atmosphere

Supplementary Materials:

Wilson K. Gichuhi and Lahiru P. Gamage

CO:CH_4 Emission Ratios

In most urban areas, the main source of anthropogenic CO_2 is fossil fuels, hence the need to evaluate urban CO:CO_2 emission ratios. For CH_4, the majority of anthropogenic emissions are associated with the agricultural sector, coal mining, waste management, and storage, and fugitive emissions are associated with natural gas transportation to urban, domestic, and industrial sectors. As a result, in addition to the CO:CO_2 emission ratios, ratios between CO and CH_4 (i.e., excess mixing ratios of CO and CH_4 above the background, XCO and XCH_4) have been utilized by several researchers to provide insights into the level of CH_4 anthropogenic emissions in a given urban region or sector [1–4]. In this section, we provide a brief overview of the CO:CH_4 ratio in Cookeville. Figure 6 shows the seasonal distribution of CO:CH_4 ratios for the years 2017, 2018, and 2019. The results are summarized in Table S4. Generally, compared to the other seasons, higher CO:CH_4 ratios are observed during the winter. The respective wintertime ratios for the years 2017, 2018, and 2019 are 8.4 ± 0.9, 7.4 ± 0.9, and 7.6 ± 0.9 ppb ppm^{-1}. The higher correlation in winter indicates common or similar sources for CH_4 and CO_2 while the moderate to low correlation values in the other seasons indicate the likelihood of other non-combustion-related sources.

Higher ground mixing ratios of CO_2 during the winter likely explain the observed higher wintertime CO:CH_4. It is important to note that near the surface, air masses are most likely not well mixed due to contributions from different point sources; hence, it may be difficult to make any definitive conclusions on the different seasonal ratios since there may be bias in the concentration levels of the air masses, depending on the strength of the nearby CH_4 sources. However, as noted in previous U.S. urban-based studies, large CH_4 enhancements over background mixing ratio emissions are dominated by leaks from the natural gas delivery infrastructure [5–9]. To put this study in context with other cities and evaluate the current knowledge on anthropogenic emissions as given by CO:CH_4 ratios, we compared our results with other urban sites. CO:CH_4 ratios of 9.1 and 7.0 ppb ppm^{-1} were observed in the Baltimore–Washington region and urban centers along the U.S. East Coast by Ren et al. [10]. and Plant et al. [11], respectively. In 2018, Anderson et al. observed respective morning and afternoon median CO:CH_4 ratios of 8.1 and 5.4 between February 21 and March 22 in Philadelphia [12].

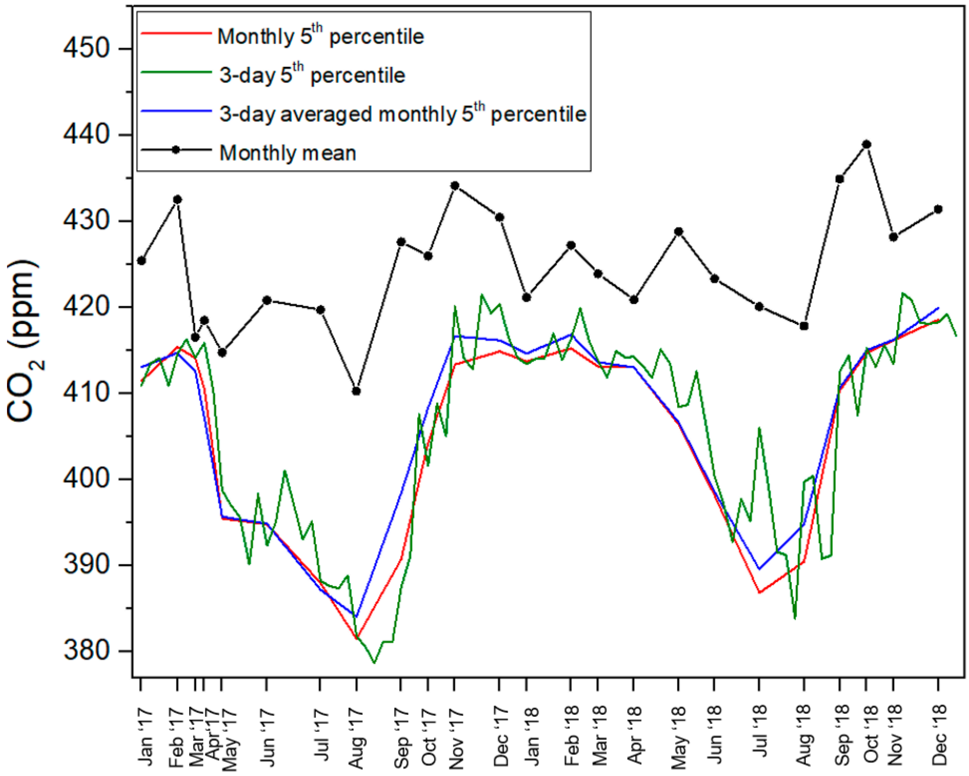

Figure S1. Fifth percentile CO_2 background mixing ratios (monthly, 3-day moving average and 3-day moving monthly average).

