



# Variability of CH<sub>4</sub>:CO<sub>2</sub> ratio at Science Park manholes

**Group 2:** *Laura Portos Amill, Socorro Margarita  
Rodrigo, Foteini Stavropoulou, Yujie Ye  
under the guidance of Hossein Maazallahi*

17 December 2020

# Background

- **CH<sub>4</sub> is a strong greenhouse gas**
  - Direct and indirect effects
- **Sources of methane in urban areas**
  - Landfills
  - Wastewater
  - Leakage of natural gas pipeline
  - Sewer systems

*Guisasola et al. (2007)*

# Background

- **Importance of measuring CH<sub>4</sub> in sewer systems**
  - Potential significant contribution to the greenhouse effect  
e.g. Gold Coast (Australia)  
Population: 540.000  
40–250 tCH<sub>4</sub> annually
  - Health and safety risks  
(incidents of explosions)

**Leaking methane gas led to French Quarter explosion and car fire, NOFD chief says**

BY MATT SLEDGE | STAFF WRITER PUBLISHED DEC 16, 2019 AT 6:39 PM | UPDATED DEC 16, 2019 AT 6:51 PM 1 min to read



1 of 6 FOLLOW US



*Guisasola et al. (2007)*

# Background

- **Factors affecting methane production in sewer systems**
  - Hydraulic retention time (HRT)
  - Pipeline geometry (i.e. surface area to volume ratio, A/V)
  - Chemical oxygen demand (COD)
  - Atmospheric Temperature
  - Presence of Nitrogen-related compounds
  - pH level

*Foley et al. (2009); Guisasola et al. (2008); Gutierrez et al. (2013)*

# Objectives

- Characterize possible methane sources from CH<sub>4</sub>:CO<sub>2</sub> ratios
- Quantify CH<sub>4</sub> emissions from manholes
  - Quantify CH<sub>4</sub> emissions of manholes failed because no accumulation was observed in the bucket

# Methods: Instrument used

One cavity ring-down spectroscopy (CRDS) analyzer Picarro Inc. model G2301

- CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O concentrations
- Integration time of approximately 1s
- Frequency of 0.3 Hz for each species



# Methods:

## Mobile atmospheric measurements

- Installed on the back seat of a 2012 Volkswagen Transporter
- Measurements taken by directing a hose into the manhole opening
- Pumped into the CRDS machine

