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Analysis of Unexpected Methane Peaks in the Urban Environment of Hamburg

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ABSTRACT

An in-depth investigation was conducted to analyze the occurrence of unexpected methane (CH_4) peaks in long-term continuous flow Isotopic Ratio Mass Spectrometer measurements (CF-IRMS) and solar-tracking Fourier transform Infrared Spectrometer (FTIR) network measurements in Hamburg. A Keeling plot analysis of the prominent methane peaks from the CF-IRMS measurements with a concentration upto 4100 ppb showed an isotopic signature of $\delta^{13}\text{C} = -60.3 \pm 0.2\text{\textperthousand}$ for Carbon-13 and $\delta\text{D} = -298 \pm 2\text{\textperthousand}$ for Deuterium, indicating microbial methane production and pointing towards wetland and water bodies emitters. Smaller peaks closer to the methane background concentration of 1921.74 ppb showed an isotope signature of $\delta^{13}\text{C} = -58. \pm 0.1\text{\textperthousand}$ for Carbon-13 and $\delta\text{D} = -291.2 \pm 1\text{\textperthousand}$, suggesting a stronger influence of methane production from thermo-genic mechanisms, with potential sources being fossil fuels and nonindustrial combustion and other anthropogenic sources. A purpose-built time-reversed Gaussian plume trans-port model using on-site measured wind data was used to model potential methane peak emission locations. The modelling indicated the most likely emission locations to be in the water bodies within and around the city, including the port, channels, and wetlands. An investigation of the water quality and water level data measured at the Elbe in the Hamburg port region showed a correlation between methane concentration in the atmos-phere and the Elbe with its tidal cycle. Correlations of meteorological data measured in the Hamburg city region and methane concentration in the atmosphere further indicate a significant influence of the water bodies in methane composition. This supports pre-vious research showing that the river produces a significant amount of methane in the upper estuary where Hamburg is located and observed that concentration in the water is enhanced with dropping water levels due to the tide. A release mechanism is postulated driven by a rapid drop in water pressure and reduced water column height allowing for methane bubble formation in water and sediments, leading to diffusion into the atmos-phere due to reduced methane oxidation potential in the shallower water column. The Elbe estuary provides optimal conditions for rapid methane emissions to the atmosphere, making the Elbe the most likely source of the significantly high concentrated methane peaks observed in Hamburg. The high methane flux from the short-release events in the Elbe were observed as peaks with CF-IRMS in situ measurements at a distance of 5 km and a height of 83 m. The FTIR sensor network located in 4 different locations in the city was also able to observe methane peaks that likely originate from the Elbe. Unfortunately, a good comparison between the two measurement approaches could not be made due to limitations in the FTIR measurements and the short deployment time.

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Chapter 1

Introduction

Methane (CH_4) is one of the most dominant greenhouse gasses (GHG) in the atmosphere and behind CO_2 , the second most important anthropogenic greenhouse gas. It has a Global Warming Potential Value (GWP) of 81 for a 20-year horizon [Forster et al., 2021], making it 81 times more potent than CO_2 for that time interval [T. Stocker et al., 2013]. Methane is released into the atmosphere in large quantities, and estimates suggest an annual emission of 363 Mt [IEA, 2023]. Various natural and anthropogenic sources produce methane and release it into the Atmosphere. Natural methane emitters are considered ones where human influence is not directly involved, such as microbial decomposition of organic materials in wetlands, volcanic activities or bound methane releases in permafrost deposits due to temperature rise [Fernandez et al., 2022]. The release of methane into the atmosphere by natural mechanisms is highly dependent on different environmental conditions, in particular, meteorological parameters such as temperature, precipitation, and solar intensity.

For natural methane emissions, methane production and release into the atmosphere depend highly on temperature. Natural methane emission (production and release) depends highly on temperature, whereby high temperatures are generally favourable for methane production [Singh et al., 2000]. However, different microbes have different optimal temperatures at which their methane production or reduction mechanisms peak. Another significant parameter is the precipitation amount and, consequently, the abundance of surface water. Some microbes live in water or moist environments, and an abundance of surface water aids their population growth. Additionally, water can help to flush organic material into the water body providing a plethora of nutrition, which promotes a large microbial population and methane production.

Anthropogenic sources are usually connected to using, transporting and treating fossil fuels, such as natural gas or oil. Fugitive releases from gas pipelines contribute to methane emissions significantly ([Schwietzke et al., 2014], [McKain et al., 2015]), along with other chemical industries and human infrastructure. This includes wastewater treatment, landfills, agriculture, and livestock. Anthropogenic methane production is differently affected by meteorological parameters than the natural ones, as the behaviour of humans mainly governs it. A well-observed example is the increase in fossil fuel consumption at colder temperatures [Javadinejad et al., 2019]. This is primarily observed in an annual cycle.

