Utilization of CH_4:CO_2 and CO:CO_2 Correlations in Deciphering Temporal Changes in Urban CH_4 and CO Emissions

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Abstract

The continued measurements of urban CH_4 and CO_2 atmospheric signals at local, regional and global levels, have continued to enhance our understanding and interpretation of carbon and methane cycles. In this study, seasonal correlation between CH_4 and CO_2 (CH_4:CO_2) and CO and CO_2 (CO:CO_2) are evaluated within an urban setting. The linear regression analysis is used to determine seasonal correlations between the respective tracer gas and CO_2. The NOAA HYSPLIT model is utilized in determining the origin of the air masses that contribute to the observed emission ratios and the consistent diurnal mixing ratio patterns throughout the year. These mixing ratio measurements are simultaneously and continuously taken in site near the Cookeville city (36.1628° N, 85.5016° W), which is located within the greater Eastern Highland Rim region of Tennessee. Both the correlation co-efficient (R^2) and emission ratios (ppb:ppm^{-1}) of CO and CO_2 for the winter season are reasonably high compared to all the other seasons, which is indicative of elevated anthropogenic emissions during the winter that are supplemented by high winter respiratory fluxes. For the years 2017 and 2018, CO:CO_2 winter emission ratios were about 5 times higher than in the summer. Even though the CH_4 mixing ratios are different for each season, the calculated CH_4:CO_2 seasonal emission ratios do not show high variations throughout the year, with monthly averaged seasonal values ranging between 4.85 to 4.93 ppb:ppm^{-1}.

Introduction

- The temporal changes in atmospheric CO and CH_4 are a result of an overall balance between the emissions and sinks.
- Synoptic-Scale Variation (SSV) in the mixing ratio of one chemical species is usually associated with SSVs of other species that have similar regional emission distributions.

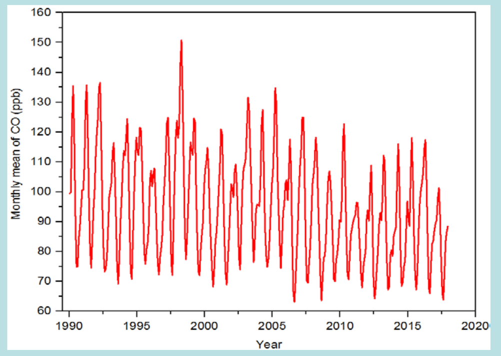

Figure 1: The monthly mean CO measured at Mauna Loa, USA (19.53 N, 55.57° W).

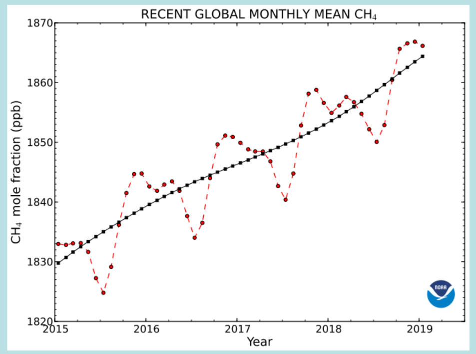

Figure 2: Seasonal variations and recent global trend of atmospheric CH_4.

Source: Ed Dlugokencky, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/)

- Therefore, specific chemical species with relatively well quantified sources can be used to constrain emission estimates of other species with poorly quantified (Example: CO:CO_2, CH_4:CO_2).
- Urban cities are responsible for a large share of greenhouse gas emissions.
- Local urban atmosphere exposes to local and regional emissions and transporting outside air masses.

