Characterisation of $\delta^{13}CH_4$ source signatures from methane sources in Germany with two different sampling strategies

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Motivation

- Global long-term measurements show an accelerating increase rate of atmospheric CH_4 since 2007 ([1], Fig. 1a).
- At the same time the isotope ratio in the atmosphere is shifting towards more depleted values (Fig. 1b)
- Each source type has a different isotopic signature, depending on production processes and origin.
- Thus, the isotopic composition measured in the atmosphere contains information about the sources that contribute to the measured mole fraction.
- Especially at the local and regional scale, the measurement of the atmospheric isotope ratio of CH_4 provides information on the composition of CH_4 emissions.
- However, this requires a good understanding of local and regional isotopic source signatures.
- By combining the knowledge of isotopic source signatures with observations of greenhouse gas isotopes in the atmosphere, it is possible to infer emission budgets as well as observed atmospheric trends in mole fraction and isotopic composition (e.g. [2], [3], [4] and [5]).

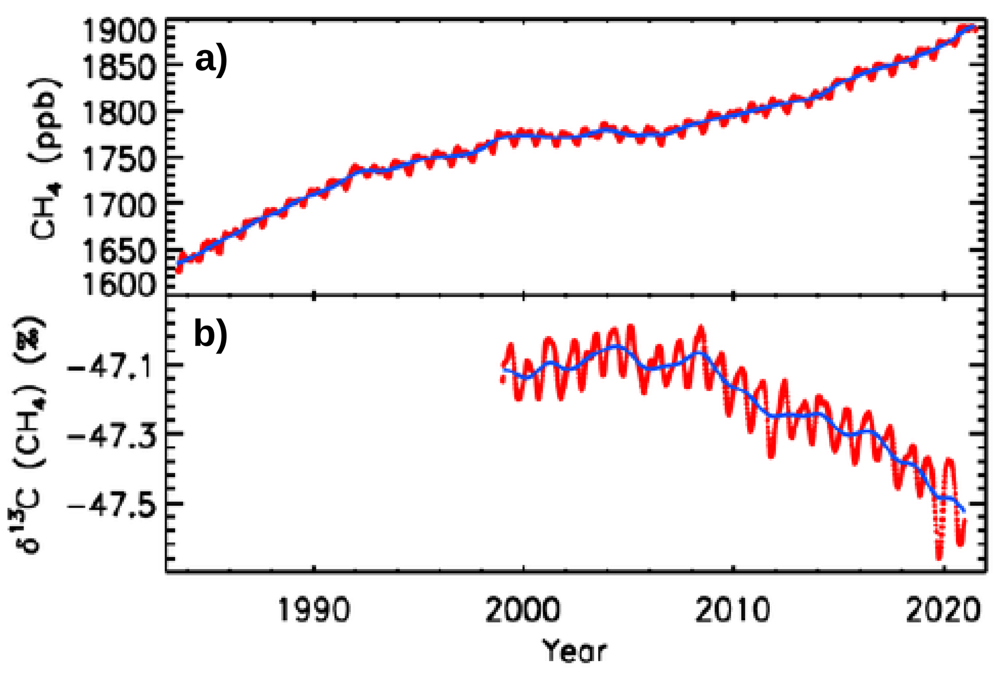


Figure 1: a) Global average methane mole fraction and **b)** methane isotope measurements from the NOAA Global Greenhouse Gas Reference Network marine boundary layer sites. The blue line shows annual average mole fractions, while the red symbols are monthly averages showing the seasonal cycle. CH4 isotopes are measured by the Institute of Arctic and Alpine Research at the University of Colorado Boulder.[1]

Instrumentation and Measurements

- Samples are measured at a CRDS analyser (G2201-i, Picarro) for 30 minutes.
- Sample gas is dried via a Nafion dryer or cooling trap before entering the analyzer.
- First 10 minutes of each measurement are flagged due to flushing and stabilization time.
- Allan standard deviation was used to determine the optimum averaging period (20 minutes average to reach Allan std for $\delta^{13}CH_4$ of 0.25 ‰).
- Single-point calibration strategy.
- Correction for cross sensitivity with H_2O/C_2H_6 and CH_4 dependence.

