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Characterization of biogas plants in Germany: methane emission rate quantification and isotopic source signatures

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Abstract

The development of biogas as a renewable energy source in Europe and especially in Germany, the largest biogas producer in Europe, requires an appropriate strategy to quantify potential methane (CH₄) losses to ensure the sustainability of renewable energy production in the biogas sector. In addition to high uncertainties in emission factors, there is little information on the temporal variation of CH_4 emissions from biogas plants. To evaluate this issue, CH_4 emissions were assessed across 65 biogas production sites in Germany using mobile measurements combined with a Gaussian dispersion model. The quantified CH_4 emission rates ranged from 0.3 to 255 kg h⁻¹. A significant environmental problem is the uncontrolled release of methane into the atmosphere, which is approximately 5 %(median of all analyzed biogas plants) of the methane produced. To ensure the reliability and consistency of the results, the measurement and quantification method used has been thoroughly tested and refined through controlled CH_4 release experiments. These experiments helped to identify and mitigate potential sources of uncertainty. As a result, the method demonstrated an overall accuracy of 30 % in quantifying emission rates. Additionally, the isotopic source signature (δ^{13} CH₄) was determined for 18 biogas plants, revealing a wide range of values between -62.7 % to -39.6 %, strongly influenced by the feedstock used.

Zusammenfassung

Die Entwicklung von Biogas als erneuerbare Energiequelle in Europa und insbesondere in Deutschland, dem größten Produzenten von Biogas in Europa, erfordert eine geeignete Strategie zur Quantifizierung potentieller Methanverluste (CH_4) , um die Nachhaltigkeit der erneuerbaren Energieerzeugung im Biogassektor sicherzustellen. Neben großen Unsicherheiten bei den Emissionsfaktoren gibt es nur wenige Informationen über die zeitliche Variation der CH₄-Emissionen aus Biogasanlagen. Um dieses Problem zu untersuchen, wurden die CH₄-Emissionen an 65 Biogasproduktionsstandorten in Deutschland unter Verwendung mobiler Messungen und eines Gauß'schen Dispersionmodells ermittelt. Die quantifizierten Emissionsraten reichen von 0.3 bis 255 kg CH_4 h⁻¹. Ein erhebliches Umweltproblem ist die unkontrollierte Freisetzung von Methan in die Atmosphäre, die etwa 5 %(Median aller analysierten Biogasanlagen) des erzeugten Methans ausmacht. Um die Zuverlässigkeit und Konsistenz der Ergebnisse zu gewährleisten, wurde die verwendete Messund Quantifizierungsmethode durch kontrollierte CH₄-Freisetzungsexperimente gründlich getestet und weiterentwickelt. Diese Experimente trugen dazu bei, potenzielle Unsicherheitsquellen zu identifizieren und zu reduzieren. Im Ergebnis zeigte die Methode eine Gesamtgenauigkeit von 30 % bei der Quantifizierung der Emissionsraten. Darüber hinaus wurde die isotopische Quellsignatur ($\delta^{13}CH_4$) für 18 Biogasanlagen bestimmt. Diese weisen eine breite Spanne von Werten zwischen -62.7 ‰ bis -39.6 ‰ auf, welche stark durch das verwendete Substrat beeinflusst wurden.

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Chapter 1

Introduction

The Earth's climate is, next to other factors, strongly dependent on the Earth's radiation balance - the balance between energy received from the sun and energy emitted by Earth. Some of the energy emitted by the Earth is trapped by greenhouse gases (GHGs), causing heat retention. The accumulation of GHGs in the atmosphere therefore leads to changes in the radiation balance and alters climate and weather patterns on both regional and global scales, and ultimately results in global warming.

In order to keep the possible risks of global warming as low as possible, world leaders at the UN Climate Change Conference concluded under the historic Paris Agreement in 2015, to limit the mean global surface temperature increase since pre-industrial era well below 2 °C, and if possible below 1.5 °C (UNFCCC [2015]). In addition to natural sources, such as volcanic activity, forest fires, wetlands and the release of gases through decomposing organic material, it is above all the anthropogenic contribution that is responsible for the continual increase in GHG concentrations in the atmosphere and thus for the progressive global warming (Saunois et al. [2024]). Particularly since the industrial era, humans have been contributing to climate change through the combustion of fossil fuels and the related emissions of carbon dioxide (CO_2) and methane (CH_4) . The Mauna Loa Observatory on the US island of Hawaii has been measuring the mole fraction of carbon dioxide in the atmosphere since 1958 (Keeling and Graven [2021]), and the National Oceanic and Atmospheric Administration (NOAA) has been measuring the mole fraction of methane in the atmosphere since 1983 (Lan et al. [2024]). Based on these atmospheric measurements, emissions are estimated using 'top-down' approaches. This can be done using a variety of techniques, ranging from simple box models with trace gas measurements (Levin et al. [2011]) to more complex inverse models that simulate gas mole fractions from atmospheric transport and a priori inventories (Bergamaschi et al. [2022], Crippa et al. [2024]). Top-down estimates are improved in particular by dense networks of monitoring stations, such as the NOAA Global network or the European Integrated Carbon Observation System (ICOS), that provide highly accurate data on greenhouse gas concentrations (NOAA, ICOS).

To get a picture of emissions as well as finding the most effective mitigation strategy, in addition to the EU other countries of the United Nations Framework Convention on Climate Change (UNFCCC) have committed themselves to report annual National Inventory Reports (NIRs) on greenhouse gas emissions. These emission inventories are based on 'bottom-up' methods for quantifying greenhouse gas emissions. They are compiled from statistical data on sources such as animal populations or fuel consumption, and from specific emission factors used to estimate emissions from different categories (Crippa et al. [2019], IPCC [2023]). However, this approach can be subject to considerable uncertainty due to unaccounted sources or significant spatial and temporal variations. Uncertainties in the bottom-up approach to methane emissions in the global budget range from 8 to 210 Tg CH₄ per year (Saunois et al. [2024]). For this reason, independent verification of emission inventories is essential. On-site measurements and quantification of emissions from specific sources offer a flexible and independent method for this purpose. While some emission sources, such as methane emissions from cattle, are well understood and based on accurate emission factors and known data regarding population size and distribution, other sources, such as unintended leaks in the gas distribution system or from technical installations like biogas plants, are more challenging to quantify and in need of further investigation.

Data from such measurements are critical for understanding, for example, the role of methane as a greenhouse gas and its impact on climate change. Emitted into the atmosphere, CH_4 is a significant and the second most important anthropogenic GHG, after CO_2 . Anthropogenic methane is mainly released by fossil resource extraction and processing, but also by waste decomposition and digestive processes in livestock and agriculture. Its global warming potential is 29.8 times larger than that of CO_2 on a time scale of 100 years (IPCC [2023]). This and the fact that methane is reduced in the atmosphere by oxidation within 12 years (IPCC [2023]) bring methane into the focus of scientists and policy makers in the understanding and fight against climate change. Global long-term records of atmospheric methane mole fraction reveal a nearly continuous increase since pre-industrial times. Since 2014 the mole fraction increases with a particularly extreme growth rate of 12.5 ± 0.4 ppb CH₄ per year (Lan et al. [2024]). Around the same time, δ^{13} CH₄ (isotope ratio ${}^{13}C/{}^{12}C$) has shifted to significantly more ${}^{13}C$ -depleted values Schaefer et al. [2016]. Each type of methane source has a different isotopic signature, depending on the production processes and origin. Thus, the isotopic composition measured in the atmosphere contains information about the sources that contributed to the measured mole fraction. The shift to more negative δ^{13} CH₄ values indicates that biogenic CH₄ sources, with their lighter isotopic signature than fossil sources, becoming an increasing factor influencing the observations (Schaefer [2019]).

Given the increase in biogenic methane in the atmosphere, these type of sources are becoming a focus of interest. Biogenic methane is produced through the anaerobic digestion of organic material by microorganisms. The increasing global demand for energy, combined with the dwindling reserves of fossil fuel and the goal of reducing greenhouse gas emissions, is shifting the focus to the generation of energy from renewable sources. In addition to energy generation from wind power and solar energy, biomass in particular is one of the most important renewable energy sources. It accounts for 50 % of Germany's renewable final energy supply due to its diverse uses (solid/gaseous fuels for heating purposes, biofuels in transport or biogas for electricity generation) (Umweltbundesamt [2025]). The method of anaerobic digestion offers the possibility of processing organic feedstock and converting it into biogas, biomethane, electricity, heat and fertilizer, thereby simultaneously managing and recycling the increasing quantities of organic waste and reducing the need to use fossil fuels. In this way, resources are utilized efficiently and, above all, continuously in order to cover the increasing energy demand and at the same time protect the environment (Fagerström et al. [2018]). Biogas contains 50 to 70 % methane and, therefore, methane losses from leaks, accidental releases and improper management practices can occur during biogas production its distribution and use. When these losses are factored into the GHG emissions calculation, they can have a substantial effect on the overall sustainability of biomethane (Scheutz and Fredenslund [2019], Olczak et al. [2025]). Due to the large number of over 9,600 biogas plants with an installed capacity greater than 7,000 MW in Germany (dena [2023]) and the environmental and economic factors of unintentional methane losses, it is particularly important to accurately estimate methane emission rates and analyze plant conditions in order to determine the climate change benefits. Several studies in Europe (e.g. Adams et al. [2015], Liebetrau et al. [2013], Fredenslund et al. [2018], Scheutz and Fredenslund [2019], Bakkaloglu et al. [2021], Fredenslund et al. [2023], Wechselberger et al. [2025], Olczak et al. [2025]), Canada (Flesch et al. [2011], Baldé et al. [2016], Baldé et al. [2022]) and Australia (Reinelt et al. [2022]) have already shown that the CH_4 loss (ratio of emitted to produced CH_4) can have a significant impact on the GHG balance of biogas plants. For instance, Fredenslund et al. [2023] reported an average CH_4 loss rate of 4.7 % for 44 agricultural biogas plants in Denmark, with a range spanning from 0.3% to 40.4%. The study by Wechselberger et al. [2023], on the other hand, focused on CH₄ losses from different biogas plant technologies. However, the studies vary in the types of facilities covered, the methods used for measurement, the scope, and the geographical coverage. While Germany ranks second in the world after China in terms of the number of biogas plants, the current state of research on emission measurements in Germany remains limited.

Achieving the goals of the Paris Agreement requires a clear understanding of where and how much of each greenhouse gas is being emitted, to enable targeted strategies to reduce anthropogenic emissions. As such, greenhouse gas mole fractions can be used to estimate the amount of emissions. My dissertation addresses these challenges by investigating CH_4 emissions from 65 biogas plants in Germany, resulting in the largest study of measured biogas plants in Germany to date.

This thesis is structured in three main chapters. After briefly introducing the theoretical background and measurement technique in chapters 2 and 3, chapter 4 focuses on the uncertainty analysis of the measurement method applied in this thesis. Results from controlled CH_4 release experiments obtained by applying a Gaussian plume model (GPM) were compared with the actual release rates and thus the uncertainty of the method was analyzed in detail. Additionally, this chapter presents the results of an international

blind-release campaign conducted to test the method in the field. Finally, a best-practice strategy is implemented for mobile measurements and data evaluation, following the results obtained during the controlled releases.

The application of the method for CH_4 emission quantification of 65 biogas production sites in Germany is described and discussed in chapter 5. The investigated plants differ in terms of age, installed biogas production capacity, feedstock, site structure and biogas utilization. The results are then related to the production rates of the respective plants to calculate a CH_4 loss rate and are compared with the results of similar scientific studies. Furthermore, long-term emission monitoring at a local biogas plant between 2018 and 2024 were analyzed and interpreted.

To expand the database on δ^{13} CH₄ isotopic source signatures from biogenic sources, samples were taken from 20 biogas plants. The sampling was done directly at the plants themselves or inside the emission plume. The isotope results were placed into context and are subject of chapter 6.

Chapter 7 concludes the thesis with the main findings and a summary highlighting the sustainability of German biogas plants (and their GHG balance) in a larger context.

Chapter 2

Methane as a greenhouse gas and the principle of atmospheric dispersion

2.1 Global methane cycle

Global observation networks for atmospheric GHG measurements play an important role in tracking the concentration of these gases over time. Monitoring GHG levels is essential to understand long-term trends and detect changes in emission patterns, allowing for early responses to potential climate impacts. To make accurate statements about the development of greenhouse gases in the atmosphere and their contribution to climate change, a dense network of measurement stations with harmonized and well-calibrated high-quality data is needed. The Global Atmosphere Watch (GAW), which is managed by the World Meteorological Organization (WMO), coordinates data collection from over 400 stations spread across more than 80 countries [WMO]. The largest international monitoring network is operated by NOAA, with a focus on greenhouse gas measurements (CO₂, CH₄, N₂O) in North America and four observatories at different latitudes (Barrow, Mauna Loa, Samoa and South Pole) and a global flask sampling program at 188 stations (NOAA). Similarly, ICOS is a network within Europe with many stations monitoring atmospheric data, mostly from fixed stations or tall towers (ICOS). All of these networks contribute significantly to the monitoring of CO₂ and CH₄ mole fractions in the atmosphere.

Methane is typically reported as 'dry air mole fraction', which is defined as the number of methane molecules divided by the total number of molecules in a sample, after water vapor has been removed. This mole fraction is expressed in nanomoles per mole (nmol mol⁻¹), or parts per billion (ppb), where 1 ppb corresponds to one methane molecule out of every billion molecules in an air sample. The mole fraction of methane in the atmosphere has increased by a factor of about 2.7 since pre-industrial times as a result of human activity. In 2024, the global average mole fraction of methane was 1929 ppb [Lan et al. [2024]]. The continuing upward trend of methane mole fraction is evident from globally-averaged,

monthly mean data collected from marine surface sites by the Global Monitoring Division of NOAA's Earth System Research Laboratory, which has shown a current annual growth rate of 10.01 ± 0.58 ppbCH₄ yr⁻¹ [Lan et al. [2024]] (Figure 2.1).

Despite its relatively short atmospheric lifetime, ranging from 9.1 to 11.8 years [IPCC [2023]], methane is a highly potent greenhouse gas. Its effective radiative forcing is 0.54 W m⁻² (IPCC [2023]), making it a significant contributor to global warming. Over a 100-year period, CH₄ has a global warming potential 29.8 times greater than that of CO₂ (IPCC [2023]). These factors underscore the urgency of continued monitoring and mitigation efforts to manage methane emissions effectively in the context of climate change, as reducing methane emissions can lead to rapid success in mitigating the greenhouse effect.



Figure 2.1: Globally-averaged, monthly mean atmospheric methane abundance determined from marine surface sites from the Global Monitoring Division of NOAA's Earth System Research Laboratory [Lan et al. [2024]]. The red circles are globally averaged monthly mean values. The black line show the long-term trend, where the average seasonal cycle has been removed.

2.1.1 Global methane budget

The CH_4 mole fractions presented in the previous chapter were derived from global and regional monitoring networks and are key input parameters for the top-down approach to determine GHG emissions. The top-down method relies on atmospheric observations and inverse modeling to draw conclusions about emissions and provides a comprehensive perspective on the GHG methane once it entered the atmosphere. In contrast, the bottomup approach is based on detailed data about specific sources and their activities. These estimates often involve the combination of emission factors and activity data in various sectors, such as industry, transportation, and agriculture. Both approaches are complementary, as they provide different insights into the sources, sinks, and trends of methane in the atmosphere.

To develop effective mitigation strategies for methane, it is crucial to identify the relevant sources and sinks that influence its atmospheric concentration. A comprehensive description of the global methane budget, incorporating both top-down and bottom-up estimates, is provided by Saunois et al. [2024]. A detailed overview of the individual sources and sinks of the budget is shown in Fig. 2.2. According to Saunois et al. [2024], the atmospheric increase of methane from 2010 to 2019 implies global methane emissions of 575 (553-586) Tg CH₄ per year in the top-down approach. Of these, anthropogenic sources account for 65 % of total emissions, with a contribution of 359 (333-395) Tg CH_4 yr^{-1} . The majority of anthropogenic emissions are related to agriculture (rice cultivation and ruminants) and waste management, followed by fossil fuel extraction. The formation of methane through incomplete combustion of biomass- and soil-carbon during wildfires and biofuels makes the smallest contribution to the anthropogenic emissions. Natural methane emissions from wetlands and inland freshwater dominate the non-anthropogenic sources, contributing 165 (145-214) Tg CH_4 yr⁻¹. These natural emissions are highly sensitive to environmental factors such as temperature and water levels, and as such, they are expected to respond to ongoing global warming (e.g. Nisbet et al. [2016], Gloor et al. [2021], Zhang et al. [2023], Nisbet [2023]).

The removal of methane from the atmosphere primarily occurs through a series of chemical reactions with hydroxyl radicals (OH), which are predominantly located in the troposphere. This sink is responsible for the removal of approximately 521 (485-532 Tg CH₄ yr^{-1} from the atmosphere. Hydroxyl radicals are short-lived and are variable in their spatial and temporal distribution, which increases the uncertainty associated with this methane sink (Rigby et al. [2017]). In addition to atmospheric oxidation, a smaller fraction of methane is removed through oxidation processes in soils. This global methane budget for the years 2010-2019 results in an annual atmospheric growth rate of 21 (19-33) Tg CH₄ yr^{-1} .

Methane emissions can also be categorized based on their formation processes. Biogenic methane represents the largest source category and is produced in anaerobic environments. In addition to wetlands, rice paddies, oxygen depleted-or starved freshwater reservoirs (like dams) this also includes digestive systems of ruminants and termites. Biogenic methane is also produced during the decomposition of organic waste in landfills, waste water treatment and manure management. Thermogenic methane is produced during geological processes over long timescales. While volcanic activity naturally releases thermogenic methane, anthropogenic emissions of this type are mainly caused through the exploitation and use of fossil fuels such as coal, oil, and natural gas. Pyrogenic methane is the smallest source category and released from biomass burning.

The complexity of the methane cycle and the difficulties in accurately quantifying its global budget are particularly emphasized by the interactions between methane sources and sinks. The sensitivity of natural CH₄ sources, such as wetlands and permafrost, to climate change is an important factor to better predict and mitigate the effects of climate change, especially in the near future. Additionally, an accurate understanding of the contributions from various anthropogenic sources remains an ongoing challenge. Especially, on regional to local scales, there can be large deviations and uncertainties in the methane emission inventories (e.g. Lan et al. [2021b]). NIRs (e.g. Günther et al. [2024]) or independent sources like the EDGAR database (Emissions database for global atmospheric research, Crippa et al. [2024]) provide information on a country's greenhouse gas emissions. Sometimes estimates based on emission inventories do not match with the atmospheric observations. Therefore, atmospheric monitoring networks in combination with inverse modeling are important to track methane emissions on a national scale and to verify and improve NIRs (Bergamaschi et al. [2022]).



Figure 2.2: CH₄ inventory balance for the years 2010 - 2019 as published by the Global Carbon Project 2024 [Saunois et al. [2024]].Both bottom-up (left) and top-down (right) estimates are provided for each emission and sink category in Tg CH₄ yr⁻¹, as well as for total emissions and total sink.

2.1.2 Isotopic composition of CH₄

While atmospheric mole fractions and thus total global emissions can be well defined by a global monitoring network, estimates of emissions by source sector are still subject to major uncertainties. In particular, regional to national emission estimates pose a challenge here (Stavert et al. [2021], Schulte et al. [2024]). Measurements of the isotopic composition of methane fractions of less abundant isotopes (¹³C, ¹⁴C and D (D = ²H)) allow better monitoring of the global CH₄ budget and the distribution of emissions by source sectors and countries.

Atoms of the same element which differ only in the number of their neutrons are called isotopes. Molecules of the same kind can be composed of different isotopes and thus have a different isotopic composition. These molecules have slightly different physical and chemical properties due to their different masses. These different properties result in lower mobility of the heavier isotope, as $v \propto \sqrt{(m^{-1})}$ and higher binding energies. Overall, this leads to slower reaction rates and diffusion, which in turn leads to shifts in the relative abundances of isotopes during physical phase transitions or chemical reactions. This process is called isotope fractionation and changes the isotopic composition of a sample [Mook [2000]].

Measuring and determining methane isotopes (e.g. 12 CH₄, 13 CH₄, 14 CH₄, 12 CH₃D) is a well-established method to determine the contribution of different sources to the increasing methane emissions on a global and regional scale and to assign the related source types (e.g. Dlugokencky et al. [2011], Schaefer [2019], Hoheisel et al. [2019], Menoud et al. [2022], Mannisenaho et al. [2023]). Knowing the ratios of the stable carbon isotopes ($^{13}C/^{12}C$) allows assumptions about possible sources and reaction pathways in a system. In general, one isotope is more abundant than the others. For carbon, this is ^{12}C with a relative abundance of about 98.8 %, whereas ^{13}C has a relative abundance of only 1.1 %. The isotope ratio is calculated as follows:

$$R = \frac{abundance \ of \ rare \ isotope}{abundance \ of \ abundant \ isotpope}$$
(2.1)

e.g. ${}^{13}R = [{}^{13}C]/[{}^{12}C]$. The so-called delta notation is a more convenient way to make this ratio comparable, so the isotope ratio is related to an international reference standard:

$$\delta = \frac{R_{sample}}{R_{standard}} - 1 \tag{2.2}$$

The official international standard for ${}^{13}\text{C}/{}^{12}\text{C}$ is the VPDB, the Vienna Pee Dee Belemnite, with a ratio of $R_{standard} = 0.0111802 \pm 0.0000028$ (Werner and Brand [2001]). Since δ is usually a very small number and therefore normally given in permil [%].

Since methane is formed in multiple processes and is subject to different fractionation, the stable isotope ratio can range widely, predominantly between -13 to -70 ‰ [Ciais et al. [2013]]. The formation processes distinguish between three different types of methane, whereby a clear source attribution by isotopic signature is not always possible, since there

is some overlap between the categories (Kirschke et al. [2013]). Thermogenic and pyrogenic CH₄ is generally more enriched with ¹³C ranging between -45 to -25 % and -25 to -13 %, respectively. Biogenic CH₄ has a more depleted isotopic signature ranging between -55 to -70 %.

Figure 2.3 shows the δ^{13} C isotopic source signature of different methane emitters in Europe, based on the European Methane Isotope Database (Menoud and et. al. [2021], Menoud et al. [2022]). The database characterized 734 locations over eight countries. Twelve categories are presented, with biogenic sources being the most common. The δ^{13} CH₄ values range from -96.1 ‰ (wetland) to -19.6 ‰ (fuel combustion).

The atmospheric isotope ratio of δ^{13} CH₄ is currently at -47.67 ± 0.01 ‰ (Michel et al. [2024]). In the years 1990-2000, δ^{13} CH₄ in ambient air shows a trend towards less negative values due to the increased emissions of fossil methane (Lowe et al. [1994], Rice et al. [2016], Schaefer et al. [2016]), whereas in recent years (2010-today) a trend towards more negative δ^{13} CH₄ has been observed, as shown in Fig. 2.4 (Schaefer [2019]). This indicates a recent increase in biogenic methane in the atmosphere, which has a lighter isotope source signature compared to fossil methane. This trend has been described in several studies documenting an increasing proportion of biogenic methane in the atmosphere in the context of global climate change (wetlands and permafrost thawing) and more intensive agricultural activities (Schaefer et al. [2016], Schaefer [2019], Nisbet et al. [2016], Nisbet et al. [2019], Nisbet [2023], Michel et al. [2024]). These changes in δ^{13} CH₄ reflect the increasing importance of biological sources of methane emissions and provide important clues to the source of methane contributing to global warming.



Figure 2.3: Isotopic source signatures in δ^{13} CH₄ of different methane emitters in Europe based on European methane isotope database (Menoud et al. [2022], Menoud and et. al. [2021])



Figure 2.4: Trends in atmospheric mole fraction of global CH₄ (Lan et al. [2024]) and δ^{13} CH₄ records from Baring Head, New Zealand, and global average (Schaefer et al. [2018]). Vertical blue lines indicate the start and end of the source-sink imbalance anomaly. Blue shading indicates the CH₄ plateau. Figure adapted from Schaefer [2019].

2.2 Dispersion of gases in the atmospheric boundary layer

In order to analyze the impact of specific emission sources on air quality and climate, it is important to make predictions about the behavior of possible GHG emissions and their distribution in the atmosphere. Released gases are transported in the air in downwind direction and expand both horizontally and vertically due to diffusion caused by turbulent eddies in the atmosphere. Mathematical models are used to describe the spatial and temporal distribution of these gases in the atmosphere (Hanna [1982]). A large number of models with varying degrees of physical complexity have been developed, of which the Gaussian plume model (GPM) under the assumption of homogeneous atmospheric conditions, is the most commonly used in practice, as a result of its simplicity (e.g. Ars et al. [2017], Bakkaloglu et al. [2021], Kumar et al. [2021], Korbeń [2021], Stavropoulou et al. [2023]). By describing the dispersion of the gas in the atmosphere, the GPM allows conclusions to be drawn together with corresponding measurements about the emission rate of the investigated source, which is in the interest of this thesis.

2.2.1 Gaussian plume dispersion model

A number of simplifying assumptions are made in order to apply the Gaussian model (Venkatram and Thé [2003], Abdel-Rahman [2008]). Firstly, it is assumed that particles are emitted from a point source at a constant emission rate Q and are transported in the air by the wind at a speed u, with no other source or sink of the dispersing material after (no decay, deposition or chemical transformation). The particles distribute perpendicular to the wind direction by turbulent diffusion in the form of a Gaussian distribution for the assumption of constant meteorological conditions between source and measurement point. To calculate the time-averaged concentration field, it can be assumed that the x- and y-axis span a horizontal plane of a cartesian coordinate system with the point source in the origin (z=0) and the x-axis is oriented in the direction of the mean wind direction as it is shown in Fig. 2.5.

$$C(x, y, z) = \frac{Q}{2\pi\sigma_y\sigma_z u} exp[-\frac{y^2}{2\sigma_y^2}] [exp[-\frac{(z-h_s)^2}{2\sigma_z^2}] + exp[-\frac{(z+h_s)^2}{2\sigma_z^2}]]$$
(2.3)

Equation 2.3 (Sutton [1932], Turner [1970]) describes the relationship between emission rate Q [kg m⁻³] and CH₄ mole fraction above background C [μ g m⁻³] of the gas released at a given point (x, y, z). Other parameters included in the equation are wind speed u [m s⁻¹], location and height of the CH₄ source h_s [m] and the dispersion coefficients σ_y and σ_z in the horizontal (y) and vertical (z) directions. The effect of a reflective ground surface is taken into account by placing an image source at z = -h_s (Seinfeld and Pandis [2006]). For the parametrization of the dispersion coefficients σ_y and σ_z following Briggs [1973] and Hanna et al. [1982], the meteorological conditions are used and transferred into stability classes based on the definitions of Pasquill, Gifford and Turner (Turner [1970]). Since the dispersion parameters are an expression of the turbulence in the atmosphere, the values of σ become larger with larger eddies in an unstable atmosphere and smaller



with a stable atmosphere in which the eddies are smaller.

Figure 2.5: Schematic drawing of a Gaussian distribution of a pollutant released in the atmospheric boundary layer from a point source. This scheme is a re-illustration by Andersen [2021] of the figure originally published by Leelőssy et al. [2014]

Based on the empirically derived plume dispersion formulations of Pasquill [1961] and modified by Gifford and Turner (Turner [1970]), the Pasquill-Gifford stability classes (PGSC) are used as an indicator of atmospheric stability. Since turbulent mixing in the atmosphere is driven by wind shear and buoyancy, the stability classes are related to wind speed as an indicator of shear-induced turbulence, and to incoming solar radiation as an indicator of sensible flux-induced turbulence. The stability classes are arranged into six categories A-F, ranging from extremely unstable atmospheric conditions (A) to moderately stable conditions (F) as presented in Table 2.1. The classes (A-D) correspond to the atmosphere during the day and E-F correspond to the night time. Class D is neutral and can also be used during day or night for overcast conditions regardless of the wind speed. To derive the stability class, the incoming solar radiation is specified by Turner [1970] as follows: "Strong incoming solar radiation correspond to a solar altitude greater than 60° with clear skies; slight insolation to a solar altitude from 15° to 35° with clear skies.[...] Incoming radiation that would be strong with clear skies can be expected to be reduced to moderate with broken (5/8 to 7/8 cloud cover) middle clouds and to slight with broken low clouds" (Turner [1970], p. 6). A more recent categorization of solar radiance according to Riddick et al. [2022a] is strong > 1000 W m⁻², moderate = 500-1000 W m⁻² and slight < 500 W m^{-2} . The wind speed u corresponds to a reference height of $z_2 = 10$ m and needs to be adjusted from the measurement height to the reference height since wind does not flow with same speed at all heights caused by surface friction. Therefore, the wind speed as a function of height in the atmospheric boundary layer can be calculated using the wind

profile power law:

$$u(z_2) = u(z_1) \left(\frac{z_2}{z_1}\right)^p \tag{2.4}$$

According to Hsu et al. [1994] a typical value for p on land is 0.14. The dispersion coefficients or standard deviations σ_y and σ_z describe the horizontal and vertical mixing of the released pollutant and are an estimate for the turbulence (Hanna et al. [1982], Venkatram and Thé [2003]). The Briggs parametrization is an analytical expression for the coefficients and based on observed diffusion patterns after averaging each point over approximately 30 minutes (Briggs [1973]). With longer averaging times, the plume boundaries become more 'smeared'. This is mainly due to the shift in wind direction, although gradual changes in mean wind speed also affect the diffusion pattern. The parameters are calculated like it follows:

$$\sigma_y = \frac{\alpha_y x}{\sqrt{1 + \beta_y x}} \tag{2.5}$$

$$\sigma_z = \alpha_z \ x(1 + \beta_z \ x)^\gamma \tag{2.6}$$

The parameters α , β , γ depending on the PGSC and x is the distance downwind to the source (Korsakissok and Mallet [2009]). For rural settings, the Briggs parametrization is given as in Table 2.2 listed.

Surface wind	Day			Night	
speed (at 10 m)		Solar radiation			
in m s ^{-1}	Strong	Moderate	Slight	$\geq 4/8$ low cloud	$\leq 3/8$ cloud
< 2	А	A-B	В		
2-3	A-B	В	\mathbf{C}	E	\mathbf{F}
3-5	B-C	\mathbf{C}	D	E	\mathbf{F}
5-6	C-D	D	D	D	\mathbf{E}
> 6	С	D	D	D	D

Table 2.1: Pasquill-Gifford stability classes for atmospheric stability classification into six categories according to Pasquill [1961]. For overcast conditions during day or night stability class D is recommended. Here as reported in Turner [1970].

Stability class	σ_y (m)	σ_z (m)
A	$0.22x(1+0.0001x)^{-1/2}$	0.20x
В	$0.16x(1+0.0001x)^{-1/2}$	0.12x
C	$0.11x(1+0.0001x)^{-1/2}$	$0.08x(1+0.0002x)^{-1/2}$
D	$0.08x(1+0.0001x)^{-1/2}$	$0.06x(1+0.0015x)^{-1/2}$
E	$0.06x(1+0.0001x)^{-1/2}$	$0.03x(1+0.0003x)^{-1}$
F	$0.04x(1+0.0001x)^{-1/2}$	$0.016x(1+0.0003x)^{-1}$

Table 2.2: Briggs parametrization for rural conditions. The coefficients σ_y and σ_z depend on the stability class and the downwind distance x. Values from Hanna et al. [1982].

2.2.2 Limiting factors

Due to its simplicity and, thus, low computational capacity of the GPM, the applicability of the model is limited. The GPM is based on theoretical formulae relying on many assumptions and developed from limited data sets and therefore source scenarios, averaging times, meteorological conditions, underlying surfaces and distance are documented as limiting model parameters (e.g. Hanna et al. [1982], Wilson et al. [1976]).

The calculation of the dispersion parameters σ_y and σ_z as function of discrete stability classes and downwind distance results often in low accuracy (Kahl and Chapman [2018]) as the Pasquill-Gifford curves are based only on a few diffusion experiments known as the Prairie Grass project (Haugen [1959]). The release experiments were carried out on flat terrain near ground-level and the concentrations were measured less than 1 km downwind and are difficult to transfer to complex terrain situations (Abdel-Rahman [2008]). The PGSC provide a simple and useful approach to estimate atmospheric stability. However, several key factors can significantly affect gas dispersion that are not accounted for in the PGSC, leading to some limitations (Kahl and Chapman [2018]). Elements such as air mass fetch (Crawford et al. [2016]) and synoptic weather conditions (Luna and Church [1972]) are not considered in the classification. Furthermore, they do not account for variations in the thermal properties of soils, including the formation of heat islands (Gifford, F.A.) or changes in surface roughness (Bowen [1994], Panofsky and Dutton [1984]). As the stability classes are not measurable physical parameters and are arranged stepwise, they can introduce significant uncertainties into dispersion modeling.