## Additional info:

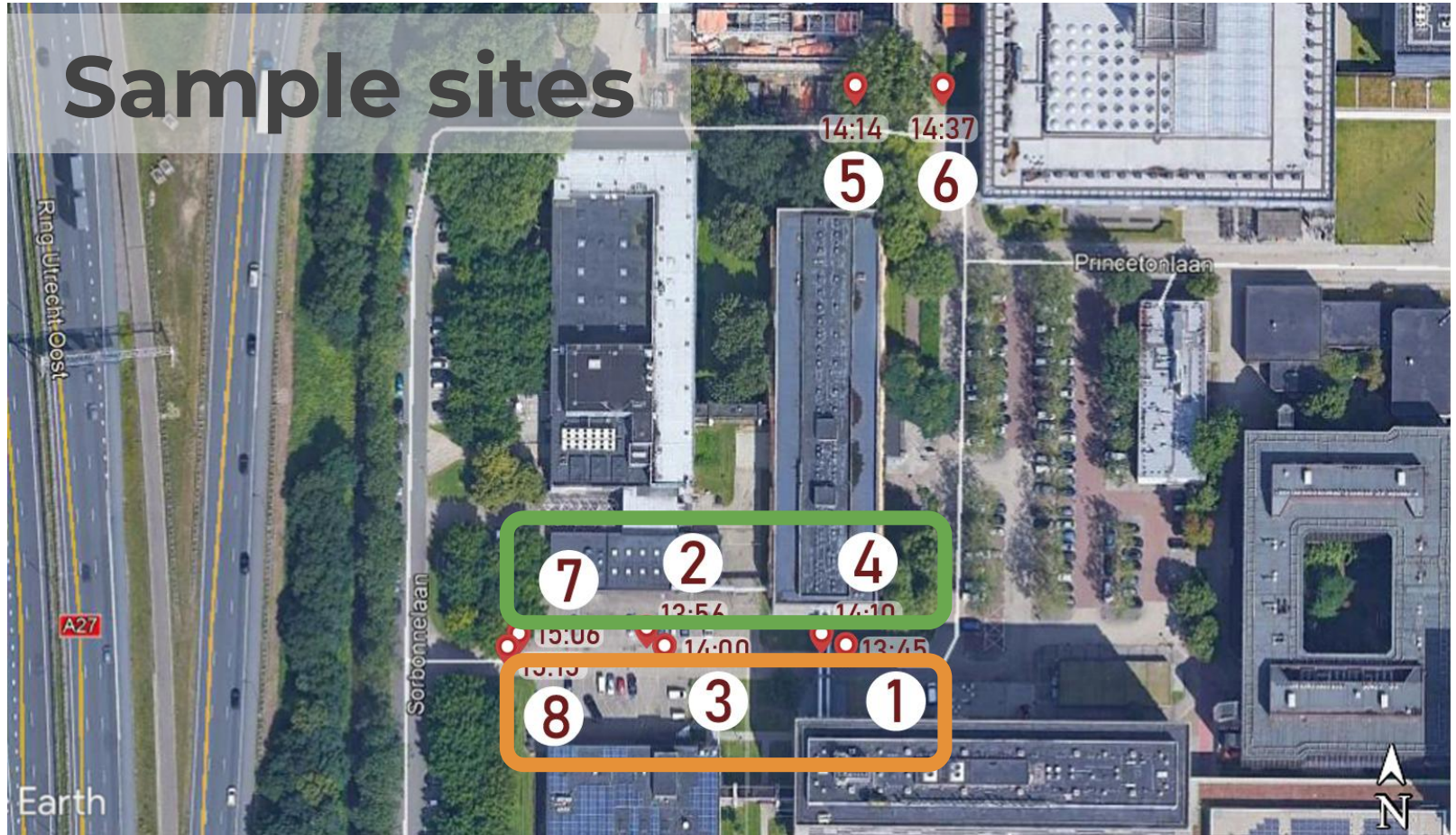
### Isotopic signatures

- Isotope-ratio mass spectrometry





# Sample sites







# Manhole info

- **4 November 2020:**  
Sampling date
- #1-4 and #6-8: Manholes
- #5: Storm drain