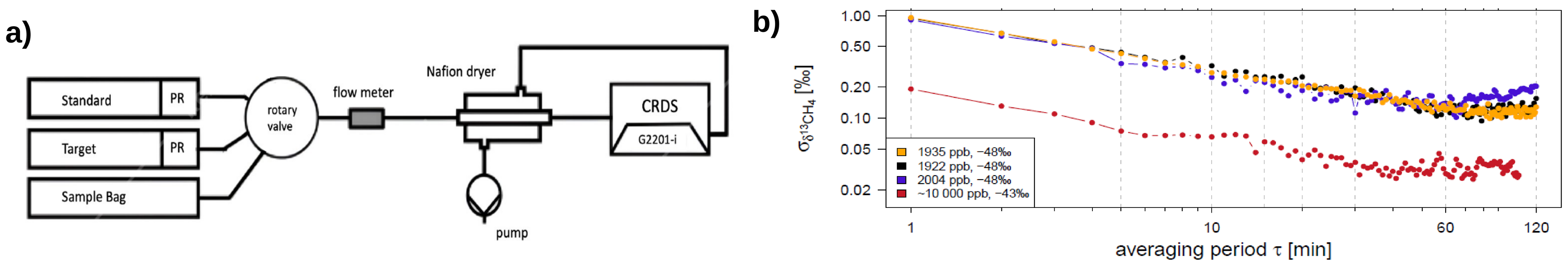


Figure 2: a) Schematic overview of experimental set-up for sample measurements in Heidelberg **b)** Allan standard deviation of CRDS G2201-i determined from four cylinders. One cylinder contains 10 ppm CH_4 (red) and the others around 2 ppm (black, blue, orange) [4].

Sampling Strategy and $\delta^{13}CH_4$ determination

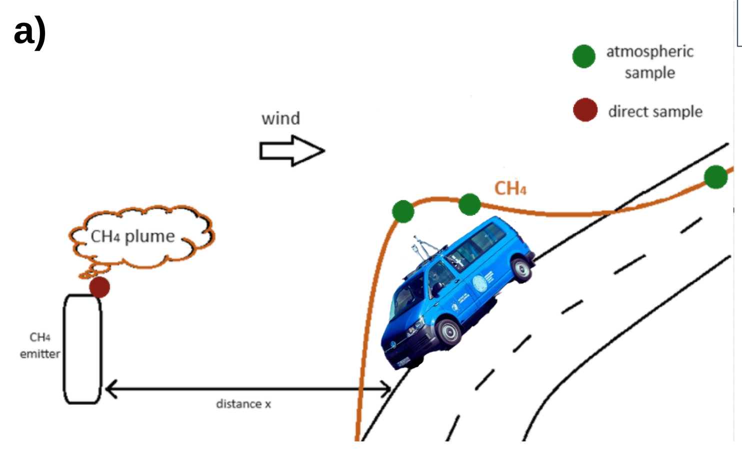
Sampling Strategy

Direct sampling at the emission source

⬇

Dilution in synth. air to ~10 ppm CH_4

During mobile measurements ambient **atmospheric** air c_a near the source is sampled



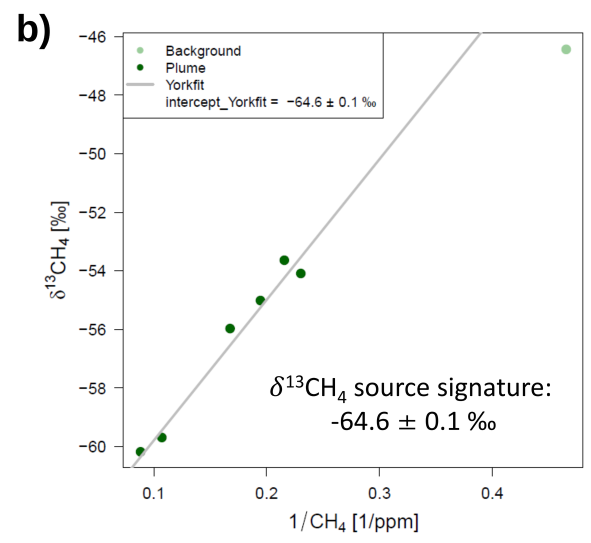


Figure 3: a) Schematic overview of sampling strategies directly at the emitter or in the plume **b)** Keeling plot with York fit through $\delta^{13}CH_4$ values of background (lightgreen) and plume (darkgreen) sample meaurements.

Sample containing mixing of atmospheric background c_b and methane source mixing ratio c_s

$$c_a = c_b + c_s$$

Mass conservation

$$\delta^{13}C_a c_a = \delta^{13}C_b c_b + \delta^{13}C_s c_s$$

Keeling approach

$$\delta^{13}C_a = c_b(\delta^{13}C_b + \delta^{13}C_s)(1/c_a) + \delta^{13}C_s$$