The analytical power-law equations for σ_y and σ_z by Briggs [1973] are independent of release height and surface roughness and are applicable for distances between 100 m and 10 km. Near the source the concentration levels reach infinity (Abdel-Rahman [2008]).

Furthermore, at low wind speeds the results are affected by meandering of the plume and the dispersion calculation is less reliable than for wind speeds over 2 m s⁻¹ (Essa et al. [2005], Mortarini et al. [2016]). This was investigated more closely by Wilson et al. [1976], who concluded that increased horizontal diffusion caused by the variability of wind direction at low wind speeds leads to increased dilution of the plume by meandering. In addition, vertical mixing is enhanced by low wind speeds and surface roughness. This results in a poorly performing model at low wind speeds since the dispersion parameters are underestimated.

Variation in the plume behavior is expected simply due to atmospheric variability (Caulton et al. [2018]). Therefore, the averaging interval should be sufficient long to allow the plume emissions to reach a steady-state, but at the same time short enough, to not miss significant changes in wind speed. Figure 2.6 demonstrates how the concept of time-averaging appears on the data. In the literature, 10 minutes is given as an appropriate time interval for data averaging (Stockie [2011]).



Figure 2.6: Differences in instantaneous and time-averaged concentration profiles of emitted pollution plumes in (a) top-down and (b) side perspective as illustrated by Andersen [2021]

2.3 Absorption spectroscopy

Field measurements require reliable determinations of the gas concentration in the ambient air. There are a number of different methods that can be used to measure greenhouse gases in the atmosphere. These include gas chromatography (GC) (Schmidt et al. [1996]) and Fourier transform infrared spectroscopy (FTIR) (Hammer et al. [2013]), as well as mass spectrometry (Röckmann et al. [2016]) and cavity ring-down spectroscopy (CRDS) (Hoheisel and Schmidt [2024]). Greenhouse gases can now also be measured from space using the remote sensing technique with satellites such as GOSAT (Butz et al. [2011]). Absorption spectroscopy is the basis of many of the instruments used today. A detailed description of the phenomenon based on the quantum mechanical approach is described in Bransden and Joachain [2014], while only a brief overview of absorption and energy transition is given in this section.

Molecules have quantized energy levels that are defined by their electronic, vibrational and rotational states. These levels are specific to each molecule and depend on its chemical structure. Absorption spectroscopy is based on the fundamental principle that electromagnetic waves are absorbed by molecules at a certain wavelength if it matches a ro-vibrational excitation energy. Absorption lines are generally classified according to the type of quantum mechanical change in the molecule or atom. For example, rotational lines are caused by a changing rotational state of a molecule, which typically occurs in the microwave spectrum. Mostly found in the infrared range are vibrational lines corresponding to a change in the vibrational state of the molecule. Electronic lines correspond to an excitation of the electronic state of an atom or molecule and are typically found in the visible and ultraviolet range. A combination of these states (e.g. rotational-vibrational transitions) result in new absorption lines at the combined energy of the two excitations. The absorption spectrum is characterized by the molecule-specific properties of the gas and its components, so the mole fraction and the isotope ratio of different gas components can be determined. Due to shifts in the absorption lines caused by the mass dependence, the abundance of different isotopologues can also be accurately determined. Lambert-Beer's law states that there is a linear relationship between the concentration of a material and its absorption. The relationship between the intensity of incident light $I_0(\lambda)$ and the intensity of light passing through the material $I(\lambda, d)$ can be described as:

$$I(\lambda, d) = I_0(\lambda) \cdot exp[-d \cdot \alpha(\lambda)] \quad with \ \alpha(\lambda) = \sigma(\lambda) \cdot C$$
(2.7)

with the path length d through the absorbing medium and the absorption coefficient $\alpha(\lambda)$, which is given by the product of the effective cross section $\sigma(\lambda)$ and the concentration C(Platt and Stutz [2008]).

The detailed measurement technique of the two instruments used in this thesis is briefly described below.

2.3.1 Cavity ring - down spectroscopy

In order to be able to use the absorption properties of a medium and determine the concentrations of one or more components of a sample such as CH₄, the light intensity after passing the sample is usually measured with the help of a photodetector. Therefore, one or more lasers, with wavelengths tuned to the absorption spectra of the gas components of interest, are directed into an optical cavity and reflected several times between highly reflective mirrors to increase the effective path length. It is important that the pressure and temperature inside the cavity are controlled and stabilized. The photodetector measures the amount of light exiting through one of the mirrors and generates a signal that is directly proportional to the intensity in the cavity. After a threshold is reached at the photodetector, the laser is switched off and the exponential drop is measured. The decay or ring-down time ($\alpha = \frac{1}{c\tau}$) of the cavity with and without absorption by the target gas species can be calculated and compared to obtain information about the concentration of the sample component (Crosson [2008], Rella et al. [2015a], Hartmann et al. [2018]).

The CRDS analyzer (G2201-i, Serial No. 1317-CFIDS-2034, Picarro, Inc., Santa Clara, CA) uses CRDS and allows precise measurements of ${}^{12}\text{CH}_4$, ${}^{13}\text{CH}_4$, ${}^{12}\text{CO}_2$, ${}^{13}\text{CO}_2$, H_2O and C_2H_6 in the ppb range with a time resolution of 3.7 s as well as calculations of $\delta^{13}\text{CH}_4$ and $\delta^{13}\text{CO}_2$ values.

The CRDS G2201-i uses three different temperature-tunable lasers with wavelength 1600 nm absorbed by ${}^{12}CO_2$ and ${}^{13}CO_2$, 1651 nm absorbed by ${}^{13}CH_4$ and 1659 nm absorbed by ${}^{12}CH_4$, ${}^{13}CO_2$ and H_2O (Dinger [2014]). The laser is tuned to several points across the spectral absorption line of the relevant gases and ring-down measurements are made at all these points. To maximize accuracy, the path length is increased to over 20 km using three highly reflective mirrors (> 99.99 %). The photodetector, which measures the ring-down in real time, is located behind one of the mirrors. To determine the absorp-

tion at a specific wavelength, the decay time of an empty cavity needs to be compared with the decay time of a cavity containing a sample. The measurements in an 'empty' cavity is simply taken by shifting the light to wavelengths that are not absorbed by the target species. Subsequently, the instrument performs a continuous comparison of the ring-down times, which are then used by the software to calculate the absorption lines. A mathematical fit to the shape of these absorption lines are then used to calculate the gas concentration from the height of the absorbance peak. The temperature of the cavity is controlled to $45 \pm 0.00003^{\circ}$ C, while the pressure is actively stabilized at 148 ± 0.02 Torr (20 kPa) (Picarro Inc., Manual, Picarro Inc.). The standard device operates with a gas flow of approximately 25 standard cubic centimeters per minute (sccm), although the device is capable of accommodating flows between 5 and 400 sccm (Rella et al. [2015a]).

2.3.2 Optical feedback - cavity enhanced absorption spectroscopy

Optical feedback cavity-enhanced absorption spectroscopy (OF-CEAS) is based on a similar spectroscopic measurement technique. However, the linewidth of the emission from the laser source is reduced and the frequency is locked. This is achieved by coupling the laser frequency to a cavity resonance mode, whereby the resonant field of the cavity is fed back to the laser facet, which acts as an external source for injection excitation. In addition to the longer path length caused by the cavity, these feedback effects can amplify the signals transmitted through the cavity and the sensitivity is significantly increased (Ventrillard et al. [2017], Manfred et al. [2015], Morville et al. [2005]).

In this study we measure with an OF-CEAS analyzer (LI-7810, Serial No. TG10-1110, LI-COR, Nebraska, USA). This trace gas analyzer measures the mole fractions of CH_4 , CO_2 and H_2O in air at a sampling rate of 1 Hz in the ppb range. Again, three highly reflective mirrors are arranged in a V-shaped cavity to increase the effective path length. The laser discretely jumps from one cavity resonance mode to the next, which are evenly spaced a few kHz apart. The spectral ranges of the three gases to be analyzed are covered in less than 0.25 seconds. Each scan uses two ring-down times (decay of light intensity in the cavity), one at the beginning and one at the end, to normalize the signal. A photodiode behind one of the mirrors detects the intensity transmitted by the mirror and compares its signal with that of the reference photodiode to calculate the absorption for each resonance mode. Finally, the gas concentration is computed by an algorithm comparing the measured absorption spectra with the internal high-resolution spectra. Typically, the analyzer operates with a cavity temperature around 55 °C and a cavity pressure around 40 kPa. The nominal flowrate is 250 sccm but can be reduced to 70 sccm with the help of a reduced flow adapter kit (LI-COR [2020]).

The theoretical absorption spectra taken from the database 'HITRAN' in the near infrared of ${}^{12}CH_4$, ${}^{13}CH_4$, CO_2 , and H_2O , are shown in Fig. 2.7. The areas in which the CRDS and OF-CEAS measuring device have set their laser frequencies are indicated additionally. Several physical factors can influence the accuracy, precision, and stability of measurements obtained from optical atmospheric trace gas spectrometers. In addition to temperature and pressure variations, fluctuations in the laser wavelength can affect line shape and contribute to errors in peak height. Furthermore, spectral interferences may arise from other vibrational absorption lines corresponding to different gas species present in the background gas matrix. Spectral models employed to fit the measured absorption spectra may not fully compensate for these cross-sensitivities, thereby affecting the measurement accuracy. Previous studies focusing on CRDS (Rella et al. [2015a], Hoheisel et al. [2019], Grandke [2022], Pfau [2023], Hahn [2024]) and OF-CEAS (Leggett et al. [2019], Nelson [2020], Wietzel [2021]) have conducted various tests to assess instrument drift, cross-sensitivity, and potential correction factors. These tests have been specified for our instruments and are subject to regular verification and adjustment as necessary. To correct for potential instrument drift and assure accurate and precise results, measurement data can be calibrated by assessing one or more calibration gases and applying a response function (Hoheisel [2021]). A more comprehensive description of this application is available in A.1.



Figure 2.7: Theoretical line spectra of ${}^{12}\text{CH}_4$ and CO_2 in the near-infrared in relation to the isotopologues specific natural abundance. Data shown was provided by the openaccess HITRAN database (Gordon et al. [2022]). Key regions of the operational regimes of both analyzers used in this thesis are highlighted in red and orange, respectively.

Chapter 3

Measurement setup and quantification method

3.1 Mobile CH_4 measurement setup

Methane emissions can be quantified using different measurement techniques and evaluation methods. In this thesis, a Gaussian distribution of methane dispersion in the atmospheric boundary layer is assumed for the quantification of methane emission rates. This assumption, which can be modeled inversely as previously described in section 2.2.1, allows emission rates to be estimated in combination with atmospheric in-situ measurements. One method for determining emission rates is based on mobile measurements of atmospheric CH_4 mole fraction during plume crossings, which are then modeled using a Gaussian plume model. This method will be referred to as the GPM method. In this thesis, mainly mobile measurements of this type were carried out. In addition, the Other Test Method (OTM) 33-a was occasionally used to complement the results. This method is also based on the assumption of a Gaussian distribution of the trace gas in the atmosphere, but its application relies on stationary measurements. A detailed explanation of the implementation of the GPM method can be found below, following the description of the measurement setup, while the OTM33-a method is provided in the Appendix B.3.

The determination of methane emission rates in my thesis is mainly based on the mobile measurements carried out as part of my thesis, but also includes the analysis of data collected in the studies of Hoheisel et al. [2019], Kammerer [2019], Seyfarth [2021] and Korbeń [2021]. During the period from 2016 to 2024, analyzed in this thesis, the mobile measurement setup has been subject to changes. Table 3.1 provides an overview of the different measuring instruments and the time they were used together with their specifications.

Between 2016 and 2020, a CRDS analyzer (G2201-i, Picarro, as described in section 2.3.1) was installed in a van for mobile atmospheric measurements of CH₄, CO₂ and H₂O, as well as the isotopic composition of δ^{13} CH₄ and δ^{13} CO₂ (Hoheisel et al. [2019], Korbeń [2021]). These measurements were conducted with a temporal resolution of 0.27 Hz and a flow rate of 0.16 L min⁻¹. The repeatability of the analyzer, as a function of CH₄ mole fraction,

was determined by Hoheisel et al. [2019]. The Allan standard deviation (σ), which is the square root of the Allan variance (σ^2) (Werle et al. [1993]) for raw CH₄ data (3.7 s intervals), ranged from 0.34 to 2.69 ppb for CH₄ mole fractions between 1.9 and 10 ppm (Hoheisel et al. [2019]). The mobile CH₄ and CO₂ measurements were calibrated against the international WMO scale (Dlugokencky et al. [2005]) through regular calibration gas analyses. Laboratory calibration of the mobile setup was carried out by performing preand post-campaign measurements of a standard gas (UHEI4_3). Detailed descriptions of the mobile system and calibration procedures is described by Hoheisel et al. [2019].

Instrument	Measured species	Temporal resolution [Hz]	Precision	Date of use
LI-7810 (Li-Cor) ¹	$\begin{array}{c} CH_4, CO_2, \\ H_2O \end{array}$	1	0.4 ppb (1 s, 2 ppm CH_4), 1 ppb (1 s, 10 ppm CH_4)	Since 10/2019
G2201-i (Picarro) ²	$\begin{array}{c} \mathrm{CH}_4,\mathrm{CO}_2,\\ \mathrm{H}_2\mathrm{O},\\ \delta^{13}\mathrm{C}\text{-}\mathrm{CH}_4,\\ \delta^{13}\mathrm{C}\text{-}\mathrm{CO}_2 \end{array}$	0.27	0.34 ppb (3.7 s, 2 ppm CH ₄), 2.7 ppb (3.7 s, 10 ppm CH ₄)	Until 09/2019
Vantage Pro2 (Davis Instruments) ³	ws, wd, T, h, p	0.16	$1 \text{ m s}^{-1} \text{ or } 5\%$ (ws)	Until 05/2018
Ultrasonic 3D- anemometer USA-1 (Metek) ⁴	ws, wd, T, u, v, w	10	$\pm 0.01 \text{ m s}^{-1}$ (ws)	Since 01/2019
MaxiMet GMX500 2D- anemometer (Gill) ⁵	ws, wd, T, h, p	1	$3~\%~(\mathrm{ws})$	Since 05/2018
GPS logger (Navilock) ⁶	Lat, Long, Altitude	1	2.5 m	Until end 2020
GPS logger (BasicAirData) ⁷	Lat, Long, Altitude, Speed	1	3 m	Since beginning 2020

Table 3.1: Specification and time span of used measurement instruments.⁽¹ Wietzel [2021], ² Hoheisel et al. [2019], ³ Davis, Manual, ⁴ Metek, Manual, ⁵ Gill Instruments, Manual), ⁶ Navilock, Manual), ⁷ BasicAirData)

Since 2020, the mobile measurements of CH_4 and CO_2 have been conducted using an OF-CEAS trace gas analyzer (LI-7810, LI-COR, as described in section 2.3.2), which offers a higher temporal resolution of 1 Hz and a flow rate of 0.31 L min⁻¹. This analyzer is capable of measuring CH_4 mole fractions in the range of 0.1 to 100 ppm, CO_2 in the range of 1 to 10,000 ppm, and H₂O from 100 to 60,000 ppm (LI-COR [2020]). The Allan standard deviation for this device was also determined by Wietzel [2021]. For CH_4 , the Allan standard deviation for 1-second data was found to be between 0.41 and 1 ppb for mole fractions of 2 and 10 ppm, respectively. A detailed characterization of the OF-CEAS analyzer, including instrument drift, as well as pressure and humidity dependencies, was carried out by Nelson [2020] and Wietzel [2021] in 2020.

In the past two years, one standard gas (Pic14_1) has been measured regularly with the OF-CEAS analyzer to monitor the stability and drift of the instrument (Korbeń et al. [2022], Wietzel and Schmidt [2023]). Standard gas measurements were averaged over the respective measurement duration (typically 20 minutes) after excluding a 10-minute stabilization period. As shown in Fig. A.1, there was no significant drift in the CH₄ mole fractions, with a mean value of 2024 ± 5 ppb. As the application of the Gaussian dispersion models required only the relative CH₄ mole fraction (after background subtraction), no drift correction was applied to the high-resolution second data of the OF-CEAS measurements.

To perform mobile in-situ measurements, a vehicle was equipped with one of the trace gas analyzers together with a mobile and/or stationary wind sensor and a GPS system. At the vehicle roof, the air inlet was mounted on a roof system at 2.7 m above ground, protected from the inflow of large dirt particles by a fine mesh net. Through a 1/4" Teflon tube, ambient air was pumped continuously from the inlet on the vehicle roof to the trace gas analyzer inside the van. Time shifts of all recording devices were corrected and adjusted during the data analysis as well as time delay caused by dead volume of the tubing system.

Meteorological parameter, such as temperature, humidity, pressure, wind speed and direction, were recorded with a 2D-anemometer (MaxiMet GMX500, Gill Instruments Ltd., Lymington, UK) mounted on the roof of the vehicle near the inlet or/and a 3D ultrasonic anemometer (USA-1 Sensor, METEK Meteorologische Messtechnik GmbH, Elmshorn, Germany) or a stationary weather station (Vantage Pro2, Davis Instruments) located near the emitter in an open area without major obstacles. Figure 3.1 shows the roof system with air inlet and mobile anemometer mounted on the van as well as the CRDS analyzer inside the van.

For measurements based on the stationary OTM33-a method, the 3D-anemometer is used and placed in the main wind direction downwind of the emitter. In addition, an air inlet (1/4") Teflon tube with protected inlet) is attached to the tripod on which the Metek is positioned and connected to the OF-CEAS analyzer located under the tripod. This allows data to be recorded every second in the center of the emission plume at a height of 2.8 m. As the 2D-anemometer (Gill) is mounted on the roof of the vehicle, an internal correction is applied for wind speed and wind direction adjustment during vehicle movement. According to the manufacturer (Gill Instruments, Manual), this allows the data to be recorded with a temporal resolution of 1 Hz and an accuracy of $\pm 3\%$ at wind speeds up to 40 m s⁻¹ and a resolution of 0.01 m s⁻¹ (wind speed) and 1° (wind direction), respectively. Unlike the 2D-anemometer, the 3D-anemometer (Metek) is completely stationary and is powered by external batteries when mounted on a tripod in 2.8 m height above ground. The 3D-anemometer measures not only the horizontal wind speed, but also the vertical component with a resolution of 0.01 m s^{-1} (up to 50 m s⁻¹) and the wind direction with a resolution of 0.4° . The temporal resolution is up to 25 Hz, but the frequency is set to 1 Hz when used for emission rate determination (Metek, Manual). The uncertainty in orientation is 5° in the field tests (Kammerer [2019]). In the earlier mobile measurements before 2018, another stationary weather station (Davis) recorded all relevant wind data for later analysis. The Davis measured the speed and direction of the wind by a wind vane and cup anemometer with a time resolution of up to 1 minute. The resolution for wind speed was 0.4 m s^{-1} with a nominal accuracy of 1 m s⁻¹ or 5 % (whichever is greater). For wind direction, the resolution was 1° with an 3° accuracy (Davis, Manual).



Figure 3.1: Mobile setup for atmospheric in situ measurements with (a) roof system mounted on the van with 2D anemometer and air inlet and (b) CRDS analyzer equipped inside the van.

3.2 Application of the GPM for CH_4 emission quantification

To determine the CH_4 emission rate from the mole fraction recorded during plume crossings, a GPM is applied. This process is schematically summarized in a flowchart in Fig. 3.2.

For the analysis, input parameters are defined for each specific measurement, such as the meteorological conditions, the location of the source and the inlet height (detailed list of all parameters is included in Fig. 3.2). The GPS coordinates are transformed into a cartesian coordinate system. The origin is set at the point source and the system is oriented so that the peak maximum is aligned with the y-axis (y=0). The recorded mole fractions are converted from ppm to kg m⁻³ (as function of temperature and molar mass (M_{CH4}=16.04 g mol⁻¹) and the background mole fraction is calculated to continue only using the CH₄ excess. This is done by applying a weighted regression (IDPmisc package; Ruckstuhl et al. [2001]) through each single data point including the CH₄ mole fraction at 4 min before and after each data point (Wietzel and Schmidt [2023]). For the application of the GPM, the data analysis follows mainly the method developed by Kammerer [2019], which was validated and refined by controlled release experiments in Mannheim and Heidelberg, as described in detail in the following chapter 4.

From the input parameters, such as coordinates and averaged wind data, and the apriori emission rate, the corresponding CH_4 mole fractions are calculated using the Gaussian model. The diffusion parameters σ_y and σ_z are calculated based on the PGSC classification and Briggs parametrization (section 2.2.1). To minimize the influence of wind fluctuations following Albertson et al. [2016], both the measured and the modeled mole fractions (C(x, y, z)) are integrated along the transect pathways. For this purpose, the start and end time of each plume transect is defined and it is examined that the peak is completely present within the specified time interval (background-peak-background). To obtain an estimated emission rate Q_{est} for each individual transect, the measured integral I_{meas} is divided by the modeled integral I_{mod} and multiplied by the input release rate Q_{in} (set to 1 g h^{-1} in the evaluations of this work). A determination coefficient (R^2) greater than 0.5 is used as a criterion for a valid comparison between the measured and modeled plume for each transect, in order to accept the transects (Korbeń et al. [2022]). Only transects that passed the quality check are included in the calculation of the average emission rate for a specific emitter. Finally, the mean value, the median, the standard error of the mean and the median, calculated from the standard deviation (std) and median absolute deviation (mad) (3.1b) are reported for each set of transects at a specific emission source.

$$SE(mean) = \frac{std}{\sqrt{n}}$$
 (3.1a)

$$SE(median) = \frac{mad}{\sqrt{n}}$$
 (3.1b)



Figure 3.2: Flowchart describing the application of the GPM as used in an R script to calculate an estimated CH_4 emission rate based on CH_4 mole fraction measurements recorded during mobile surveys.
Chapter 4

Best practices and uncertainties in the quantification of CH_4 emissions by controlled release experiments

Analyzing measurement data from mobile platforms using a dispersion model to calculate CH₄ emission rates has the advantage that measurements can be carried out on the roads outside the facilities, without the need for direct access by the operator. It is important to test the method used for emission quantification by sampling a known release rate before investigating unknown emission sources. This allows the method's capabilities, limitations and uncertainties to be carefully examined. Controlled release experiments have already been conducted in several studies to support the development, testing and improvement of atmospheric measurement and modeling techniques for the detection, localization and quantification of CH₄ emissions (e.g. Foster-Wittig et al. [2015], Hirst et al. [2017], Ars et al. [2017], Caulton et al. [2018], Kumar et al. [2021], Morales et al. [2022]). However, differences in local conditions and measurement devices require a thorough examination of the method to ensure that it is adapted to individual needs. To estimate the uncertainty of our measurement and modeling setup, a large number of uncertainty analyses with controlled release experiments were carried out in Mannheim (MA) and Heidelberg (HD). The experiments cover the years 2018 to 2023, reflecting technological adaptations in our research team. The 2018-2020 release experiments were performed by J. Kammerer and P. Korbeń and detailed analyses of these can be found in Kammerer [2019] and Korbeń [2021]. As part of this thesis, the release experiments were re-evaluated in harmonized manner and new findings applied. The emission rates are calculated according to section 3.2. The relative deviation is given as the estimated emission rates divided by the actual release rate. While the evaluation using the GPM is analyzed in detail in the following section, results from the OTM33-a measurement during HD3 are discussed in Appendix B.3.1. The following section is based on the study by Wietzel et al. [2025] submitted to Atmospheric Measurement Techniques, to which further details have been added.

4.1 AirField Heidelberg campaign 2023 and re-evaluation of release experiments from 2018 and 2020

4.1.1 Site descriptions, controlled releases and atmospheric conditions

Between October 11 and 13, 2023, a three-day controlled release campaign was carried out on a former airfield in Heidelberg, Germany (longitude: 49.391954° , latitude: 8.654846° , altitude a.s.l.: 105 m). As shown in Fig. 4.1, the airfield, located to the southwest of Heidelberg, covers an area of 400 m by 400 m. To the west, several hangars and a tower are located, while open fields extend to the north and east. The site is predominantly surrounded by agricultural fields and individual residential buildings. Two biogas plants are located approximately 700 m to the northeast. To reduce the possible influence of methane emissions in the northeast, methane releases were only conducted when the wind was directed from the south or southwest. The selection of measurement days was based on wind direction and other favorable meteorological conditions, including wind speeds of at least 1 m s⁻¹ and the absence of precipitation.

Two 10-liter high-pressure cylinders (release tank 1 and 2) filled with CH_4 (> 99.5 % CH_4) were used on site. To simulate a methane point source, one cylinder was connected to a flowmeter (Yokogawa Rotameter, model RAGL) and a 3-meter tubing. The flow rate was adjusted between 0.1 and 0.7 kgCH₄ h^{-1} and the end of the tubing was placed between 1 m and 2.5 m above the ground. The CH_4 cylinders were weighed before and after each gas release (model DS30K0.1 balance, Kern & Sohn GmbH, Balingen, Germany, readability 0.1 g) to cross check the flowmeter measurements. Both methods of flow rate determination were in good agreement. In order to exclude the influence of other emitters, the background mole fraction of CH_4 was confirmed by measurements close to the release point before the start of each release. Mobile ground-based measurements were performed as described in chapter 3 for atmospheric measurements using the OF-CEAS analyzer. Subsequently, the data were analyzed using the GPM and OTM33-a methods as described in section 3.2 and B.3. During three performance days, 22 releases with an average duration of 15 minutes were carried out with variations in driving speed, distance between release point and inlet, number of point sources and source positioning. The average wind speed during the three days was 1.9 m s^{-1} , predominantly from the south, and temperatures ranged from 17 to 24 °C.

Additionally, the dataset was complemented by three release experiments conducted as part of previous studies (Kammerer [2019], Korbeń [2021]). Re-evaluating these experiments within the scope of this thesis allowed for a more in-depth analysis and increased the statistical dataset. The three controlled CH_4 release experiments took place in November 2018, September 2020 and October 2020 at a parking lot in Mannheim (longitude: 49.470816°, latitude: 8.514822°, altitude a.s.l.: 89 m). The site is a flat area measuring 750 m by 250 m, free of significant obstacles (Fig. B.1). To the north is a local airport, while to the south, between the parking lot and the highway, there are trees and bushes. During these three experimental days, 17 releases were conducted, with variations in the measurement vehicle, driving speed, and the distance between the release point and the inlet. The release rates ranged between 0.1 and 0.6 kgCH₄ h⁻¹.

Table 4.1 provides an overview of the most important underlying conditions during all six release experiments analyzed in this thesis.



Figure 4.1: (a) Color-coded map of former airfield site with driving possibilities (yellow) and area for stationary measurements (orange). The map was created using leaflet for R (©Esri). (b) Windrose showing the frequency of wind speed by wind direction for all three days in October, 2023, of the stationary 3D anemometer measurements.

ID	Date	Location	Instrument	Anemometer	
MA1	28.11.2018	Mannheim	CRDS	Metek	
MA2	10.09.2020	Mannheim	OF-CEAS	Gill + Metek	
MA3	22.10.2020	Mannheim	OF-CEAS	Gill + Metek	
HD1	11.10.2023	Heidelberg	OF-CEAS	Gill + Metek	
HD2	12.10.2023	Heidelberg	OF-CEAS	Gill + Metek	
HD3	13.10.2023	Heidelberg	OF-CEAS	Gill + Metek	
	Temperature	Meteorological	Wind speed	Number of	
	$[^{\circ}C]$	condition	[m/s]	releases	
MA1	5	overcast	2.8	5	
MA2	22	sunny	1.7	6	
MA3	19	cloudy	1.9	6	
HD1	21	sunny	2.2	9	
HD2	20	overcast	1.2	9	
HD3	22	sunny	2.4	4	

Table 4.1: Overview of controlled CH_4 release experiments performed between 2018 and 2023 in Mannheim (MA) and Heidelberg (HD)

4.1.2 Analysis of experimental setup, driving strategy and averaging methods

Different wind sensors and two distinct trace gas analyzers were employed during the time period 2016-2024 (see chapter 3). Accurate measurement of atmospheric trace gas mole fractions is essential for the calculation of emission rates. Therefore, the response time of gas analyzers is critical, especially in dynamic environments where trace gas mole fractions change rapidly. The CRDS analyzer, used for mobile ambient air measurements of CH_4 and CO_2 between 2016 and 2020, has a lower data acquisition frequency (0.27 Hz) and is more optimized for isotope measurements. In contrast, the OF-CEAS analyzer, used from 2020 onward, has a faster data acquisition frequency (1 Hz), which is better suited to applications that require rapid detection of mole fraction changes, such as flux measurements. It is important to consider the response time of the instrument in the context of real-time (in situ) measurements and how this might influence the accuracy of emission rate calculations.

The response time of the CRDS and OF-CEAS analyzers were investigated during one mobile survey, in which both analyzers performed simultaneously with different temporal resolutions. The faster analyzer (OF-CEAS) recorded higher mole fractions, while the peak measured by the slower analyzer (CRDS) was broadened. An example peak is shown in Fig. B.2 (a), which shows the modeled peak structures in addition to the measured CH₄ enhancements measured with both instruments at the same time during a plume crossing. We found that for our two analyzers the peak heights are different, but the area under the integrated molar fraction curve integrated over time remains consistent (Table B.2 (b)). Takriti et al. [2021] also investigated the effect of analyzer response time on mole fraction measurements by conducting mobile surveys using two gas analyzers. They consider that if the mole fraction in the ambient air changes rapidly, the slower instrument in particular may miss the true peak height in real time. By using the peak area to calculate an emission rate as already applied by Mønster et al. [2014] and Korbeń et al. [2022], we can ensure that the emission rates derived from measurements with the two different instruments remain consistent and comparable.

Influence of driving speed and choice of mobile vehicle

The duration of measurements and, consequently, the measured peak area, is directly influenced by the driving speed - as the driving speed decreases, the area of the peak measured during one transect increases. Even though the estimated emission rate is adjusted by multiplying the methane enhancement with the distance of the individual data points and thereby minimizing the influence of speed on the data (see 3.2), a precise investigation during field measurements remains. To test the impact of vehicle speed on measurement results, two measurements, each consisting of 10 transects, were conducted during the HD2 campaign at a distance of 25 m, with driving speeds of 20 km h⁻¹ and 50 km h⁻¹. Lower driving speeds allow a better resolution of the peak, with 8 data points at 20 km h⁻¹ compared to only 5 data points at 50 km h⁻¹ (see Fig. 4.2 (a) and (b)). The peak

height for peaks measured at 50 km h⁻¹ is on average only 2/5 of the maximum peak height of peaks measured at 20 km h⁻¹. This is shown in Fig. 4.2(c) as a time series of the measurement together with the corresponding calculated CH₄ emission rates.

Although no significant deviation from the actual release rate is observed in both scenarios, a lower driving speed improves the temporal resolution of mole fraction measurements, which may enhance data accuracy. Based on these findings, it is recommended that field measurements are conducted at driving speeds below 30 km h⁻¹, whenever possible.

The lightweight and compact OF-CEAS trace gas analyzer allows also measurements on foot and by bicycle (Wietzel and Schmidt [2023]). Walking measurements offer a useful tool for directly identifying emission sources on site, while bicycle measurements provide an effective complement to the application of the GPM, particularly when roads are inaccessible by car. The subject of the MA2 investigations was also the comparison between the choice of measurement vehicle (car or bicycle) used for mobile CH_4 measurements.

For this purpose 8 and 12 transects were driven by bike and car, respectively, and the resulting data was analyzed. Although the bicycle measurements show a more variable emission rate estimation as indicated by a higher standard deviation (bike: 0.51 ± 0.27 kgCH₄ h⁻¹, car: 0.47 ± 0.09 kgCH₄ h⁻¹), measurements agree with the true release rate of 0.4 kgCH₄ h⁻¹ within their uncertainties (Fig. B.5). Based on these results, the bicycle setup is considered a suitable and reliable alternative for conducting mobile ambient air measurements, particularly in areas where access by car is limited.

Influence of downwind distance on emission rate estimate

The location of accessible roads varies for each CH_4 emitter, resulting in the plume being crossed at different distances. Therefore, it is important to analyze the emission estimate as a function of the distance between the emission source and the measurement point to account for this in the planning phase.