The methane present in the atmosphere is always a mixture of different emitter types, particularly in densely populated regions.

Identifying and quantifying these emitters is of utmost importance to understand and predict the mechanisms that govern climate change and subsequently be able to create informed legislation to rein in runaway emissions.

Hamburg is the second-largest city in Germany, with a population of around 2.5 million. The city has various urban uses, including typical residential areas with high and low-density neighbourhoods and extensive industrial, commercial, and port spaces. These industrial areas also include oil and gas refineries. Additionally, the city also provides numerous natural environments like parks and gardens. The extensive network of rivers, channels, lakes, ports and wetlands is a unique feature for a city located 70 km inland from a coast. This region also has many interconnected fleets, historic harbours, and channels freely connected to the river Elbe. Some of them completely dry out for some amount of time during the tide cycle, exposing a deep sediment-rich ground. The river/lake Alster and other contributing rivers join the Elbe by locks and controlled water management systems.

The most prominent water body is the river Elbe. The Elbe connects the city to the North Sea, providing Europe's third-largest port, the Hamburg port, with a year-round navigable offshore shipping route. It has a diverse system of methane emission sources that contribute to the methane composition in the air.

It is known that the Elbe is a significant methane emitter [Matoušů et al., 2019]. The methane concentration in its water and methane release into the atmosphere varies for the entire river and is affected by various factors.

The river originates in the "giant mountains" in the Czech Republic. The first section is a natural fast-flowing river experiencing no impact by human influences. The river has no significant methane emissions in this region as the natural methane oxidation mechanisms are balanced with its production and influx mechanisms. In the second section, the river is heavily used for industrial purposes in the Czech Republic and severely impounded. The water carries high concentrations of methane due to pollution, while the availability of natural regeneration areas that facilitate microbial methane oxidation is limited.

The third section describes the Elbe as a lowland river flowing through Germany. The banks are only stabilized by groynes, and the river is significantly naturalized with free-flowing characteristics. In this section, the microbial methane production is kept in check with its countering oxidation processes, resulting in a low methane concentration in the water and, consequently, low atmospheric diffusion rates.

Some heavily impounded human-made structures are present throughout the river, including harbours, locks, and weirs. These sections form methane hotspots, as methane production is rampant due to the disturbed flow of the river and heavy pollution. At the same time, the oxidizing mechanisms are repressed. The reason for the inability of oxidation is not fully understood and is likely multifactorial ([Matoušů et al., 2019], [Bednářík et al., 2019].)

The river Elbe estuary starts at the city of Hamburg and stretches down to the North Sea into the Waddensea, experiencing different environmental factors and mechanisms that drive its methane production and reduction mechanism. The upper estuary, including Hamburg's port, is defined by the heavily impounded region around Hamburg

and experiences significant variations in water level due to the tide. While no significant methane transfer occurs from the saltwater of the Waddensea to the very nutrient-rich freshwater in the upper estuary due to insufficient mixing [Matoušů et al., 2019]. The water in this region has a short turnover time, with a very high methane concentration, similar to other harbours and human-altered segments upstream. The water has high pollution and biomass concentration from industry, agriculture, and other human and natural influences upstream and in the region. This high concentration of pollutants and biomass significantly enhances the methane production mechanisms while hindering the Oxidation mechanisms. High heterotrophic activity is related to remineralization processes of high loads of labile organic matter, and it has been shown by Matoušů et al., 2019 that the methane concentration in the upper estuary correlates with BOD-7 (a measure of bioavailability of degraded organic matter).

This is further amplified by its short turnover time, where the oxidation processes have little time to take effect and efficiently remove methane from the system.

The river is significantly widened in the lower estuary, with an extensive network of connected marshlands. The marshlands have methanogenic bacteria that are well-adjusted to the colder climate of northern Germany. Those can be found in oxic as well as in anoxic soil layers, resulting in a methane production peak at 10 °C and 20 °C [Wagner, 1997]. The low-temperature peak production occurs due to reduced methane oxidation at low temperatures. Marshlands systems usually peak in a 30 °C region in warmer climates. The water turnover time is significantly longer, providing good conditions for methane oxidation and greater methane diffusion into the atmosphere, resulting in a ten times lower methane concentration than in the upper estuary [Matoušů et al., 2019]. A significant amount of the methane in the lower estuary originates from the Waddensea, as the tides flush highly methane-enriched water into the estuary. The well-functioning oxidation processes in this region would otherwise dominate the methane balance.

Low water levels in the river and high temperatures enhance microbial activity and thus decrease oxygen levels in the water. This can, for example, be observed in the seasonal cycle.