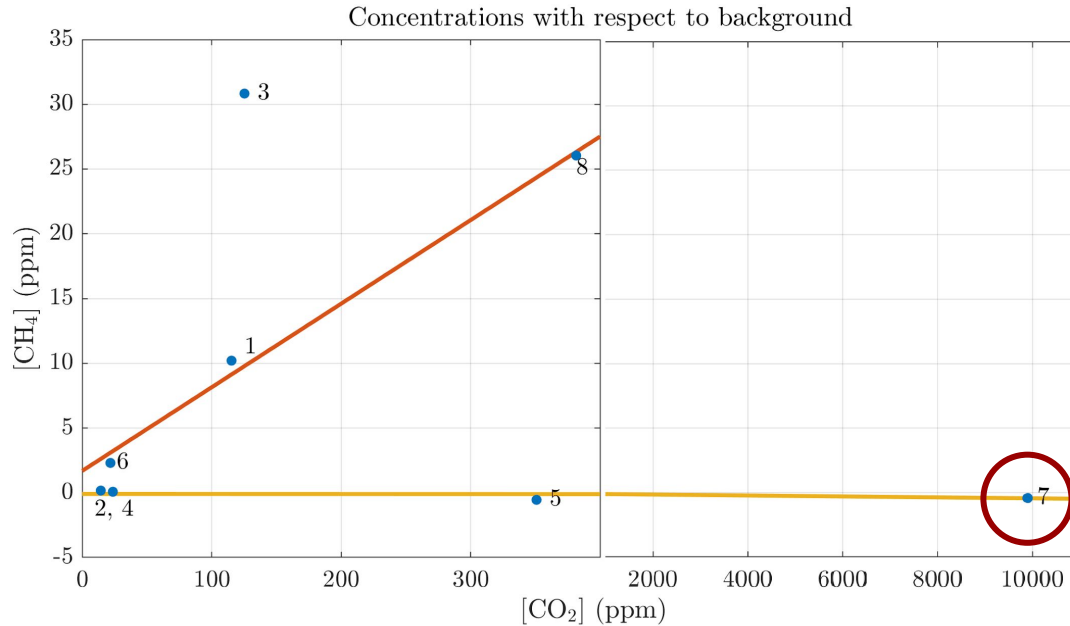
## Isotope data

- #1, #3, and #5 have isotope measurements
- Background

# CH<sub>4</sub> and CO<sub>2</sub> concentrations

	CO <sub>2</sub> (ppm)	CH <sub>4</sub> (ppm)
<b>Background</b>	420 ± 5.00	2.00 ± 0.01
<b>1</b>	536 ± 8.00	12.2 ± 2.70
<b>2</b>	435 ± 3.00	2.17 ± 0.01
<b>3</b>	546 ± 13.0	32.8 ± 2.40
<b>4</b>	444 ± 7.00	2.07 ± 0.01
<b>5</b>	771 ± 1.00	1.45
<b>6</b>	442 ± 13.0	4.30 ± 0.80
<b>7</b>	103 · 10 <sup>2</sup> ± 20.0	1.56
<b>8</b>	802 ± 21.0	28.1 ± 0.90

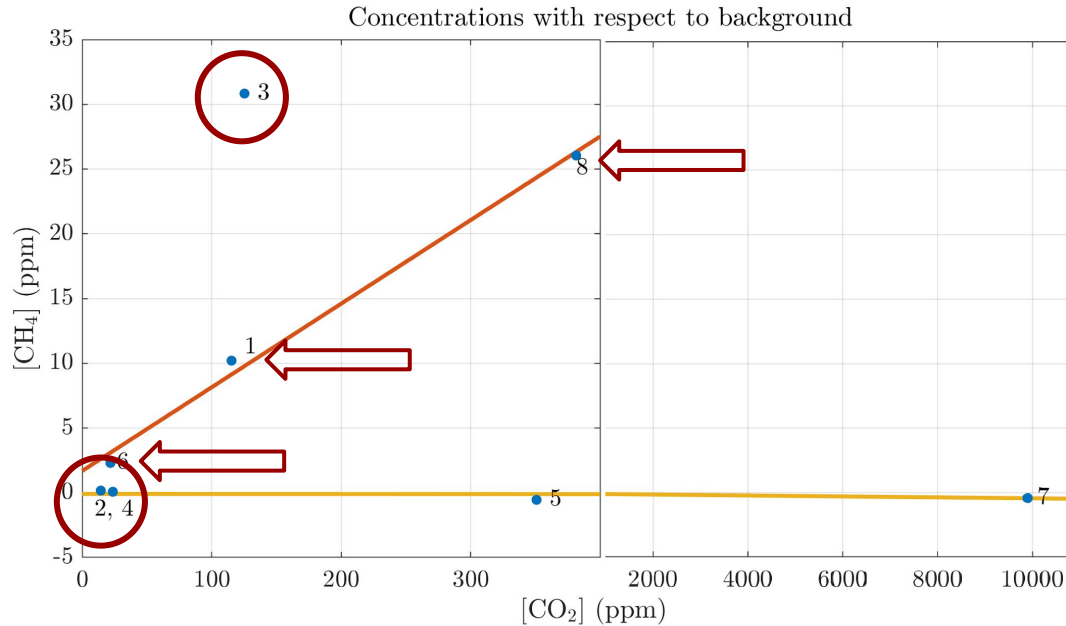
# CO<sub>2</sub> and CH<sub>4</sub> concentrations above background



- #s 1, 6, 8:  
CH<sub>4</sub>:CO<sub>2</sub> = 65 ppb/ppm
- #3:  
CH<sub>4</sub>:CO<sub>2</sub> = 246  
ppb/ppm (*corrected from presentation*)
- #s 2, 4, 5, 7:  
CH<sub>4</sub>:CO<sub>2</sub>  $\cong$  0 ppb/ppm
  - Microorganisms can oxidize methane in sewers
  - Thought to be a weak sink