Under stable meteorological conditions, distances of 100 m, 250 m and 310 m to cross the plume were tested during MA1 with a release rate of 0.6 kgCH₄ h⁻¹ and wind speeds over 3 m s⁻¹. The time series of the measured CH₄ mole fraction is shown in Fig. 4.3 with highlighted peaks measured at the different distances. The average enhancement above background was ~ 200 ppb at 100 m (blue), ~ 60 ppb at 250 m (yellow) and ~ 40 ppb at 310 m (green). In addition the estimated emission rates are illustrated in comparison to the actual release rate. No significant difference between the emission rate estimation in the three different distances investigated can be seen.

However, measurements closer to the emission source in distances of 14 and 36 m were tested during MA3 and finally a large range from 5 to 260 m was tested during HD2. The average CH₄ emission rate during MA3 at a distance of 14 m was 0.77 ± 0.23 kg h⁻¹ and at 36 m 0.34 ± 0.06 kg h⁻¹, respectively, with a release rate of 0.36 kgCH₄ h⁻¹. MA3 already shows that very close measurements of 14 m from the source lead to an overestimation of the emission rate by twice the actual rate (Fig. B.3).



Figure 4.2: Upper two panels show example peaks of measured and modeled CH_4 mole fraction at driving speeds of (a) 20 km h⁻¹ and (b) 50 km h⁻¹. Lower panel (c) shows controlled release experiment HD2 time series with CH_4 mole fraction measured at different speeds highlighted (blue = 20 km h⁻¹, yellow = 50 km h⁻¹) and determined emission rates in comparison to actual release rate for the different driving speeds.



Figure 4.3: Controlled release experiment MA1 time series with CH_4 mole fraction measured at different distances (blue = 100 m, yellow = 250 m, green = 310 m) and determined emission rates in comparison to actual release rate for the three different distances.

In even more extreme cases, such as the scenario in HD2 with measurements conducted at only a distance of 5 m, it is no longer possible to make a realistic estimate of the emission rate applying the GPM (Fig. B.4). In this case the CH_4 emission rate is overestimated by more than 1000% (the same result was found at MA2 at 4 m distance).

This behavior is consistent with model expectations. The Briggs parametrization (Briggs [1973]) used to calculate the dispersion coefficients is based on measurement distances between 100 m and 10 km and the concentration values tend to increase and finally reach infinity near the source, due to the parametrization of the diffusion coefficients (Abdel-Rahman [2008]). In addition to the limitation introduced by the Briggs parameterization, the accuracy of the GPS position (\pm 3 m) can also affect the emission rate determination, especially at short distances.

This shows, while the GPM model is effective at distances greater than 20 m, close-range measurements, especially below 20 m, can introduce substantial errors and are unsuitable for accurate emission rate estimation in our case. For successful implementation of the GPM and obtain reproducible results, it is essential to maintain an appropriate distance from the emission source, sufficiently far to avoid plume interference, yet close enough to clearly capture distinguishable methane peaks. In this respect, with our measurement and modeling setup, we would only accept measurements taken at a distance greater than 20 m from the emitter.

This result differs from the studies of Day et al. [2014], who found no dependence in four controlled release experiments at downwind distances between 15 and 30 m from the source. Rella et al. [2015c] also found no correlation between the estimated CH_4 emission rate and wind direction at a distance of 15 to 150 m in measurements at oil and gas wells.

Number of transects and averaging method

Field campaigns for methane emission investigation require a precise sampling strategy to ensure accurate emission rate estimations. The optimal number of transects (plume crossings) to achieve reliable results, while minimizing the sampling time is an important factor. We investigate the convergence of the determined CH_4 emission rate as well as the standard deviation as a function of the number of transects based on the release experiments.

A set of 30 transects from the release experiment HD1 is used and an increasing number of randomly selected transects are taken from the set n times to calculate the corresponding average total emission rate. This process is repeated n times to obtain a distribution of mean values and standard deviations. The convergence of the calculated emission rate and its standard deviation is then analyzed in relation to the number of transects averaged. Figure 4.4 shows box and whiskers plots for the median and mean, respectively. In some cases significant deviations from the nominal release rates were estimated. Note that the uncertainties shown in the box plots correspond to the distribution of the calculated mean or median values (uncertainty due to the limited number of transects) and therefore do not reflect the accuracy (influence of systematic error) of the measurement.

The results indicate that as the number of plume transects increases, the standard deviation decreases, and precision improves. A notable reduction in variance is observed after approximately 10 transects, with additional transects only leading to a slow reduction in the variance of the results. At 10 transects, the standard deviation decreases by 80 %, but only decreases by an additional 10 % by extending up to 20 transects. Based on these observations from the field experiment, the number of transects required to achieve reliable results by decreasing the influence of atmospheric variability, while keeping measurement time within reasonable limits was identified as ten.

A similar result was described by Kammerer [2019] with findings from MA1 and is in agreement with Caulton et al. [2018], who also suggested 10 transects as optimal. This result is also consistent with recommendation for a 10-minute averaging interval to achieve steady-state plume emissions by Stockie [2011] as mentioned in section 2.2.2, since the GPM does not depict the instantaneous turbulent structures on fine spatial and temporal scales. This finding supports the averaging over 10 transects as an effective approach to ensure robust emission rate determination.

When 10 or more transects are conducted, a question arises regarding whether the mean or the median is the most suitable method for averaging to determine the emission rate per measurement at a CH₄ source. Figures 4.4(a) and 4.4(b) clearly demonstrate that the mean is closer to the actual release rate (indicated by the dashed red lines). In this example, the median converges to a value 22 % lower than the CH₄ release rate, while the mean is only deviating by 3 %. Figure 4.5 provides a summary of all release experiments conducted between 2018 and 2023, comparing the deviation of determined methane emission rates to the actual release rate. The red values are calculated with the mean, while blue presents the median values. The median tends to underestimate the values



Figure 4.4: Convergence of the (a) mean and (b) median plume rate by averaging randomly selected transects from one set conducted during release experiment HD1. The actual release rate is shown as dashed red line. Box and whiskers plots show the average, 25th and 75th percentile, and minimum and maximum values of the means obtained for each number of transects. Outliers are shown as black dots. The standard deviation of the average values is included in blue.

more than the mean, as it is less sensitive to extreme values or outliers. While the median represents the central value of a dataset, it does not account for very high or low emission estimates, which may bring the mean closer to the actual release rate. In contrast, the mean incorporates all values, including extreme estimates, thus better reflecting the true emission rate in cases with outliers. Variations in the values observed during controlled release experiments are attributed to atmospheric variability, as fluctuations in the release rate can be excluded. However, variations in methane emission rates in field conditions cannot be ruled out. Similar to the previous analysis of HD1, the mean proves to be more accurate than the median, with average deviations from the release values of 36 % for the mean and 43 % for the median. When measurements below a distance of 20 meters are excluded as suggested in the previous section, the deviation reduces to 30 % for the mean and 37 % for the median.

Based on the findings from the release experiments and to account for fluctuations in

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emission rates and atmospheric variability during measurement campaigns, the mean will be used to represent the emission rate throughout the remainder of the study. Nevertheless, both the mean and median were calculated in all analyses, as significant deviations between these values may indicate potential issues or changes during the measurement process. It is important to note that the determined emission rates in Fig. 4.5 show no influence by changes in the measurement setup between MA1 and MA2.



Figure 4.5: Scatterplot for comparison of determined methane emission rates during the different release experiments to the actual release rate for mean values (red) and median values (blue). Releases conducted at 14 m distance during MA3 are excluded from the average values.

Influence of meteorological parameters on calculated emission rates

During the eight years of the mobile surveys analyzed in this dissertation, different wind sensors, including stationary (Davis and Metek) and mobile set-ups (Gill) were used for wind measurements. For the GPM, continuous in situ measurements of wind speed with sufficient temporal resolution and high accuracy are required as input parameter in its application. The calculated emission rate is proportional to the wind speed (Eq. (2.3)). The stability class and thus indirectly the dispersion coefficients σ_y and σ_z also depend on the wind speed. In two comparison campaigns of the wind sensors, all three sensors used over time were first set up as static, and in a second comparison the mobile sensor was compared with a stationary one during the HD3 release experiment.

In February 2019, simultaneous measurements were taken by Kammerer [2019] using three weather stations located at the roof of the Institute of Environmental Physics to compare wind data. Data were recorded in seconds (Metek, Gill) and minutes (Davis) and averaged

over hourly means as wind vectors (Fig. 4.6(a)). The results from the 2019 measurements indicated that the wind speeds measured by the Gill and Davis instruments were slightly lower than those recorded by the Metek station. On average, the Metek measured wind speeds of 2.4 ± 1.5 m s⁻¹, while the Gill recorded 2.1 ± 1.3 m s⁻¹, and the Davis 2.2 ± 1.7 m s⁻¹. However, these differences, were not statistically significant. The differences in wind direction were also not significant during the measurement period.

A further comparison measurement in 2023 focused on evaluating the performance of the mobile Gill anemometer during vehicle motion, to verify the internal correction that accounts for the driving wind and vehicle alignment. At the same time the stationary Metek anemometer was set up nearby. When both the Gill and Metek anemometers were stationary (Fig. 4.6(b)), the data were comparable, with the Gill measuring an average wind speed of $2.1 \pm 1.1 \text{ m s}^{-1}$ (wind direction: $174 \pm 26^{\circ}$) and the Metek measuring 2.4 \pm 0.9 m s⁻¹ (wind direction: 169 \pm 20°). The difference in the wind speed values was similar to that recorded in 2019. However, during vehicle movement, especially during acceleration phases, the Gill showed more variability in wind speed with 2.5 ± 1.5 m s⁻¹ and wind direction: $207 \pm 124^{\circ}$ compared to the Metek with a mean wind speed of 2.5 \pm 0.9 m s^{-1} and wind direction of $176 \pm 19^{\circ}$. Figure 4.6(b) shows the corresponding time period with driving times highlighted in gray. Once the vehicle reached a constant speed, the wind measurements from the Gill were in agreement with those from the stationary Metek instrument. The uncertainty (calculated as the standard deviation of the 1 s values) is lower when the car does not move, especially in the wind direction. However, the mean values do not appear to be affected. Nevertheless, the driving speed should be maintained when driving through the plume in order to avoid being influenced by acceleration phases, which may introduce additional uncertainty into emission rate calculations. The wind direction in particular appears to be more strongly affected. Its influence on the emission estimation will be discussed in a later section.

Inaccurate wind data can introduce significant errors, as the Gaussian equation (Eq. 2.3) shows a linear relationship between the inverse of wind speed and the emission rate. This means that the relative uncertainty in the emission rate is likely to be similar to the relative uncertainty in the wind speed. Caulton et al. [2018] demonstrated that using carefully measured, on-site in situ wind data greatly enhances the accuracy of CH_4 emission rate estimates, compared to relying on modeled wind fields that may not accurately represent the site or NOAA wind data.



Figure 4.6: Wind speed (top) and wind direction (bottom) measured with the Gill (blue), Metek (green) and Davis (red) instruments (a) installed stationary on the roof of the Institute of Environmental Physics, averaged hourly (February 2019) and (b) mobile (Gill) and stationary (Metek) secondly data during the HD3 release experiment (October 2023). The gray areas highlight the periods, when the car was moving.

Wind parameter averaging method

Wind variability is a critical factor in the dispersion and detection of atmospheric plumes, often leading to deviations in the lateral positioning of transects. This phenomenon, known as the 'meander effect', arises from atmospheric eddies that are larger than the diameter of the plume. Accurate wind direction determination is essential for reliable emission rate calculations. Caulton et al. [2018], Kumar et al. [2021] and Korbeń et al. [2022], find that using geographic coordinates to determine the wind direction from the location of the maximum peak concentration during a transect and the emitter can provide a more accurate representation of the plume behavior and a better reproduction of the modeled peaks, than directly measured wind data

To evaluate this, ten transects from HD1 were analyzed using the two distinct anemometer setups - the stationary anemometer positioned at a fixed location (Metek) and the mobile anemometer mounted on a vehicle (Gill) moving along the transects. Figure 4.7(a) presents the anemometer data for wind direction averaged across the transects as well as the modeled wind direction, based on the geographical coordinates. The modeled wind direction and stationary measurements (Metek) were in good agreement with and average deviation of less than 13°, while the mobile wind sensor (Gill) deviated significantly with 84° on average. This characteristic behavior of the Gill has already been described in section 4.1.2. These differences are then directly reflected in the calculated emission rates as shown in Fig. 4.7(b). The emission rates calculated using the stationary anemometer do not show significant variations when comparing measured and modeled wind directions with an average $0.63 \pm 0.18 \text{ kgCH}_4 \text{ h}^{-1}$ and $0.61 \pm 0.18 \text{ kgCH}_4 \text{ h}^{-1}$, respectively. In contrast, the mobile anemometer's wind direction measurements lead to a notable overestimation of the emission rates with an average of $133 \pm 103 \text{ kgCH}_4 \text{ h}^{-1}$. For modeled wind direction on the other hand the calculated emission rate with $0.41 \pm 0.10 \text{ kgCH}_4 \text{ h}^{-1}$ does not deviate significantly from the release rate set to 0.5 kgCH₄ h⁻¹. These results emphasize that wind direction variability, caused by vehicle movement as well as other factors such as an emometer placement or external influences like buildings and passing vehicles, impacts emission rate calculations. The approach proposed by Caulton et al. [2018] and Kumar et al. [2021], and employed by Korbeń et al. [2022], using modeled wind direction based on geographic coordinates, provides a valuable method for compensating for such variability and improving the accuracy of emission rate estimates.

Several studies average wind parameters, especially wind speed, over different time periods (e.g. Riddick et al. [2022b], Kumar et al. [2021], Albertson et al. [2016]). Korbeń et al. [2022] averaged the wind speed separately for each plume crossing, which usually lasts between 30 and 90 seconds. To assess the impact of wind speed averaging, two different methods were tested: (1) averaging the wind speed over each individual transect or (2) averaging the wind speed over a set of transects (minimum of 10 transects). In the first case, the transects are considered separately calculating an average transect wind speed (TWS). In the second case, the measured wind speed is usually averaged over a period of

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Figure 4.7: (a) Measured wind direction for the Metek and Gill instruments in comparison to modeled wind direction for 10 transects conducted during HD1. (b) Bar plot showing the corresponding emission rates calculated using measured and modeled wind direction for the Metek and Gill instruments, respectively, compared to the actual release rate.

20 to 30 minutes and this mean wind speed (MWS) is applied to all peaks and used to calculate the corresponding emission rate.

To compare the two methods, a set of transects from HD1 is shown in Fig. 4.8 presenting a bar plot with the actual release rate and the estimated release rates of single transects calculated via MWS and TWS using wind measurements from (a) Metek and (b) Gill.

No significant differences were found between the two methods, particularly with the Metek, as the time periods during the release experiments were short ($\sim 20-30$ minutes) and no noticeable wind changes were observed. The same applies to the Gill, as the accelerating phases were excluded from the TWS calculation, and any discrepancies during acceleration were averaged over the entire MWS measurement. Nevertheless, TWS is selected for wind speed calculations as it allows a more immediate response to potential wind changes, especially during longer measurement periods (> 1 hour), as it is often the case during field campaigns.

Parametrization of Pasquill stability class

To relate measured methane mole fractions to emission rates, it is essential to understand the stability of the atmospheric boundary layer. In the context of this thesis, atmospheric stability is categorized into a PGSC for the application of the GPM method (Table 2.1). This categorization describes the dispersion characteristics of the atmosphere and is represented in the Gaussian model by the dispersion parameters σ_y and σ_z , as described in detail in section 2.2.1. The classification influences the dispersion behavior of the atmosphere as a fundamental in the GPM. According to Pasquill [1961] the stability of the atmosphere can be described in a simplified way using wind speed and observations of the position of the sun and cloud cover as a proxy for the solar radiation (based on conditions in England). The Pasquill-Gifford classes are simple and straightforward, yet they overlook crucial factors influencing atmospheric stability (Kahl and Chapman [2018]; section

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Figure 4.8: (a) Averaged wind speeds over a set of transects (MWS), or averaged over each transect separately (TWS) for the Metek and Gill instruments are shown for 10 transects performed during HD1. (b) Bar plot showing the emission rates calculated via mean wind speed (MWS) and transect wind speed (TWS) with wind measurements conducted using the Metek and Gill instruments, respectively, compared to the actual release rate.

2.2.2). As the PGSC are not measurable physical parameters and their categorization is gradual, they can significantly influence the dispersion model, leading to considerable uncertainties in the determination of the emission rate (Haggagy and Shazly [2008]).

When considering transitions between neighboring stability classes (such as B-C or C-D), the dispersion properties can change significantly, leading to uncertainties in the categorization. This is demonstrated by modeling peaks across stability classes A to D in Fig. B.6, keeping all other parameters unchanged. The results show that as the stability class increases, the dispersion peak becomes narrower and higher. This reflects that in more stable atmospheric conditions (higher stability classes) the air is dispersed less strongly, due to higher wind speeds and lower solar radiation.

Choosing a wrong stability class can lead to significant errors, as the model describes the dispersion and therefore the distribution of emissions inaccurately. This is reflected in a remaining uncertainty of 40 % in the values presented in Table B.1, if an incorrect stability class is assigned. For example, the stability class during MA1, where methane was released with a rate of 0.6 kg h⁻¹, was C, which results an emission rate of 0.55 \pm 0.06 kgCH₄ h⁻¹. If category B had been selected instead, the CH₄ emission rate would be 0.87 \pm 0.11 kg h⁻¹, and if category D had been selected, the emission rate would be 0.38 \pm 0.04 kg h⁻¹. Thus, the choice of the correct PGSC for the GPM is of great importance. Uncertainties in the categorization, especially at transitions between neighboring stability classes, can lead to considerable errors in the calculations and thus affect the practical application of the model.

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Riddick et al. [2022a] used direct measurements of solar radiation to slightly modify the classification. They defined strong solar radiation as $> 1000 \text{ W m}^{-2}$, moderate between 500 and 1000 W m⁻², and weak for solar radiation below 500 W m⁻². As part of the release experiments, the effect of different parametrization of the stability classes on the calculated emission rates was assessed. For Riddick et al.'s slightly modified classification, solar radiation data recorded at the weather station of the Institute of Environmental Physics in Heidelberg (latitude: 49.4172553°, longitude: 8.67437285°, altitude a.s.l.: 36 m) were used. The emission rates for each release were calculated using both stability class approaches and compared with the release rates as Fig. 4.9 is showing for MA1. The calculated emission rates using the original Pasquill classification were influenced by the overcast condition on the experimental day, leading to all releases during MA1 being assigned to stability class D. This resulted in an average deviation of 36 % from the true release rates. In contrast, when using the modified approach with measured solar radiation, all CH_4 releases were assigned to stability class C due to moderate wind speeds and low solar radiation levels. Using the measured solar radiation instead of cloud cover reduced the average deviation in calculated emission rates to 8 %, resulting in a more accurate emission rate quantification.

When applied to all release experiments, the modified classification resulted in emission rate estimates that were, on average, 20 % closer to the actual rate than those resulting from the original categorization, although the difference was smaller when there was no overcast condition. Based on this observation, the largest differences tend to occur during overcast conditions, as was the case during MA1. A general categorization in stability class D according to the Pasquill method can result in significant deviations from the true release rate.

This findings highlight the advantages of direct measurement of solar radiation according to Riddick et al. [2022a], providing a more reliable approach to stability classification, minimizing uncertainty in emission rate calculations. Despite these improvements, the categorization process can still be subject to uncertainties, especially when transitioning between adjacent stability classes (e.g., B-C or C-D).



Figure 4.9: Bar plot with actual release rate and estimated release rates for the calculation categorized according to Pasquill [1961] (original) and Riddick et al. [2022a] (modified) from MA1.

4.1.3 Special cases

Application of GPM on a two-point source

During field measurements at emission sources, it happens that multiple peaks or a doublepeak structure in the CH₄ mole fraction along a transect are observed. This can be attributed to the presence of a second emitter whose plume is also detected downwind, or to multiple spatially separated emission points at a single emitter, such as in the case of several leaks or technical treatment points from which methane is released (Caulton et al. [2018]). In the second case, with no other CH₄ source influencing the measurements, two point sources can be placed on a facility to estimate a total emission rate from the corresponding emitter. For this purpose, the possibility of a second source was introduced into the GPM script by Kammerer [2019], allowing each source to be assigned an individual input emission rate (Q_{in}) and position. While both sources are processed as separate point sources, their contributions are summed within the model. This approach enables the calculation of the total absolute emission, although the relative emission contributions must be specified within the algorithm.

The application of this approach was investigated in the HD1 and HD2 experiments, where two methane cylinders were placed 20 meters apart as distinct emission sources. The release rates were set to 0.3 and 0.6 kgCH₄ h^{-1} . Two distinct scenarios were observed: in some cases, peak-background-peak structures were detected, while in others, the plumes from both release points overlapped, resulting in either a single peak or a double peak. Fig. 4.10(a) shows for one transect from HD2, the measured methane mole fraction above background (green) and the model fit (blue) occurrence of two separate peaks. Although two sources were given the GPM was unable to replicate the observed peak structure. As a result, this peak was excluded from the emission rate calculation based on the \mathbb{R}^2 criterion ($\mathbb{R}^2 \ge 0.5$). To avoid this problem, one possible solution is to define and analyze each plume individually within the GPM, which results in a better agreement with the measurements and an acceptable model fit. In contrast, Fig. 4.10 (b) presents another transect from HD2 where a double peak structure was observed, indicating that the plumes from the two sources had overlapped, but the individual peak maxima remained distinguishable. In this case, the model with the input of two-point sources successfully reproduced the observed peak structure.

These results suggest that the GPM with two separate point sources as input, where the contributions from each source are summed, is most effective in scenarios where the double-peak structure cannot be clearly separated. However, for cases where the peaks can be distinctly separated and the background mole fraction is reached between the peaks, it is recommended to calculate the emission rate for each point source individually.



Figure 4.10: Measured and modeled CH_4 enhancement above background along two transects during HD1 with a simulated two-point source from two release cylinders. (a) represents a rare case where despite two clearly measured peaks the model is unsuccessfully due to underlying environmental factors and (b) showing overlapping plumes forming a double peak structure and a successful model fit.

Release point close to building

Buildings and other obstacles can significantly affect airflow and plume dynamics. Emission sources are often located at technical facilities, such as biogas plants or wastewater treatment plants, in environments with buildings or other obstructions. These structures influence the determination of emission rates , which is important to consider when applying the GPM. In the HD3 release experiment, this scenario was modeled by positioning the release source near a building. Methane was released at a rate of 0.3 kg h⁻¹, and the presence of the building blocked the free inflow of air masses and prevented direct removal of methane by wind, as the release outlet was located 1 m above the ground on the downwind side of the structure. Eleven transects were driven at a speed of 30 km h⁻¹, with an average distance of 30 m between the release point and the air inlet.

The model demonstrated a good ability to replicate the measured CH₄ mole fraction, so that, contrary to expectations, the results show good agreement with the actual release rate. The calculated mean emission rate was 0.32 ± 0.04 kgCH₄ h⁻¹ (~ 7 % deviation to actual release rate), based on the analysis of 10 accepted transects.

This result indicates that the model is also applicable in more complex environments where obstacles influence plume behavior and airflow, which increases the reliability of the model as a tool for assessing emission rates in difficult environments. However, it remains important to evaluate environmental factors on a case-by-case basis when determining emission rates and analyzing the impact of technical installations.

4.2 TADI campaign 2024

The energy company TOTAL developed the test center TotalEnergies Anomaly Detection Initiatives (TADI) at Lacq in southwestern France to "[...] bridge(s) the gap between laboratory tests and on-site deployment for gas detection, and quantification of atmospheric emissions [...]" (X. Marcarian, Head of R&D, TADI). The TADI site offers the possibility to test different greenhouse gas measurement technologies for the detection and quantification of emissions in a controlled environment. Located within the multicompany platform Induslacq (longitude: 43.41282°, latitude: -0.64265°, altitude a.s.l.: 94 m), TADI has already been used for this purpose in earlier studies (e.g. Watremez et al. [2020], Kumar et al. [2021], Bonne et al. [2024]). Various pieces of industrial equipment (e.g. pipes, valves, tanks, lines, wellheads, flares) installed on the site are used to reproduce a range of different leakage scenarios. On this facility infrastructure a single-blind validation of methane-sensing technologies with independent testing of satellite, aircraft, drone and ground sensors was organized by Stanford University (Adam Brandt and Audrey McManemin) in collaboration with TotalEnergies during summer 2024.

In the same week as our campaign participation, measurements were also taken by a drone team, a stationary team and a satellite team. Under the premise of blind testing, the results of all teams were reported centrally to Stanford University, with the evaluation conducted without knowledge of the release rates or the exact location of the source. Stanford summarized the results of all participants in an UN report (McManemin et al. [2025]). During the first analysis and calculation of CH₄ emission rates within six weeks of the campaign, the background calculation was incorrect due to a bug in the software code. This error affects measurements conducted during release rates below 2 kgCH₄ h⁻¹ and is negligible for higher rates and it has been corrected for in the recalculated results in this thesis. However, as Stanford only accepts the first reported values in the 'blind' experiment, the calculated release rates below 2 kgCH₄ h⁻¹ in this thesis and in the UN report may differ slightly.

4.2.1 Site description, controlled releases and atmospheric conditions

We participated in a one-week controlled blind release campaign from June 24 to 28 with our mobile measurement setup for methane emission quantification and the data was analyzed using the GPM and OTM33-a methods as described in section 3.2 and section B.3. The measurement setup was installed as described in the chapter 3 on atmospheric measurements in a car that was driven on roads 50 to 400 m downwind of the release area. Since our LI-7810 OF-CEAS trace gas analyzer was at the manufacturer for repair from April to July 2024, they provided us a loaner instrument of the same type, with which the measurements were carried out during the campaign. A 2-liter calibration cylinder (Pic6_3) was taken along for stabilization control of the loaner. The CH₄ measurements of the standard gas showed only a slight fluctuation of ± 1 ppb (see Fig. B.7 in the Appendix), confirming a stable behavior of the analyzer. Each release lasted approximately 45 minutes, with 5 to 10 minute breaks in between and methane was emitted in a controlled manner (5 % uncertainty) between 0 and 200 kgCH₄ h⁻¹. In addition to the release rate, the position of the point source varied over an rectangular area of 40 m x 60 m and heights between 0 and 6.5 m above ground. The point sources corresponded to different types of equipment and release scenarios: horizontal or vertical piping, manholes, open ended lines, under insulation, control boxes, flanges, drilled plugs and valves at pipe racks, flares, tanks, scrubbers and product skids. For safety reasons the release area was not accessible to participants. Figure 4.11 (a) shows a top-down view on the site including the release area and possible accessible roads for measurements. During five performance days 35 releases were carried out and we obtained measurements during 34 releases. Ambient air measurements were performed continuously while the car drove alongside the platform at an average speed of 15 km h⁻¹. The number of plume crossing varied between 10 and 26 and were in several cases carried out at two different distances.

A 3D anemometer was installed close to the release area to obtain reliable measurements of the meteorological parameters at a height of 2.8 m above ground-level. In the case of a stationary measurement, this 3D wind sensor was placed inside the plume together with the instrument for the duration of the release (Appendix B.12). The average wind speed during the five days was 1.9 m s⁻¹, mainly directing from the north. On several days low wind speeds were measured ($< 2 \text{ m s}^{-1}$) during the releases, which came along with quickly changing wind directions (Fig. 4.11(b)). The temperature ranged from 18 to 33 °C and all releases were conducted during daytime.

4.2.2 Campaign results

As the campaign was a blind release test and neither the release rate nor the release location were known during the first round of evaluation of all 34 releases, the point source was placed in the center of the release area (latitude: 43.4128249° , longitude: -0.6426542°) at a height of 2 m above ground. After the exact release location and the respective controlled release rate for each release was communicated, a second round of evaluation was carried out in which the data sets were re-evaluated taking into account the exact release location and height as input for the GPM. In addition to the comparison with the actual release rate, other aspects such as release location, meteorological conditions, background mole fraction, measurements at two different distances were investigated in detail. The release with the lowest release rate and the zero release carried out as part of the TADI campaign were considered as special cases and are discussed separately later in this section. During individual releases the stationary meteorological weather station was affected by data gaps during battery changes. These short term interruptions in the data were supplemented during the evaluation by linear interpolation of the data set. Anemometer performance and further supplementary material of the TADI campaign can be found in Appendix B.2, providing a table with information on the actual release rates, the number of transects driven and peaks accepted for evaluation, the meteorological parameters for each of the



Figure 4.11: (a) Color-coded map of Induslacq site with release area (light blue), possible area for stationary OTM33-a measurements (orange) and roads accessible to drive (yellow). The map was created using leaflet for R (©Esri). (b) Windrose showing the frequency of wind speed by wind direction for all five days of the stationary 3D anemometer measurements.

releases as well as the stability class selected and the estimated emission rates (\pm SE). As no data on solar radiation was available on site, the stability class was determined using the original Pasquill classification. For a local time from 12 to 16 pm a strong incoming solar radiation was considered and for the other a moderate incoming solar radiation based on solar altitude and cloudiness.

Release location

Accurate estimation of methane emission rates requires precise knowledge of source position and release height. Variations in these parameters can influence the calculation of emission rates, but during field measurements the exact source location is not always well known. This section analyses the impact of source position and release height adjustments on the accuracy of methane emission rate estimates. The analysis examines the shift in the relative distance between the release point and the inlet and the impact on the calculated emission rates for 34 CH_4 releases.

After position adjustments were done with the known locations, the relative distance between the release point and the inlet changes by an average of 11 % (range: 0.1-38 %), whereby only two releases were affected by a change greater than 30 %. The average distance between source and inlet was 109 m for the unknown source position and 103 m for the known source position while the release location shifted between 1 and a maximum of 29 m after adjustment. The actual release heights varied between 0 and 6.5 m. The majority of releases (30 out of 34) took place at heights between 1 and 3 m. Only four releases were at either 6.5 m or directly above ground. The emission rates were estimated both with and without adjusting for the source position and height. These adjusted rates were compared to the actual release rates for each release.

Figure 4.12 shows the estimated versus actual release rates (dark gray) for all 34 CH₄ releases, as calculated without knowing the exact release location (dark blue) and adjusted for known source position (light blue). To provide a more detailed view of the position adjustment, Fig. 4.13 shows the deviation before and after position adjustment, once for the difference in the x-y plane (4.13(a)) and once for the height difference in the z plane (4.13(b)). A better agreement with the actual release rate after source position adjustment was shown for 15 of the 34 releases, with the best result for RE2_8 with a calculated emission rate of 2.78 ± 1.43 kgCH₄ h⁻¹ before and 1.73 ± 0.21 kgCH₄ h⁻¹ after location adjustment compared to the actual CH₄ release rate of 1.48 kg h⁻¹. The 20 m misplacement resulted in 68 % higher deviation of emission rate determination than with correct source position.



Figure 4.12: Comparison of the actual and estimated emissions rates of 34 releases given in kgCH₄ h⁻¹. Estimated rates are given as mean of the corresponding determined transect values. During releases marked with a red asterisk, the wind speed was below 1 m s⁻¹.

For the four releases with height differences of more than 2 m (releases with heights of 6.5 m and 0 m), resulted in a quantification improvement of 20 %. RE2_1 showed a calculated emission rate of 1.28 ± 0.18 kgCH₄ h⁻¹ before, and 0.81 ± 0.08 kgCH₄ h⁻¹ after a height adjustment of 2 m, resulting in a 60 % lower deviation in the emission rate determination after the adjustment. The CH₄ release rate was set to 0.77 kg h⁻¹.

In general the improvements were small, resulting in an average improvement of 6 % of the relative deviation. The results indicate that as long as measurements are taken at a sufficient distance of more than 100 m, adjusting the source position in the x-y plane has on average a relatively small effect on the calculated methane emission rate. However, in some cases an improvement of up to 70 % was observed. In contrast, changes in the

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Figure 4.13: Barplots showing the average deviation in emission rates relative to the release rate, based on measurements conducted during TADI campaign. The results are grouped into categories (a) ranging from distance adjustment below 15 m to distance adjustment over 20 m between unknown and known source location and (b) ranging from small height adjustment below 0.5 m to high height adjustment of over 2 m between unknown and known source height.

z-plane of more than 2 m already lead to larger changes in the emission rate calculation. The rest of this chapter refers to the results based on the analyses with the exact position of the source.