While no apparent relation to suspended particular matter can be seen, the sediment, on the other hand, plays a significant role in the methane cycle. Methanotrophs, for example, reduce CH₄ emissions from the sediments. And one can observe from tidal activities that resetting the sediments significantly increases methane production due to the reintroduction of biomass and ions to the sediments [Bednářík et al., 2019]. The types of methane-producing microbes can vary significantly due to the type of sediments and vary significantly throughout the river, allowing them to form hotspots.

The water level also contributes to the methane balance. Low water levels reduce the ability of the water to oxidize the methane due to its lower water column height over the sediments. In the Elbe estuary, the methane concentration in the water is correlated to falling water levels due to the tide. It is reaching its peak at the lowest water level. [Harrison et al., 2017] have shown that the fast reduction of the water level increases the methane concentration and, consequently, its emission to the atmosphere.

A possible explanation is that the thick sediment layers can accumulate a large amount of methane. The drop in pressure due to the reduction in water column height causes

the methane to form bubbles, which are released from the sediments, travel up to the surface and escape to the atmosphere. The reduced water column height can no longer oxidize most of this methane, consequently defusing the methane into the atmosphere. The exact condition required for such a surge in methane emission is not yet detailed. It is most likely a function of sediment characteristics, water depth, lowering rate, etc. For the Elbe estuary, it is estimated that 5–41 % of the total methane loss in the water is attributed to active methane oxidation. The remaining part is released into the atmosphere due to diffusion [Matoušů et al., 2019].

The United Nations environment programme (UNEP) measurement campaign aimed to quantify the emissions in the city region of Hamburg, Germany. While providing the opportunity to compare and validate different data acquisition approaches with the best bottom-up inventories currently available.

The campaign was conducted between 01.08.2021 and 1.04.2022, with some short 1-3 day maintenance breaks. High-time-resolution mass spectrometer measurements were conducted during the campaign, focusing on deuterium (^2H) and Carbon 13 (^{13}C) isotopes. The measurement was stationary and positioned near the city centre on the roof of the Geomatikum building owned by Hamburg University with a measurement inlet height of 83 m fig. 1.1. A series of additional analyses were conducted for the shorter period

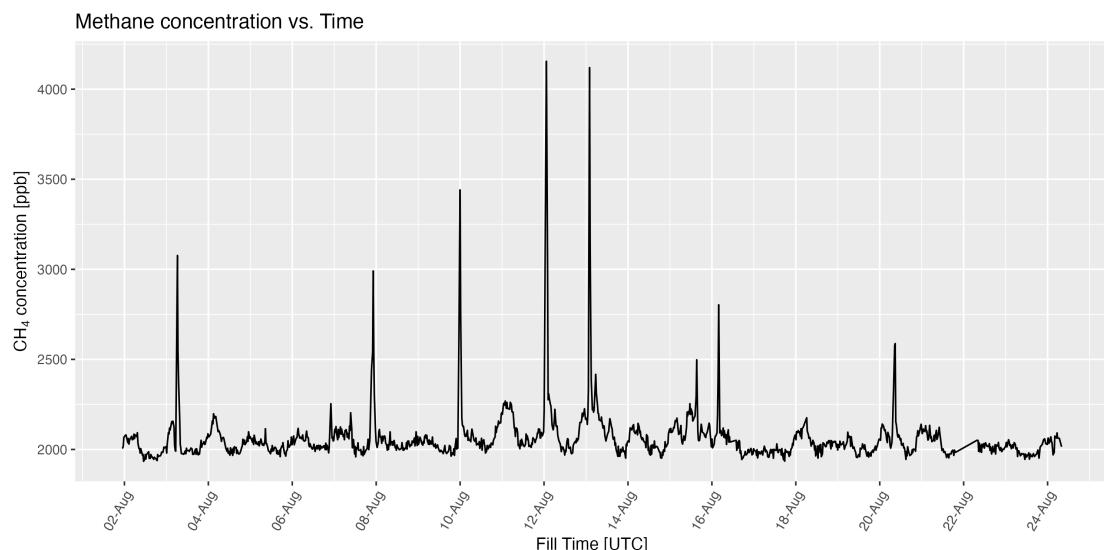


Figure 1.1: Section of CF-IRMS in situ measurement showing the timeline of methane concentrations measured in Hamburg Geomatikum (83m above ground) from 02.08.2021 to 24.08.2021.

of 27.07.2021 to 9.09.2021. These include a solar-tracking Fourier Transform Infrared Spectrometer (FTIR) Network with four EM27/Sun spectrometers in and around Hamburg. This network enabled a differential total column measurement using the Bayesian inverse modelling approach. A Leosphere Windcube 200S Doppler wind LIDAR was deployed to improve the transport modelling of the Bayesian inversion by correcting the

atmosphere boundary layer height and the wind direction of the wind model. Mobile methane measurements by car and boat were also conducted to validate and improve the inventory for the uses as prior in the Bayesian inverse modelling. A Picarro model G2301 measured mole fractions of CH₄, CO₂ and H₂ at a frequency of 0.3 Hz, and a Picarro model G4302 measured mole fractions of C₂ H₆, H₂O and CH₄ at a frequency of 1 Hz. The mobile measurements mainly focused on the industrial and port region in the south of Hamburg, filling the gaps left by a previous measurement campaign with the same approach that primarily focused on the residential areas to the north.