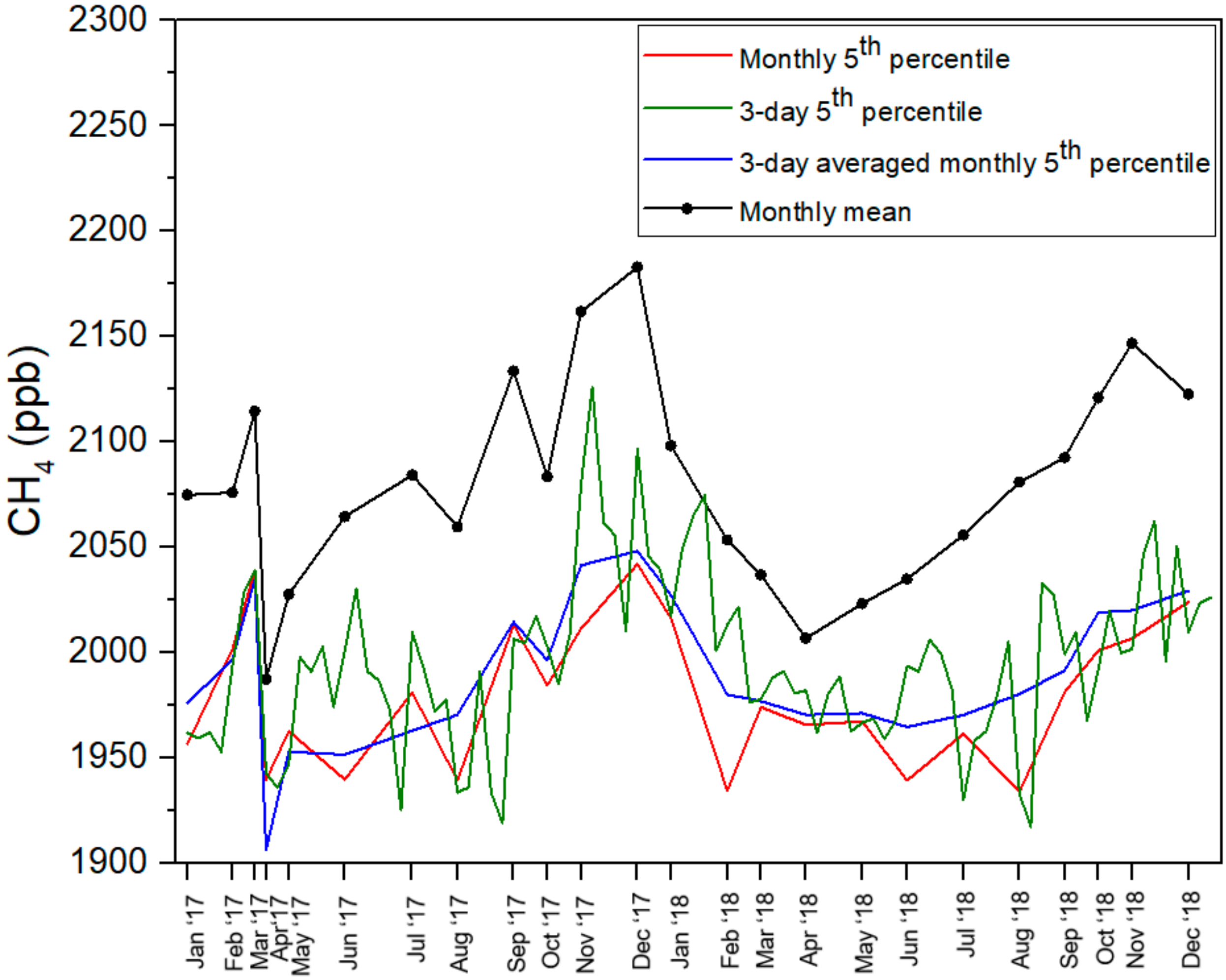

Figure S2. Fifth percentile CH_4 background mixing ratios (monthly, 3-day moving average and 3-day moving monthly average).