*Liu et al. (2016)*

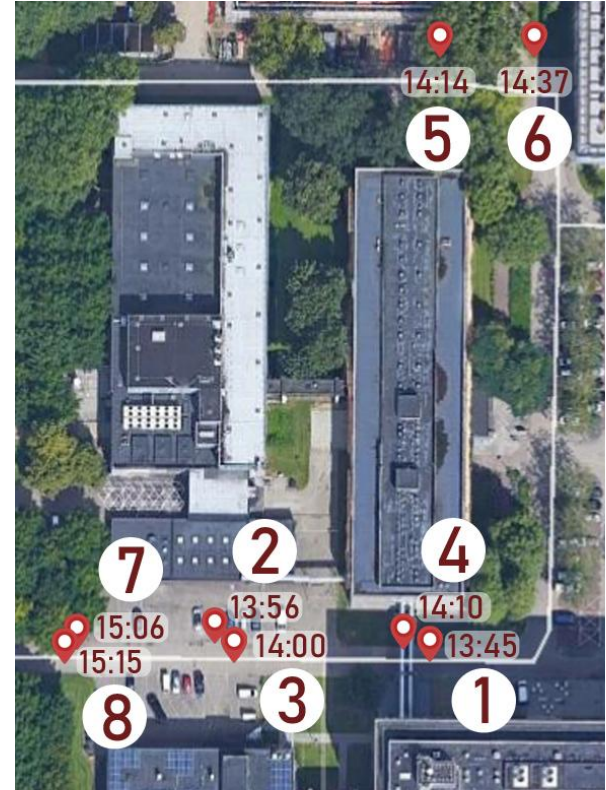
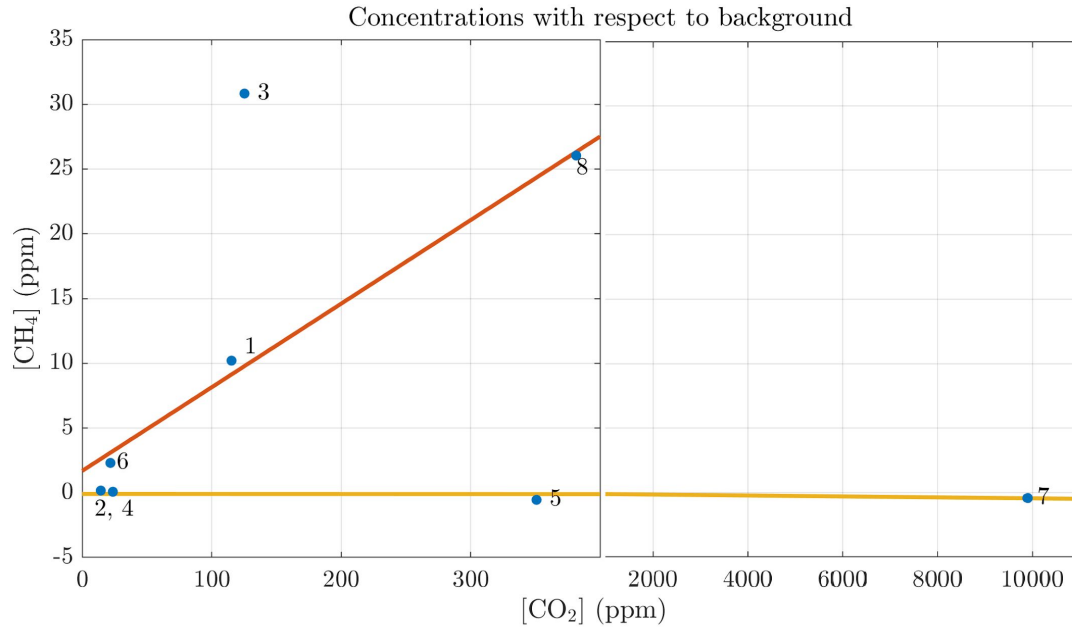
# CO<sub>2</sub> and CH<sub>4</sub> concentrations above background