The Isotope measurements and, to some extent, the FTIR measurement yielded some surprising results for their methane concentration that could initially not be explained. In particular, some seemingly randomly occurring high methane concentration peaks were observed. These peaks had a dry air mole fraction of up to 4500 ppb, while the average background was around 2000 ppb. The duration of the peaks was also concise, lasting for only around 0.5-3 h. The current global average mole fraction of methane is at 1921.74 ppb (January 2023) [Lan et al., 2022].

By investigating the chemical composition of the methane by the Keeling method from Air sampled during the peaks, it was concluded that emission sources were due to natural microbial methane production mechanisms, pointing towards wetlands and water bodies.

A purpose build particle transport model pointed towards the source of emissions within the city region, encompassing the port, fleets, channels, and wetlands.

The occurrence of the peaks has been successfully correlated to the water level of the Elbe, as these regions experience strong water level fluctuations due to tidal effects. [Harrison et al., 2017] shows that a fast-dropping water level can trigger significant methane emissions into the atmosphere at freshwater reservoirs. Additionally, [Matoušů et al., 2019] shows that the methane concentrations in the water of the river Elbe increase at dropping water levels.

Further correlations of meteorological and water quality data with the methane concentration in the air provide an overall concrete conclusion of the origin of methane peaks. Linking it to the water bodies and wetlands in and around the city due to a complex interplay of man-made riverbank impoundments, pollution in the water, flow characteristics of the river sediment depositions and tidal influences.

The river Elbe is currently underrepresented in methane inventories, such as in the TNO GHGco inventory. This is also suggested by Forstmaier et al., 2023, in which the methane modelling is significantly improved by including the river in the inventory with an estimation.

The fluctuations of methane release by rivers and wetlands due to tidal effects are not well investigated and understood yet but are of great interest for an accurate methane budget estimation. This thesis investigates the observable effects of methane emissions in the Elbe and attempts to correlate the methane concentrations in the air with the tidal effects on the Elbe. Moreover, this thesis provides ideas for further research to improve methane monitoring in the Hamburg region and the Elbe.

Chapter 2

Methods

2.1 The UNEP Campaign

This thesis was conducted as part of the United Nations environment programme (UNEP) measurement campaign. This project aimed to quantify the total type-based (natural and anthropogenic) methane emissions of Hamburg [Forstmaier et al., 2023]. Three measurement types were deployed during this campaign: 1. A total column-based Fourier-Transform Infrared Spectrometer network, deployed from 27.07.2021 to 9.09.2021; 2. A continuous-flow isotope ratio mass spectrometer (CF-IRMS) measurement at the Geomatikum, deployed from 01.08.2021 to 1.04.2022; 3. A mobile dual Cavity Ring-Down Spectrometer measurements by car and boat, deployed from 09.08.2021 to 21.08.2021. The FTIR sensor network is part of the Munich Urban Carbon Column Network (MUCC-Net) and was relocated for the measurement campaign to Hamburg. The coordination and deployment were provided by the Technische Universität München (TUM) from Andreas Forstmaier (TUM) and Jia Chen (TUM). The sensors used in the MUCCnet are solar-tracking absorption spectrometers (Bruker, EM27/SUN) that enable column-averaged dry air mole fractions measurements of CO₂, CH₄, and O₂ [Chen et al., 2016]. A Bayesian inverse modelling approach was used to estimate the location and type-based methane emissions. The TNO GHGco inventory [Super et al., 2020] was used as prior information for the Bayesian approach. The inventory was further improved for modelling using the results of the mobile survey. The ERA5 model [Hersbach et al., 2023] was used to model the transport by the atmosphere, and wind-LiDAR measurements were used to correct this model further. The wind-LiDAR deployed was the Leosphere Windcube 200S Doppler Wind-LiDAR provided and operated by Norman Wildmann from the Deutsches Zentrum für Luft- und Raumfahrt (DLR) [Wildmann et al., 2020], [Vasiljević et al., 2016].