Summary

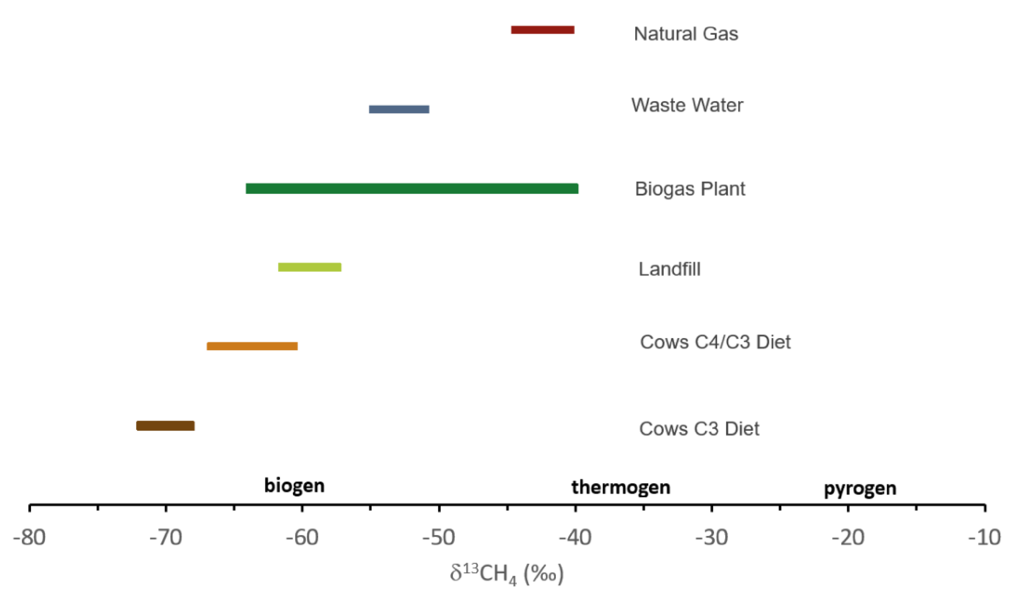


Figure 4: Determined $\delta^{13}CH_4$ isotopic source signature of different CH_4 emission sources. Biogenic sources as cows have more depleted values than emissions from thermogenic sources like natural gas. Biogas plants in particular have a wide range of isotope values.

- Application of two different sampling strategies to determine the isotopic source signature ($\delta^{13}CH_4$).
- Direct sampling is an easy and reliable way to get isotopic information but often not accessible.
- Precise determination of the isotopic signature in the plume via Keeling plot method together with the York fit.
- For accurate results, a careful characterisation of the CRDS analyser and an appropriate measurement duration is required.
- Limitation factor of $\delta^{13}CH_4$ source signature determination is plume mole fraction above background and sample quantity.
- Keeling method mostly in good agreement with measured isotope ratios of direct samples.
- Biogas plants have a particularly large range in isotope signature, as $\delta^{13}CH_4$-values depend on substrates fed.

$\delta^{13}CH_4$ Values of different CH_4 Sources

*preliminary results

Emission source	Location	Sample	Period of time	Number of sample locations	$\delta^{13}CH_4$ (‰)	
Natural Gas	Heidelberg	direct	2016-2018	1	-43.3 ± 0.8	
Natural Gas	Heidelberg	direct	2022-2024	1	-42.8± 1.3	-42.6±0.4 ‰
Natural Gas	Stuttgart	direct	2019/2020	1	-41.8 ± 0.2	
WWTP	Heidelberg	direct	2024	1	-52.5 ± 0.2*	
WWTP	Heidelberg	atmospheric	2024	3	-53.0 ± 2.0*	
WWTP	Stuttgart	direct	2020	1	-52.7 ± 0.9	-52.9±0.4 ‰
WWTP	Stuttgart	atmospheric	2020	2	-54.5 ± 1.3	
Sewer System	Heidelberg	atmospheric	2023	16	-51.9 ± 2.2	
Biogas Plant	Heidelberg	direct	2023/2024	3	-62.5 ± 0.4*	
Biogas Plant	Heidelberg	atmospheric	2023/2024	5	-59.5 ± 1.4*	
Biogas Plant	Heidelberg	atmospheric	2016/2017	AirCore[4]	-62.4 ± 1.2	
Biogas Plant	Rottal	direct	2022/2023	2	-45.1 ± 0.1*	-56.6±3.2 ‰
Biogas Plant	Altbierlingen	direct	2023	3	-58.2 ± 1.1*	
Biogas Plant	Mardorf	direct	2024	2	-39.9 ± 0.1*	
Biogas Plant	Bad Rappenau1	direct	2024	2	-64.1 ± 0.1*	
Biogas Plant	Bad Rappenau2	direct	2024	1	-61.3 ± 0.3*	
Cowshed	Weinheim	atmospheric	2017-2019	AirCore[4]	-64.9 ± 1.6	
Cowshed	Ladenburg	atmospheric	2019	3	-63.1 ± 2.5	-63.6±0.7 ‰
Cowshed	Mardorf	atmospheric	2024	2	-62.5 ± 0.1*	
Pasture cows	Schauinsland	atmospheric	2018	AirCore[4]	-71.0 ± 1.0	-71.0±1.0 ‰
Landfill	Sinsheim	direct	2017	1	-59.5 ± 0.1	-59.5±0.1 ‰

References and Acknowledgements

[1] NOAA, 2022; State of the Science FACT SHEET Methane and Climate Change
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[4] Hoheisel, A., et al. (2019), An improved method for mobile characterisation of δ13CH4 source signatures and its application in Germany, Atmos. Meas. Tech., 12, 1123–1139, 2019. https://doi.org/10.5194/amt-12-1123-2019
[5] Schaefer, Hinrich et al. "A 21st-century shift from fossil-fuel to biogenic methane emissions indicated by $^{13}CH_4$." Science (New York, N.Y.) vol. 352,6281 (2016): 80-4. doi:10.1126/science.aad2705

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