Range of release rates

As a good complement to the release experiments in Heidelberg and Mannheim, where only emission rates below 1 kgCH₄ h⁻¹ were generated, the TADI experiment was able to test larger ranges with release rates between 0 and 200 kgCH₄ h⁻¹. As 29 releases were carried out at rates above 1 kgCH₄ h⁻¹, we were able to test our method for emission rate quantification at higher values. Figure 4.14 shows the relative deviation of the emission rates from the release rate as a function of the release rate, excluding the zero and 0.01 releases. In the lowest range below 1 kgCH₄ h⁻¹, which was already tested during controlled release experiments in Mannheim and Heidelberg, the average deviation is 10 %. At higher rates the average deviation varies between 29 % and 45 %. The largest relative deviation of 104 % was observed at RE5_1. Here, CH₄ was released at a rate of 2.98 kg h⁻¹ and our measurements showed an emission rate of 6.07 ± 1.11 kg CH₄ h⁻¹. The smallest relative deviation of 1.7 % was observed at RE4_3, where 0.57 kg h⁻¹ of CH₄ was released and 0.58 ± 0.19 kg h⁻¹ was calculated.

These results show not only that our method is suitable for detecting and quantifying both medium and high emission rates, but also that it works particularly well at low emission rates. For example, the relative deviation during the TADI campaign of 10 % for releases below 1 kg CH_4 h⁻¹ is even lower than the deviations in the previously discussed release experiments in Mannheim and Heidelberg, which deviated on average by 30 % from the release rate. However, it should be noted that the measurement results are based on multi-factorial correlations.



Figure 4.14: Barplot showing the average deviation in emission rates relative to the release rate, based on measurements conducted during TADI campaign. The results are grouped into seven categories, ranging from very low CH_4 rates (< 1 kg h⁻¹) to very high CH_4 rates (> 50 kg h⁻¹), as observed during the campaign.

Measurements during different wind speeds

During the five-day campaign, wind speeds between 0.8 and 4.4 m s⁻¹ were recorded. For routine measurements, we avoid mobile measurements at wind speeds below 2 m s⁻¹ as higher wind speeds reduce the probability of plume meandering. During the TADI campaign, however, we carried out our measurements in all weather conditions. Wind speeds below 2 m s⁻¹ occurred in 40 % of the releases. Figure 4.15 shows the relative deviation of the calculated emission rate from the release rate as a function of wind speed. Careful evaluation of our results from the TADI campaign shows very good results, with deviations of 25 % from the actual release rate based on the 11 release experiments analyzed at wind speeds of 1 m s⁻¹ to 2 m s⁻¹. Only in two cases, measured below a wind speed of 1 m s⁻¹ (RE3_1 and RE5_3), deviate the results significantly and underestimate the actual release rate by about 80 % and 55 %, respectively.

Several studies (Essa et al. [2005], Mortarini et al. [2016], Wilson et al. [1976]) indicate that wind speeds below 2 m s⁻¹ already lead to poor model performance due to increased plume meandering, which could not be confirmed by our results. In contrast, there is a clear influence on the quality of emission rate determinations at wind speeds below 1 m s⁻¹. This means that the meteorological restrictions of our method can be relaxed to a wind speed limit of > 1 m s⁻¹ for mobile surveys.

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Figure 4.15: Barplot showing average deviation to release rate for emission rates determined based on measurements conducted during releases with different prevailing wind speeds.

Variability in background mole fraction

Background methane variability can significantly affect the accuracy of emission rate calculations, particularly at lower release rates where the relative effect of background variability is more prominent. In contrast, higher release rates, characterized by larger methane enhancements during plume crossings, reduce the relative effect of background variability on emission rate estimates (Caulton et al. [2018]). For release rates below 2 kg CH₄ h⁻¹, emissions were sensitive to background variability, with calculations showing a 10-30 %overestimation in CH_4 emission rates when a 10 ppb offset was applied to the background CH_4 mole fraction (see also white paper by Wietzel et al. in McManemin et al. [2025]). A more qualitative analysis of simultaneous measurements of CH_4 and CO_2 mole fractions help to differentiate release plumes from nearby emissions in the Induslacq area. During event RE1_1, a clear drop in background methane (15 ppb) and CO_2 (8 ppm) was observed, likely due to increased vertical air mixing from rising temperatures (see Fig. 4.16(a)). In contrast, releases RE3_1 and RE2_1 showed methane fluctuations of \pm 100 ppb in CH₄, with similar changes in CO_2 mole fraction (see Fig. 4.16(b)). This variability, alongside corresponding changes in the CO_2 mole fraction, suggests that the observed variations are likely due to emissions from other small emitters at the Induslacq site.

Overall we confirmed, that background methane variability creates uncertainties in emission rate estimates, especially at low release rates as described by Caulton et al. [2018]. While moving background calculations help mitigate this, emissions from nearby sources can complicate plume detection, particularly when plumes overlap. Further analysis, including CO_2 data, can help to improve plume identification and emission quantification at the site.



Figure 4.16: Time series of measured CH_4 (black) and CO_2 (green) mole fractions with CH_4 background fit in blue during release (a) RE1_1 (b) RE3_1 and (c) RE2_2.

Measurements at different distances

During the TADI campaign, eleven methane releases were measured at different distances on two separate days. On the second release day, easterly winds were present, increasing from 1.4 to 2.6 m s⁻¹, throughout the day. Once wind speeds exceeded 1.5 m s⁻¹, measurements were taken at approximately 70 m and 130 m from the release area. The average emission rate at the farther location was estimated to be 7 % higher than at the closer one. On the fourth day, the highest wind speeds of the week, 4.4 m s⁻¹, from the west, were recorded. In addition to close-range measurements at 90 m, measurements were conducted at a distance of 450 m along a road to the east of the site. The maximum peak mole fraction at this distance was roughly a quarter of the maximum peak mole fraction measured at a distance of 90 m. On this day, the average estimated emission rate at the farther road was 25 % lower than at the closer one. It is important to note that only 3 out of 10 transects at the more distant road were included in the calculations, due to the road alignment, which complicated measurement. Despite these limitations, the GPM accurately predicted the emission rates at both distances with minimal deviations.

Therefore, the results confirm that the GPM remains effective in estimating CH_4 emission rates over a wide range of distances, as long as clear CH_4 peaks are detectable. This finding aligns with previous studies from the Heidelberg and Mannheim release campaigns, where the GPM produced consistent emission rate estimates, even as measurement distance varied between 20 and 300 m. The observed differences in maximum peak mole fractions at varying distances, particularly on the fourth day, highlight how wind speed and plume dispersion affect methane detection. However, the model's ability to provide reliable emission rate estimates underscores its value in field studies.

Zero-Release

Zero-release experiments are intended to simulate the absence of methane emissions and are usually used as control cases in emission monitoring studies. However, in the present campaign, unexpected methane peaks were detected during a zero-release test (RE3_8) conducted at the TADI site, although the organizers claimed that no has been released. Figure 4.17(a) shows a stable background CH_4 mole fraction of about 2030 ppb, with distinct CH_4 peaks between 90 ppb and 950 ppb. These peaks were repeatedly observed to the southwest of the release area, consistent with the north-easterly winds observed, as illustrated in Fig. 4.17(b). Although the car with the mobile measurement setup circled the release area, no methane was detected on the upwind side of the platform, indicating that the source of the detected methane was not located behind the release area. In addition, the CO_2 mole fraction remained stable throughout the test, as shown in Fig. 4.17(a), indicating that no other significant emissions, such as from another point source, were present and supporting the hypothesis that the detected methane was the result of a release at the TADI site. As no other significant sources of methane were identified, it is concluded that the detected methane emissions are due to an unanticipated release from the designated area, although it was stated that no release of CH_4 has occurred. The methane emission rate was estimated assuming a point source at the central position of the release area, as the exact source location remained unknown. The calculated emission rate was 0.53 ± 0.13 kgCH₄ h⁻¹. The finding of this thesis questions the claim of a zero release for RE3_8. Further investigations would be necessary to assess the underlying causes of these discrepancies.

Another unclear case is release RE3_5, where the lowest CH₄ release rate was reported with 0.01 kg h⁻¹. Methane enhancements above background mole fraction up to 290 ppb were measured (Fig. B.9), although the wind was more unstable than during the zero release. However, since both releases took place on the same day, it cannot be ruled out that an unintentional leakage may have influenced the actual release, since a CH₄ emission rate of 0.14 ± 0.03 kg h⁻¹ was determined and the release rate was therefore overestimated by more than 1500 %. Both releases were excluded from the overall analysis.



Figure 4.17: (a) Time series of measured CH_4 (black) and CO_2 (green) mole fractions with CH_4 background fit in blue during zero release (RE3_8). (b) Map with color-coded CH_4 mole fractions along the driving route. The map was created using leaflet for R ($\bigcirc Esri$).

4.3 Summary and recommendations

In this thesis, a method of mobile measurements combined with a GPM was investigated in detail during six controlled CH_4 release experiments and an additional blind-release campaign. The findings of these experiments, where the true release rates were known, helped to improve and standardize the measurement method and emission rate calculation using the GPM.

The influence of various factors, including the measurement setup, driving strategy and adjustments in the evaluation process using the GPM were analyzed in detail with the releases performed between 2018 and 2023 in Mannheim and Heidelberg. The comparison of the results with two different trace gas analyzers and several anemometers showed no significant influence on the results. This means that the time series of mobile measurements and emission rate determination can be harmonized over the entire study period (2016-2024). The driving strategy could also be adjusted to minimize the impact on the result and increase accuracy. In addition, the averaging method was investigated and the influence of meteorological parameters on the quantification of emission rates was examined in more detail.

After a detailed consideration of all these factor, the release tests show that the uncertainty of emission rate determination by the GPM method with our measurement setup is within 30 %. This result can only be achieved by following good measurement practices, including appropriate distance from the emission source, accurate meteorological data and optimized driving strategies. A graphical summary of the results as a percentage deviation from the true release rate is presented in Fig. 4.18. Figure 4.18(a) shows the results as box and whisker plots. In Fig. 4.18(b), the deviation is shown as a histogram, showing the deviation of the calculated rate from the true rate represented as a normal distribution with a maximum close to 0 (with a slight tendency of underestimation). This supports the assumption that if an emitter is measured several times under different conditions, the mean value of the calculated emission will stabilize close to the true emission value.

While the capabilities of our own release set-up were limited to low release rates of less than 1 kg CH₄ h⁻¹, the TADI campaign allowed us to test our method at CH₄ release rates from 0 to 200 kg h⁻¹. Furthermore, it was a blind release experiment, where neither the release rate nor the location of the source was known initially.

Figure 4.19(a) shows a box and whisker plot of the mean deviation of the emission estimate from the actual emission rate for each day of the campaign. Day five stands out as having a particularly large variation, since low wind speeds and changing wind directions caused a larger dispersion. This variation is significantly lower under better measurement conditions with more stable wind conditions, such as those that prevailed on day four. The mean deviation of all releases (excluding 0 and 0.01 releases) is 32 %. The plot of the normal distribution in Fig. 4.19(b) clearly shows that the values deviate to about the same extent both upwards and downwards, and are therefore distributed around 0 %. The independent release campaign at the TADI site reproduced and confirmed the results of our previously discussed controlled release experiments. This demonstrates the successfully application of the GPM method in combination with mobile measurements.

The experiments provided valuable information that contributed to the reliability of mobile sampling as an effective method for emission quantification. It was shown that the mobile sampling method described here, in combination with the GPM, can be used to determine the emission rate with an accuracy of 30 %.

To better limit the uncertainty in Gaussian emission estimates derived from mobile platforms, the following improvements are recommended and have been used in emission rate determinations throughout this thesis wherever possible:

- Wind measurement on-site with a mobile anemometer, ideally supplemented by a stationary anemometer, to enhance the accuracy of wind data.
- Solar radiation measurement helping to determine the atmospheric stability class and improving model predictions.
- Minimum wind speed of 1 m s^{-1} , due to increased plume meandering
- A minimum of 10 transects should be conducted to account for atmospheric variability and ensure robust results.
- Low driving speeds, best below 30 km h⁻¹, and high temporal resolution of instruments.
- Maintain a sufficient distance from the emission source, with a recommended minimum of 20 m, to avoid near-field distortion in emission estimates.
- Background mole fraction and possible co-emitted CO₂ can provide indications of interfering emissions from other sources.

Table 4.2 provides an overview of the parameters analyzed in the controlled release experiments and their influence on the uncertainties of the emission rate determination. It is important to note that this applies to the measurement setup and modeling method used in this thesis and is recommended to be repeated for other equipment and methods. Subsequently, verification of the measurement and modeling setup by controlled release experiments will ensure a reliable and repeatable method for emission rate determination.

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Figure 4.18: (a) Boxplot for comparison of determined methane emission rates during the different release experiments (MA and HD) to the actual release rate for mean values. Boxes represent the first and third quartile of the data, while whiskers extend to the largest value that is within 1.5 times the interquartile range. (b) Histogram illustrating the distribution of mean estimated emission rates relative to the actual release rate across all six controlled release experiments conducted between 2018 and 2023. The black curve represents the normal distribution of the data, calculated using the mean and standard deviation.



Figure 4.19: (a) Boxplot for comparison of determined methane emission rates during the different TADI campaign days to the actual release rate for mean values. Boxes represent the first and third quartile of the data, while whiskers extend to the largest value that is within 1.5 times the interquartile range. (b) Histogram illustrating the distribution of mean estimated emission rates relative to the actual release rate across whole TADI campaign. The black curve represents the normal distribution of the data, calculated using the mean and standard deviation. In these illustrations, the zero and 0.01 release are excluded.

Catagony	Incontainty course	Observed uncertainty level		
Category	Uncertainty source	High	Medium	Low
Sotup	Analyzer			Х
betup	Anemometer			Х
	Number of transects ≥ 10		Х	
	Distance to source < 20 m	Х		
Driving strategy	Distance to source > 20 m			Х
	Driving speed $< 50 \text{ km h}^{-1}$			Х
	Vehicle (bike or car)			Х
	Wind speed $< 1 \text{ m s}^{-1}$	Х		
Meteorological	Wind direction		X	
parameter	TWS/MWS			Х
	Stability class		X	
	Release height		Х	
Analysis	Release location		X	
	Background (small CH_4 signal)		X	
Special eages	2-point source			Х
special cases	Building			Х

Table 4.2: Tested parameters and their associated uncertainty levels based on controlled release experiments. Influence on emission rate estimate: high \geq 40 %, medium 10-40 %, low \leq 10 %.

CHAPTER 4. BEST PRACTICES AND UNCERTAINTIES IN THE QUANTIFICATION OF CH_4 EMISSIONS BY CONTROLLED RELEASE EXPERIMENTS

Chapter 5

Methane emission rates from biogas plants in Germany

5.1 The role of biogas: production, potential, and regulations

Methane emissions account for 12% of the EU's total greenhouse gas emissions (Fernandez [2022]) and need to be urgently reduced in order to meet the targets in the energy sector by 2030. Biogas plants are technical installations designed to collect and use methane produced by anaerobic digestion processes for energy production. This helps to reduce CH₄ emissions by decomposing bio waste, agricultural residues and animal manure into biogas.

In addition to environmental factors, the 2021 energy crisis and energy security concerns have increased political support for biogas in gas import-dependent regions such as Europe, as biogas is a renewable energy source. The EU aims to produce 35 billion cubic meters (bcm) of biomethane per year by 2030, a more than tenfold increase in less than a decade (COM [2022]). Nevertheless, there are debates within European countries about the expansion of biogas production inside the renewable energy sector. On the one hand, there are ongoing concerns regarding the availability of sustainable feedstock and its transport, as well as the methane emissions associated with the production, storage and utilization of biogas. A study by Bakkaloglu et al. [2022a] suggest that methane emissions along the biogas supply chain are underestimated. The Renewable Energy Directive (EU) 2018/2001 (RED II) already considers some specific emission sources as digestate management, engine exhaust and upgrading. But operational and fugitive emissions are not included at this time (Buffi et al. [2024]).

Fugitive methane emissions are particularly challenging as they are largely avoidable and require further mitigation efforts. Several methane mitigation models suggest that biogas production can make a significant contribution to reducing methane emissions from the livestock and waste sectors (e.g. Shindell et al. [2024], EPA [2019], UNEP and CCAC [2021]). However, this is only effective if biogas production helps reduce, rather than increase, methane emissions.

5.1.1 Processes and structure of a biogas production facility

Biogas plants utilize the process of anaerobic digestion (AD) to generate renewable energy from biodegradable materials. The resulting biogas consists of 50-70 % CH₄, 30-50 % CO₂, and trace amounts of H₂O, hydrogen sulfide (H₂S), and ammonia (NH₃) (UN-FCCC/CCNUCC [2012]). Some plants upgrade biogas to biomethane by removing impurities such as CO₂ and H₂S, achieving a purity level greater than 90 % CH₄, which is comparable to the quality of natural gas (Xie et al. [2020]). The biogas can either be used directly on site in a combined heat and power (CHP) unit for electricity and heat generation or, after upgrading to biomethane, be injected into the natural gas grid, enabling its use across the electricity, heat, and transport sectors, regardless of location. Biogas is produced from a wide range of organic materials, including biogenic waste and residual materials from agriculture and forestry (such as animal manure, crop residues, leaves, and grass), municipal solid waste from households and industry, wastewater sludge, and specially cultivated energy crops (e.g., maize, sugar beet, wheat). The composition and yield of the biogas produced varies depending on the choice of feedstock and the design of the plant.

The organic material is decomposed by different bacterial populations under the absence of oxygen and converted into biogas. This long and complex decomposition process can be divided into four phases (Kirchner [2023]):

- 1. Hydrolysis: polymeric macromolecules (carbohydrates, fats, proteins) within the biomass are broken down by enzymes.
- 2. Acidogenesis: organic acids (mainly carboxylic acids) and alcohols are formed by degrading the shorter compounds formed during hydrolysis.
- 3. Acetogenesis: Microorganisms convert previously formed substances into acetic acid and its dissolved salt (acetate).
- 4. Methanogenesis: (5.1a) acetic acid is decomposed by methanogens (methane-producing bacteria) to methane and (5.1b) methane and water are formed from elemental hydrogen and CO₂.

$$CH_3COOH \rightarrow CO_2 + CH_4$$
 (5.1a)

$$\mathrm{CO}_2 + 4\mathrm{H}_2 \to \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O} \tag{5.1b}$$

The amount and composition of biogas produced is influenced not only by feedstock, but also by the time given to the bacteria and the temperature in the digester. The more time bacteria have and the higher the temperature, the more complete the digestion and the more biogas is produced. Mesophilic biogas production takes place at 30-40 °C and thermophilic biogas production at 50-60 °C (Jain [2019]).

Figure 5.1 illustrates a schematic representation of the structure of a biogas plant. The incoming organic material is first pre-treated, where larger particles are shredded into smaller pieces. The various components are then mixed to create a homogeneous substrate. In some plants, particularly when processing food waste, the substrate is heated to eliminate potential pathogens. Once prepared, the material is fed into the digesters (num-
ber depending on the size of the plant), initiating the anaerobic methane formation process as described previously. This process is facilitated by continuously stirring the material and maintaining a stable temperature to ensure homogeneity and efficiency throughout the entire volume. The biogas produced is collected above the digestate.



Figure 5.1: Schematic layout of a biogas plant with different process stages and use for the gas produced under anaerobic conditions.

Certain systems divide the process into two stages, with a primary heated digester followed by a non-heated post-digester. Depending on the specific technology, the digestate remains in these stages for a period of 30 to 90 days before being transferred to a separate storage tank, where it is stored until it can be used as a natural fertilizer on fields. The collected biogas leaves the digester and passes through a dehumidification and scrubbing system, typically employing activated carbon, to remove harmful gases such as H_2S .

Along with renewable electricity generation, the combustion of biogas in a CHP unit also produces heat. This heat not only helps sustain the optimal conditions for bacterial activity within the plant but is also often utilized in a range of alternative applications. For example, it is frequently used in agricultural processes such as cheese production and drying, or it is integrated into small-scale district heating systems to supply heat to public buildings or homes. Some plants are equipped with an extra gas storage tank, allowing additional storage of biogas. In the absence of such storage or a second CHP, the biogas has to be flared during engine maintenance, resulting in a loss of energy. As an alternative to on-site energy production, biogas can be upgraded to biomethane and injected into the natural gas grid, providing a sustainable energy solution (Jain [2019], Envitech (a)).

5.1.2 Biogas and its potential as renewable energy source

According to the Federal Environment Agency (Umweltbundesamt, UBA), renewable energies accounted for 22.4 % (514 TWh) of Germany's total energy demand in 2024, with 47 % (240 TWh) of renewable energy generated from biomass (UBA - AGEE-Stat [a]). Europe is the largest producer of biogas, with Germany being the dominant market, holding two-thirds of Europe's total biogas plant capacity, which amounted to 33.56 TWh electricity and 18.4 TWh heat generation in 2022 (Reinholz and Schmidt [2023]). Currently, more than 9,600 biogas production facilities in the agricultural and waste sector (excluding sewage gas) are operated in Germany (dena [2023]). The electricity production of a biogas plant depends on the volume of gas produced and its methane content. While the number of biogas plants only increased by a 15 % between 2012 (8,300) and 2022 (9,600), the average plant capacity almost doubled from 400 to 760 kWel (DBFZ-Report Nr. 50 [2023], dena [2023], IAEA-Country Report [2024]). New biogas plants are becoming larger and existing plants are expanded, while smaller plants from the pioneering days of biogas production are decommissioned.

As shown in Fig. 5.2(a), the majority of German biogas plants are operated in Baden-Württemberg and Bavaria (with less than 370 kWel per plant), accounting for 10 % and nearly 30 %, respectively. An additional 20 % of plants are located in Lower Saxony. At the same time, however, the majority of installed capacity is located in northern and eastern Germany (> 500 kWel per plant), where biogas plants have become part of new, large renewable energy parks (DBFZ-Report Nr. 50 [2023]).

The digestion of manure and organic waste used as input in biogas plants produces CH_4 and CO_2 , which would otherwise be emitted freely into the atmosphere. While CO_2 is also released into the environment when the biogas is combusted in power plants, it has previously been captured by the plants used as feedstock. In this view, the conversion of biogas into electricity appears to be carbon-neutral. However, greenhouse gases are still emitted from the fields, the operation of the machinery and possible gas leaks. Therefore, the actual GHG footprint of a biogas plant depends largely on its operational management and especially the leakage.

Subsidies under the Renewable Energy Act (Erneuerbare-Energien-Gesetz, EEG) led to strong growth in biogas production in the early 2000s, with maize being cultivated on a large scale as the main substrate. To counteract this, a limit of 60 % was introduced in 2012 on the amount of maize and cereal grain that could be used as feedstock, which largely slowed the expansion of biogas plants. As part of the EEG 2023, this limit was raised to 30-40 % and is to be increased further (UBA-EEG). Contrary to its often negative image, however, biogas can play a crucial role in the energy transition. It can be stored and is available even when solar or wind energy cannot be produced, and it is also able to replace fossil natural gas. While meeting ecological criteria, it therefore can be a promising alternative to fossil fuels and a supplement to other renewable energies. Biogas is also produced at waste water treatment plants and landfills, where it can be used to generate energy. However, energy crops still provide half of the feedstock for biogas plants and are responsible for more than two-thirds of the energy produced (Rensberg et al. [2023]).

For larger plants, it can be profitable to upgrade the biogas to biomethane. This is chemically identical to natural gas and can be injected into the existing gas grid. There are currently around 250 such plants in Germany, covering 1 % of German gas consumption (Nelles et al. [2023]). The CO₂ removed during processing can be captured (bioenergy with carbon capture) and thus removed from the CO₂ cycle. Such negative emissions are necessary to achieve climate neutrality.



Figure 5.2: (a) Locations of biogas and upgrading plants in operation in Germany, excluding biogas upgrading plants; (Rensberg et al. [2023]); (b) Development of biogas production sites differentiated by size classes, gross electricity generation and total installed plant output; output class 70/75 kW: up to 2012, plants \leq 70 kW, from 2012 onwards, expansion of small slurry plants \leq 75 kW included.(Rensberg et al. [2023])

5.1.3 Possible methane emissions and the RED II directive

Even though renewable energy sources, such as biogas, are increasingly promoted as a sustainable alternative, biogas plants also carry considerable risks and under incorrect operation their impact may be counterproductive for the environment. In addition to avoid ing global warming impacts, there is also an economic motivation to avoid emissions, as the release of methane results in a loss in energy production and lower profits for operators. The Renewable Energy Directive 2018/2001 (RED II) (Parliament and the Council of the European Union [2018]) described sustainability criteria along its full supply chain. Therefore, all emission sources should be monitored and mitigated to reduce methane losses. In order to do this, however, it is first necessary to know where and how much methane is emitted. Buffi et al. [2024] lists the most important sources of methane emissions from biogas plants as following:

- 1. feedstock storage (direct emissions through decomposition on air)
- 2. digestate storage (continuing digestion process outside digesters)
- 3. exhaust of CHP engine (due to incomplete combustion)
- 4. methane slip during upgrading process
- 5. leakages (piping, valves, tanks, digesters)
- 6. unintentional releases (safety, incorrect operation, maintenance)

While RED II considers specific continuous sources such as 1 to 4, it does not include unintentional, fugitive emissions such as 5 and 6. Further, it also does not explicitly include a specific calculation for CH₄ losses from biogas and biomethane production (European Parliament [2018], p. 100). The data on methane losses, which serve as emission factor values for biogas and biomethane, have been reviewed and updated by Buffi et al. [2024], and are presented in Table D.8. Based on these updated factors, the average methane loss in a biogas production facility ranges from 2% to 20%, depending on variables such as feedstock type, biogas utilization, and operational management. The UBA - AGEE-Stat [b] reports an average methane loss of 5 % of the methane produced in these plants, which escapes uncontrolled into the atmosphere. Recent studies have identified even higher methane loss rates, ranging from 0.02 % to 40.6 %, during both the biogas production and energy generation processes (Hrad et al. [2015], Holmgren et al. [2015], Baldé et al. [2016], Maldaner et al. [2018], Fredenslund et al. [2018], Scheutz and Fredenslund [2019], Kvist and Arval [2019], Bakkaloglu et al. [2021], Hrad et al. [2022], Reinelt et al. [2022], Fredenslund et al. [2023] and Wechselberger et al. [2025]). This underlines the ongoing debate about the use of biomass digestion for energy production, despite the general consensus that it is a step towards replacing fossil fuels.

5.2 Measurement site description

Mobile atmospheric measurements were carried out between May 2022 and August 2024 to quantify the methane emission rates of 63 biogas and upgrading plants in Germany. Additionally, mobile measurements by Seyfarth [2021] and Korbeń [2021] at two other sites were re-assessed. A map of all 65 sites, where measurements were performed, is presented in Fig. 5.3. Biogas plants were mainly surveyed in the Rhine-Neckar region up to Frank-furt (23 plants), with one-day campaigns always starting from Heidelberg (indicated in red). In addition, 21 biogas plants in the Ehingen-Donau region (zoom-in) were surveyed on a total of four multi-day measurement campaigns, with 14 plants being visited several times. Measurement campaigns were also conducted in south-west Baden-Württemberg and northern Germany.

The plants investigated were selected on the basis of criteria such as road accessibility, geographical location and prevailing wind direction. They represent a broad spectrum of German biogas plants in terms of age, type (agricultural or waste), production capacity, as well as in feedstock, site layout and prevailing biogas utilization technologies. Given that there are around 9,600 biogas plants in Germany (Reinholz and Schmidt [2023]), the 65 plants included in the study represent less than 1% (0.07 %) of the total. But they represent a spectrum, with 59 agricultural biogas plants and 5 plants using food waste. Twelve of the plants upgrade the biogas to biomethane and inject it into the natural gas grid or utilize it in other forms. The installed electrical capacity ranges from 75 kW to 8,500 kW. Biogas plants that are operated continuously at full power are the exception today (FNR (b)). In general, the engines are flexibilised (operated according to a schedule), e.g. the CHP units run in particular at times when it's economically profitable. This flexibility means that the engine can be started even during periods of unfavorable electricity prices, or an additional engine, typically available for times of higher energy demand, can be switched on when the biogas storage tank reaches a critical filling level. This avoids the otherwise necessary flaring of the gas.

Tables are included in appendix D.3, outlining all plants analyzed in this thesis, along with technical details. Data for biomethane producing plants are based on the German Energy Agency (dena) biomethane feed-in atlas, which shows the year of commissioning, plant capacity and amount of biomethane fed into the natural gas grid (dena, Einspeiseatlas). Corresponding biogas plant data were collected from the Core Energy Market Data Register, which shows year of commissioning, production capacity and electricity production (MaStR). Additional information was obtained through operator interviews and supplementary online research.



Figure 5.3: Locations of the biogas plants investigated in Germany. Blue dots represent agricultural biogas plants, while green dots indicate agricultural biomethane plants. Red dots mark waste-based biogas production facilities. Heidelberg, the starting point of all measurement campaigns and the site of the biogas plant where a long-term measurement time series was recorded, is highlighted in yellow. A zoom-in on the Ehingen-Donau region provides a more detailed view of the investigated biogas plants in that area.

The primary input materials are categorized into energy crops, manure, and organic waste. Energy crops are mainly composed of maize silage, with other key inputs including whole crop silage from grass, grain, or sugar beet. The term 'manure' covers solid manure, cattle and chicken slurry, as well as other solid and liquid residues from animal farming. Biogenic waste includes mainly food leftovers and bio waste from industry and households but also agricultural residuals. Methane content and biogas volume depend on the feedstock (LfL, FNR - Fachagentur Nachwachsende Rohstoffe e.V. [c], FNR (a)). Maize silage and other energy crops provide relatively little methane with a volume fraction of about 52 % of the biogas, but a high biogas amount of about 200 m³ per tonne. Bio waste and food waste provide between 100 and 160 m³ of biogas per tonne with an average methane content of 60 %. Depending on the type of manure, the biogas volume can contain more than

60 % methane. But due to the relatively low biogas output of 20 to 100 m³ per tonne of manure, energy crops are often used as co-substrate to increase the amount of biogas produced. This results in an average CH_4 volume fraction of about 55 %.

From the knowledge of the amount of electricity generated in the CHP units, it is possible to deduce the volume of methane and biogas required for corresponding electricity production on the basis of certain assumptions. The calculation in Eq. D.1 assumes a methane content in the biogas of 52 % (for energy crops), 55 % (for manure), and 60 % (for organic waste), and an electric efficiency of 38 % for the combustion engines (Gustafsson et al. [2024]). In addition, a methane density of 0.67 kg m⁻³ and the lower CH₄ heating value of 50 MJ kg⁻¹ are used.

Based on this calculation, the biogas production rates range between 40 and 3,600 m³ h⁻¹, with the largest plant located in Güstrow (northern Germany), converting biomethane into around 9,000 tonnes of bioLNG per year. To provide a clear overview, the biogas plants are categorized by size ('small', 'medium' and 'large'). The 'small' category includes 14 plants with electricity production of up to 250 kW, which corresponds to a biogas production rate of about 150 m³ h⁻¹. The 'medium' category contains 22 plants with an electricity production ranging from 250 to 520 kW, or roughly 150 to 300 m³ h⁻¹ of biogas. Further 17 biogas plants are classified as 'large' with over 520 kW and 300 m³ biogas per hour, whereby upgrading plants are considered separately.

5.2.1 Consideration of individual local conditions

The solar radiation used to determine the stability class, as proposed in section 4.3, is derived from data from the Institute for Environmental Physics in Heidelberg for measurements in the vicinity of Heidelberg or the nearest measuring station of Germany's National Meteorological Service (Deutscher Wetterdienst, DWD). The measurements on the roof of the institute are recorded with a resolution of 10 min and indicate solar radiation in $[W m^{-2}]$. The data for the measured global radiation from stations of the National Meteorological Service are given in $[J cm^{-2}]$ as a 10-minute sum. The data set used is averaged over the respective measurement period in order to apply the stability parametrization.