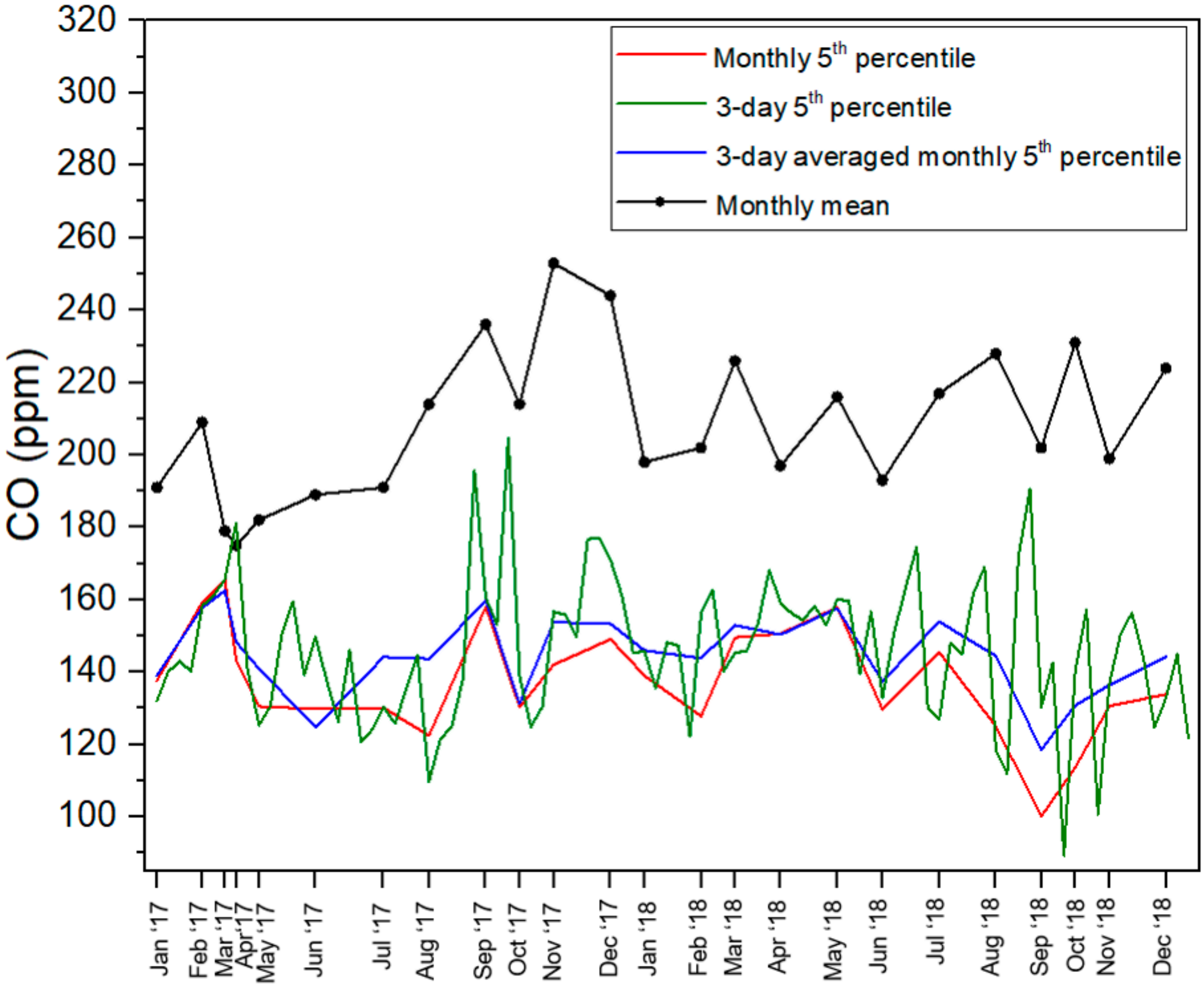

Figure S3. Fifth percentile CO background mixing ratios (monthly, 3-day moving average and 3-day moving monthly average).