- #s 1, 6, 8:  
CH<sub>4</sub>:CO<sub>2</sub> = 65 ppb/ppm
- #3:  
CH<sub>4</sub>:CO<sub>2</sub> = 246  
ppb/ppm (*corrected from presentation*)
- #s 2, 4, 5, 7:  
CH<sub>4</sub>:CO<sub>2</sub>  $\cong$  0 ppb/ppm
  - Microorganisms can oxidize methane in sewers
  - Thought to be a weak sink

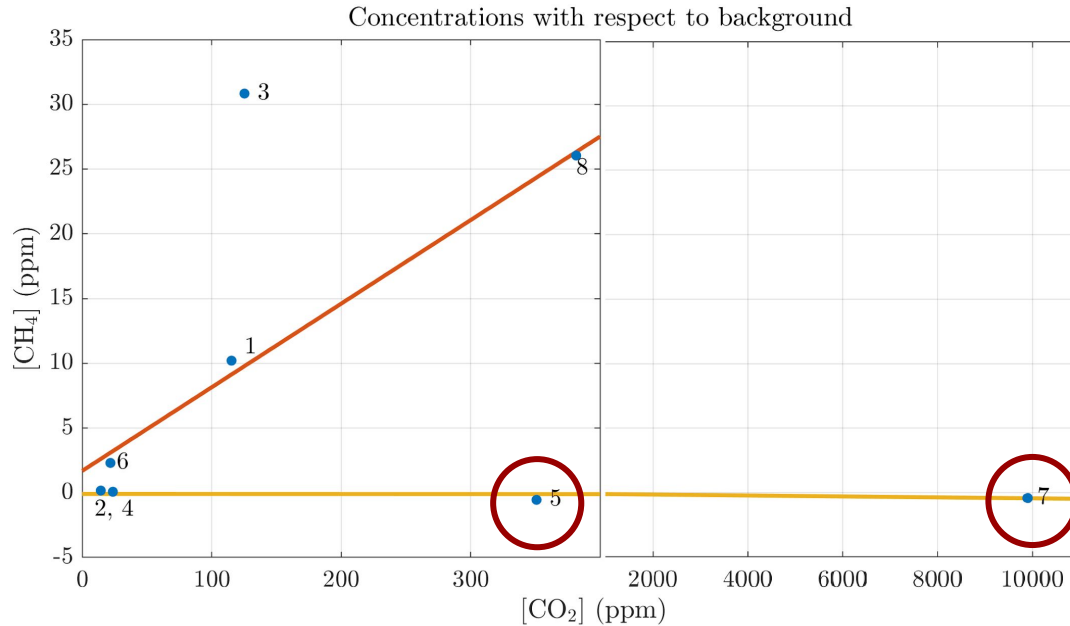
*Liu et al. (2016)*

# CO<sub>2</sub> and CH<sub>4</sub> concentrations above background



*Liu et al. (2016)*

# CO<sub>2</sub> and CH<sub>4</sub> concentrations above background



- #s 1, 6, 8:  
CH<sub>4</sub>:CO<sub>2</sub> = 65 ppb/ppm
- #3:  
CH<sub>4</sub>:CO<sub>2</sub> = 246  
ppb/ppm (*corrected from presentation*)
- #s 2, 4, 5, 7:  
CH<sub>4</sub>:CO<sub>2</sub>  $\cong$  0 ppb/ppm
  - Microorganisms can oxidize methane in sewers
  - Thought to be a weak sink

*Liu et al. (2016)*

# CH<sub>4</sub>:CO<sub>2</sub> ratio -- This experiment vs. previous studies

Source	Combustion-related/ Open roads	Gas field
<b>CH<sub>4</sub>:CO<sub>2</sub> ratio (ppb/ppm)</b>	Hamburg: 3.2±3.9 <small>Maazallahi et al., 2020</small> Utrecht: 9.8 ±5.8 <small>Maazallahi et al., 2020</small> 4.6 x 10 <sup>-2</sup> <small>Popa et al., 2014</small> 0.41 <small>Nam et al., 2004</small> 0.3 <small>Naus et al., 2018</small>	13 <small>Tait et al., 2013</small>