It is important to acknowledge the challenges encountered during the measurement process. The best practice outlined in section 4.3 provide a valuable guideline to ensure consistency and comparability of measurements. Nevertheless, several complications occurred during the measurements, including geographic conditions (e.g., hilly terrain), traffic conditions that required adjustments in driving speed for safety reasons, changing weather conditions (e.g., rain) that reduced the number of transects conducted, and changing wind patterns that sometimes interrupted the measurements. In addition, the presence of short-term emission sources (e.g. field fertilization) occasionally interfered with the measurement process and led to interruptions. To be able to identify measurements where the best practice was not applicable, they are indicated in gray in the Tables in Appendix D.4. Some of the investigated biogas plants are located in close vicinity to cowsheds. If it is not possible to separate the peaks because of overlapping plumes of cowshed and biogas plant, the CH₄ emission rate of the cows in the immediate vicinity is subtracted from the determined total emission (see sect. 4.1.3). This is done by multiplying the number of cows by the emission factor from enteric fermentation for dairy cows of 0.016 kgCH₄ per cow per hour. This emission factor is based on UBA reporting (UBA [2023], p.479, Table 256 [140.8 kgCH₄ animal place⁻¹ yr⁻¹]).

5.3 Investigation of CH₄ source locations on site

Individual on-site leak detection walking surveys were conducted at seven biogas plants. With the consent of the plant operators, these facilities were systematically investigated using the OF-CEAS trace gas analyzer, functioning as a 'sniffer', to examine the technology and units at various stages of the production process. (see Fig. D.2). Unintentional methane emissions, such as those resulting from technical or human failure, were identified as leaks. These leaks typically occur in gas-carrying pipelines, gas-tight containment units (e.g., substrate and digestate storage tanks), digesters, valves, and gas storage tanks. Additionally, non-defective methane emission sources were identified, including methane produced in non-gas-tight substrate or digestate storage tanks before entering or after leaving the digester, process ventilation, and methane slip from CHP units. While emission rates for these sources were not quantified during the surveys, the primary objective was to identify typical source locations within this type of technical installation. After completing the surveys, the biogas operators were informed of the detected CH₄ leakages and point sources, enabling them to address and mitigate these emissions.

In three additional biogas plants, emission sources were identified either through prior reports from the plant operators or through supplementary measurements conducted by a team from Queen Mary University of London (UK team). This team used an optical gas imaging camera (Opgal, EyeCGas 2.0) and a handheld remote methane laser detector (RMLD-IS) to detect leaks at the respective sites as described in more detail in the study by Olczak et al. [2025]. At four sites, walking surveys were performed simultaneously using both the OF-CEAS and the instruments of the UK team (Olczak et al. [2025]). All sites with respective identified emission sources are summarized in Table 5.1, which provides the locations and categories of the sources (small, medium, major). Additionally, Fig. D.3 in the Appendix shows the locations of the emission sources across all of the surveyed plants. Major emission sources were classified based on CH_4 mole fractions exceeding 200 ppm, recorded while the air inlet was positioned at the corresponding location for a minimum of 2 minutes. The medium category includes methane sources where the recorded methane values did not increase over 200 ppm during the measurement period but reached at least 50 ppm. Small emission sources are those with measured CH_4 mole fractions below 50 ppm.

Since no emission rate quantification was performed and the measurements were influenced by factors such as wind and the unknown exact source location, this part of the study should be considered only as a qualitative overview. Its primary aim was to identify the typical locations of major emission sources and categorize them accordingly. It is important to note that some leakages may have been overlooked or were inaccessible during the survey.

At the seven biogas plants, where walking measurements were carried out with the OF-CEAS analyzer, 16 individual leaks and emission sources were identified. The two sites, where leak detection is based only on the detection equipment of the UK team, have a greater number of sources (5 and 7 identified emission points respectively). This may indicate that these detection methods are more effective at identifying a wider range of sources, as the OF-CEAS is limited to short distances. In contrast, the methane camera and handheld detector can detect more distant sources beyond the range of the OF-CEAS. However, the high number of identified emission sources of BM-11 and BG-31 appear to be exceptions, as no additional sources were detected with the gas camera at the other facilities, where simultaneous surveys were conducted with the UK team. Furthermore, the OF-CEAS method was able to detect smaller sources that fell below the detection limit of the camera and laser detector. Therefore, the number of sources is not due to the detection method, but to the individual condition of the investigated plants.

In total, 29 point sources were identified, with 10 (35%) classified as 'major', 8 (28%) as 'medium', and 11 (38%) as 'small'. In addition to leaks at the CHP engine, vents were the main sources of major emissions (feeder, pressure relief valve (PRV)). Leaks in the membrane roof or pipe connections were also identified as major emission sources. However, the causes of leakages were diverse and could only be pinpointed to a limited extent.

In published studies on the investigation of biogas production facilities in Germany, Austria, Switzerland, Sweden, Denmark and Australia with regard to emission sources, PRVs and non-gastight digestate storage tanks were named as particularly frequent causes (Liebetrau et al. [2013], Fredenslund et al. [2018], Hrad et al. [2022], Reinelt et al. [2022], Wechselberger et al. [2023]). These were also identified in individual cases during our surveys. In addition to temporary leaks, there are also continuous emissions. A study by Wechselberger et al. [2023] has shown that approximately 1.6 % of the produced methane is released from the CHP exhaust through incomplete combustion and can therefore assumed as a significant emission source. Kvist and Aryal [2019] are describing in their study a methane slip between 0.04 and 1.97 % for upgrading units, depending on the upgrading technology. However, Olczak et al. [2025] estimated that 76 % of CH₄ emissions are avoidable.

Walking surveys have revealed a variety of causes for methane leaks in biogas plants, making the precise positioning of the emission source for inverse modeling a challenge. However, CH_4 emissions from the CHP exhaust often serve as a significant source and thus provide a solid starting point for an evaluation strategy when specific emission sources are unknown. For further analysis to quantify CH_4 emission rates at different biogas plants, leakage information was used for source placement where possible. However, in the case of plants without a detailed on-site investigation, the point source was located close to the CHP unit and/or other critical process locations derived mainly from the main wind direction and the findings of this section.

Biogas	Source of	# Detected	Emission source location		
ID	detection	sources	small	medium	major
BG-03	OF-CEAS, UK team	3	ventilation (post- digester)	digestate storage	leak at pressure gauge (CHP)
BG-09	OF-CEAS, UK team	3	slurry tank	membrane (post- digester)	leak (CHP)
BG-20	OF-CEAS	1	substrate mixing	/	/
BG-27	OF-CEAS, UK team	3	sewage drain	/	membrane (post- digester), shut flup (digester)
BG-29	OF-CEAS, UK team	2	venting (post- digester)	/	leak (CHP)
BG-30	OF-CEAS	3	substrate mixing	valve/pipe (digester to post digester)	valve/pipe (AC)
BG-38	OF-CEAS, UK team	1	pipe (digestate storage)	/	/
BM-11*	UK team	5	digester pump room (2x)	membrane (post- digester), biogas upgrader	ventilation (feeder)
BG-31*	UK team	7	slurry tank, PRV (post- digester)	Sewage drain, membrane (post- digester), stirrer (post- digester)	PRV (gas storage), digester roof
BG-04*	operator	1	/	/	pipe (feeder to digester)

Table 5.1: Emission source locations detected at ten biogas plants. The emission strength classification of the sources is based on measured CH_4 mole fractions. Measurements conducted by the UK team are referenced to Olczak et al. [2025]. For those marked with an asterisk (*), CH_4 mole fractions have not been measured with the OF-CEAS analyzer and the classification is based on information reported by UK team or plant operator.

5.4 Whole-site CH_4 emission quantification of 65 biogas plants in Germany

The quantitative analysis of methane emissions from biogas plants is necessary for evaluating the environmental impact of biogas plants. The CH_4 emission rates of a total of 65 biogas plants in Germany are estimated and their losses are systematically quantified. In addition, the long-term variation of emission rates at a local biogas plant is investigated and the influence of the number of measurement campaigns on the accuracy of emission quantification is examined.

5.4.1 Long-term CH_4 emission rate variation at a local biogas plant

At a local biogas plant (BG-20) the total CH_4 emissions were repeatedly measured twelve times in two years as part of this thesis. However, since 2016, atmospheric measurements have also been carried out regularly at the plant. By re-evaluating this measurements from Hoheisel et al. [2019] and Korbeń [2021] and extending the measurements, a longterm series over an eight-year period of emission monitoring could be analyzed, including in total 31 measurement campaigns.

The biogas plant investigated in long-term measurements is located in Heidelberg, in the south-west of Germany (longitude: 49.39849°, latitude: 8.662816°, altitude a.s.l.: 110 m). Figure 5.4 shows the location of the plant, with position of the emission source indicated as a blue dot based on walking surveys (section 5.3). A detailed schematic of the site highlights the locations of the anaerobic digesters, biogas storage, and the CHP unit, while vehicle-accessible roads are marked in vellow. The biogas plant is specialized in the disposal of organic waste, particularly from the food industry and households. Constructed in 2001, the plant consists of two 500 m^3 digesters, where organic waste and energy crop silage are processed into biogas under anaerobic conditions. The biogas production is 240 $m^3 h^{-1}$ (97 kgCH₄ h⁻¹), which is subsequently converted into electricity and heat by a 500 kW CHP unit. The electricity is supplied to the local grid, while the generated heat is used on-site and in the surrounding buildings connected to the plant. The digestate is spread as organic fertilizer to agricultural fields. The operating temperature within the digesters is maintained around 38 °C (mesophile), with an average digestion cycle duration of 90 days. A biogas storage, with a capacity of approximately $1,500 \text{ m}^3$, ensures continuous operation of the CHP unit and prevents significant fluctuations in electricity production. A special characteristic of the plant is that the two anaerobic digesters are located underground, with continuous ventilation provided to the accessible maintenance room to ensure air quality.

The data recorded during a total of 31 measurement campaigns at this site, between August 2016 and August 2024, were initially evaluated with different focuses and methods: 2016-2018 (isotopic source signature only, Hoheisel et al. [2019]), 2019-2021 (emission rates with different model configurations, Korbeń [2021]), and recent measurements conducted as part of this work between 2022 and 2024. As part of this thesis, all measured data were evaluated using the standardized approach with the GPM.



Figure 5.4: Map of the biogas plant site near Heidelberg, with the emission source location used for running the GPM marked in blue. A zoomed-in schematic view of the plant highlights the locations of the digesters, biogas storage, and CHP unit. Roads accessible for driving are marked in yellow. The map was created using leaflet for R (©Esri).

Results and discussion

In total, the methane plume was crossed 372 times on 31 separate days, with 239 (64 %) of these transects on 26 measurement days accepted in the final analysis. On average 12 plume crossings were performed per site visit, though the number varied from 3 to 36. The reasons why measured transects were not included in the final evaluation, were not completed transects (turning inside the plume), or an insufficient correlation between the model output and the measurement. During these plume crossings, maximum CH₄ mole fractions varied between 2.3 and 51.9 ppm. The GPM, together with the defined evaluation criteria, was used to estimate the CH₄ emission rates from the recorded CH₄ mole fractions. The daily mean CH₄ emission rates, with standard errors of the mean, were calculated from the individual transect emission estimates. These values, shown in Fig. 5.5, ranged from 0.6 to 13.6 kgCH₄ h⁻¹ and are documented more detailed in Table D.4.

At the same time as the change in the trace gas analyzers used throughout the measurement process indicated by a red dashed line in Fig. 5.5, the driving strategy was adjusted, to ensure that at least 10 transects were completed per measurement. The results from the release experiments show a significant reduction in standard deviation of the emission rate when driving 10 or more transects. In the years 2016 to 2019, only 8 transects were driven on average (5 accepted), whereas from 2020 onward an average of 19 transects were driven (12 accepted), some of them at two distances. In addition, from 2024 onward, the more accurate stationary wind measurement station was set up during plume crossings. This trend is particularly noticeable in the error bars of the biogas plant emission rates, where the uncertainty decreased from an average 40 % to 12 % after the changes were implemented. This finding is consistent with results from our release experiments (chapter 4) and the work of Caulton et al. [2018], summarizing that 10 transects reliably constrain the influence of atmospheric variability on emission estimates.

The average CH₄ emission rate for the biogas plant was estimated to be 5.9 ± 0.5 kg h⁻¹ ($52 \pm 4 \text{ t yr}^{-1}$). Overall, the calculated emission rates showed greater variability until the end of 2021, with measurements exceeding 10 kgCH₄ h⁻¹. Starting in 2022, a more consistent mean value emerged (5.0 ± 0.5 kgCH₄ h⁻¹), with the rates fluctuating only slightly. In 2022, the gas storage tank cover was renewed (operator interview), which could have contributed to the lower and less variable emissions observed thereafter, through the use of new low-emission technologies. In the further course of this work, the emission rate of this biogas plant only refers to the 12 measurements carried out between 2022 and 2014. This is to allow comparability with the other biogas plants analyzed during the same period.



Figure 5.5: Estimated mean CH_4 emission rate values from a biogas plant for each measurement day between the years 2016 to 2024, calculated using a GPM. The dashed red line indicates a change in the trace gas analyzer used for ambient air measurements (from CRDS to OF-CEAS analyzer). Hoheisel [2017] carried out measurements between 2016 and 2018 (light blue), followed by Korbeń [2021] (blue), who carried out measurements between 2018 and 2021. These measurements have been re-evaluated and supplemented with new measurements (green) as part of this thesis.

5.4.2 Influence of campaign frequency on emission rate quantification

Among the 65 biogas production sites analyzed, the emission rate calculations for 65 % (n = 42) of the plants were based on a single measurement campaign. For 15 % (n = 10) of the sites, two separate campaigns were conducted, while for 20 % (n = 13) of the plants more than two campaigns were conducted to determine the CH₄ emission rates. When multiple campaigns were carried out, the emission rates were averaged, and the associated error was quantified through error propagation. It is important to note that the errors discussed in this chapter refer only to the statistical uncertainty, which is derived from the number of plume transects conducted during the measurement campaigns. These errors reflect the variability in the data arising from the sampling process, rather than from any systematic factors, which are discussed in detail in chapter 4.

Long-term measurements at BG-20 showed that CH_4 emission rates typically remain stable over time under normal operational conditions, with no major fluctuations. This consistency in emission behavior is a critical finding, suggesting that a single measurement campaign can generally provide an accurate representation of emission rates. To further investigate the impact of the number of measurement campaigns on the emission rate calculation, the percentage standard deviation of the averaged emission rates for different numbers of campaigns conducted at one site is presented in Fig. 5.6. Despite some observed variation between campaigns, the data does not indicate a clear trend in improved accuracy with an increasing number of measurements. This observation implies that additional campaigns beyond a single measurement do not substantially enhance the precision of the emission rate estimation.

Therefore, we conclude that the emission rates derived from a single measurement campaign at biogas plants are both valid and representative. This conclusion is supported by the observed stability of methane emission rates over time during typical plant operations, indicating that a single, well-executed measurement can reliably reflect the plant's CH_4 emissions. Additionally, this method does not require direct access to the site, making it even more practical and effective for emission monitoring. As a result, to the best of my knowledge, this study represents the largest analysis of CH_4 emission rates from biogas plants in Germany to date, conducted in a single study.



Figure 5.6: Boxplot for comparison of standard deviation in percentage of mean CH_4 emission rate during different numbers of campaigns. Boxes represent the first and third quartile of the data, while whiskers extend to the largest value that is within 1.5 times the interquartile range.

5.4.3 Estimated CH_4 emission rates

The total CH₄ emission rates for all the biogas plants studied are presented in Appendix D.4 and range from 0.28 to 255 kgCH₄ h⁻¹. These rates are visualized in Fig. 5.7 and D.4, colored by plant size. For small plants the CH₄ emission rates range from 0.98 to 7.0 kg h⁻¹, with a mean of 3.5 ± 0.7 kgCH₄ h⁻¹. Medium-sized plants show emission rates between 0.28 and 9.7 kg h⁻¹, with a mean of 3.5 ± 0.6 kgCH₄ h⁻¹. Large plants show emission rates between 0.45 and 99.1 kg CH₄ h⁻¹, with a mean of 14.6 ± 6.0 kgCH₄ h⁻¹. The largest variation is observed for biomethane plants, where emission rates range from 1.66 to 255 kg CH₄ h⁻¹, with a mean of 38.9 ± 20.2 kg CH₄ h⁻¹. As illustrated in Fig. 5.7, four plants reported total CH₄ emissions exceeding 50 kg h⁻¹, while all other plants emitted below 30 kg h⁻¹.

The highest emission rate $(255 \pm 47 \text{ kgCH}_4 \text{ h}^{-1})$ was recorded at the biomethane plant BM-01, which also has the highest gas production rate $(1,206 \text{ kgCH}_4 \text{ h}^{-1})$, nearly seven times the average production $(178 \text{ kgCH}_4 \text{ h}^{-1})$ of all plants. However, locating the exact emission source at BM-01 is challenging due to the plant's large area of 320,000 m², with various processing steps occurring across multiple locations. In addition, BM-01 is unique in this study. Since 2023 it converts its biomethane into bioLNG, which is used as fuel for the transport of heavy goods (Envitech (b)). The second-highest emission rate (99 \pm 10 kgCH₄ h⁻¹) was measured at biogas plant BG-02, which began operation in 2008 with two CHP units, and later added a third unit in 2011. The plant is located near a cowshed housing approximately 450 cows. However, emissions from the cows, which constitute only

a small portion of the total, were accounted for and subtracted using an emission factor to ensure that the reported CH₄ emission rate is entirely attributable to the plant itself. BM-03, with the third-highest emissions $(64 \pm 5 \text{ kgCH}_4 \text{ h}^{-1})$, also holds the third-highest gas production rate at 700 kgCH₄ h⁻¹. No other methane sources were identified that could have influenced the emission measurements at this site. The fourth-highest emission rate $(53 \pm 9 \text{ kgCH}_4 \text{ h}^{-1})$ was measured at BG-04, where a known major leak had been present at the time of the measurements (as detailed in Table 5.1).

On average, the total CH_4 emission rate across all 65 biogas plants is 12.9 ± 0.5 kg h⁻¹ (mean) and 4.9 ± 0.8 kg h⁻¹ (median). The analysis of CH_4 emission rates across different biogas plant sizes reveals a wide range of emission values, with the highest emissions observed at plants with a high CH_4 production rate, indicating that CH_4 emission rates vary significantly based on plant size and production capacity. Additionally, we found that the four largest emitters contribute to more than half of the total emissions from all the facilities analyzed.



Figure 5.7: Barplot showing determined CH_4 emission rates in kg CH_4 h⁻¹ according to the four biogas facility categorizations. The 'small' category includes 14 plants with electricity production ≤ 250 kW (biogas rate ≤ 150 m³ h⁻¹). The 'medium' category has 22 plants producing between 250 and 520 kW (biogas rate from 150 to 300 m³ h⁻¹). 'Large' includes 17 plants with electricity > 520 kW and biogas > 300 m³ h⁻¹, with upgrading plants classified separately.

5.4.4 Determined CH₄ loss rates

For each of the surveyed plants a CH_4 loss rate in [%] was calculated from the determined emission and production rates according to the equation of Fredenslund et al. [2023]:

$$CH_4 loss = \frac{Q_{est}}{Q_{prod} + Q_{est}}$$
(5.2)

with the estimated total CH_4 emission rate Q_{est} of each facility divided by the sum of the emission rate and the CH_4 production rate Q_{prod} . The measured total CH_4 emission was added to the calculated production (Eq. 5.2), as most emissions are usually not included in the measured gas production of the plants, which is typically determined as CH_4 to grid or gas flow to CHP (Grebe et al. [2024]).

The calculated CH₄ loss rates range between 0.8 % and 38.4 %. Small biogas plants with an average of 11.9 \pm 2.7 % (median: 8.8 \pm 1.9 %) tend to have higher loss rates compared to larger production facilities as shown in Fig. 5.8 and Fig. D.5. Medium-sized plants have an average loss rate of 4.0 \pm 0.7 % (median: 2.9 \pm 0.6 %), while large plants emit on average 7.0 \pm 1.7 % (median: 5.1 \pm 1.0 %) of their produced methane into the atmosphere. The 12 upgrading sites in this study have an average CH₄ loss of 5.8 \pm 1.6 % (median: 4.2 \pm 0.8 %). This means that biogas plants in the medium category show the lowest loss rates.

Several factors contribute to these observed differences. A significant proportion of the smaller agricultural biogas plants (9 out of 14) predominantly utilize manure as feedstock. Manure produces higher methane emissions compared to energy crops, particularly during storage prior and after digestion (Wechselberger et al. [2025]). However, this would also be the case if the manure was stored on the farm until it was spread on the fields. Smaller plants also showed higher CH_4 loss rates in the study by Fredenslund et al. [2023]. These increased losses were mainly attributed to open digestate storage tanks lacking gas collection systems. In Germany, regulations demand that digestate must be stored in gastight systems for at least 150 days (combined time in the digester and gastight storage), which generally mandates closed digestate storage (Buffi et al. [2024]). However, an exception exists for small manure-based plants, which, according to the EEG 2012, are not required to store their digestate in a gastight manner (Grebe et al. [2024]). This regulatory exception could contribute to higher methane emissions, as the lack of a gastight storage requirement and the high proportion of manure-based feedstock, may result in the elevated emissions observed in these plants (Wechselberger et al. [2025], Buffi et al. [2024], Vechi et al. [2023]).

Further, with the exception of one, all smaller biogas plants operate at full capacity, without operational flexibility. As a result, these plants consistently run their CHP units at full load. Non-flexible plants, operating at full capacity, are more likely to flare gas. This is because they generally do not have large gas storage tanks or additional engines to capture excess gas during emergencies or CHP maintenance. Additionally, many small plants are integrated into farms and are often used for self-supply purposes. Consequently, the level of expertise and economic efficiency may not be as high as in larger facilities. Also financial constraints associated with replacing equipment and implementing low-emission technologies can have a significant impact on emission levels.

Medium-sized plants often have these flexible operating characteristics. Most of the interviews were conducted with operators of medium-sized biogas plants. They confirmed that in many cases their plants are subject to voluntary annual leakage inspections by third parties. Additionally, some operators perform routine self-inspections, which significantly reduces the likelihood of undetected leaks.

Biogas plants categorized as 'large' or 'upgrading' are generally subject to more stringent regulations due to their larger biogas production volumes. These facilities are typically operated by energy companies or their subsidiaries, with dedicated staff, comprehensive statistical tracking, and optimization for maximum economic efficiency. Furthermore, energy crops remain the dominant feedstock in these plants, which tends to result in lower emissions during storage in clamp silos, in contrast to the higher emissions associated with manure storage in smaller plants.



Figure 5.8: Boxplot showing determined methane loss rates according to the four biogas facility categorizations. The 'small' category includes 14 plants with electricity production $\leq 250 \text{ kW}$ (biogas rate $\leq 150 \text{ m}^3 \text{ h}^{-1}$). The 'medium' category has 22 plants producing between 250 and 520 kW (biogas rate from 150 to 300 m³ h⁻¹). 'Large' includes 17 plants with electricity > 520 kW and biogas > 300 m³ h⁻¹, with upgrading plants classified separately. Boxes represent the first and third quartile of the data, while whiskers extend to the largest value that is within 1.5 times the interquartile range.

Exceptions to these trends are found in BM-01 and BM-12, particularly within the 'upgrading' category, as indicated by the outliers shown in Fig. 5.8. BM-01, previously identified in the preceding section as having the highest measured emission rate, is a large, complex plant where bioLNG is produced from processed biomethane. This extended stages of processes increases the potential for emissions, particularly during the manual filling of trucks with the bioLNG, which can cause additional methane emission.

BM-12, which was surveyed on four separate campaigns, showed high CH₄ mole fractions in each survey. During two measurements, CH₄ mole fractions above 40 ppm were recorded when crossing the plume. In 2023 and 2024, emission rates were larger than 20 kgCH₄ h⁻¹ during the first three visits, with a significantly lower value of 5.7 kgCH₄ h⁻¹ during the last campaign. As no contact with the operator could be established for further clarification, the exact cause of these emissions remains uncertain. But at least one major leak, which was repaired before our fourth campaign, is very likely.

The other two outliers among the large plants are BG-02 and BG-04, which have already been discussed in the preceding section due to their significant emission rates.

The highest CH₄ loss was observed in a small biogas plant (BG-52) with a capacity of 75 kWel, which is part of a farm including 180 cows. Even after accounting for and subtracting the emissions from this additional source, the reported CH₄ loss still amounted to 38.4 \pm 6.9 % of the methane produced at this site.

The results of this study indicate that biogas plants feeding mainly manure show the highest average CH₄ loss rates, accounting for $9.7 \pm 2.4 \%$ (median: $7.8 \pm 1.5 \%$) of CH₄ production (n = 17). This is followed by plants based on energy crops, which show an average CH₄ loss of $6.0 \pm 0.9 \%$ (median: $4.2 \pm 0.5 \%$, n = 43). The observed difference in methane losses between manure-based and energy crop-based plants is consistent with the findings of Wechselberger et al. [2025]. The lowest average loss rate is observed for biowaste treatment plants with $3.8 \pm 0.7 \%$ (median: $4.1 \pm 0.9 \%$, n = 5). Furthermore, this study shows that it is technically possible to limit CH₄ losses to less than 1 %, although relatively high loss rates were observed in many plants.

5.4.5 Comparison to recent literature

A total of 117 measurement campaigns were conducted over 48 different days at 65 biogas production sites, during which plumes were crossed 2,016 times. Methane mole fractions ranged from 2.01 to 56.5 ppm, recorded as the maximum values of the plume peaks. This resulted in emission rates between 0.3 and 255 kgCH₄ h⁻¹. The range of measured methane emissions in this study was larger than in previous studies, such as those conducted in the UK (0.02 to 58.7 kgCH₄ h⁻¹, n = 10) by Bakkaloglu et al. [2021], and in Denmark (1.9 to 81.2 kgCH₄ h⁻¹, n = 44) by Fredenslund et al. [2023]. This variation can be attributed to the larger number of sites studied in this thesis and the presence of one production site with an exceptionally large emission rate, which also is one of the largest plants in Europe.

In general, direct comparisons between studies should be made with caution, as there are differences in facility types, measurement methods, scope, and geographic locations. The average emission rate of 12.9 ± 0.5 kg h⁻¹ in this study falls within the range of values reported in literature for studies with a larger number of investigated sites (n \geq 10). For instance, Scheutz and Fredenslund [2019] reported an average of 10.4 kgCH₄ h⁻¹,

Bakkaloglu et al. [2021] reported 15.9 kgCH₄ h⁻¹, and Fredenslund et al. [2023] reported an average of 14.4 kgCH₄ h⁻¹. Given that the mean value in this study is strongly influenced by the four highest emission rates, the median value may provide a more accurate representation of the emission rates for the majority of the investigated biogas plants. The median emission rate across all plants was 4.9 ± 0.8 kgCH₄ h⁻¹, offering a more reliable measure of emissions from most plants.

The observed CH₄ loss rates varied between 0.8 % and 38.4 % resulting in an average loss rate of $6.8 \pm 0.9\%$ and in a median of 5.0 ± 0.6 %. Table 5.2 provides a summary of methane loss rates from whole-site measurements at various biogas plants, primarily in Europe, compared to this study. The observed differences in methane losses between manure-based and energy crop-based plants have been discussed in detail in the previous section and align with the findings of Wechselberger et al. [2025]. The average loss rate for biowaste treatment plants is 3.8 ± 0.7 % and is therefore higher than the loss rate reported in the study by Bakkaloglu et al. [2021] for UK waste plants. Based on a review of existing studies, Buffi et al. [2024] suggested emission factors (CH₄ loss rates) between 2.3 % and 19.7 %, depending on feedstock, biogas utilization, and best or standard practice management. Overall, the data obtained in this study are in good agreement with previous estimates for emission factors based on CH₄ loss rates, although significant deviations were observed in some individual cases.

Study	Country	Method	Number of plants	Feedstock	Range of loss rate [%]	Average loss rate [%]
Fredenslund et al., 2018	Denmark	Remote sensing, Tracer release	3	manure	1.4 - 3.3	2.2
Fredenslund and Scheutz, 2019	Denmark	Tracer release	13	agricultural	0.4 - 8.6	2.4
Bakkaloglu et al., 2021	UK	GPM	9	6x agricultural 3x waste	0.3 - 8.1 0.02 - 6.8	4.8 2.1
Reineit et al., 2022	Australia	Static chamber	2	/	8.1 - 10.5	9.3
Hrad et al., 2022	Germany	Tracer release, inverse modeling	2	agricultural (energy crops)	1.2 - 2.2 (only off-site)	1.7
Fredenslund et al., 2023	Denmark	Tracer release	44	agricultural	0.3 - 40.6	4.5
Wechselberger et al., 2025	EU	Remote sensing, statistical	88	49x manure 14x energy crops 11x biowaste	0.3 - 5.5 0.3 - 6.5 0.4 - 4.8	1.9 2.8 1.8
				17x manure	0.4 - 38.4	$9.7 \pm 2.4 \\ (7.8 \pm 1.5)$
This study	Germany	GPM	65	43x energy crops	0.3 - 25.0	$\begin{array}{c} {\bf 6.0} \pm {\bf 0.9} \\ (4.2 \pm 0.5) \end{array}$
				5x biowaste	2.1 - 5.4	3.8 ± 0.7 (4.1± 0.9)

Table 5.2: Comparison of studies on CH_4 loss rates at various biogas plants in Europe and Australia. The average loss rates for this study are given as the mean for three primary feedstock types together with the standard error of the mean and the median in brackets.

5.5 Summary and outlook

Through mobile measurements of methane emissions at 65 biogas plants in Germany, this study determined that, on average, 4.9 kg h⁻¹ or 5.0 % of the methane produced is emitted into the atmosphere (median of all investigated sites), with significant variations observed between individual sites. This result aligns with the estimate provided by the Federal Environment Agency, that biogas plants emit approximately 5 % of the methane they produce. Results from this cross-sectional survey provide valuable data for up-scaling methane emissions from German biogas plants. Directly extrapolating the emission rate from an average emission per biogas plant of 43.8 t of CH₄ per year and taking into account the 9,600 installations operating in Germany, results in approximately 420 kt of CH₄. Alternatively, we can estimate that the 33.56 TWh of electricity generated from biogas plants in Germany in 2022 corresponds to roughly 5,917 kt of biomethane. Applying the calculated loss rate of 5 % yields an estimate of around 320 kt of methane emissions annually from biogas plants. Compared to the total methane emissions in Germany amounted to approximately 1,600 kt in 2022 (UBA [2023]), biogas plants are responsible for about 20 % to 26 % of the national methane emissions.

Direct measurements of methane concentrations at specific process stations within individual biogas plants indicate that a significant portion of these emissions could be mitigated. A study by Olczak et al. [2025], which involved simultaneous mobile measurements, identified that up to 76 % of methane emissions from biogas plants could be reduced through improvements in plant operation and design. This highlights a critical opportunity for emission mitigation, as many sustainability assessments of biogas production have not sufficiently accounted for methane emissions from leaks or considered the impact of different management practices (Lehtoranta et al. [2024]).

The sustainability of a biogas plant depends on several factors. In addition to methane emissions, other climate-relevant gases are usually recorded in the GHG balancing of biogas plants. All recorded gases such as carbon dioxide, methane, nitrous oxide and ammonia are converted into so-called CO_2 -equivalents. The type of substrates used for biogas production plays a crucial role. For instance, the use of manure, waste, and residual materials generally results in no additional GHG emissions and can even provide a climate benefit. as these materials would release methane into the atmosphere through open digestion in landfills or on farms. However, the cultivation, farming, and transportation of energy crops for biogas production can generate additional GHG emissions. The technical design of the biogas plant must also be considered, including factors such as the efficiency of the CHP unit and the technical processes involved in biogas treatment. Furthermore, the extent to which thermal energy from biogas combustion is utilized, as well as the implementation of air pollution control technologies (e.g., catalytic converters or post-combustion systems), the plant's own electricity demand, and heat storage capacities, are all important factors in the sustainability assessment. The sustainability of individual plants can therefore vary significantly, depending on factors such as the design and equipment of the biogas plant (e.g., gas-tight covering of digestate storage, airtightness of biogas and methane-carrying components), which can have a substantial impact on emissions.

A study by Scheutz and Fredenslund [2019] on Danish biogas plants revealed that CH_4 emissions, even with a loss of 5 %, already represent the largest share of the plants' carbon dioxide impact, surpassing the contributions from energy consumption and the transport of feedstock and digestate. The study further estimates that biogas plants with particularly high losses (> 15 %) could be net emitters of greenhouse gases. This would be the case for eight of the 65 biogas plants analyzed in this thesis. In a new joint study with the Queen Mary University of London we analyzed 31 biogas plants across Germany, Poland, and the UK, calculating the carbon footprint of each (Olczak et al. [2025]). We find, that 4 out of the 11 German plants examined were net emitters, with three of these plants having emissions (CO₂-equivalent) higher than the average emissions from the German electricity grid. Both studies observed considerable variability across the sites, a trend that is also confirmed by the present study.