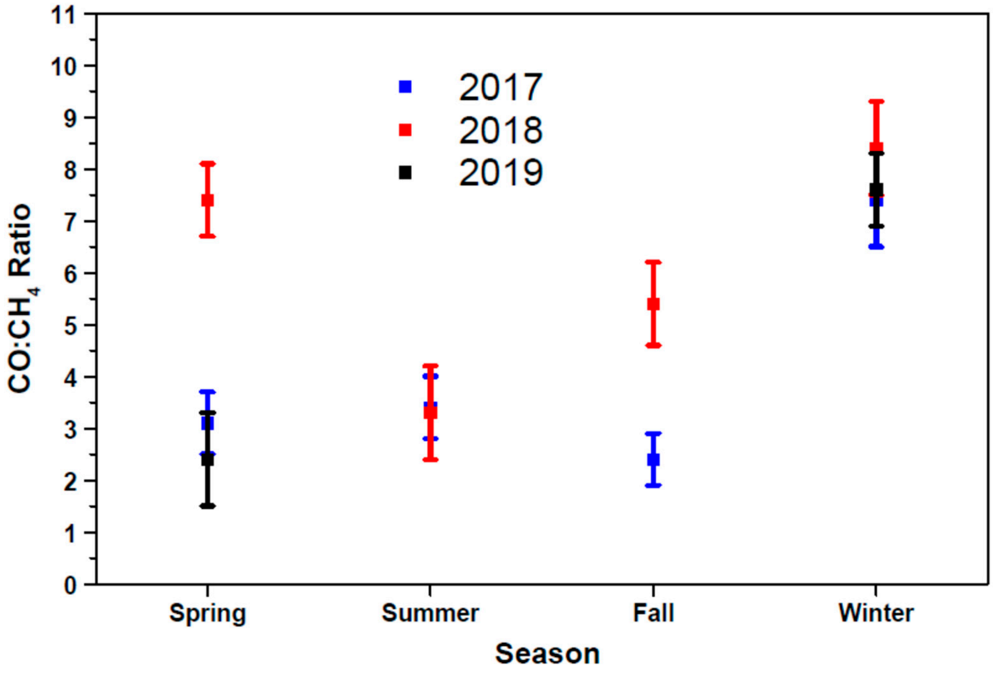

Figure S4. Seasonal $CO:CH_4$ ratios in ppb ppm^{-1} observed between 2017 and 2019.

Table S1. Estimated contributions to the urban CO sink and biogenic source by the respective OH + CO, OH +CH_4, and OH + isoprene oxidation reactions, utilizing a maximum [OH] of 2×10^7 molec./cm^3.

Species	Transit Time (s)	k_{OH} (cm^{3}mol^{-1}s^{-1})	Estimated Mole Fraction (nmolmol^{-1})	γ_{OH} (% C)	γ_{OH} Molecule of CO per Molecule of Species (VOC)	Yield OH (nmomol^{-1})	Total CO (nmolmol^{-1})
CH_4	t = 3600 s	6.40×10^{-15}	1900	0.96	0.96	0.84	0.84
Isoprene	t = 3600 s	1.0×10^{-10}	9	0.38	1.90	17.1	17.1
	t = 3600 s	1.0×10^{-10}	9	0.6	3.0	27	27
	t = 5040 s	1.0×10^{-10}	9	0.38	1.9	17.1	17.1
	t = 5040 s	1.0×10^{-10}	9	0.6	3.0	27	27
CO sink by OH	t = 3600 s	1.44×10^{-13}	160	N/A	N/A	−1.65	−1.65

Table S2. Estimated contributions to the urban CO sink and biogenic source by the respective OH + CO, OH + CH_4, and OH + isoprene oxidation reactions, utilizing a minimum [OH] of 1×10^6 molec./cm^3.

Species	Transit Time (s)	k_{OH} (cm^{3}mol^{-1}s^{-1})	Estimated Mole Fraction (nmolmol^{-1})	γ_{OH} (% C)	γ_{OH} Molecule of CO per Molecule of Species (VOC)	Yield OH (nmomol^{-1})	Total CO (nmolmol^{-1})
CH_4	t = 3600 s	6.40×10^{-15}	1900	0.96	0.96	0.042	0.042
Isoprene	t = 3600 s	1.0×10^{-10}	9	0.38	1.90	5.2	5.2
	t = 3600 s	1.0×10^{-10}	9	0.6	3.0	8.2	8.2
	t = 5040 s	1.0×10^{-10}	9	0.38	1.9	6.7	6.7
	t = 5040 s	1.0×10^{-10}	9	0.6	3.0	10.7	10.7

CO sink by OH	t = 3600 s	1.44×10^{-13}	160	N/A	N/A	−0.08	−0.08

Table S3. Seasonal $CO:CH_4$ ratio and correlations.