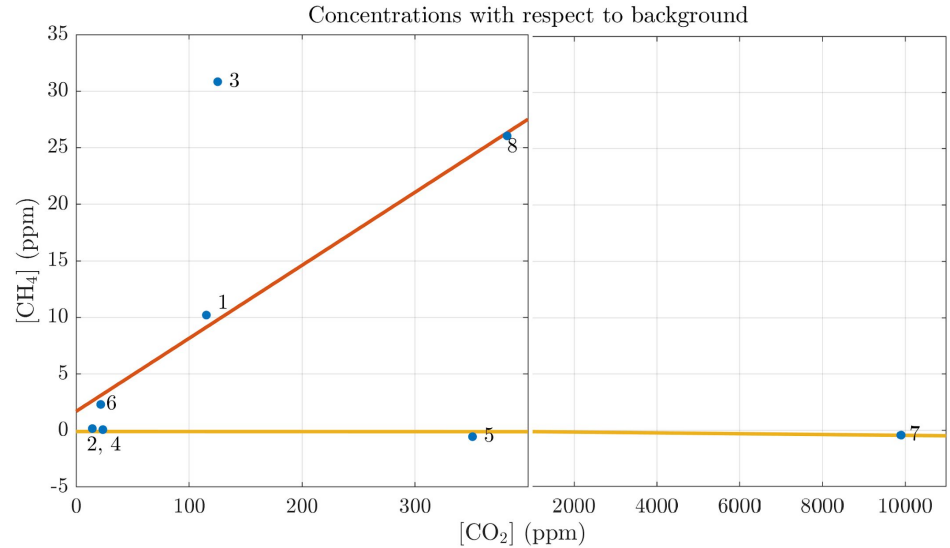
- #s 1, 6, 8:  
CH<sub>4</sub>:CO<sub>2</sub> = 65 ppb/ppm
- #3:  
CH<sub>4</sub>:CO<sub>2</sub> = 246  
ppb/ppm (*corrected  
from presentation*)
- #s 2, 4, 5, 7:  
CH<sub>4</sub>:CO<sub>2</sub> ≈ 0 ppb/ppm
  - Microorganisms can oxidize methane in sewers
  - Thought to be a weak sink



# Isotope data

## Manholes 1, 3, and 5

- $\delta D = -264\text{‰}$
- $\delta^{13}C = -51\text{‰}$
- Indicates bacterial source (*Fries et al., 2018*)



# Conclusions

- Within close proximity, manhole CH<sub>4</sub>:CO<sub>2</sub> indicates different sources/“families”
  - Interesting for future work
- CH<sub>4</sub> concentrations can be significantly lower than background
- Emissions indicate microbial/biogenic sources

# References

- Fries A.E., Schiffman L.A., Shuster W.D., Townsend-Small A.: Street-level emissions of methane and nitrous oxide from the wastewater collection system in Cincinnati, Ohio\*, Environmental Pollution 236, 247-256, <https://doi.org/10.1016/j.envpol.2018.01.076>, 2018
- Guisasola A., Sharmaa K.R., Kellera J., Yuana Z.: Development of a model for assessing methane formation in rising main sewers, Water Research 43, 2874-2884, <https://doi.org/10.1016/j.watres.2009.03.040>, 2009
- Guisasola A., de Haas D., Keller J., Yuan Z.: Methane formation in sewer systems, WATER RESEARCH 42, 1421–1430, <https://doi.org/10.1016/j.watres.2007.10.014>, 2008
- Liu Y., Ni B., Sharma K.R., Yuan Z.: Methane emission from sewers, Science of the Total Environment 524-525, 40-51, <https://doi.org/10.1016/j.scitotenv.2015.04.029>, 2016
- Maazallahi H., Fernandez J. M., Menoud M., Zavala-Araiza D., Weller Z. D., Schwietzke S., von Fischer J.C., Denier van der Gon H., and Rockmann T.: Methane mapping, emission quantification, and attribution in two European cities: Utrecht (NL) and Hamburg (DE), Atmos. Chem. Phys., 20, 14717–14740, <https://doi.org/10.5194/acp-20-14717-2020>, 2020
- Tait D.R., Santos I.R., Maher D.T.: Atmospheric radon, CO<sub>2</sub>, and CH<sub>4</sub> dynamics in an Australian coal seam gas field, AGU Fall Meeting abstracts A53H-06, 2013