The Isotope Ratio Mass Spectrometer system at the Geomatikum was provided by the Universiteit Utrecht and operated by Carina van der Veen. The Spectrometer used was a ThermoFinnigan MAT Deltaplus XL isotope ratio mass spectrometer, alternating ²H and ¹³C measurements with a frequency of 20 min. The measured isotope ratios were analysed using a Keeling plot approach and compared for identification to a stable isotope ratio database of isotope measurements of known source types [Menoud et al., 2021].

The mobile measurement survey deployed two Cavity Ring-Down Spectrometers, the Picarro model G2301 and a Picarro model G4302. Additionally, methane plumes were analysed by sample bags for their source attribution. The bags were examined with the

isotope ratio spectrometer in the Geomatikum. Hossein Maazallahi from the Universiteit Utrecht conducted the mobile measurement survey. This survey completes a campaign conducted with the same instrumentation in 2020 in the northern part of Hamburg, which is primarily constituted of residential areas [Maazallahi et al., 2020]. It focused on the southern regions with mostly industrial and port areas, surveying 1567 km.

2.2 Continuous-flow isotope ratio mass spectrometry (CF-IRMS)

The isotopic ratio signatures of Deuterium (δD) and Carbon-13 ($\delta^{13}C$) were measured by using a Continuous-flow isotope ratio mass spectrometry (CF-IRMS). Isotope measurements are well suited to provide additional information about the production mechanism of methane since different sources emit CH₄ with a characteristic and, in many cases, distinct isotopic composition.

The system used is described in great detail by Brass and Röckmann, 2010 and will hence only be outlined briefly here [Brass and Röckmann, 2010]. The method used is designed for a multi-month operation with minimal user interaction. Apart from liquid nitrogen refilling, which is used for cooling, the process is fully automated and continuously measures autonomously. Besides a few short 1-3 day maintenance breaks in which the furnace had to be replaced, the setup measured uninterrupted for the extended time period from 01.08.2021 to 1.04.2022. The isotope ratio determination procedure follows seven steps of extracting and purifying methane before analysing it with the mass spectrometer. [Brass and Röckmann, 2010]:

1. The air is sampled with a fixed volume of 40 mL.
2. Methane is pre-concentrated to separate it from the bulk air. The separation process is performed by cooling the air to -130 °C, which leads to the condensation of CH₄, while N₂ and O₂ stay gaseous and can be separated mechanically. The remaining air is then heated to -85 °C, at which CH₄ returns to its gas phase, whereas N₂, O₂, CO₂, H₂O and other condensable gases stay solid/liquid and are again mechanically separated by valves.
3. The CH₄ is focused in a small volume by re-cooling it. This also ensures a better separation from the O₂, N₂, and CO₂, which can harm the conditioning of the furnaces or interfere with the mass spectrometry. By reheating the CH₄, the release peak can be shortened, which ensures a high enough concentration in later processes.
4. The CH₄ is gas chromatographically separated by a PoraPLOT Q column from the remaining gas components.
5. CH₄ is converted to either CO₂ or H₂, and the two processes are alternated with a 20 min frequency. The CH₄ is combusted into CO₂ for the $^{13}C/^{12}C$ ratio analysis. In this process, the CH₄ is broken into CO₂ + H₂O. For the $^2H/^1H$ ratio analysis,

the CH₄ is converted to C + 2H₂ via pyrolysis. This process uses highly purified Helium (purity 5.0) as a transport medium.

6. The converted CH₄ is injected into the mass spectrometer via an open split interface.
7. The mass spectrometer measures the molecular ion current ratios; The peak areas are evaluated for a methane concentration analysis.

