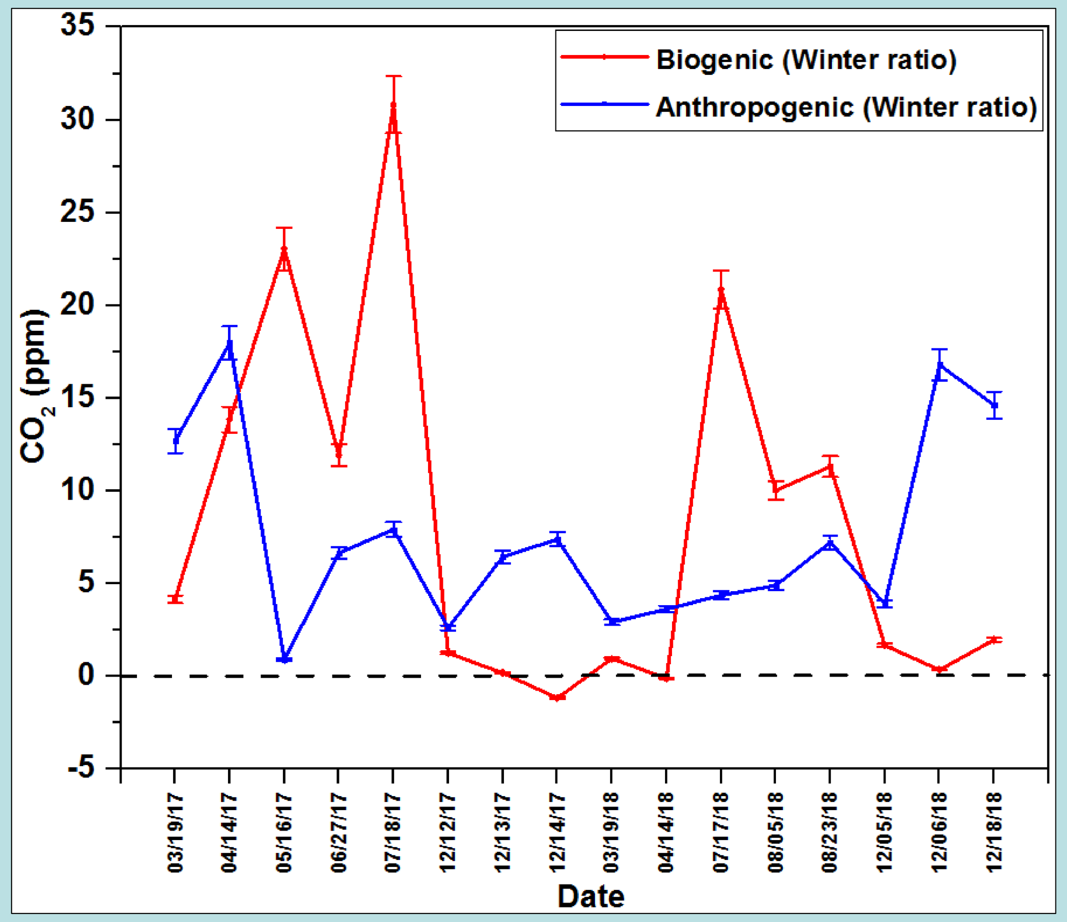

Figure 7: Daily mean variations of biospheric (red) and anthropogenic (black) CO_2 determined by using wintertime β values.

Conclusions and Future Directions

- During the winters, when the biospheric CO_2 fluxes are close to zero, mostly correlated (r^2 = 0.9) anthropogenic β values were observed.
- This study demonstrates the potential of a CO-based technique over $^{14}CO_2$-based technique method in quantifying CO_{2An}.

Selected References

- Turnbull, J. C.; Sweeney, C.; Karion, A.; Newberger, T.; Lehman, S. J.; Tans, P. P.; Davis, K. J.; Lauvaux, T.; Miles, N. L.; Richardson, S. J.; Cambaliza, M. O.; Shepson, P. B.; Gurney, K.; Patarasuk, R.; Razlivanov, I., Toward quantification and source sector identification of fossil fuel CO2 emissions from an urban area: Results from the INFLUX experiment. J. Geophys. Res. Atmos. 2015, 120, (1), 292-312.
- Churkina, G., Modeling the carbon cycle of urban systems. Ecol. Model. 2008, 216, (2), 107-113.
- Briber, B. M.; Hutyra, L. R.; Dunn, A. L.; Raciti, S. M.; Munger, J. W., Variations in Atmospheric CO2 Mixing Ratios across a Boston, MA Urban to Rural Gradient. Land 2013, 2, (3), 304.

Acknowledgement

- Financial support from Tennessee tech Faculty start-up grant
- Faculty development grant from College of Arts and Science
- Support from Chemistry department, TTU