In conclusion, the results of this study highlight the need for targeted actions to reduce methane emissions in the biogas sector. Optimizing plant operation, improving plant design and addressing leak detection and repair could significantly reduce the environmental footprint of biogas production. These improvements are essential to increase the sustainability of biogas as a renewable energy source and to minimize its contribution to the German methane budget.

Chapter 6

Stable isotopic methane signatures for source identification

6.1 Principle of isotopic source signature determination

Measured enhancements in atmospheric CH_4 can originate from different sources, each with distinct isotopic signatures that reflect their origin and the production processes, which involve different fractionation mechanisms that alter the isotopic composition (Kirschke et al. [2013]). The stable isotopic signature of CH_4 emissions can be determined using different sampling strategies. One method involves sampling directly at the methane source, while the other involves sampling within the emission plume. With the first approach, the $\delta^{13}CH_4$ values measured can be directly attributed to the source. With the second approach, the $\delta^{13}CH_4$ signal is diluted in ambient air, which has a different $\delta^{13}CH_4$ signature. Therefore, additional analysis is required to trace the signal back to its original isotopic source signature.

In this thesis, the Keeling approach (Keeling [1958]; Keeling [1961]) in combination with the York fit (York et al. [2004]) as described by Hoheisel et al. [2019] is applied to determine the stable isotopic source signature of a CH₄ emission source, when the sampled CH₄ mole fraction is smaller than 60 ppm. For samples containing more than 60 ppm no further approach is necessary, as the measured values already reflect the corresponding δ^{13} CH₄ source signature (Zeleny [2023]).

Assuming that the measured methane mole fraction (CH_{4meas}) is the result of the combination of the background methane mole fraction (CH_{4bg}) and the source mole fraction (CH_{4s}) , and taking into account the conservation of mass, the following relationship applies:

$$CH_{4meas} = CH_{4bg} + CH_{4s} \tag{6.1}$$

and

$$\delta^{13} CH_{4meas} \cdot CH_{4meas} = \delta^{13} CH_{4bg} \cdot CH_{4bg} + \delta^{13} CH_{4s} \cdot CH_{4s}$$
(6.2)

Rearranging these equations gives the following:

$$\delta^{13}\mathrm{CH}_{4\mathrm{meas}} = \mathrm{CH}_{4\mathrm{bg}} \cdot \left(\delta^{13}\mathrm{CH}_{4\mathrm{bg}} - \delta^{13}\mathrm{CH}_{4\mathrm{s}}\right) \cdot \frac{1}{\mathrm{CH}_{4\mathrm{meas}}} + \delta^{13}\mathrm{CH}_{4\mathrm{s}} \tag{6.3}$$

Equation 6.3 follows the form y = mx + b. This means that the isotopic source signature δ^{13} CH_{4s} corresponds to the intercept of a linear regression graph when the values of δ^{13} CH_{4meas} are plotted against CH⁻¹_{4meas}, which is also referred to as a Keeling plot. The York fit (York et al. [2004]) was selected for the analysis in this thesis because it minimizes the weighted distance between the data points and the fitted line, accounting for uncertainties in both the x and y coordinates. The accuracy of the analyzer and the CH₄ enhancement over the background have a significant impact on the uncertainty of the source signature determined using the Keeling plot method and the York fit (Hoheisel et al. [2019]).

6.2 Isotopic δ^{13} CH₄ composition of biogas

Data from isotopic measurements of methane (12 CH₄, 13 CH₄, CH₃D) are often used in atmospheric modeling to understand the individual contributions of different methane sources to the global and regional CH₄ budget (e.g. Bousquet et al. [2006], Röckmann et al. [2016], Hoheisel et al. [2019], Hoheisel and Schmidt [2024]). As already explained in section 2.1.2, the δ^{13} C values of atmospheric methane have shifted towards more negative values since 2007 (e.g. Schaefer et al. [2016], Nisbet et al. [2019], Lan et al. [2021a], Hoheisel and Schmidt [2024]). However, the exact reason for this negative trend has not yet been clearly identified, and there are considerable uncertainties in the isotopic signatures of the sources due to large temporal variations and regional specifications (e.g. Sherwood et al. [2017], Menoud et al. [2022]).

Biogenic methane, which is predominantly produced by the microbial degradation of organic materials under anaerobic conditions, shows a significantly lower enrichment in ¹³C (and D) with typical δ^{13} CH₄ values ranging between -80 ‰ and -40 ‰ (Lowry et al. [2020]) compared to pyrogenic (-25 to -13 ‰) and thermogenic (-45 to -25 ‰) methane sources. These differences result from the isotopic fractionation process that occurs during anaerobic digestion (AD) of organic material or CO₂ reduction (e.g. Bergamaschi et al. [1998], Levin et al. [1993], Levin et al. [1999], Zazzeri et al. [2015], Sherwood et al. [2017], Lowry et al. [2020] Xueref-Remy et al. [2020]).

This isotopic fractionation process in methanogenesis is influenced by a variety of parameters, including the type and population density of microorganisms, pH, nutrient availability, $CH_4:O_2$ ratio, temperature, and the presence of inhibitory chemicals and inorganic nitrogen (Templeton et al. [2006], Polag et al. [2015], Bakkaloglu et al. [2022b]). The German waste sector is increasingly recycling more material and redirecting more biodegradable waste from landfill to AD and composting plants (Umwelbundesamt [2024]). This change, which involves the biological processes, making it necessary to study the signatures of the waste sources in order to link them to the corresponding processes. In biogas plants where these microbial processes are specifically used, the isotopic signature of the methane that is produced plays a central role in better understanding and optimizing the underlying biological processes. Analyzing the δ^{13} C values of methane samples from biogas plants can provide valuable insights into the efficiency of AD and the type of feedstock used (Nikolausz et al. [2013], Bakkaloglu et al. [2022b]). Additionally, isotope measurements can help identify potential disruptions in the digestion process and assess the impact of operational parameters, such as temperature or pH, on the microbiome and methane production (Polag et al. [2015]). On a regional scale, isotope analysis allows for more accurate attribution of methane emissions to specific sources and helps quantify the contribution of biogas plants to GHG emission reductions with greater precision.

In the following, the ¹³C stable isotope signature of methane in biogas plants is summarized and examined in more detail based on the δ^{13} CH₄ source signature of 20 biogas plants. The sampling and measurement of the methane are based on different sampling and calibration strategies, which are discussed in detail in the following section. These methods are important for the accuracy of the isotope analysis, as they ensure that the obtained data reflect the specific conditions of each biogas plant and that the results are comparable with existing databases.

6.2.1 From sampling to data evaluation

Sampling strategy

Several sampling strategies are used to determine the isotopic signature of CH₄ sources. Besides direct sampling at the source (Menoud et al. [2022]), the plume can be sampled at some distance and then measured in the laboratory (Zazzeri et al. [2015]), or mobile measurements can be carried out with an AirCore system (Lopez et al. [2017], Hoheisel et al. [2019]). As part of this thesis, direct sampling was carried out at eight biogas plants and samples were taken in the plume at a total of 20 biogas plants for δ^{13} CH₄ determination in the laboratory using the CRDS analyzer.

Direct biogas sampling was performed using a short tube connecting the outlet valve of the corresponding CH₄ source to a 1-L Tedlar bag (Tedlar with poly-propylene valve with septum, RESTEC). Plume samples were collected at distances between 30 and 200 m in 3-L Tedlar bags (see Fig. 6.1). During the filling process, large dust particles are already filtered out by a 7 μ m filter at the inlet of a portable pumping system with magnesium perchlorate drying. Background air was typically collected before or after plume air sampling, upwind of the sources, or outside the plume where low CH₄ mole fraction was measured. To ensure that background or plume air was collected, the atmospheric CH₄ mole fraction was measured in-situ in parallel with the filling of the sample bags. Direct biogas samples are collected in pairs and in case of plume samples 2 to 6 samples with different CH₄ mole fractions were taken.



Figure 6.1: (a) Schematic illustration showing two possible sampling strategies applied in this thesis for δ^{13} C isotopic signature determination of a CH₄ emission source.(b) Pumping system for filling Tedlar bags with atmospheric samples for a later measurement in the laboratory.

Measurement setup

Measurements of the sample bags were carried out using the CRDS G2201-i analyzer. Gas from the calibration cylinders or sample bags flows through a 16-port rotary-valve (model: EMT2CSD-16UWE, Valco Vici, Switzerland), a flow meter and a Nafion tube (PermaPure) for further drying into the CRDS analyzer. The flow used for calibration and sample measurements is typically between 40 to 50 mL min⁻¹. After passing through the cavity, the gas is directed by a vacuum pump through the outer tube of the Nafion. By using this Nafion setup, the water vapor mole fraction is reduced to values below 0.08 % without affecting the measured CH_4 mole fraction or its isotopic composition (Hoheisel [2021]). A schematic of the setup is shown in Fig. 6.2.

Samples of biogas with a CH₄ concentration between 50 and 65 % and biomethane of up to 98 % have to be diluted to 10 ppm before entering the CRDS analyzer. This is done by diluting a small amount of the sample with 3 L of synthetic air, resulting in a mixture with a CH₄ mole fraction of approximately 10 ppm. According to Hoheisel et al. [2019], the measurement accuracy for δ^{13} CH₄ is highest within this range ($\sigma^2 = 0.06$ % for a 10 min averaging period) and decreases for mole fractions at atmospheric levels ($\sigma^2 = 0.4$ % for a 10 min averaging period). Therefore, for samples with CH₄ mole fractions below 3.5 ppm, measurements should be extended to 40 minutes instead of the 30 minutes typically used for direct samples, in order to improve the accuracy of the averaged δ^{13} CH₄ value. Since each sample is measured twice and the flow rate is typically between 40 and 50 mL min⁻¹, atmospheric samples require a larger volume. As a result, atmospheric samples are collected in 3-L bags, while direct samples are filled in 1-L bags.



Figure 6.2: Laboratory setup for sample measurements to determine δ^{13} CH₄ values of methane sources, as illustrated by Grandke [2022].

Data analysis

The CRDS analyzer records data every 3.7 seconds, which are then averaged to one-minute values. Since 2022 we monitored a CH₄ concentration dependence on the measurement of δ^{13} CH₄, which was examined and tested by Pfau [2023] and Hahn [2024]. After discussion with the manufacturer, we identified the instrument-specific calibration offset parameter, as described by Rella et al. [2015b], as the cause of the significant change in 2022. A brief overview of the issue and its handling is provided in Appendix C. This parameter adjustment was integrated into the analysis, and the affected data were recalculated and provided by Feuerle (personal communication) for the relevant time period from October 2022 to May 2024 (offset parameter = 0 instead of -0.00555535148055). For analysis in this thesis, the recalculated one-minute δ^{13} CH₄ values are used.

Before the analysis of the minutely CH_4 and $\delta^{13}CH_4$ values of the sample measurements, invalid data points are identified and excluded. The first ten minutes after each sample gas change are discarded to account for cavity flushing and stabilization. Since the samples do not contain ethane (C_2H_6) and the air is dried before entering the cavity, no additional corrections are required, which would otherwise be necessary as noted by Hoheisel et al. [2019].

To minimize the influence of instrument drift, the samples are calibrated. The calibration gases (Table A.1) used in this study are compressed air with atmospheric mole fractions. Given the wide range of methane mole fractions present in the samples, different calibration strategies are implemented. In the case of our instrument with its individual characteristics, the one-point calibration (Appendix A.1) with a standard gas containing ~ 10.5 ppm CH₄ is performed during the evaluation process for all samples with a CH₄ mole fraction above 3.36 ppm. The calibration standard used is either Sib1_8 with a δ^{13} CH₄ value of -43.6 % or Sib8_5 (available since 2023) with a δ^{13} CH₄ value of -59.4 %, depending on the δ^{13} CH₄ value of the sample. Background and other atmospheric samples with mole fractions below 3.36 ppm CH₄ are calibrated via one-point calibration using the Pic3_1 standard with a CH₄ mole fraction of 2 ppm and an isotopic signature of approximately -48 %. The threshold value of the sample methane mole fraction, that determines the calibration strategy is based on the simplified assumption of a constant offset parameter as discussed in Appendix C. The correction of the δ^{13} CH₄ values by the new offset parameter depends on the CH₄ mole fraction and is subject to small variations over time, contrary to the assumption. When calibrating samples with different CH₄ mole fractions, the influence of a not optimally selected offset parameter on the correction of the δ^{13} CH₄ value at 3.36 ppm with a 2 ppm standard is as large as with a 10.5 ppm standard. Therefore, to minimize the influence of the offset parameter on the δ^{13} CH₄ values, samples below 3.36 ppm CH₄ are calibrated with our 2 ppm standard, while samples above 3.36 ppm are calibrated with one of our standards at approximately 10.5 ppm (personal communication M. Feuerle). For the determination of δ^{13} CH₄ reference values, flasks filled with our calibration gases were analyzed at the Max Planck Institute (MPI) for Biogeochemistry in Jena (δ^{13} CH₄ ± 0.05‰). These analyses provide a link between our measurements in Heidelberg and the VPDB isotopic scale (Sperlich et al. [2016]).

Since isotope measurements can be influenced by a range of factors, precise characterization of the measuring instrument used and an adapted calibration strategy are essential in order to obtain accurate and reliable results.

Finally, the Keeling approach is applied to the atmospheric samples for each sampling day where the biogas plant was approached separately and then averaged for each site.

6.2.2 Isotopic source signature of 18 biogas plants in Germany

To determine the δ^{13} CH₄ source signature, 256 sample bags were filled at 20 biogas plants in Germany and analyzed in the Heidelberg laboratory. In the cases where significant discrepancies were observed between the first and second measurements of a given sample, the second measurement was discarded to ensure the reliability of the data. However, if the measurements were consistent, the data were processed and analyzed. The methane enhancements observed during plume sampling varied widely, ranging from 160 to 11,040 ppb above the background CH₄ mole fraction. Analysis using Keeling plots showed higher uncertainties of the isotopic source signature that increases with decreasing enhancements. Two example of a Keeling plot is shown in Fig. 6.3, where panel (a) shows a CH_4 enhancement of 870 ppb in the plume samples relative to the background samples. In contrast, panel (b) illustrates a case with only 60 ppb CH_4 enhancement, making it not possible to reliably extract the isotopic source signature. Only events where at least one plume sample exceeded 200 ppb above background were considered for further evaluation of the Keeling plots and the minimum number of samples in the plume was set to three. This led to the exclusion of seven calculated source signatures: four due to insufficient CH_4 enhancements and three because only two samples were available. Consequently, atmospheric sampling results are missing for four biogas plants, with one (BG-01) being completely excluded from the evaluation. For the remaining three affected plants, direct samples are available.



Figure 6.3: Keeling plots based on bag samples filled within the emission plumes of two different biogas plants. Panel (a) shows an example with sufficiently high CH_4 enhancements in the plume relative to the background, allowing for a reliable isotopic source signature. In contrast, panel (b) shows an example with insufficient methane excess, making it impossible to accurately determine the isotopic source signature using the Keeling approach.

The results of the stable δ^{13} C signature of the analyzed methane from biogas plants are listed in Table 6.1 and shown in Fig. 6.4(a). Atmospheric δ^{13} CH₄ source signatures based on the sample bags filled in the whole-site emission plumes of 19 biogas plants and determined using the Keeling approach range from -63.8 % to -35.7 %. The measured values of the direct samples of biogas collected on site at eight plants range from -62.7 % to -39.6 %.

The direct samples were mostly collected before the gas was led into the CHP unit. At certain sites, additional samples were collected at different process points and in the vicinity of individual emission sources. All values for the different sampling locations are listed in Table E.1 in the Appendix. For direct samples of biogas collected at the digesters and before and after the activated carbon treatment as done at BG-03, BG-29 and BG-30, no significant differences in isotopic composition were observed when compared to the samples taken at the CHP unit. This suggests that no fractionation of the methane occurs during the removal of impurities from the biogas. At an upgrading plant (BM-06), both biomethane samples (post-upgrading) and raw biogas samples (pre-upgrading) were also collected, and similarly, no significant differences were observed.

Samples collected from individual emission sources, such as the feeder, manure storage, and digestate storage, exhibited more distinct δ^{13} CH₄ signatures. Notably, at BG-09, BG-29, and BG-30, significant differences in the isotopic source signatures were observed when comparing samples taken from the manure storage or feeder to those collected from biogas after the fermentation process. In several instances, sampling occurred over multiple campaigns, resulting in different values, which may contribute to larger errors. This variability suggests potential changes in feedstock or alterations in the AD process, highlighting the dynamic nature of the emissions and the importance of consistent sampling to account for such variations.

At five biogas plants, a comparison between the results from different sampling strategies was conducted. The δ^{13} CH₄ values obtained from atmospheric and direct samples showed no significant deviations at two sites, while notable discrepancies were observed at three plants. Specifically, for BG-20, which had a particularly large number of samples collected, and BG-27, the δ^{13} CH₄ values based on both strategies agreed well. In contrast, for the remaining three plants, deviations of more than 10 % were observed between the atmospheric and direct measurements. These discrepancies can be partly attributed to the specific sampling conditions at each site. At BM-06, for instance, the sampling location was in close proximity to a second biomethane plant (BM-07), resulting in a sample influenced by methane emissions from both plants. Therefore, it is likely that the isotopic signature of the sample was affected by the emissions from the second biogas plant. Similarly, at BG-29, located near a cowshed, the proximity to the cowshed influenced the isotopic composition of the samples. A direct sample taken inside the cowshed showed a δ^{13} CH₄ value of -55.5 \pm 0.6 ‰, closely matching the atmospheric sample of -55.4 \pm 1.0 %, suggesting that the methane emissions in the plume were primarily sourced from the cowshed. For BG-38, no additional emission source was identified. One potential explanation for the observed discrepancy is that methane excess in the atmosphere could have originated from emissions at a different stage of the biogas process than the stage where the direct sampling occurred, as was observed and discussed for several other plants. However, the exact cause of this deviation remains uncertain.

From the results, it can be concluded that atmospheric and direct sampling methods generally provide consistent δ^{13} CH₄ values across various biogas plants. However, significant discrepancies can arise in certain cases, primarily due to the influence of nearby emission sources, such as other biogas plants or livestock facilities (e.g., cowsheds), which can alter the isotopic composition of methane in the plume. Accurate identification and characterization of these additional emission sources are essential for ensuring reliable interpretation of δ^{13} CH₄ values in atmospheric samples. Therefore, for further analysis, values that are likely affected by a second methane source have been excluded (marked by gray-colored values in Table 6.1). This includes the atmospheric sample from BG-16, where the presence of a nearby pig farm and its associated manure storage most likely influenced the isotopic signature, as methane from pig manure typically shows a δ^{13} CH₄ signature between -70 ‰ and -60 ‰ (Dalby et al. [2020]). Nevertheless, with careful sampling techniques and the absence of additional methane sources that could alter the isotopic signature, it is indeed possible to accurately determine the source signature by collecting and analyzing samples directly from the plume.

Plant ID	Feedstock	Sampling strategy	$\delta^{13}\mathbf{CH}_4$ source signature [‰]	
		(# samples)	${f Atmospheric}$	Direct
BG-03	Organic waste (solid and green waste)	direct (4)	/	-62.7 ± 0.2
BG-09	Mixed (cattle manure, maize silage)	direct (1)	/	-42.1 ± 0.1
BG-20	Organic waste (food waste, grass and maize silage, manure)	atmospheric (21), direct (19)	-60.6 ± 1.9	-61.4 ± 1.7
BG-27	Mixed (pig manure, maize silage)	atmospheric (3), direct (8)	-57.4 ± 0.5	-58.4 ± 2.1
BG-29	Mixed (maize and grass silage, manure)	atmospheric (3), direct (4)	-55.4 ± 1.0	-39.6 ± 0.2
BG-30	Mixed (maize and grass silage, manure)	direct (8)	/	-43.8 ± 0.9
BG-38	Organic waste (food waste, silage)	atmospheric (4), direct (2)	-45.6 ± 0.7	-59.9 ± 0.3
BM-06	Energy crops (maize and grass silage, agricultural residues)	atmospheric (3), direct (4)	-45.6 ± 0.2	-55.3 ± 0.1
BG-04	Energy crops	atmospheric (4)	-56.1 ± 2.1	
BG-11	Mixed	atmospheric (4)	-59.9 ± 1.7	
BG-15	Energy crops	atmospheric (4)	-35.7 ± 1.4	
BG-16	Mixed	atmospheric (7)	-63.8 ± 0.5	
BG-22	Mixed	atmospheric (7)	-51.7 ± 1.1	
BG-23	Mixed	atmospheric (6)	-48.9 ± 1.1	
BG-35	Energy crops	atmospheric (3)	-41.2 ± 2.0	
BG-44	Mixed	atmospheric (3)	-56.5 ± 0.6	
BM-04	Mixed	atmospheric (7)	-56.9 ± 0.3	
BM-10	Energy crops	atmospheric (11)	-43.6 ± 1.1	
BM-12	Energy crops	atmospheric (8)	-43.0 ± 2.1	

Table 6.1: δ^{13} CH₄ source signature of 19 biogas plants, with samples collected either directly on-site or within the plume, and determined using the Keeling approach. Atmospheric sample results, indicated in gray, are likely influenced by a secondary emission source, affecting the isotopic signature.

Plume samples from 12 additional biogas plants were analyzed using the Keeling approach, with BG-16 excluded for the reasons previously mentioned. The observed wide range of δ^{13} CH₄ values, spanning from -62.7 % to -35.7 % (Fig. 6.4 (a)), can be partially explained by classifying the data according to the feedstock employed (Fig. 6.4(b)). Biogas plants primarily utilizing energy crops as feedstock show the highest δ^{13} CH₄ values, with an average of -45.9 ± 8.1 %. This trend is primarily attributed to the dominant use of maize in energy crop-based biogas systems. As maize is a C4 plant, it exhibits a ¹³C content that is 10 to 15 \% higher than that of typical C3 plants, resulting from fractionation during photosynthesis (Levin et al. [1993]). As a consequence, the mean isotopic signature of the methane produced by these plants is enriched in 13 C, leading to the higher observed δ^{13} CH₄ values. However, since 2012, the proportion of maize that can be used as input material has been limited to 30-40 % (UBA-EEG). As a result, energy crops are often mixed with manure, leading to a larger range of δ^{13} CH₄ values, from -59.9 ‰ to -39.6 ‰, with an average of -50.9 ± 7.6 %. This variability reflects the contribution of both feedstock types: as the proportion of manure increases, the CH₄ isotopic composition becomes more depleted in ¹³C. In contrast, food waste-based biogas plants have the most depleted δ^{13} C values in their methane, with an average of -61.4 ± 1.4 ‰.

These results highlight the influence of feedstock composition on the stable isotopic signature of methane produced in biogas plants. The observed variations in δ^{13} CH₄ values between different plant types emphasize the complexity of biogas production and its dependence on the substrates used. In addition, these results provide valuable insights into the sustainability of biogas plants, as isotopic signatures can not only help to trace the sources of methane emissions, but also to identify the specific feedstock used.

The findings are in line with previous studies, such as that of Bakkaloglu et al. [2022b], where 26 biogas plants were analyzed together with various other waste sources in the UK. In that study, δ^{13} CH₄ values ranged from -64.4 % to -44.3 %, with a mean of -54.6 \pm 5.6 %. Similarly, the most enriched values were observed in maize-fed agricultural biogas plants, while food and municipal waste, as well as mixed feedstock plants, showed more depleted values. The study by Nikolausz et al. [2013], which analyzed the isotopic composition in methanogenic pathways of laboratory biogas reactors in Germany, reported a broader range of values from -68.4 % to -31.3 %. Again, more ¹³C-enriched values were recorded when the digesters were filled with maize silage, while chicken manure led to strongly ¹³C-depleted values. Bezyk et al. [2024] investigated a municipal solid waste treatment plant in Poland and measured CH_4 mole fractions and corresponding $\delta^{13}C$ values at different treatment installations. CH_4 produced in the biogas plant fed with kitchen waste had a mean δ^{13} CH₄ value of -62.2 \pm 0.8 % and was therefore similar to the mean value of -61.4 ± 1.4 % determined in this study for organic waste-based biogas plants. The EMID database, which lists the stable isotope signatures of various European methane sources, also contains a large selection of biogas plants studied. (Menoud and et. al. [2021]). The ¹³C values in methane from 42 biogas plants, ranging from -64.4 % to -45.1 % are given in EMID.

Based on the results of our study and in line with previous research, the feedstock is identified as a key factor influencing the stable isotopic composition of the methane produced in biogas plants. However, it is important to note that in biogas plants, methane is produced through methanogenesis under anaerobic conditions via various metabolic pathways. Therefore, the δ^{13} CH₄ signature in anaerobic digesters is influenced not only by the feedstock type but also by factors such as loading rates, the amount and activity of the methanogenic population, and operating conditions like temperature, pH, and hydraulic retention time (Laukenmann et al. [2010], Polag et al. [2015], Lv et al. [2018]).

Although the wide range of δ^{13} CH₄ values measured at biogas plants allows for the attribution of emissions to specific plants at a local level, it complicates the quantification of methane emissions from biogas facilities on a larger regional or global scale.



Figure 6.4: δ^{13} CH₄ source signature of 18 biogas plants (a) for different carbon isotopic signature categories and (b) relating to different feedstock substrate material, such as organic (food) waste (n = 3), mixed (n = 9), including energy crops and manure, and energy crops (n = 6). Boxes represent the first and third quartile of the data, while whiskers extend to the largest value that is within 1.5 times the interquartile range.

6.2.3 Long-term δ^{13} CH₄ variation at a local biogas plant

At the same biogas plant (BG-20), where long-term monitoring of CH_4 emission rates has been carried out, the isotopic source signature has also been subject to regular analysis. The δ^{13} CH₄ values were measured and determined for 22 separate days between 2016 and 2024. Between 2016 and 2019 δ^{13} CH₄ measurements of methane from the biogas plant were carried out by Hoheisel [2017] and Korbeń [2021]. During this period, the CH_4 and δ^{13} CH₄ values are measured in situ with a CRDS analyzer when crossing the emission plume. Simultaneously to the in-situ measurements, a secondary split-off flow directed ambient air through an AirCore system. This configuration allowed the re-measurement of air with a higher temporal resolution for short time intervals. The δ^{13} CH₄ signature of the methane source was subsequently determined using the Keeling approach, based on the non-averaged data obtained with the AirCore setup. A comprehensive description of the mobile measurement setup and data evaluation method is provided by Hoheisel et al. [2019]. After 2020, the CRDS instrument was no longer used for mobile measurements and was primarily dedicated to ambient air measurements in the Heidelberg laboratory (Hoheisel and Schmidt [2024]). Since 2023, the bag sampling method described earlier has been applied for subsequent measurements at this particular biogas plant. In addition, samples were taken directly on site at different stages of the biogas production process, such as both digesters and CHP unit.

Results of δ^{13} CH₄ long-term analysis

As part of this study, a total of 57 sample bags were filled and analyzed, including 22 direct samples. Given that direct samples always were collected in pairs, 11 δ^{13} CH₄ isotopic values are available for the period from January 2023 to August 2024 based on the direct samples. Additionally, two direct samples were collected in February 2017 by Wald [2017] and analyzed by Hoheisel et al. [2019]. The remaining 35 samples were obtained either from the entire plume or from more specific plume locations, such as the feeder or the digester room, over the course of eight sampling days. The time series was further complemented by 14 days of daily averaged isotopic source signature values derived from a total of 70 AirCore measurements.

The isotope values are plotted against the date of sampling in Fig. 6.5 and are listed in E.2. The determined δ^{13} CH₄ values range from -64.1 % to -54.7 % with a mean value of -61.3 ± 2.1 %. Considering both the plume and direct samples and distinguishing between the three different study periods, the mean for the study period of Hoheisel et al. [2019] is -62.4 ± 1.2 % with a range from -64.1 % to -60.2 % (n = 9). For the study period of Korbeń [2021], the average is -61.7 ± 2.3 % with values between -64.0 % and -57.1 % (n = 7). The greatest variation is found in the analyzed period of this thesis with -63.8 % to -54.7 % and a mean value of -60.6 ± 2.2 % (n = 22).

A slight but not significant enrichment of ¹³C in the isotope values can be seen in the mean values compared to the earlier study periods. However, the most recent values in Fig. 6.5 show some of the most enriched signatures of the complete monitoring period. In particular, one of the last direct samples, which was taken at digester 1, shows an

atypically high δ^{13} CH₄ value of -54.7 ‰. From personal correspondence with the operator of the biogas plant it is known that there were problems with the digestion process of the methanogenic bacteria on this day as the digesters were overfed. This enriched value may reflect this problem.

The use of stable δ^{13} C-values in methane as an early indicator of such process instability was investigated in the study by Polag et al. [2015]. They continuously monitored the ¹³CH₄ values in a full-scale continuous stirred-tank reactor operated under mesophilic conditions for a six-month period, while varying organic loading rates (maize and cattle manure). The δ^{13} CH₄ values showed a high dynamic range associated with short-term feeding events and long-term fluctuations in organic load. Especially in the process state, when the anaerobic digestion was under stress due to continuous overfeeding, the δ^{13} CH₄ values showed a strong increase (more than 10 ‰). This supports the hypothesis that the isotopic signature in the digester of the investigated biogas plant of our long-term study reacted due to overfeeding.

Excluding the last sample from the averaging gives a δ^{13} CH₄ mean of -61.0 ± 1.8 ‰ for the time period of this study. The mean values for the individual study periods therefore differ only slightly and resulting in a mean of -61.5 ± 1.9 ‰ for the complete observation period.


Figure 6.5: Determined δ^{13} CH₄ source signature of a biogas plant for each sampling day between the years 2016 to 2024. Values indicated in light blue are measured via plume crossings using an AirCore system and calculated using the Keeling approach (Hoheisel et al. [2019], Korbeń [2021]). Hoheisel et al. [2019] carried out measurements between 2016 and 2018, followed by Korbeń [2021], who performed measurements between 2018 and 2020. Since beginning of 2023, the isotopic source signature determination at this facility is based on the application of the Keeling approach to air sampled inside the plume in sample bags (dark blue) and analyzed in the laboratory. Direct samples are indicated in green and were filled at different process stages directly on site.

On April 26th, 2024, samples were collected from different process stages of the biogas plant. Since both digesters are fed with different primary input material, air samples were taken near both feeders, along with direct samples from each digester. Additionally, an air sample was filled in the underground digester room, located between the two digesters. A direct sample of the purified biogas was also collected just before it entered the combustion engine in the CHP unit. Finally, an air sample was taken inside the CHP unit. The results for this day are presented in Fig. 6.6.

Overall, the values for the different process stages are in the range between -60.9 ‰ and -58.6 ‰ and do not show major fluctuations. All samples show strongly depleted δ^{13} CH₄ signatures, a pattern also observed for the organic waste plants in general. Digester 1, which is mainly fed with silage (including grass and maize) and small amounts of cattle manure and organic waste, has a δ^{13} CH₄ value of -59.1 ± 0.1 ‰, making it slightly isotopically lighter than digester 2, which has a value of -60.9 ± 0.4 ‰ and is mainly fed with food waste. The 1.8 ‰ difference between the two digesters, as well as the 2.6 ‰ difference observed in the 2017 samples taken from the same digesters (Wald [2017], Hoheisel et al. [2019]), can be attributed to the proportion of maize in the feedstock of digester 1, which causes an enrichment in ¹³C compared to the methane produced in digester 2.

However, as only about 15 % of the organic load rate fed to digester 1 consists of maize (according to operator interview), the isotopic composition does not show a strong shift to more enriched ¹³C-values. The direct sample from the CHP plant, with a δ^{13} CH₄ value of -60.0 ± 0.3 ‰, is isotopically positioned between the two digester samples. This reflects the mixture of biogas produced in both digesters and subsequently combusted in the CHP unit, as indicated by the isotopic values.

This long-term monitoring has allowed the observation of several phenomena that can influence the stable isotope signature. In this case, not only is the feedstock an influencing factor on the isotope values, as described in the previous chapter, but the organic load was also identified as an important factor. These results are consistent with previously published studies on anaerobic digesters (Polag et al. [2015], Bakkaloglu et al. [2021]). In addition, the low variability of the isotope values (with the exception of the last measurement) supports the observations of the emission rates, which also show a stable picture. As this is a non-flexibilized plant, incidents such as over-feeding of a digester, if not detected in time, can lead to a failure of the plant operation and result in additional flaring or gas releases.