Techniques and Methods

Study Location

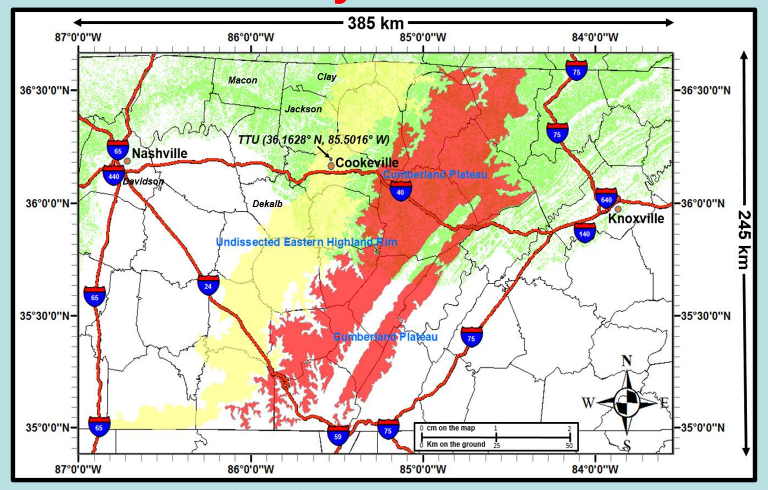

Figure 3: Map of the location and surroundings of the city of Cookeville and the study site (36.1628° N, 85.5016° W).

Cavity Ring-Down Spectroscopy

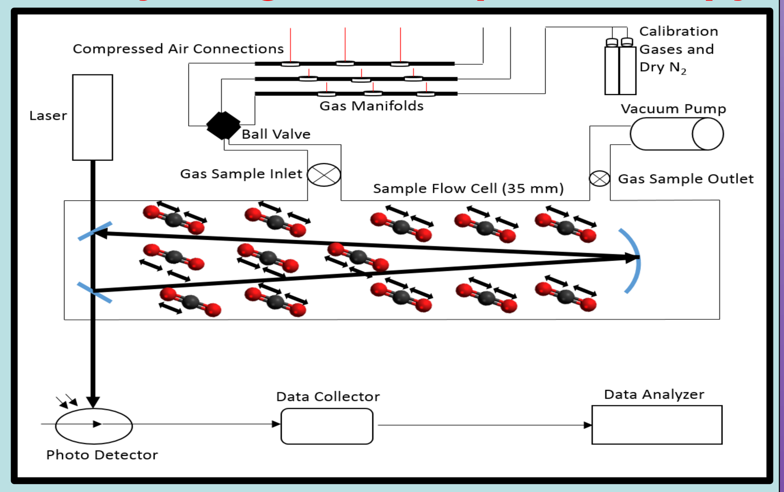

Figure 4: The schematic diagram of Cavity ring-down spectroscopy set-up and the associated components in the laboratory.

- For all the gases, Excess mixing ratio = measured daily mean - background
- Daily excess mixing ratios were used in all the correlation plots.
- Simple regression analysis (Y = mX + C) was performed (using Origin 2016 statistical software) to obtain the seasonal correlations between excess mixing ratios of respective gases.
- NOAA HYSPLIT model single backward trajectories were used to determine the dominant directions of air masses in different seasons.

Results and Discussion

Background mixing ratios

- Monthly 5th percentile mixing ratios of each gas was considered as the local background concentration.
- Monthly background mixing ratios were derived using 10-13 days continuous measurements in each month.
- The background concentrations in the winter seasons are slightly higher than in the other seasons.

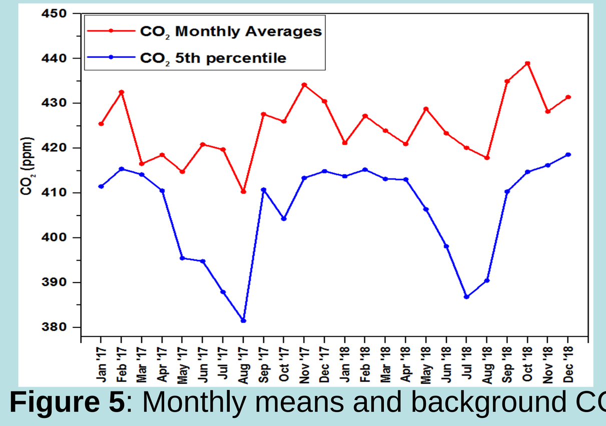

Figure 5: Monthly means and background CO_2.