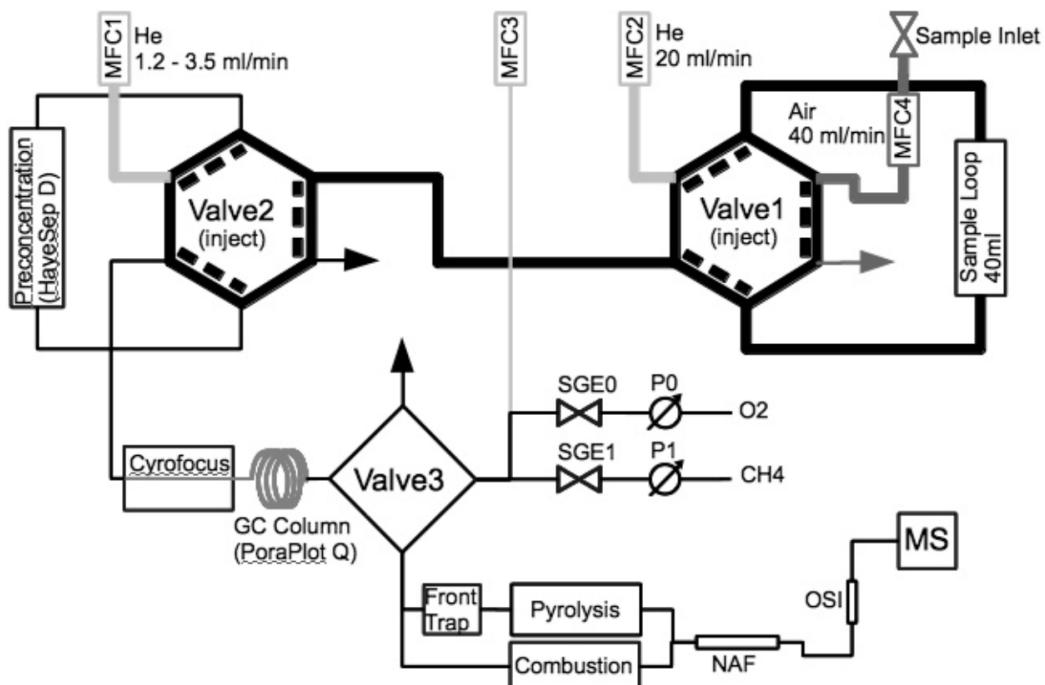


Figure 2.1: Schematics for the continuous-flow isotope ratio mass spectrometry (CF-IRMS) deployed at the Geomatikum. Methane is isolated from other air components by subsequent preconcentration, cryo-focussing and gas chromatographic separation. The separated methane is then either combusted to CO₂ (for $^{13}\text{C}/^{12}\text{C}$ ratio analysis) or pyrolyzed to H₂ (for $^2\text{H}/^1\text{H}$ ratio analysis) and injected into the isotope ratio mass spectrometer for isotopic analysis. [Brass and Röckmann, 2010]

For calibration and stability monitoring, the isotopic ratio mass spectrometer measurement is packaged into six individual measurements (Reference-Sample-Sample-Sample-Reference). A complete measurement cycle takes about 20 min, and the $\delta^{13}\text{C}$ and δD measurements are alternated. The system pressure is also measured with a pressure sensor to determine the methane concentration of the sample air.

2.2.1 Mass spectroscopy

The commonly used analytical technique of mass spectroscopy offers an excellent tool for measuring ion mass-to-charge ratios. This allows for accurate measurement of the isotope ratios in a sample, giving great insight into the production mechanisms of the molecules studied. By measuring and analysing the ratios of hydrogen (1H) to its heavier deuterium (2H) isotope and carbon (^{12}C) to its heavier carbon-13 (^{13}C) isotopes in methane, its origin can be estimated. The process is further detailed in section 2.2.2 on the Keeling plot method.

A mass spectrometer measures the charge ratio of an uncharged molecule by ionising the molecule through an electron impact. The ionised molecule now has an electric potential and can experience the effects of magnetic and electrostatic fields.

The ions are accelerated using an electric potential, resulting in a similar kinetic energy for all ions independent of their mass-to-charge ratio. A magnetic field (B) is then applied to the accelerated ions resulting in a Lorenz force experienced by the ions. Consequently, the trajectory of the ions is bent towards a circle within the magnetic field. While equal charges (q) with an equal velocity (v) experience the same Lorenz force, they do not necessarily follow the same circular trajectory and have the same radius (r). This is co-dependent on the mass (m) of the charge, i.e. the ionised molecule or atom. Hence for isotopes with larger masses, the radius of the trajectory differs from the radius of the lighter parent isotope. The heavier isotopes have a larger radius than their lighter counterpart.

$$\frac{m}{q} = \frac{r \times B}{v^2} \quad (2.1)$$

A continuous flow of ions on the magnetic field generates a mass spectrum on a detector (ion collectors), a histogram of the isotope abundance/intensity versus its mass-to-charge ratio.

The mass spectrometer measures the Isotope ratio δX , which is noted in ‰. The isotope ratio describes the ratio of two isotopes ($R = ^{13}C/^{12}C$ or $R = ^2H/^1H$) in a sample relative to the same ratio in a reference standard sample.

$$\delta X = \frac{R_{sample} - R_{standard}}{R_{standard}} \quad (2.2)$$

Due to the high cost and scarcity of well-defined and peer-reviewed reference samples, the measurements are performed against a working standard (WS). This working standard is calibrated to a small amount of a well-defined reference with the mass spectrometer that will be used in the sample measurements. The measured isotope ratio of the sample is later converted to the international isotope scale (IS) by:

$$\delta_{\frac{sample}{IS}} = \delta_{\frac{WS}{IS}} \delta_{\frac{sample}{WS}} + \delta_{\frac{WS}{IS}} + \delta_{\frac{sample}{WS}} \quad (2.3)$$

The measurement results can then be published on the international isotope scale. The uncertainty in the reference sample and the instruments have to be accounted for when such an approach is implemented. For ^{13}C , the international isotope scale is the Viana

Pee Dee Belemnite (VPDB), and for 2H , the is the Vienna Standard Mean Ocean Water (VSMOW).