Figure 6.6: Determined δ^{13} CH₄ source signatures for different process stages at the biogas plant on April 26th, 2024. Triangles represent values obtained using the Keeling approach, while circles indicate direct samples.

6.3 Summary and outlook

In this chapter, the isotopic signatures of methane emissions from biogas plants were analyzed, revealing significant variations in δ^{13} CH₄ values across different facilities. The results show a large range in δ^{13} CH₄ signatures, making it difficult to establish a straightforward link between atmospheric $\delta^{13}CH_4$ values and methane emissions from the biogas sector. These variations are largely attributed to differences in feedstock composition. Biogas plants feeding energy crops, often with maize silage as primary substrate (C4 plant), yield more ¹³C-enriched methane, while biogas plants using manure or mixed substrates produce more ¹³C-depleted methane. This finding is consistent with previous studies in the UK and Germany, such as those by Bakkaloglu et al. [2022b] and Nikolausz et al. [2013], which also report a wide range of isotopic values depending on the feedstock used. The analysis also emphasized the impact of microbial methane producers in anaerobic digesters. The metabolism of methanogens plays a crucial role in isotopic fractionation, meaning that not only the feedstock but also microbial population and activity can influence the isotopic profile of methane (Polag et al. [2015]). This was particularly evident in the long-term study, where overfeeding led to significantly more enriched ¹³C values compared to other years, during which the plant was operated without major incidents. In addition to feedstock and microbial activity, other tracers, such as the CH_4 to CO_2 ratio (Poulsen et al. [2017]) and $\delta^{13}CO_2$ values (Lv et al. [2014]), could provide further insights into the underlying processes occurring in biogas plants. For example, the CH_4 to CO_2 ratio could indicate whether CH_4 emitted from biomethane plants is due to leakage before or after upgrading.

Another key observation was the variation in methane enhancements during plume sampling, ranging from 60 to 11,040 ppb. The uncertainty in Keeling plot analysis was found to be greater at lower enhancements. It became clear that a methane excess of at least 200 ppb is required to reliably determine the isotopic signature. Furthermore, the accuracy of the isotopic signature improves with the number of samples collected, highlighting the importance of comprehensive sampling for robust analysis.

Overall, this chapter underscores the complexity of attributing methane emissions to specific biogas plants based only on δ^{13} CH₄ values. While different emission sources on site, feedstock type and microbial activity are critical factors, further research using additional tracers and a larger number of samples will be necessary to refine emission source attribution in the biogas sector on an international scale.

Chapter 7

Summary and conclusion

With a global warming potential 28 times greater than that of CO_2 , methane is a significant driver of global warming (IPCC [2023]). Accurate quantification of methane emissions is essential for developing and targeting effective mitigation strategies. However, many aspects of CH₄ emissions, particularly at the regional level, remain insufficiently quantified. This thesis provides a detailed insight into the quantification of CH_4 emission rates from the biogas sector by mobile measurements in combination with the application of a Gaussian plume dispersion model. In the scope of this thesis, this combined method has been tested and improved using controlled CH_4 release experiments. A best practice approach to our measurement setup and application objectives was developed from the key findings. The aim of the method is to be able to estimate the CH_4 emission rate of the investigated methane source from the measured atmospheric methane enhancements. For this purpose, instruments with a temporal resolution of 1 Hz are used to measure the CH_4 mole fraction in the ambient air while passing through the CH_4 emission plume of an emitter and to record the atmospheric conditions on site. Evaluation of the results of six controlled release experiments has contributed to a better understanding of the influence of various factors on the determination of the emission rate and to develop a strategy to minimize uncertainties. Thus, with sufficiently high statistics, accurate meteorological data and optimized driving strategies, including an appropriate distance from the emission source, the method shows an overall accuracy of 30 % for emission rate quantification.

While the capabilities of our own release setup were limited to low CH_4 release rates of less than 1 kg h⁻¹, participation in the TADI campaign allowed us to test our method at CH_4 release rates from 0 to 200 kg h⁻¹. The TADI campaign 2024 was a single-blind, controlled release experiment designed to provide an international comparison of different measurement instruments and methods for quantifying methane emissions. During our five-day participation, with a total of 34 perceived releases for which neither the release rate nor the release location were known at the time of the initial evaluation, we were able to achieve a good performance in international comparison (McManemin et al. [2025]). Moreover, we were able to confirm the results from our previously conducted release experiments and extend the accuracy of approximately 30 % to higher release rates. Overall, the quantification method demonstrated simple and flexible implementation in the field. This allowed the investigation of a large number of biogas sites within the time frame of the thesis. Using the previously verified GPM method, 65 biogas production plants in Germany were measured and analyzed. Germany produces approximately 8.8 bcm of biomethane per year (based on 33.56 TWh electricity produced in 2022 Lauf et al. [2023]), which is 42 % of the European market (21 bcm in 2022 Association [2023]) and 22 % of the world market (40 bcm in 2021) (WBA [2024]). This makes Germany the second largest producer of biogas, with a total of 9,600 plants (Gustafsson et al. [2024]), making it necessary to understand and account for methane emissions from the biogas sector in order to understand Germany's methane budget. As a renewable energy source, biogas is part of the sustainable RED initiative, so it is particularly important to investigate and verify the sustainability of the production sites. The surveyed biogas sites covered a wide range of plants in terms of age, production capacity, as well as in feedstock, site layout and prevailing biogas utilization technologies. An average CH₄ emission rate of 7.0 \pm 2.0 kg h⁻¹ was calculated for biogas plants and an average emission rate of 38.9 \pm 20.2 kg h⁻¹ for biomethane plants. Overall, the emission rates varied between 0.28 and 255 kgCH₄ h^{-1} . The annual methane production rate of each plant was calculated based on the electricity produced in the CHP units by the combustion of biogas and the amount of biomethane injected into the natural gas grid. This, in turn, allowed the CH_4 loss rate to be determined using the previously calculated CH₄ emission rates, indicating the percentage of the total produced methane that is emitted into the atmosphere.

A CH₄ loss rate of 5 % of the produced methane per plant emitted to the atmosphere was found, a value consistent with the one reported by the Environmental Federal Agency (UBA - AGEE-Stat [b]). This amount of methane emissions can have a significant impact on the sustainability of biogas production. These results indicate that up to 30 % of national methane emissions in Germany are caused by emissions from biogas plants. The fact that a large proportion of these methane emissions to the atmosphere are caused by leaks and improper operational management indicates that this emissions are partly avoidable and can be minimized through careful and regular monitoring.

The sustainability of biogas plants is influenced by a range of factors. The entire process chain of plant operation is taken into account, from the cultivation of feedstocks to their storage, as well as the management of digestate and the application of fertilizers. The choice of substrates used in biogas production is particularly important. If the feedstock is not based on agricultural residues or food waste, but instead primarily consists of energy crops grown and processed specifically for this purpose, it can have significant impact on the sustainability. As a result, the sustainability of each plant can differ considerably, also depending on factors such as the design and operational features, including the sealing of digestate storage and the airtightness of the biogas system. These factors can have a considerable effect on emissions. While it is relatively straightforward to meet the RED II sustainability criteria when using manure and organic waste, the use of energy crops as feedstock does not always guarantee the same level of sustainability (Buffi et al. [2024]). Therefore, this study emphasizes the pressing need for improvements in the biogas sector. Further investigations are recommended, not only to support and expand upon the findings of this thesis but also to monitor and assess the future development of the biogas sector, enabling the implementation of appropriate mitigation strategies if necessary. It is essential to adapt the methane emission quantification methods to the local conditions and measurement setup, and continue to study these methods. Therefore, conducting regular release experiments is recommended to generate a consistent and comprehensive dataset. Since biogas plants contribute to the local methane budget and can cause local pollution events, the stable isotopic source signature can offer valuable insights for accurately attributing the contribution of local emitters to the overall methane budget (Hoheisel and Schmidt [2024]). Methane produced through anaerobic digestion in biogas plants exhibits a wide range, spanning nearly 30 ‰, from -62.7 ‰ to -35.7 ‰, as measured in this thesis across 18 different plants. Other studies have observed even larger ranges, such as -68.4 % to -31.3 % (Nikolausz et al. [2013]). The δ^{13} CH₄ values mainly depend on the amount of fractionation on the specific reaction pathway. In this thesis, especially the feedstock substrate was found to be a major factor to influence the isotopic composition of the produced methane and therefore could offer good possibilities for source identification on a local level. $\delta^{13}CH_4$ source signature of separate plants can therefore be used to deduce the digestion process and type of feedstock.

In summary, this thesis highlights both the potential and the limitations of biogas plants as a renewable energy source. By using atmospheric mobile measurements in combination with a Gaussian plume model, CH_4 emission rates from 65 biogas plants were quantified. The findings raise concerns regarding the sustainability of biogas plants, as they have the potential to make up a large proportion of Germany's CH_4 emissions and high loss rates contribute to increased climate risks, in addition to posing significant hazard potentials. Independent measurements for the validation of emission factors as often used for oil and gas production sites, are also essential tools in the biogas sector, to inform and support plant operators and policymakers in achieving climate targets.

However, biogas plants offer substantial potential when managed effectively, as they not only prevent the release of methane through the open decomposition of manure and biowaste but also generate electricity, heat, and biofuel. Their flexibility in operation further positions them as a valuable complement to other renewable energy sources, such as wind, solar, and water energy. With the launch of the Global Methane Pledge in 2021, which has been joined by around 100 countries, including the US and the EU, the urgency of reducing methane emissions has reached the political level (COP27 - Global Methane Pledge [GMP]). Participating countries have committed to reduce anthropogenic methane emissions by 30 % by 2030 compared to 2020 levels. To address this, the EU Methane Regulation was introduced in August 2024, mandating measurement and reporting requirements for the fossil energy production and transport sectors. This thesis emphasizes the need for similar obligations to be applied to biogas production, especially for plants that are currently not covered by the Methane Regulation.

Appendix A

Calibration of CH_4 and $\delta^{13}CH_4$ measurements

A.1 Single-point calibration

In this thesis a single-point calibration is applied on samples measured in the laboratory on the CRDS analyzer. Therefore, the sample measurements are calibrated against the most recent calibration measurements before and after the sample measurement. An average value is calculated for each calibration measurement. A calibration value, $X_{intStd}(t_n)$, is determined for each time point (t_n) at which a sample is measured, $X_{meas}(t_n, by linear$ interpolation between the averaged calibration measurements. Each measurement data $point, <math>X_{meas}(t_n)$, is calibrated using an individual calibration line.

In the single-point calibration, this interpolation is represented as a linear relationship between the nominal calibration gas value, X_{nomStd} , and the interpolated calibration gas value, X_{intStd} . The calibration line is extended through the origin, and the sample measurement, X_{meas} , is calibrated using the following equation:

$$X_{\rm cal}(t_n) = \frac{X_{\rm nomStd}}{X_{\rm intStd}(t_n)} \cdot X_{\rm meas}(t_n)$$
(A.1)

aulindan	cylinder	\mathbf{CH}_4	$\delta^{13}{ m CH}_4$	\mathbf{CO}_2	$\delta^{13} \mathbf{CO}_2$
cynnder	number	[ppm]	[‰]	[ppm]	[‰]
Pic3_1	-	$2.004^{-2)}$	-48.1 ²⁾	475.55^{2}	-11.6 ²⁾
Target	-	$1.77^{-1)}$	$-47.99^{\ 2)}$	$366.7^{(1)}$	-8.8 ²⁾
$Sib1_8$	-	$10.953 \ ^{1)}$	-43.60^{1}	$402.03^{(1)}$	$-9.86^{1)}$
$Sib8_5$	-	$10.768^{-4})$	$-59.43^{(4)}$	440.0^{4}	$-9.78^{(4)}$
Deuste1	D563597	$9.92^{-3)}$	$-37.33^{(4)}$	<1.00	-
Deuste2	D484277	$10.05^{-3})$	-40.4 ⁴)	<1.00	-
Release1	D42NRR3	>99.5~%	$-41.89^{(4)}$	<1.00	-
Release2	D48W7DP	>99.5~%	-41.75 ⁴⁾	<1.00	-
UHEI4_3	D860391	$1.935^{-2)}$	$-47.89^{\ 2)}$	448.59^{-2}	-11.05 ²⁾
Pic14_1	-	$2.016^{-1)}$	$-48.39^{(1)}$	432.74^{-1}	-9.71 ¹⁾
Pic6_3	-	$2.082^{(1)}$	-48.48 ¹⁾	453.11^{-1}	-10.18 ¹⁾

Calibration standards A.2

Table A.1: Specification of gas cylinders used in this thesis. Indices mark different laboratories where the values were determined:

¹⁾ CRDS using Pic3_1 as calibration gas, $(\delta^{13} \text{ CH}_4: \pm 0.2 \%, \delta^{13} \text{CO}_2: \pm 0.06 \%)$ ²⁾ MPI Jena, IRMS: WMO Scale, $(\delta^{13} \text{ CH}_4: \pm 0.05 \%, \delta^{13} \text{CO}_2: \pm 0.02 \%)$ ³⁾ Deuste-Steininger: (CH₄, CO₂: ±2 %) ⁴⁾ CRDS using Sib1_8 as calibration gas, $(\delta^{13} \text{ CH}_4: \pm 0.2 \%, \delta^{13} \text{CO}_2: \pm 0.06 \%)$





Figure A.1: Measurement of calibration gas (Pic14_1) with the OF-CEAS analyzer between May 2022 and April 2024. Mean values of each calibration measurement with their standard deviation are shown in blue for CH_4 and red for CO_2 . Black lines indicate the mean values of all measurements for CH_4 and CO_2 , respectively.

Appendix B

Controlled CH_4 release experiments

B.1 Supplementary material on Mannheim and Heidelberg controlled release experiments



Figure B.1: Location of carpark in Mannheim for release experiments performed in 2018 and 2020. The map was created using leaflet for R (©Esri).



Figure B.2: (a) Example of a measured CH_4 excess^{*} during plume crossing with OF-CEAS (yellow) and CRDS (green), as well as modeled gauss fits to data in red and blue, respectively. (b) Corresponding integrals from measured and modeled data, as well as the calculated emission estimate. *This measurement was performed beyond the release experiments (Nelson [2020]) and is shown here for illustrative purposes only, without going into the data in more detail.



Figure B.3: Controlled release experiment MA3 time series with CH_4 mole fraction measured at different distances highlighted (blue = 14 m, yellow = 36 m) and determined emission rates in comparison to actual release rate for the different distances.



Figure B.4: Controlled release experiment HD2 time series with CH₄ mole fraction measured at different distances highlighted (blue = 4 m, yellow = 25 m, green = 50 m, light red = 70 m, light blue = 120 m and red: 260 m) and determined emission rates in comparison to actual release rate for the different distances. For visualization purposes, the y-axis is cut at 0.8 kgCH₄ h⁻¹ but the estimates for 4 m distance (highlighted in blue) exceed 1000 kgCH₄ h⁻¹.



Figure B.5: Controlled release experiment MA2 time series with with CH_4 mole fraction measured by bike (8 transects) in blue and by car (11 transects) in yellow and determined emission rates in comparison to actual release rate for the different vehicles.



Figure B.6: Measured and modeled cross sections of GPM during CH₄ plume crossing downwind of the source at a distance of x = 40 m, u = 2.5 m s⁻¹, T = 20 °C, z = 2.5 m and h = 1 m for different stability classes (A-D) at HD1.

stability	mean	accepted	mean relative to
class	$[kgCH_4 h^{-1}]$	transects	actual rate [%]
А	1.62 ± 0.22	29	271
В	0.87 ± 0.11	37	145
С	0.55 ± 0.06	43	92
D	0.38 ± 0.04	44	63
\mathbf{E}	0.23 ± 0.03	44	39
F	0.15 ± 0.02	40	25

Table B.1: Mean emission rate estimates (absolute and relative to the actual rate of 0.6 kgCH₄ h⁻¹) for 47 transects driven during the experiment MA1 for the stability classes A to F.

B.2 Supplementary material on TADI campaign



Figure B.7: Measured CH_4 mole fraction at different days of 2-liter calibration cylinder (Pic6_3) for stabilization control of LI-7810 (loaner) during TADI campaign 2024.

Release	Release	Release	Emission	Wind	Stability
ID	height	rate	estimate	speed	\mathbf{class}
	[m]	$[kgCH_4/h]$	$[kgCH_4/h]$	[m/s]	
RE1_1	0.6	0.59	0.55 ± 0.11	1.7	A-B
RE1_2	1.3	136.6	91.1 ± 14.5	2.1	A-B
RE1_3	1.1	24.8	9.4 ± 2.8	2.3	A-B
$RE1_4$	2.4	0.89	0.93 ± 0.28	2.3	A-B
$RE1_5$	1.1	46.2	55.0 ± 4.9	2.5	A-B
$RE1_6$	6.5	19.23	19.7 ± 8.1	1.8	A-B
$RE1_7$	1.8	32.18	20.4 ± 5.5	2.5	В
RE2_1	0	0.77	0.81 ± 0.08	1.4	A-B
RE2_2	1.2	1.95	1.66 ± 0.32	1.6	A-B
$RE2_3$	1.8	8.2	9.81 ± 1.37	1.9	A-B
$RE2_4$	1.1	32.1	42.2 ± 6.2	2.5	A-B
$RE2_5$	1.8	50.4	75.3 ± 7.9	2.8	В
$RE2_6$	1.1	21.7	22.6 ± 3.2	2.2	A-B
$RE2_{-7}$	1.1	54.9	75.4 ± 8.9	2.6	A-B
$RE2_8$	1.2	1.48	2.02 ± 0.34	2.5	В
RE3_1	3.0	1.62	0.31 ± 0.11	0.8	A-B
RE3_2	1.5	1.33	1.27 ± 0.30	1.1	A-B
RE3_3	6.5	9.71	5.01 ± 1.33	1.3	A-B
$RE3_4$	-	4.83	-	-	-
$RE3_5$	0.6	0.01	0.17 ± 0.04	1.7	А
RE3_6	1.1	44.0	34.1 ± 7.3	2.1	A-B
RE3_7	1.8	8.55	5.41 ± 1.57	2.3	В
RE3_8	-	0	0.53 ± 0.13	2.9	В
RE4_1	1.1	37.6	43.4 ± 4.4	1.5	A-B
$RE4_2$	1.1	42.1	28.1 ± 5.3	3.2	B-C
$RE4_{-}3$	2.4	0.57	$0.58 \pm 0.24^*$	2.7	D
$RE4_4$	1.8	8.55	$7.11 \pm 2.32^*$	3.0	D
$RE4_5$	1.8	13.9	17.3 ± 3.4	3.3	В
$RE4_6$	1.1	37.6	61.4 ± 10.7	4.4	В
$RE4_7$	1.3	81.3	114 ± 19	3.9	В
$RE4_8$	0.6	1.44	$0.92 \pm 0.24^*$	3.3	D
$RE5_1$	0.5	2.98	6.07 ± 1.11	1.6	A-B
$RE5_2$	1.2	0.32	0.23 ± 0.03	1.4	A-B
$RE5_3$	1.3	189	85.1 ± 12.4	1.0	A-B
$RE5_4$	6.5	19.23	29.3 ± 8.3	1.1	A

Table B.2: Overview of all relevant conditions during the one-week TADI 2024 campaign with 35 releases and determined emission rate estimates. Methane emission rates marked with an asterisk (*) are calculated using the OTM33-a method, while the rest are based on GPM.

Comparison of wind sensors during TADI campaign

A comparison of the performance of the Gill and Metek wind sensors was previously conducted in section 4.1. However, both anemometers were also deployed and used during the TADI campaign. Therefore, a further brief evaluation was made regarding the performance of both mobile and stationary anemometers in relation to the CH_4 emission estimates based on their measurements. The comparison showed that the performance of both instruments was similar, with an average deviation of 30 % between the calculated mean and the true release rate^{*} for both the Metek and Gill sensors. In only three instances did the measured wind speed differ by more than 1 m s⁻¹, which caused significant discrepancies in the calculated emission rates. These exceptional cases, highlighted in Fig. B.8 by a orange box around the affected release rate on the x-axis, emphasize the sensitivity of emission estimates to wind speed variations.

Overall, however, the results from both anemometers were in good agreement, indicating that the data provided were comparable for emission rate calculations. The occasional discrepancies observed in the three outlier cases suggest that variations in wind speed can have a notable impact on emission rate estimates, underscoring the importance of precise wind speed measurements for accurate emission calculations. Despite these exceptions, the overall consistency between the two instruments supports the reliability of the emission estimates derived from the TADI campaign, reinforcing the consistency of the results observed in earlier experiments conducted in Mannheim and Heidelberg (section 4.1).



*without 0 and 0.01 release

Figure B.8: Comparison of the actual and estimated CH_4 emissions rates with different anemometer (Metek-stationary; Gill-mobile). Estimated rates are given as mean of the corresponding determined transect values. Green circles indicate a data outage with the Metek (missing values were interpolated). During releases marked with a red asterisk, the wind speed was below 1 m s⁻¹. Orange boxes indicate measured wind speed differ by more than 1 m s⁻¹ between Metek and Gill.







(b)

Figure B.9: (a) Time series of measured CH_4 (black) and CO_2 (green) mole fractions with CH_4 background fit in blue during release with 0.01 kg CH_4 h⁻¹ release rate (RE3_5). (b) Map with color-coded CH_4 mole fractions along the driving route. The map was created using leaflet for R (©Esri).

B.3 Other Test Method 33-a

The second method to estimate emission rates of a point-source, also based on the Gaussian approach, is the Other Test Method (OTM) 33-a. A more detailed description and its application can be found in the studies by Brantley et al. [2014], Thoma and Squier [2014], Robertson et al. [2017], Omara et al. [2018], Edie et al. [2020] and Heltzel et al. [2020]. Developed by the US Environmental Protection Agency (EPA), the concept is based on stationary measurements of mole fraction of a trace gas as a function of the wind direction (Thoma and Squier [2014]). The method is similar to the GPM method, but instead of moving the analyzer through the plume, it uses high-resolution mole fraction and wind measurements at a stationary point aligned with the main wind direction, facing downwind of the source. The wind transports the plume towards the observation point and the variability in the wind direction during the measurement causing a Gaussian distribution of the measured gas mole fraction relative to the wind direction (see Fig. B.10). This means that the highest mole fraction of the measured gas occurs in the main wind direction in to which the measurement setup is aligned (Thoma and Squier [2014], Omara et al. [2018]). For the application and analysis using this method, this thesis follows the study by Korbeń et al. [2022]. Wind speed and direction as well as an atmospheric stability class (Point Gaussian Indicator (PGI)) are determined from the meteorological measurements for data analysis. The PGI values are calculated and averaged using the standard deviation of the wind direction and the standard deviation of the vertical wind speed (turbulence intensity), according to the EPA guideline. The maximum methane mole fraction C is determined applying a Gaussian fit on the mean methane mole fraction as a function of binned wind direction. Equation B.1 can then be used to calculate the CH_4 emission rate Q.

$$Q = 2\pi\sigma_y \sigma_z uC \tag{B.1}$$

where σ_y and σ_z are the horizontal and vertical dispersion coefficients, u is the mean wind speed, and C is the maximum mole fraction from the Gaussian fit. To ensure data quality, three Data Quality Indicators (DQI) are considered: (1) the position of the fitted peak methane mole fraction should be within $\pm 30^{\circ}$ of the source direction to detect possible interference, (2) the average CH₄ enhancement in the plume should be greater than 200 ppb to ensure that there was no background variation, and (3) the Gaussian fit curve should correlate with the integrated measurements with an R² value greater than 0.8 to detect possible interference and obstructed wind flow conditions and avoid capturing multiple sources in a single plume (Brantley et al. [2014]); Omara et al. [2018]). The uncertainty is calculated using uncertainty propagation for Eq. B.1, considering the uncertainties of the horizontal and vertical dispersion coefficients, the calculated wind speed and the modeled methane mole fraction.



Figure B.10: Top-down view on example illustrating a representative gas concentration profile in terms of wind direction. This figure is a re-illustration of the originally figure by Thoma and Squier [2014] with elements of Andersen [2021].

B.3.1 OTM33-a during AirField campaign

An additional measurement was conducted during the AirField campaign to validate the OTM33-a method. A comprehensive uncertainty analysis, measurement duration assessment, and validation of the stability class averaging methodology were previously carried out by Korbeń [2021]. The OTM measurements from the MA2 and MA3 campaigns in 2020 have been analyzed and discussed in detail in his thesis, and are only briefly referenced here for context. To ensure the robustness of the measurement setup and its evaluation with this method, a further OTM measurement was conducted during HD2 in 2023. Methane was released with a rate of 0.3 kg h^{-1} and measurements were conducted with the OF-CEAS trace gas analyzer in combination with the 3D-anemometer at a distance of 50 m downwind from the release point. The measurement duration was one hour, with an average wind speed of 2.2 m s^{-1} and atmospheric conditions indicated a PGI of 4. For improved repeatability, the analysis was conducted using 20-minute moving intervals (Korbeń [2021]). The Gauss fit applied to the measured CH_4 enhancement above the background versus binned wind direction, is shown in Fig. B.11. The measurement successfully met all three criteria of DQIs, with an average CH_4 enhancement of 175 ppb above background and an \mathbb{R}^2 of 0.96. Consequently, the data were considered reliable and were accepted for further analysis. The emission rate calculation, based on the data collected, resulted in an estimated methane emission rate of 0.36 ± 0.14 kgCH₄ h^{-1} . This value deviates by approximately 20 % from the actual release rate of 0.3 kgCH₄ h^{-1} , indicating a minor overestimation. This is consistent with the findings of Korbeń [2021] (and Edie et al. [2020]), who similarly observed slight overestimation in emission rate calculations when applying the OTM method to small release rates during MA2 and MA3 in 2020 with the same measurement setup.

The results confirm the validity of the OTM33-a method in determining methane emissions under controlled conditions, with small deviations from the actual release rate. The



method's precision and reliability, as evidenced by the DQIs and the calculated emission rate, provide strong support for its application in field campaigns to point sources.

Figure B.11: CH₄ enhancement above background against binned wind direction, where 0° corresponds to the main wind direction. The original 1-Hz CH₄ mole fractions are plotted as black dots, the mean CH₄ mole fractions averaged over a wind direction bin of 10° as blue dots and the corresponding Gaussian fit in red (R² = 0.96).

B.3.2 OTM33-a during TADI campaign

Three OTM33-a measurements were performed as part of the TADI campaign. All of these measurements took place on the fourth day of the campaign, as the most stable wind conditions were present on this day, which is a requirement for the conduction of OTM measurements. The measurements were carried out at a distance of 120 m from the release point and lasted 45 minutes each. Based on the parametrization according to the standard deviation of the wind direction and the turbulent intensity (section B.3), these measurements were assigned to PGI 4.

The comparison of results before and after the release location adjustment in the OTM measurements reveals a significant improvement: the average deviation from the true release rate decreases from 34 % to 8 %. All three releases show a significant improvement in accuracy compared to the true value. Therefore, it can be concluded that, in this case, the adjustment of the release location, including the source position and distance to it, has a greater impact on the emission rate calculation using the OTM method compared to the GPM method. Korbeń [2021], already pointed out that the OTM method is sensitive to this parameter.

According to the DQI ($\mathbb{R}^2 > 0.8$), the measurement RE4.4 represents a non-accepted OTM measurement, as the applied Gaussian curve fit for this measurement only has an \mathbb{R}^2 value of 0.7. Although this measurement was classified as rejected, the measurement showed a not significant deviation of only 17 % from the actual release value (adjusted release location). Similar are the cases RE4.3 and RE4.8, which are rejected by the DQI of average 100 ppb above background to ensure a sufficient plume transport. But here only deviations of 2 % and 6 %, respectively, indicate that even measurements with less ideal fits and lower average CH₄ enhancement can still provide useful results that are within the uncertainty range. Korbeń [2021], suggested to lower the DQI criteria to an $\mathbb{R}^2 > 0.7$ and reduce the condition of average CH₄ enhancement from 100 ppb to 50 ppb in cases of low emission rates and distances above 100 m. This would allow to accept the performed OTM measurements during the TADI campaign. Figure B.12 shows RE4.8 as an example of processed OTM33-a data as a function of wind direction. In this case, the average wind speed was 3.2 m s⁻¹ and the average CH₄ enrichment was 0.92.

The results show that the OTM33-a method is a useful tool for estimating emission rates, even if not all DQIs are met. The accuracy of the estimation is mainly influenced by the stability of the measurement conditions and the correct location input of release point and measurement position.



Figure B.12: Example of OTM 33-a measurement for RE4_8. CH₄ enhancement above background against binned wind direction, where 0° corresponds to the main wind direction. The original 1-Hz CH₄ mole fractions are plotted as black dots, the mean CH₄ mole fractions averaged over a wind direction bin of 10° as blue dots and the corresponding Gaussian fit in red ($\mathbb{R}^2 = 0.92$).

Appendix C

Determination of δ^{13} CH₄ values and offset parameter

The CRDS G2201-i isotope analyzer was sent to Picarro in the USA for repair in July 2020. The cavity was replaced and other repairs were carried out and the instrument was returned one year later. Prior to the repair of our instrument, the CRDS G2201-i showed no significant influence of CH₄ on the reported δ^{13} CH₄ values, as discussed in Dinger [2014] and Hoheisel [2017]. Nevertheless, a significant effect was reported in the study by Miles et al. [2018] for the four instruments they analyzed. Due to significant repairs being made to our measurement device, the CRDS was re-characterized and at the time of this initial new characterization by Grandke [2022] in August 2022, no influence of CH₄ on δ^{13} CH₄ was reported.

However, during the course of 2022, a change was noticed in the regularly measured standard gas values. Figure C.1 shows the time series of the measured δ^{13} CH₄ raw values of our calibration standard (Pic3_1). It can be clearly seen that the measured values shift downwards at the end of 2022 (highlighted in gray). Repeating the tests led to the finding of a now significant effect of the methane mole fraction on the δ^{13} CH₄ isotope values. A comprehensive analysis using dilution series was carried out by Pfau [2023] and a first attempt to correct the measured δ^{13} CH₄ values was made.

Through further intensive investigation and close communication with Picarro support, it was eventually concluded that an internal offset parameter had changed. A derivation for the offset parameter is described in the study by Rella et al. [2015b], but according to Picarro it was implemented in a slightly modified form in the software of the measuring devices themselves. The δ^{13} CH₄ values were recalculated by M. Feuerle as part of his ongoing master's thesis based on the personal communication with Picarro and used accordingly throughout this thesis.



Figure C.1: δ^{13} CH₄ measurements of the calibration cylinder Pic3_1. The black vertical lines represent instances where the offset parameter was changed (from -0.00555535148055 to 0). The gray shaded area highlights the period during which the δ^{13} CH₄ values were manually recalculated using a determined offset parameter afterwards.

Appendix D

Biogas plants

D.1 Determination of CH₄ production rate

The production rates of methane and biogas can be determined via the electric production rate (P) of the CHP unit and is given in norm cubic per hour [Nm³ h⁻¹]. With the assumption of an electric efficiency (η) of 38 % and a methane content depending on feedstock of 52-60 % we can use the following equation:

CH₄ production rate =
$$\frac{P}{\eta} \cdot e$$

(D.1)
biogas production rate = CH₄ content $\cdot \frac{P}{n} \cdot e$

The energy factor (e) is given by $e = \frac{3.6}{H \cdot \rho}$ using the methane density (ρ) of 0.67 kg m⁻³ (20 °C, 1 atm) and a CH₄ heating value (H) of 50 MJ kg⁻¹. For energy crops as the primary feedstock, a methane content of 52 % in the biogas is assumed, 55 % for manure, and 60 % for organic waste. This assumption is based on the potential gas production and CH₄ content of various substrates (see Fig. D.1), where energy crops yield a higher volume of biogas but with a lower CH₄ content and a higher proportion of CO₂, whereas manure and organic waste produce less biogas but with a higher CH₄ content (LfL, FNR - Fachagentur Nachwachsende Rohstoffe e.V. [c]).



Figure D.1: Guide values for the gas production of various biogas substrates and their average methane content as provided by FNR - Fachagentur Nachwachsende Rohstoffe e.V. [c].

D.2 On-site leak surveys





(c)

Figure D.2: (a) Survey of leak and on-site emission sources with the OF-CEAS analyzer carried in a backpack system. (b) Close-up on scanning for any weak points at the digestate cover. (c) Measured methane enhancement (> 500 ppm CH_4) at a CHP unit.