Monthly Variations of CO_2, CH_4 and CO in Eastern Highland Rim

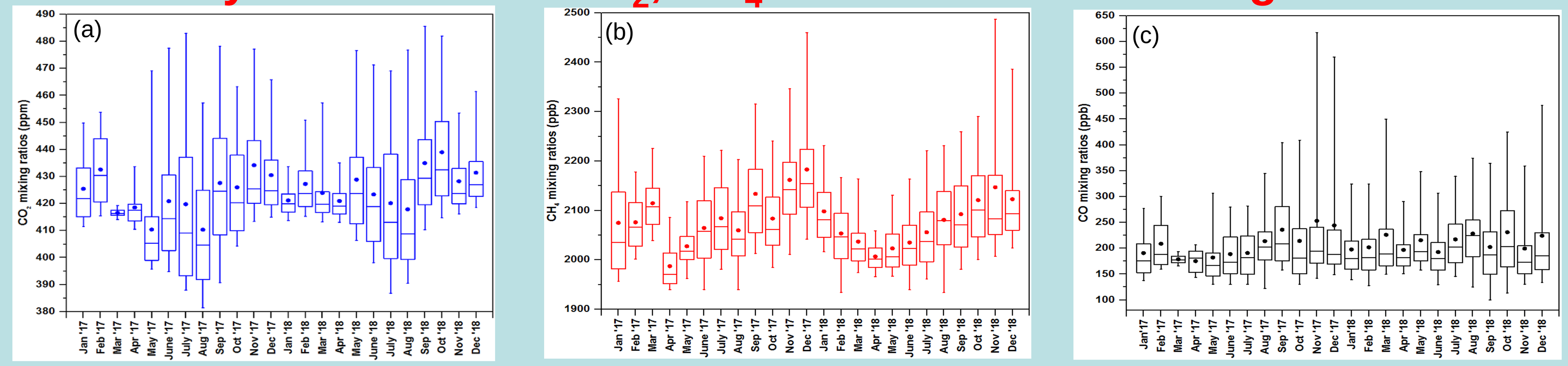

Figure 6: Box plot analysis of monthly CO_2 (a), CH_4 (b), and CO (c) mixing ratios. The dot inside the box indicates the monthly means of respective gases. The bottom and top whiskers in each box show monthly 5th and 95th percentiles respectively.

Excess CO_2 vs Excess CO in Different Seasons

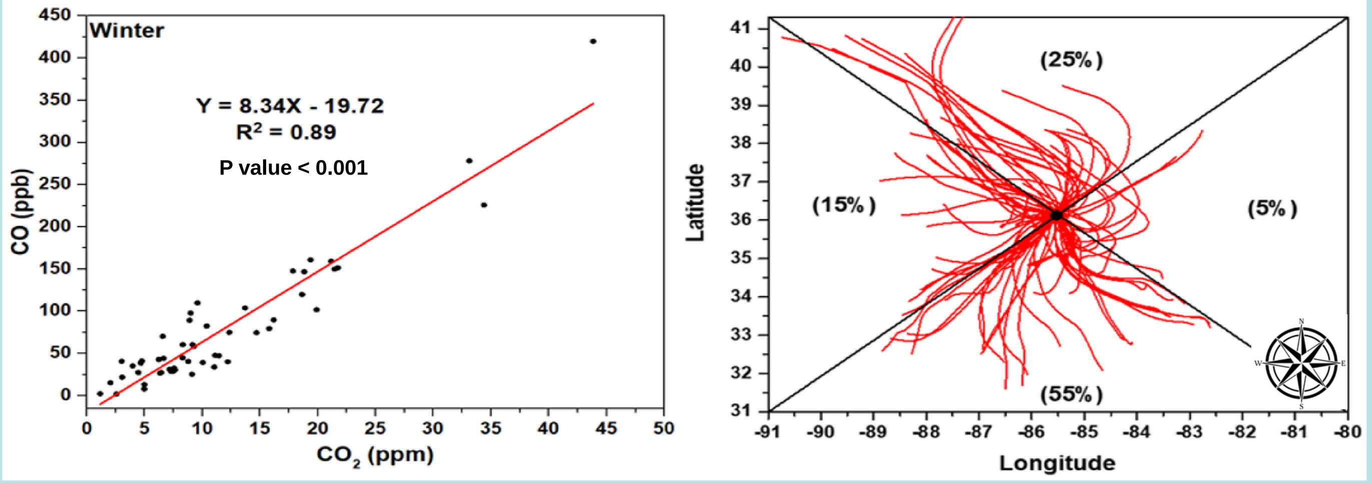

Figure 7 (a): Correlation between excess CO_2 vs excess CO in Winter and respective trajectories

- CO_2 emissions from fossil fuel combustions are high in the Winter.
- Therefore excess CO levels are high.
- CO and CO_2 Correlation is high.
- The dominant air mass direction is South relative to the measuring location.