By comparing the area of an isotope peak in the mass spectrum in the sample to a well-calibrated working standard reference of this spectrometer, the sample concentration can be calculated as follows:

$$c_{sample} = c_{WS} \frac{\text{peak area}_{sample}}{\text{peak area}_{WS}} \quad (2.4)$$

2.2.2 Keeling plot method

Charles D. Keeling showed in the 1950s that the isotopic abundance of ^{13}C and ^{18}O can be correlated to the plant-based origin of CO₂ [Charles D Keeling, 1958], [Charles D Keeling, 1960]. He devised a method for estimating the production mechanism of CO₂ by employing reference databases. This method was later adopted for methane whereby the abundance of the heavy isotopes of ^{13}C and 2H in a molecule enables the source type attribution [Menoud et al., 2021] [Menoud et al., 2022b].

For methane, a strong depression in both ^{13}C and D ($\delta^{13}C \sim -60\text{\textperthousand}$, $\delta D \sim -300\text{\textperthousand}$), for example, can be observed in biological processes like boreal and tropical wetlands, rice cultivation, ruminants and waste decomposition. Natural gas and coal mining are thermogenic processes which have a strong enrichment in both heavy isotopes ($\delta^{13}C \sim -40\text{\textperthousand}$, $\delta D \sim -150\text{\textperthousand}$). Methane from biomass burning is unusually enriched in ^{13}C ($\delta^{13}C \sim -25\text{\textperthousand}$, $\delta D \sim -230\text{\textperthousand}$). Methane extracted from gas hydrates usually is depleted in ^{13}C but enriched in D ($\delta^{13}C \sim -60\text{\textperthousand}$, $\delta D \sim -200\text{\textperthousand}$) [Brass and Röckmann, 2010]. To analyse the isotope ratios measured by the CF-IRMS using the Keeling method, the currently most up-to-date database from [Menoud et al., 2022a] is used as the comparison reference.

The mass spectrometer provides an isotope ratio δX in ‰ between the light and heavy stable isotopes. For methane, $\delta^{13}C$ for ^{13}C and ^{12}C and δD for D and 1H are used.

The Keeling plot approach is a mass balance and mass conservation approach. It considers methane concentration in the air (c_a), measured by the CF-IRMS, as a sum of the background concentration (c_b) and the concentration added by the source (c_s).

$$c_a = c_b + c_s \quad (2.5)$$

By using the isotope ratio δX for the heavy isotopes, the mass balance equation is constructed:

$$\delta_a c_a = \delta_b c_b + \delta_s c_s \quad (2.6)$$

Combining eq. (2.5) and eq. (2.6), this yields:

$$\delta_a = \frac{c_b}{c_a} (\delta_b - \delta_s) + \delta_s \quad (2.7)$$

eq. (2.7) shows a linear correlation between the measured isotopic ratio δ_a and the inverse measured concentration c_a . The Y intersect represents the isotopic ratio δ_s of the source. This value can be compared to the reference values from a database. A Keeling plot is

produced by scatter plotting a series of measurements with the Y-axis as the measured isotopic ratio and the X-axis as the inverse measured concentration. With an orthogonal distance regression line fit, the Y intersect, i.e. the isotope ratio of the source, can be obtained. For a comprehensive methane analysis, the source isotope ratio for carbon-13 $\delta^{13}\text{C}$ and Deuterium δD has to be considered. [Liu et al., 2019] For better visualisation, both isotope ratios can be plotted in a dual isotope plot, as seen in fig. 3.16a.

2.2.3 Keeling for methane peaks

To investigate if there is a difference in source attribution between the background methane and the peaks, the Keeling analysis was performed by separating the peaks and the background with a peak finder algorithm. This allowed producing Keeling plots for the total measurement, background and selected peak identification criteria separately. The results could be compared using reference isotope databases, and the emission mechanism was estimated individually.

2.2.4 Keeling analysis with wind

Any anisotropic behaviour in the methane production was identified by combining results of the Keeling method for the background and peaks isotope measurement with wind measurements.

The isotope measurements were binned according to the averaged wind direction during the measurement time. To achieve this, wind measurements at the Geomatikum provided by the Universität Hamburg were used for this. The wind measurement instruments were located very close to the isotope measurement inlet, allowing for high confidence in their repeatability.

The isotope measurement bins were in 10° wind directions. For each bin, a Keeling analysis was performed separately. The results were then plotted in a dual isotope plot with the Y intersect representing the ^2H attribution and the X representing the ^{13}C attribution. The location of the binned points indicated the methane production mechanism and emitter type when overlaying it with reference database data [Owen A. Sherwood et al., 2020] provided by the Global Monitoring Laboratory. A wide spread of the data points indicated different methane production mechanisms, while closely spaced points indicated homogeneous emitter types in all directions.