Year	Season	Correlation $CO:CH_4$ ratio (ppb ppm^{-1})	R^2
2017	Winter	7.4 ± 0.9	0.8
	Summer	3.4 ± 0.6	0.5
	Fall	2.4 ± 0.5	0.5
	Spring	3.1 ± 0.6	0.1
2018	Winter	8.4 ± 0.9	0.8
	Summer	3.3 ± 0.9	0.3
	Fall	5.4 ± 0.8	0.7
	Spring	1.9 ± 0.5	0.3
2019	Winter	7.6 ± 0.7	0.9
	Spring	2.4 ± 0.87	0.2

References

1. Parker, R.J.; Boesch, H.; Wooster, M.J.; Moore, D.P.; Webb, A.J.; Gaveau, D.; Murdiyarso, D. Atmospheric CH_4 and CO_2 enhancements and biomass burning emission ratios derived from satellite observations of the 2015 Indonesian fire plumes. *Atmos. Chem. Phys.* **2016**, *16*, 10111-10131, doi:10.5194/acp-16-10111-2016.
2. Wong, K.W.; Fu, D.; Pongetti, T.J.; Newman, S.; Kort, E.A.; Duren, R.; Hsu, Y.K.; Miller, C.E.; Yung, Y.L.; Sander, S.P. Mapping CH_4 :CO_2 ratios in Los Angeles with CLARS-FTS from mount Wilson, California. *Atmos. Chem. Phys.* **2015**, *15*, 241-252, doi:10.5194/acp-15-241-2015.
3. Huang, W.; Xiao, W.; Zhang, M.; Wang, W.; Xu, J.; Hu, Y.; Hu, C.; Liu, S.; Lee, X. Anthropogenic CH_4 emissions in the Yangtze river delta based on a "top-down" method. *Atmosphere* **2019**, *10*, 185.
4. Tohjima, Y.; Kubo, M.; Minejima, C.; Mukai, H.; Tanimoto, H.; Ganshin, A.; Maksyutov, S.; Katsumata, K.; Machida, T.; Kita, K. Temporal changes in the emissions of CH_4 and co from China estimated from CH_4/CO_2 and CO/CO_2 correlations observed at Hateruma island. *Atmos. Chem. Phys.* **2014**, *14*, 1663-1677, doi:10.5194/acp-14-1663-2014.
5. McKain, K.; Down, A.; Raciti, S.M.; Budney, J.; Hutyra, L.R.; Floerchinger, C.; Herndon, S.C.; Nehrkorn, T.; Zahniser, M.S.; Jackson, R.B.; et al. Methane emissions from natural gas infrastructure and use in the urban region of Boston, Massachusetts. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 1941-1946, doi:doi:10.1073/pnas.1416261112.
6. Hendrick, M.F.; Ackley, R.; Sanaie-Movahed, B.; Tang, X.; Phillips, N.G. Fugitive methane emissions from leak-prone natural gas distribution infrastructure in urban environments. *Environ. Pollut.* **2016**, *213*, 710-716, doi:10.1016/j.envpol.2016.01.094.
7. Alvarez, R.A.; Pacala, S.W.; Winebrake, J.J.; Chameides, W.L.; Hamburg, S.P. Greater focus needed on methane leakage from natural gas infrastructure. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 6435-6440, doi:doi:10.1073/pnas.1202407109.
8. Brandt, A.R.; Heath, G.A.; Kort, E.A.; O'Sullivan, F.; Pétron, G.; Jordaan, S.M.; Tans, P.; Wilcox, J.; Gopstein, A.M.; Arent, D.; et al. Methane leaks from North American natural gas systems. *Science* **2014**, *343*, 733-735, doi:doi:10.1126/science.1247045.
9. Brandt, A.R.; Heath, G.A.; Cooley, D. Methane leaks from natural gas systems follow extreme distributions. *Environ. Sci. Technol.* **2016**, *50*, 12512-12520, doi:10.1021/acs.est.6b04303.

10. Ren, X.; Salmon, O.E.; Hansford, J.R.; Ahn, D.; Hall, D.; Benish, S.E.; Stratton, P.R.; He, H.; Sahu, S.; Grimes, C.; et al. Methane emissions from the Baltimore-Washington area based on airborne observations: Comparison to emissions inventories. *J. Geophys. Res. Atmos.* **2018**, *123*, 8869-8882, doi:https://doi.org/10.1029/2018JD028851.
11. Plant, G.; Kort, E.A.; Floerchinger, C.; Gvakharia, A.; Vimont, I.; Sweeney, C. Large fugitive methane emissions from urban centers along the U.S. East coast. *Geophys. Res. Lett.* **2019**, *46*, 8500-8507, doi:https://doi.org/10.1029/2019GL082635.
12. Anderson, D.C.; Lindsay, A.; DeCarlo, P.F.; Wood, E.C. Urban emissions of nitrogen oxides, carbon monoxide, and methane determined from ground-based measurements in Philadelphia. *Environ. Sci. Technol.* **2021**, *55*, 4532-4541, doi:10.1021/acs.est.1c00294.