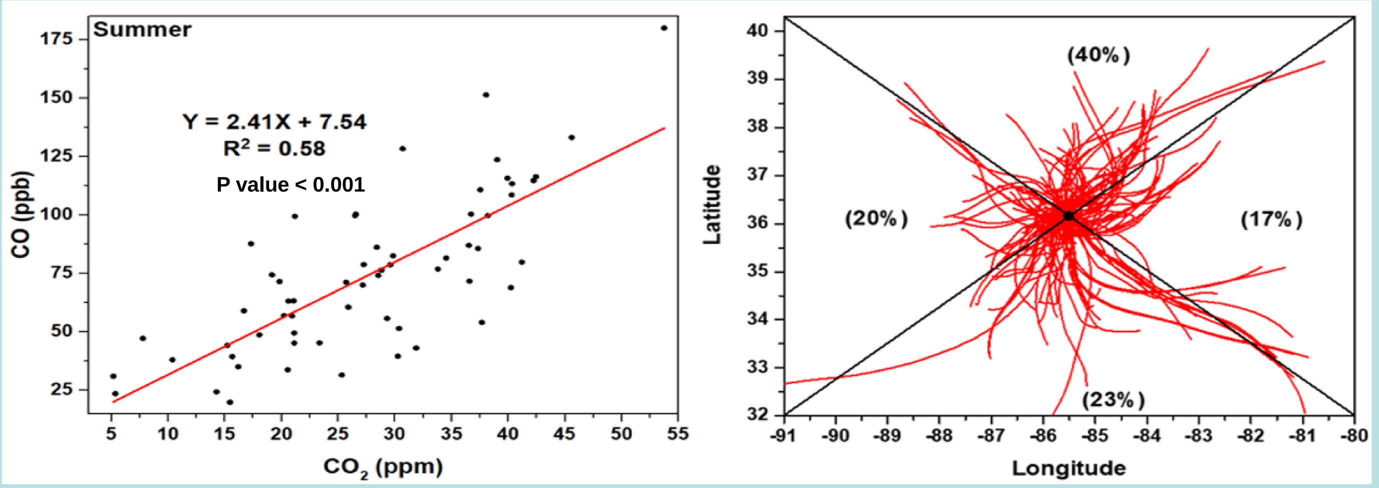

Figure 7 (b): Correlation between excess CO_2 vs excess CO in Summer and respective trajectories

- Magnitude of the dCO:dCO_2 is low in the Summer.
- CO and CO_2 Correlation is low.
- Photosynthesis effect is dominant in the Summer.
- The dominant air mass direction is North relative to the measuring location.