Figure D.3: Surveyed biogas plants with detected CH_4 emission sources marked as points with corresponding color indicating if the source is reported as major (> 200 ppm: red), medium (50-200 ppm: orange) or small (\leq 50 ppm: yellow). Emission source detection is based on measurement surveys with the OF-CEAS analyzer for biogas plant (a)-(g). Plants (h) and (i) were investigated via gas imaging and remote laser detection by the UK team and the operator of plant (j) reported one major leakage.

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Plant ID Fee BM-01 ^{1,2,3} Mc			Ctont of	D	C.Latacto	normonerrit			
$BM-01^{1,2,3} M_{\rm f}$	deral state	type	operation	f tunaty feedstock	[t/yr]	capacity [kWel]	power [kWel]	production $[m^3/h]$	production $[m^3/h]$
	eckVorp.	agr	2009 2023 LNG	energy crops	150,000	54,000	/	$3,462^{*}$	1,800
$BM-02^{1,2}$ M_{ϵ}	eckVorp.	agr	2005 2013 upgrader	energy crops	184,000	21,900	2,750	2,800	1,600
$BM-03^{1,2,4}$ M_{ϵ}	eckVorp.	agr	2006	energy crops	39,500	4,380	2,900	$2,019^{*}$	1,050
BM-04 ^{1,5,6} Ba	ıWü.	agr	2008 (I) 2011(II)	energy crops		3,600 3,900	/	1,200	700
$BM-05^{1,2}$ M_{ϵ}	eckVorp.	agr	2023	energy crops	80,000	8,500	_	1,346*	700
$BM-06^{1,2}$ M_{ϵ}	eckVorp.	agr	2018	energy crops	55,000	7,500	/	1,346*	700
$BM-07^{1,7}$ Ba	waria	waste	2009	organic waste	_	6,900	/	1,060	069
BM-08 ^{1,5,8} Ba	Wü.	agr	2011 2012 upgrader	energy crops	50,000	3,500 $3,500$	/	1,260	580
BM-09 ^{1,5,8} Ba	Wü.	agr	2006 2010 upgrader	energy crops	33,000	4,000	/	900	530
BM-10 ^{1,9} He	ssen	agr	2008 2011 upgrader	energy crops	32,500	5,130	/	820	440
BM-11 ^{1,5} Ba	Wü.	agr	2008 2014 upgrader	energy crops	/	3,700	/	650	350
$BM-12^{1,10}$ He	ssen	agr	2010	energy crops	16,000	2,270	/	360	190

Further information are based on ² Energieatlas-MV, ³ AG, ⁴ DAH Gruppe, ⁵ Energieatlas-BW, ⁶ ÈTW-Energietechnik, ⁷ schwaben-regenerativ, Badenova, ⁹ Table D.1: Technical information for surveyed biomethane plants. Biomethane production rate given as methane injected into the natural gas grid and start of operation are based on 1 dena. Einspeiseatlas. Biogas production rates marked with an asterisk (*) are calculated based on the produced biomethane rate. HEMS, ¹⁰ Oekobit

e.																											ĺ
Calc. biomethan [m ³ /h]	376	297	215	188	175	130	130	126	116	113	111	111	111	107	107	105	105	101	100	97	97	95	93	93	93	93	-townomicton
Calc. biomethane production [m ³ /h]	562	443	321	281	261	194	194	188	174	168	165	165	165	159	159	156	156	151	148	145	145	142	139	139	139	139	1 Moulatomu
Calc. biogas production [m ³ /h]	1,080	852	618	540	501	373	373	362	334	305	317	317	300	306	306	301	301	251	284	241	278	273	267	267	253	253	and hosed on
Produced power [kWel]	1,940	1,530	1,110	970	006	670	670	650	600	580	570	570	570	550	550	540	540	520	510	500	500	490	480	480	480	480	
Installed capacity [kWel]	2,580	1,600	2,200	1,200	10,850	1,440	700	690	2,100	1,220	600	1,400	600	1,000	026	780	2,550	1,080	530	510	520	520	1,400	500	500	026	-
Substrate [t/yr]			8,400	24,500		25,000		10,220	19,200																		
Primary feedstock	energy crops	energy crops	organic waste	energy crops	energy crops	energy crops	energy crops	energy crops	energy crops	manure	energy crops	energy crops	manure	energy crops	energy crops	energy crops	energy crops	organic waste	energy crops	organic waste	energy crops	energy crops	energy crops	energy crops	manure	manure	- - -
Start of oper- ation	2008	2008	2019	2007	2005	2007	2007	2012	2012	2007	2007	2011	2012	2007	2007	2008	2009	2005	2011	2002	2005	2006	2005	2006	2004	2007	-
Plant type	agr	agr	waste	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	waste	agr	waste	agr	agr	agr	agr	agr	agr	
Federal state	BaWü.	MeckVorp.	BaWü.	Hessen	BaWü.	BaWü.	BaWü.	BaWü.	Hessen	BaWü.	BaWü.	BaWü.	MeckVorp.	BaWü.	BaWü.	BaWü.	SchlHol.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	
Plant ID	$BG-01^{1,3}$	$BG-02^{1,4,5}$	$BG-03^{1,2}$	$BG-04^{1,2,6}$	$BG-05^1$	$BG-06^{1,7}$	$BG-07^{1}$	$BG-08^{1,8}$	$BG-09^2$	$BG-10^{1,8}$	$BG-11^{1,2}$	$BG-12^{1,9}$	$BG-13^{1,4}$	$BG-14^{1}$	$BG-15^1$	$BG-16^1$	$BG-17^1$	$BG-18^{1,10}$	$BG-19^{1,11}$	$BG-20^{1,3,11}$	$BG-21^1$	$BG-22^{1}$	$BG-23^{1,2}$	$BG-24^{1,12}$	$BG-25^{1} *$	$BG-26^{1} *$	• • •
Category	large	large	large	large	large	large	large	large	large	large	large	large	large	large	large	large	large	medium	medium	medium	medium	medium	medium	medium	medium	medium	

APPENDIX D. BIOGAS PLANTS

Calc. biomethane [m ³ /h]	87	83	83	83	74	74	74	20	68	68	62	60	60	47	43	41	39	37	37	37	33	29	15	15	15	15	15
Calc. biomethane production [m ³ /h]	130	124	124	124	110	110	110	104	101	101	93	00	90	69	64	61	58	55	55	55	49	43	22	22	22	22	22
Calc. biogas production [m ³ /h]	237	239	226	239	212	200	212	200	195	195	178	150	163	134	122	117	105	106	106	100	89	62	39	39	39	39	39
Produced power [kWel]	450	430	430	430	380	380	380	360	350	350	320	310	310	240	220	210	200	190	190	190	170	150	75	75	75	75	75
Installed capacity [kWel]	1,050	1,540	1,700	1,960	1,285	800	790	400	260	770	1,000	1,000	330	240	350	450	400	200	190	590	190	150	75	75	75	75	75
Substrate [t/yr]			11,360	1,300			7,500				8,580																
Primary feedstock	manure	energy crops	manure	energy crops	energy crops	manure	energy crops	energy crops	energy crops	energy crops	energy crops	organic waste	manure	energy crops	energy crops	energy crops	manure	energy crops	energy crops	manure	manure	manure	manure	manure	manure	manure	manure
Start of oper- ation	2009	2006	2009	2011	2008	2009	2010	2010	2007	2011	2020	1993	2006	2009	2013	2006	2010	2011	2007	2008	2011	2023	2019	2017	2019	2016	2018
Plant type	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	waste	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr	agr
Federal state	BaWü.	BaWü.	Hessen	BaWü.	BaWü.	BaWü.	BaWü.	SchlHol.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	Hessen	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.	BaWü.
Plant ID	$BG-27^{1,2}$	$BG-28^{1}$	$BG-29^{1,2}$	$BG-30^{1,2}$	$BG-31^{1,2}$	$BG-32^{1,8}$	$BG-33^{1,8}$	$BG-34^1$	$BG-35^1$	$BG-36^{1}$	$BG-37^1$	$BG-38^{1,2}$	$BG-39^{1} *$	$BG-40^{1,13} *$	$BG-41^{1,14}$	$BG-42^{1}$	$BG-43^1$	$BG-44^{1}$	$BG-45^1$	$BG-46^{1,15}$	$BG-47^{1,11}$	$BG-48^{1}$	$BG-49^{1} *$	$BG-50^{1,2} *$	$BG-51^{1}$	$BG-52^{1,10*}$	$BG-53^{1}$
Category	medium	medium	medium	medium	medium	medium	medium	medium	medium	medium	medium	medium	medium	small	small	small	small	small	small	small	small	small	small	small	small	small	small

Table D.3: Technical information for surveyed biogas plants, pt. 2. Produced electrical power and start of operation are based on ¹ Markstammdatenregister. Plants marked with a asterisk (*) are located in the close vicinity to a cowshed. Further information are based on ² operator interview,³ Energieatlas-MV, ⁵ Ducherower Agrar,⁶ HEMS, ⁷ Badenova, ⁸ Energieatlas-BW, ⁹ SWR aktuell Baden-Württemberg, ¹⁰Lichtner, ¹¹ Energymap, Deutsche Gesellschaft für Sonnenenergie e.V., ¹²Seiler GmbH, ¹³ Bioenergiedörfer - FNR, ¹⁴ KWA-AG, ¹⁵ Birkenhof

D.3. TECHNICAL DETAILS OF INVESTIGATED BIOGAS PRODUCTION SITES

					1	1	1						1				1	1	1						1	1	_
Distance	[m]	154	229	32	210	111	172	191	162	286	28	156	95	163	332	260	30	262	240	246	59	29	181	243	27	308	172
		D	D	A-B	D	В	C	C	Ð	в	В	C	A-B	B-C	C	A-B	В	U	C	C-D	в	A-B	Ð	C	D	B-C	D
Radiation	$[\mathrm{W} \mathrm{m}^{-2}]$	537	651	562	511	157	325	190	0	0	4	263	594	650	56	966	543	48	310	850	389	505	/	54	89	590	389
Ws	$[m s^{-1}]$	9.5	5.7	1.1	5.6	1.2	3.4	2.2	3.0	1.4	1.5	3.8	1.4	2.5	2.2	2.0	2.1	3.7	3.7	4.4	1.9	1.3	3.2	2.7	2.0	3.0	2.2
Μd	[0]	219	135	154	218	195	274	182	133	40	154	273	123	256	165	184	153	168	168	347	177	126	160	152	143	218	175
$Max CH_4$	[mdd]	3.9	3.3	3.2	2.5	10.5	2.7	7.9	22.4	2.3	19.2	6.8	18.8	6.2	3.3	4.0	6.8	3.8	3.8	3.3	13.9	14.4	13.2	12.4	15.2	2.3	10.9
#	Peaks	6	33	33	3	×	5	9	4	33	33	9	7	6	×	13	×	33	16	18	10	×	14	16	9	4	15
#	Transects	10	6	9	7	11	×	10	5 L	4	10	ç	6	16	12	22	15	36	20	20	16	11	22	24	10	21	23
o	$[\mathrm{kg} \ \mathrm{CH_4} \ \mathrm{h^{-1}}]$	3.74 ± 1.44	5.90 ± 2.52	0.58 ± 0.18	7.85 ± 6.23	3.64 ± 1.12	9.29 ± 4.32	4.97 ± 2.84	13.64 ± 4.14	4.46 ± 2.48	6.34 ± 0.32	4.10 ± 2.18	5.65 ± 2.70	10.94 ± 2.48	5.94 ± 1.19	4.54 ± 0.58	3.10 ± 0.29	6.77 ± 0.68	5.76 ± 0.58	5.69 ± 0.40	4.79 ± 0.50	4.54 ± 0.36	6.08 ± 0.61	5.00 ± 0.32	6.12 ± 1.12	4.97 ± 0.54	2.88 ± 0.32
, ,	Date	29.08.2016	08.09.2016	12.09.2016	28.09.2016	10.10.2016	02.11.2016	30.11.2016	10.01.2018	26.11.2018	17.12.2018	24.07.2019	30.01.2020	11.09.2020	12.11.2020	08.07.2022	05.10.2022	24.01.2023	16.05.2023	04.08.2023	28.09.2023	10.10.2023	18.12.2023	09.02.2024	01.03.2024	17.06.2024	07.08.2024
	.0N	1	2	n	4	5	9	7	×	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26

Long-term monitoring at a local biogas plant

Table D.4: Overview of measurements carried out between 2016 and 2024 at a local biogas plant. Hoheisel [2017] carried out measurements between 2016 and 2018 (light blue), followed by Korbeń [2021] (blue), who carried out measurements between 2018 and 2021. Measurements performed as part of this thesis are indicated in green.
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\mathbf{CH}_4	
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CH_4	loss SE	[%]	3.75	0.14	0.73	0.05	0.31	0.31	0.88	0.09	0.68	0.96	1.04	2.86
CH_4	\log	[%]	17.5	2.56	8.29	0.35	2.19	2.19	5.43	1.16	5.01	3.41	4.89	16.1
Emission	rate SE	$[\rm kgCH_4/h]$	47.0	1.50	5.20	0.25	1.453	1.45	4.10	0.34	2.43	2.87	2.47	3.75
Emission	rate	$[\rm kgCH_4/h]$	255.4	28.21	63.61	1.66	10.49	10.49	26.54	4.55	18.72	10.42	12.06	24.35
Dradmond		[kgCn4/n]	1,206	1,072	704	469	469	469	462	389	355	295	235	127
Dictonoo		[m]	640	150	130	60-100	80	80	140	2,220	810	270-450	135	110
Max	CH_4	[mdd]	9.2	4.2	7.1	10.6	13.3	13.3	11.3	2.1	2.8	5.1	7.2	57.0
Min	CH_4	[mdd]	2.0	3.4	4.8	2.1	4.3	4.3	2.2	2.1	2.2	2.14	2.9	2.4
A comtod	Accepted	peaks	14	33	33	75	15	15	34	21	14	73	x	61
Dritton		uransecus	22	14	10	119	18	18	40	21	14	102	15	20
Number of	measurement	campaigns	1	1	1	IJ	1	1	c.	1	1	IJ	1	4
	Plant ID		BM-01	BM-02	BM-03	BM-04	BM-05	BM-06	BM-07	BM-08	BM-09	BM-10	BM-11	BM-12

direction at the time of measurement, it was only possible to measure within the CH₄ plume of both together. As the plants are essentially identical in terms of Table D.5: Emission rates for all upgrading biomethane plants. BM-05 and BM-06 are located next to each other and therefore, as well as due to the given wind production capacity and gas utilization, the emission rate was split equally for both plants.

CH_4	loss SE	[%]	0.05	3.25	0.54	4.55	0.78	0.78	1.35	0.90	3.55	0.11	0.33	0.17	1.38	0.20	0.57	0.32	0.44	0.18	0.34	0.51	0.33	0.34	0.44	2.05	0.50	0.29
CH_4	$\log s$	[%]	0.29	25.03	4.08	22.07	4.07	5.07	8.02	2.56	10.89	0.40	2.96	3.22	7.79	10.15	5.47	5.14	1.07	2.05	4.21	4.92	2.12	4.55	6.71	6.31	1.79	0.98
Emission	rate SE	$[\rm kgCH_4/h]$	0.18	9.97	1.18	8.96	1.38	1.02	1.78	1.14	4.28	0.12	0.37	0.19	1.55	0.22	0.62	0.34	0.47	0.18	0.34	0.50	0.32	0.32	0.41	1.95	0.47	0.27
Emission	rate	$[\mathrm{kgCH_4/h}]$	1.08	99.07	9.16	53.26	7.41	6.94	11.33	3.33	14.22	0.45	3.37	3.68	9.34	12.05	6.17	5.67	1.13	2.12	4.35	5.02	2.10	4.53	6.70	6.27	1.69	0.92
Droduced	[] ² UTUUUU		376	297	215	188	175	130	130	126	116	113	111	111	111	107	107	105	105	101	66	97	97	95	93	93	93	93
Dietance	[m]	[TTT]	120	180	320-350	230	230	230	200	55	120	320	220-420	160	250	170-300	100-260	170	130	30	230	30-300	230-520	200	110-220	410	120	90
Max	CH_4	[ppm]	3.1	23.6	4.1	12.3	2.4	3.6	13.1	5.0	27.6	2.1	2.6	2.9	2.9	3.0	4.1	3.9	4.0	9.6	2.9	52	2.8	3.6	2.9	3.0	8.9	3.2
Min	CH_4	[ppm]	2.2	4.1	2.2	2.3	2.3	2.3	2.2	3.4	3.1	2.0	2.0	2.5	2.5	2.3	2.4	2.2	2.8	2.9	2.4	2.3	2.1	2.6	2.5	2.0	2.1	2.5
Accented	neals	cabad	14	18	34	26	9	17	11	ъ	4	6	41	6	12	31	26	46	ю	11	2	239	10	34	7	17	15	9
Driven	transacts	en der the th	20	18	44	26	10	20	13	11	21	10	63	10	14	41	30	48	14	20	10	372	17	37	16	26	21	6
Number of	measurement	campaigns	1	1	2	2	1	1	1	1	1	1	3	1	1	3	2	2	1	1	1	12	2	2	33	2	1	1
	Plant ID		BG-01	BG-02	BG-03	BG-04	BG-05	BG-06	BG-07	BG-08	BG-09	BG-10	BG-11	BG-12	BG-13	BG-14	BG-15	BG-16	BG-17	BG-18	BG-19	BG-20	BG-21	BG-22	BG-23	BG-24	BG-25	BG-26

| IOS SEL | 1.23 | 0.23 | 1.85 | 0.12

 | 0.60 | 0.66 | 0.49
 | 1.31

 | 0.08

 | 0.68 | 0.10 | 0.28 | 1.64 | 1.86 | 0.17 | 2.15

 | 0.00 | 0.58
 | 1.40 | 3.92 | 0.49 | 0.81 | 7.73
 | 1.37 | 3.14 | 6.89 | 9.75 |
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---|---|---
---|--|
| Ioss
[%] | 7.75 | 1.86 | 5.99 | 1.00

 | 2.15 | 5.29 | 2.08
 | 12.14

 | 0.92

 | 3.30 | 0.46 | 2.51 | 9.31 | 4.56 | 2.48 | 12.22

 | 9.06 | 5.53
 | 15.88 | 11.84 | 3.02 | 3.37 | 18.44
 | 6.32 | 8.61 | 38.37 | 26.76 |
| [kgCH ₄ /h] | 1.09 | 0.19 | 1.57 | 0.10

 | 0.44 | 0.49 | 0.36
 | 0.93

 | 0.06

 | 0.47 | 0.07 | 0.17 | 1.00 | 0.88 | 0.07 | 0.89

 | 0.01 | 0.21
 | 0.52 | 1.50 | 0.16 | 0.24 | 1.22
 | 0.20 | 0.471 | 1.08 | 1.57 |
| raue
[kgCH ₄ /h] | 7.33 | 1.58 | 5.31 | 0.86

 | 1.62 | 4.12 | 1.57
 | 9.65

 | 0.63

 | 2.32 | 0.28 | 1.55 | 6.17 | 2.22 | 1.09 | 5.67

 | 3.87 | 2.16
 | 6.95 | 4.95 | 1.03 | 1.02 | 3.29
 | 0.98 | 1.371 | 9.06 | 5.31 |
| $[\rm kgCH_4/h]$ | 87 | 83 | 83 | 83

 | 74 | 74 | 74
 | 20

 | 68

 | 68 | 62 | 09 | 60 | 47 | 43 | 41

 | 39 | 37
 | 37 | 37 | 33 | 29 | 15
 | 15 | 15 | 15 | 15 |
| [m] | 200-580 | 160 | 300 | 240-270

 | 170 | 360 | 260
 | 200

 | 90-130

 | 220-400 | 20 | 110 | 105 | 110 | 40 | 200

 | 270 | 660
 | 170 | 460 | 220 | 70-230 | 90
 | 50 - 300 | 560 | 190 | 260 |
| Cn4
[ppm] | 4.3 | 3.5 | 3.2 | 3.0

 | 2.4 | 2.3 | 2.5
 | 4.9

 | 3.0

 | 2.5 | 2.5 | 2.6 | 4.1 | 5.1 | 3.2 | 4.3

 | 2.6 | 2.2
 | 2.8 | 2.7 | 2.3 | 6.7 | 8.2
 | 4.2 | 2.4 | 3.7 | 3.8 |
| [ppm] | 2.2 | 2.2 | 2.4 | 2.1

 | 2.1 | 2.2 | 2.1
 | 2.8

 | 2.3

 | 2.1 | 2.2 | 2.2 | 2.8 | 2.2 | 2.3 | 2.2

 | 2.6 | 2.1
 | 2.2 | 2.2 | 2.1 | 2.2 | 2.3
 | 2.0 | 2.3 | 2.9 | 2.8 |
| peaks | 54 | 16 | 2 | 33

 | 6 | 10 | 11
 | 14

 | 23

 | 57 | e
S | 21 | 21 | × | 4 | 27

 | 1 | 8
 | 19 | 8 | 6 | 24 | 18
 | 31 | 2 | 6 | 10 |
| transects | 74 | 17 | 20 | 45

 | 13 | 11 | 20
 | 17

 | 38

 | 71 | e. | 23 | 21 | 10 | 10 | 40

 | 9 | 11
 | 25 | 17 | 10 | 33 | 20
 | 51 | ъ | 12 | 10 |
| tmeasurement
campaigns | 4 | 1 | 1 | 2

 | 1 | 1 | 1
 | 1

 | 2

 | 4 | 1 | 1 | 1 | 1 | 1 | 3

 | 1 | 1
 | 2 | 1 | 1 | က | 1
 | 3 | 1 | 1 | 1 |
| | BG-27 | BG-28 | BG-29 | BG-30

 | BG-31 | BG-32 | BG-33
 | BG-34

 | BG-35

 | BG-36 | BG-37 | BG-38 | BG-39 | BG-40 | BG-41 | BG-42

 | BG-43 | BG-44
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D.4. DETERMINED CH₄ EMISSION RATES AND LOSS RATES OF INVESTIGATED BIOGAS PRODUCTION SITES

Table D.7: Overview of measurement campaigns for biogas plants and determined CH_4 emission rates and CH_4 loss rates for all biogas plants, pt.2 (medium plants: BG-27 to BG-39, small plants: BG-40 to BG-53). At plants marked in gray, less than 10 transects were driven for CH_4 emission rate quantification, caused by complications during the measurement process.



Figure D.4: Boxplot showing determined CH₄ emission rates according to the four biogas facility categorizations. The 'small' category includes 14 plants with electricity production ≤ 250 kW (biogas rate ≤ 150 m³ h⁻¹). The 'medium' category has 22 plants producing between 250 and 520 kW (biogas rate from 150 to 300 m³ h⁻¹). 'Large' includes 17 plants with electricity > 520 kW and biogas > 300 m³ h⁻¹, with upgrading plants classified separately. Boxes represent the first and third quartile of the data, while whiskers extend to the largest value that is within 1.5 times the interquartile range.



Figure D.5: Barplot showing determined CH₄ loss rates according to the four biogas facility categorizations. The 'small' category includes 14 plants with electricity production ≤ 250 kW (biogas rate $\leq 150 \text{ m}^3 \text{ h}^{-1}$). The 'medium' category has 22 plants producing between 250 and 520 kW (biogas rate from 150 to 300 m³ h⁻¹). 'Large' includes 17 plants with electricity > 520 kW and biogas > 300 m³ h⁻¹, with upgrading plants classified separately.



Figure D.6: CH₄ loss rates plotted against CH₄ production rate, differentiating between small (n=14), medium (n=22) and large (n=17) biogas plants as well as biomethane plants (n=12).



Figure D.7: CH_4 loss rates plotted against CH_4 production rate, differentiating between primary feedstock (manure (n=17), energy crops (n=43) and bio waste (n=5)).

Plant part	Туре	Best practice [%]	Standard practice [%]	Emissions for standard practice [g CO ₂ eq/MJ]	
biogas processing	piping, maintenance, overpressure events, leaks	0.5	5.0 (<mark>0.0)</mark>	24.3	
digestate	digestate composting or storage [silage] [biowastes] [manure]	0.1 (0.0)	2.2 2.5 10.0	11.3 13.0 53.5	
management	storage with RMP measurement below the proposed default emission factor for (open) digestate storage	X = RMP * 0.25	X= RMP * 0.75	(X - 0.1) * 5.4	
	Any technology	0.0	3.0	16.2	
Biogas upgrading to biomethane	Technologies certified or measured to have < 0.2% of produced methane in the off-gas	C	.2	15.1	
	Technologies certified or measured to have < 1% of produced methane in the off-gas	1	.0	10.8	
Biogas use in CHP	Slippage of methane in the exhaust gas	1	.7		

Colours: Same as in current RED II

Newly proposed value in this study

(Current RED II value)

Table D.8: Summary of emission factors in (% of produced methane) proposed by Buffi et al. [2024] for standard and best practices for all processing steps compared to RED II values.

Appendix E

Stable isotopic source signature

Plant ID	Feedstock	$\delta^{13}\mathbf{CH}_4$ source signature [‰]
		-62.6 ± 0.2 (before AC)
BG-03	Organic waste	-62.9 ± 0.1 (CHP unit)
		-66.5 ± 1.2 (feeder)
BC 00	Mixed	$-42.1 \pm 0.1 \text{ (before AC)}$
DG-09	MIXEU	-57.1 ± 0.2 (manure storage)
		$-59.1 \pm 0.1 \text{ (digester 1)}$
		$-60.9 \pm 0.4 \; (\text{digster } 2)$
BC 20	Organic wasto	$-60.0 \pm 0.3 \text{ (CHP unit)}$
DG-20	Organic waste	-59.7 ± 0.1 (dig. room)
		-59.6 ± 1.1 (feeder 1),
		-58.6 ± 0.4 (feeder 2)
BC 27	Mixed	$-56.4 \pm 0.1 \; (digester)$
DG-21	wiixeu	-59.8 ± 1.5 (before AC)
		-39.4 ± 0.2 (before AC)
		$-39.9 \pm 0.11 \text{ (CHP unit)}$
BG-29	Mixed	-38.5 ± 1.9 (feeder),
		$-44.9 \pm 0.1 \text{ (gas storage)}$
		$-55.5 \pm 0.6 \text{ (cowshed)}$
		$-43.0 \pm 0.5 \text{ (digester)}$
		$-43.9 \pm 0.7 \text{ (before AC)}$
BC-30	Mixed	$-44.1 \pm 0.9 \text{ (CHP unit)}$
DG-90	WIIXEU	$-51.2 \pm 10.4 \text{ (feeder)}$
		$-48.2 \pm 2.6 \; (\text{leckage 1})$
		$-39.9 \pm 4.6 \; (\text{leckage } 2)$
BG-38	Organic waste	-59.9 ± 0.3 (before AC)
BM-06	Energy crops	-55.3 ± 0.1 (before upgrading)
BM-06	Energy crops	-55.4 ± 0.1 (after upgrading)

Table E.1: δ^{13} CH₄ source signature of different process stages at eight biogas plants. For BG-20 exemplary results are listed, sampled on April 26th, 2024.

No.	Date	$\delta^{13}\mathbf{CH}_4$	No. of Aircore/	Strategy	Location
		[%0]	samples		
1	29.08.2016	-62.7 ± 1.1	1	Aircore	plume
2	08.09.2016	-61.6 ± 0.4	2	Aircore	plume
3	28.09.2016	-60.2 ± 0.6	3	Aircore	plume
4	10.10.2016	-63.9 ± 0.8	2	Aircore	plume
5	30.11.2016	-63.2 ± 0.8	3	Aircore	plume
6	19.12.2016	-62.1 ± 2.3	2	Aircore	plume
7	22.02.2017	-63.3 ± 1.2	4	Aircore	plume
8	22.02.2017	-61.5 ± 0.1	2	direct	digester 1
9	22.02.2017	-64.1 ± 0.3	2	direct	digester 2
10	10.01.2018	-61.3 ± 1.5	3	Aircore	plume
11	26.01.2018	-57.1 ± 2.0	15	Aircore	plume
12	26.03.2018	-61.5 ± 0.8	3	Aircore	plume
13	24.08.2018	-61.3 ± 1.2	7	Aircore	plume
14	17.12.2018	-64.0 ± 0.5	10	Aircore	plume
15	07.02.2019	-63.6 ± 0.7	8	Aircore	plume
16	24.07.2019	-62.8 ± 1.7	7	Aircore	plume
17	24.01.2023	-62.2 ± 1.7	5	plume	plume
18	24.01.2023	-63.7 ± 0.5	2	direct	digester 1
19	16.05.2023	-61.0 ± 1.0	3	plume	plume
20	16.05.2023	-63.8 ± 0.7	2	direct	digester 1
21	16.05.2023	-63.6 ± 0.3	2	direct	digester room
22	16.05.2023	-62.6 ± 0.1	3	plume	digester room
23	08.07.2023	-60.9 ± 0.3	3	plume	digester room
24	09.07.2023	-61.8 ± 0.1	2	direct	digester 1
25	28.09.2023	-62.9 ± 1.5	3	plume	plume
26	18.12.2023	-57.0 ± 0.7	3	plume	plume
27	18.12.2023	-61.9 ± 0.1	2	plume	plume
28	26.04.2024	-60.0 ± 0.3	2	direct	CHP
29	26.04.2024	-59.1 ± 0.1	2	direct	digester 1
30	26.04.2024	-60.9 ± 0.4	2	direct	digester 2
31	26.04.2024	-59.7 ± 0.1	2	direct	digester room
32	26.04.2024	-58.9 ± 0.4	2	plume	CHP
33	26.04.2024	-59.6 ± 1.1	2	plume	feeder 1
34	26.04.2024	-58.6 ± 0.4	3	plume	feeder 2
35	08.07.2024	-59.3 ± 0.2	6	plume	plume
36	08.07.2024	-54.7 ± 0.2	2	direct	digester 1
37	08.07.2024	-59.7 ± 0.2	2	direct	digester 2

Table E.2: Overview of isotopic source signatures of measurements carried out between 2016 and 2024 at a local biogas plant. Hoheisel [2017] carried out measurements between 2016 and 2018 (light blue), followed by Korbeń [2021] (blue), who carried out measurements between 2018 and 2019. Measurements performed as part of this thesis are indicated in green.

Appendix F

Abbreviations

\mathbf{AD}	- Anaerobic digestion
a.g.l.	- Above ground level
a.s.l.	- Above sea level
bcm	- billion cubic meters
BG	- Biogas Plant
BM	- Biomethane Plant
$\mathbf{C}_2\mathbf{H}_6$	- Ethan
\mathbf{CH}_4	- Methane
CHP	- Combined heat and power
\mathbf{CO}_2	- Carbon dioxide
COP	- Conference of the Parties to the United Nations Framework
	Convention on Climate Change
CRDS	- Cavity ring-down spectroscopy
dena	- Deutsche Energie Agentur (German Energy Agency)
DQI	- Data quality indicators
DWD	- Detuscher Wetterdienst
EDGAR	- Emissions Database for Global Atmospheric Research
EEG	- Erneuerbares Energie Gesetz (Renewable Energy Act)
EMID	- European Methane Isotope Database
FNR	- Fachagentur Nachwachsende rohstoffe
FTIR	- Fourier transform infrared spectroscopy
GAW	- Global Atmosphere Watch
\mathbf{GC}	- Gas chromatography
GHG	- Greenhouse gas
GPM	- Gaussian plume model
\mathbf{H}_20	- Water
$\mathbf{H}_{2}\mathbf{S}$	- Hydrogen sulfide
HD	- Heidelberg
HITRAN	- High-resolution transmission molecular absorption database

ICOS	- Integrated Carbon Observation System
IPCC	- Intergovernmental Panel on Climate Change
\mathbf{LNG}	- Liquefied natural gas
\mathbf{LUBW}	- Landesanstalt für Umwelt Baden-Württemberg
$\mathbf{M}\mathbf{A}$	- Mannheim
MWS	- Mean wind speed
\mathbf{NH}_3	- Ammonia
NIR	- National Inventory Report
NOAA	- National Oceanic and Atmospheric Administration
OF-CEAS	- Optical-feedback cavity-enhanced absorption spectroscopy
OTM	- Other Test Method
PGSC	- Pasquill-Gifford stability classes
ppb	- Parts per billion
ppm	- Parts per million
PRV	- Pressure relief valve
\mathbf{RE}	- Release experiment
RED	- Renewable Energy Directive
TADI	- TotalEnergies Anomaly Detection Initiatives
TWS	- Transect wind speed
UBA	- Umweltbundesamt
UNFCCC	- United Nations Framework Convention on Climate Change
VPDB	- Vienna Pee Dee Belemnite
WMO	- World Meteorological Organization
WWTP	- Waste water treatment plants

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