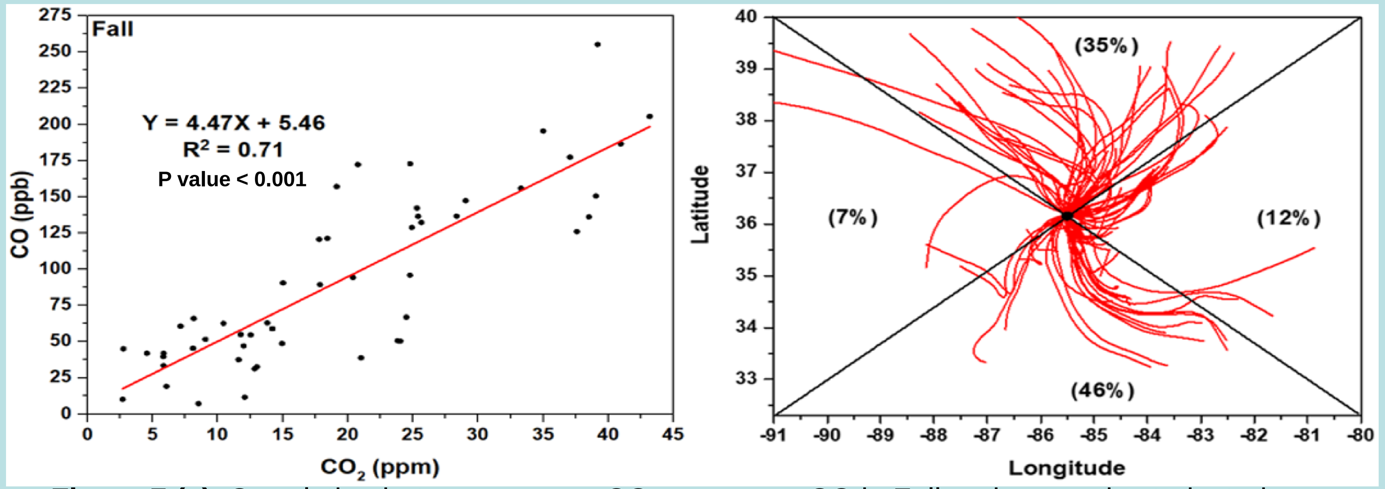

Figure 7 (c): Correlation between excess CO_2 vs excess CO in Fall and respective trajectories

- Both anthropogenic and biospheric CO_2 signals present in the Fall.
- Excess CO levels are high compared to Sprig and Summer.
- The dominant air mass direction is South relative to the measuring location.

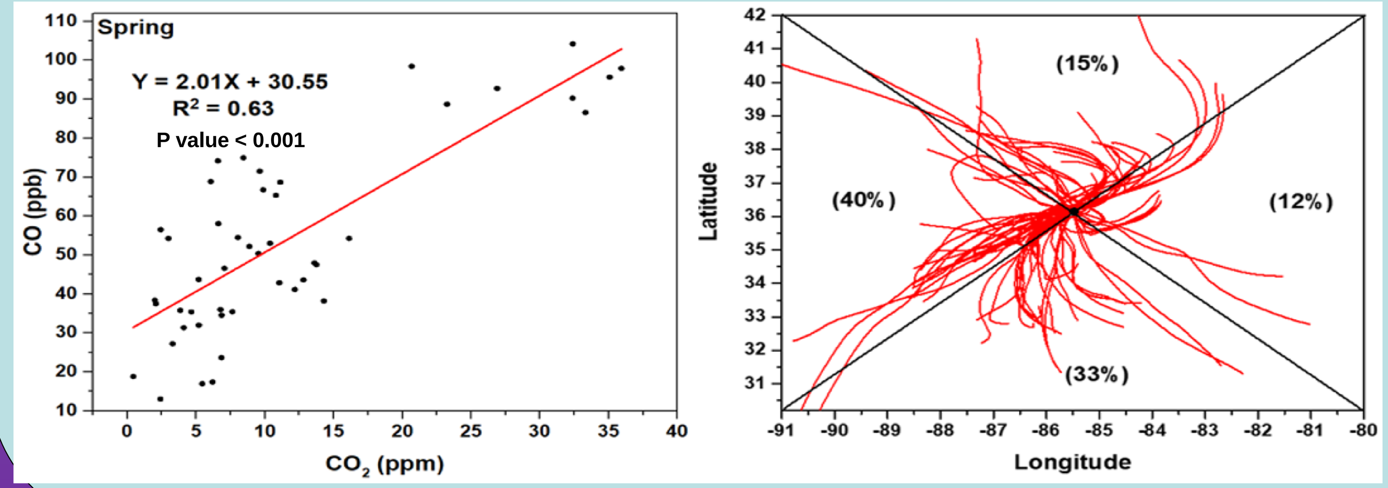

Figure 7 (d): Correlation between excess CO_2 vs excess CO in Spring and respective trajectories

- Magnitude of the dCO:dCO_2 is low in the Spring.
- CO and CO_2 Correlation is moderate.
- The dominant air mass direction is West relative to the measuring location.

Excess CO_2 vs Excess CH_4 in Different Seasons

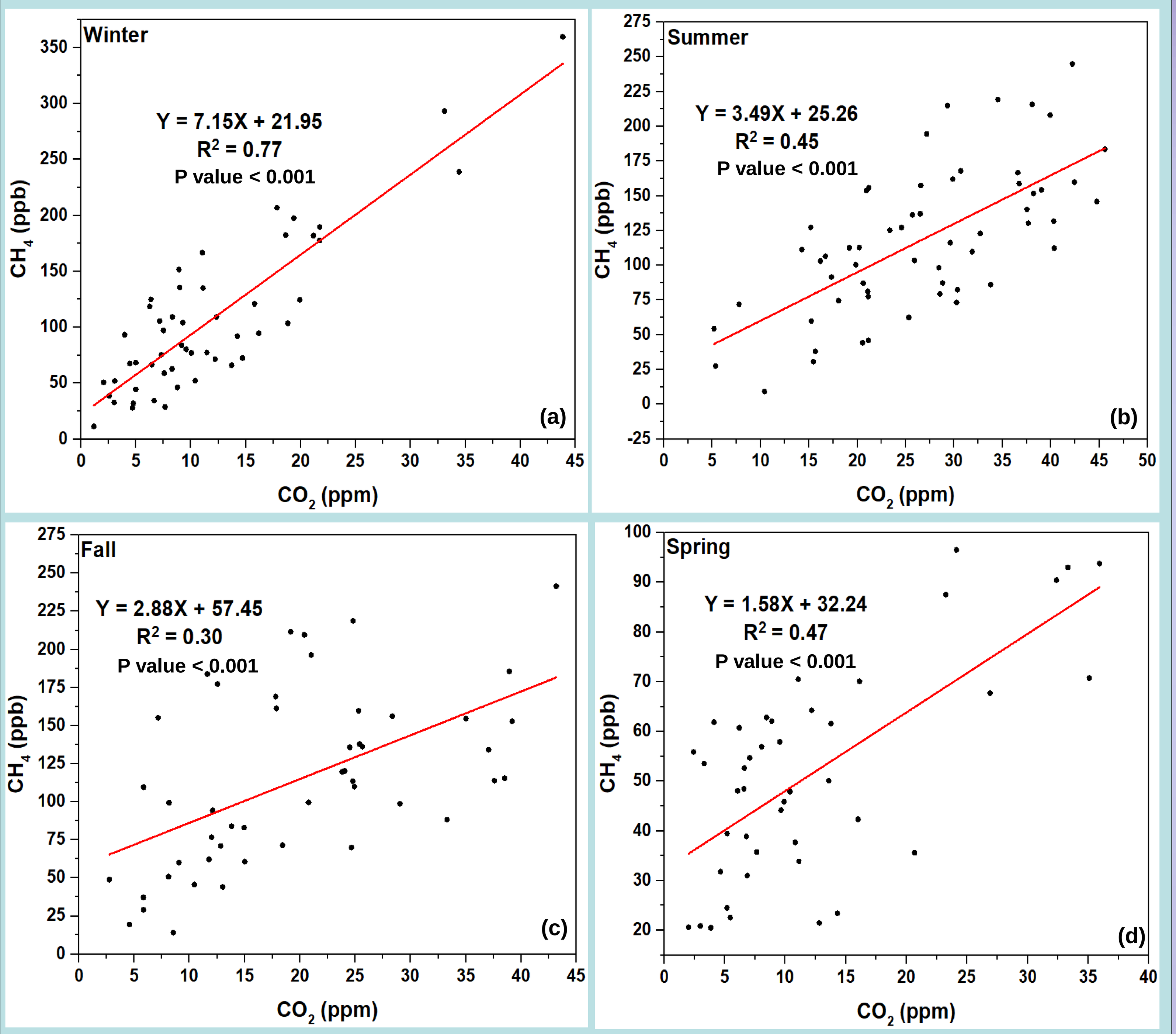

Figure 8: Regression analysis of excess CO_2 vs excess CH_4 in different seasons. (a) Winter, (b) Summer, (c) Fall, (d) Spring. Regression equations and R^2 values are shown inside the regression plot.

- In cold seasons, CO_2 retention time in the atmosphere is high due to the unavailability of photosynthesis effect.
- CO:CO_2 and CH_4:CO_2 ratio obtained in the winter is high mainly due to the increase of anthropogenic emissions.
- During the summer season CO_2 is removed rapidly from the atmosphere and there is a possibility of CO production from Isoprene.

Conclusions

- High CO:CO_2 ratio in the winter season reveals dominant anthropogenic CO_2 signal in the season.
- Air masses came from South direction relative to the study location were found to enhance the CO:CO_2 ratio.
- High CH_4:CO_2 ratio observed in the winter season could be due to the usage of natural gas for house heating.

References

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