By separating the methane peaks from the background and repeating the wind-sensible Keeling analysis, it was investigated if the peaks from different directions originate from different emitter types.

2.3 Differential column measurements

A Fourier transform infrared spectrometer network was deployed inside and around the city borders to investigate the urban greenhouse gas (GHG) emissions from the city region of Hamburg. Parts of the usually in Munich located sensor network MUCCnet have been relocated to Hamburg and were deployed for a shorter period between 27.07.2021

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to 9.09.2021. The network consists of four fully autonomous and automated enclosures. These were located about 20 km from the city centre to the East, South and West, with one enclosure close to the city centre at the Geomatikum (close to the mass spectrometer). The locations can be seen in fig. 2.2. The FTIR spectrometer enclosures operate by

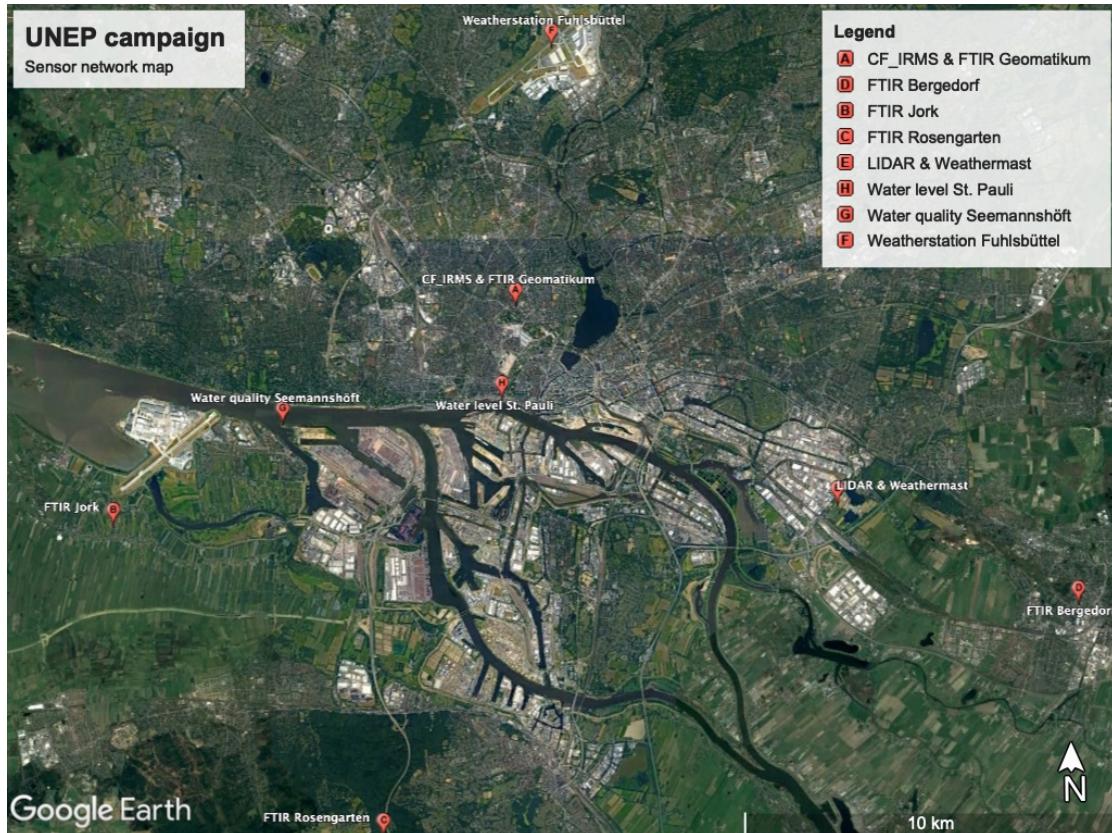


Figure 2.2: Satellite image of Hamburg with the location of the sensors deployed in the UNEP measurement campaign marked on the map. A: Geomatikum of University Hamburg with CF-IRMS, FTIR and wind measurements, B: West FTIR station in Jork, C: South FTIR station in Rosengarten, D: East FTIR station in Bergedorf, E: Weather mast and wind LiDAR both measuring wind in Billbrook, F: DWD Weather station Fuhlsbüttel, G: Water quality measurements at Seemennshöft, H: Water level measurements at St. Pauli. [Google LLC, 2023]

measuring the absorption infrared solar spectrum with a high temporal resolution of 90 seconds. In the retrieval process, they are averaged over a 10 min period to accurately calculate the CO₂, CH₄, and O₂ total column integrated dry air mole fractions.

The enclosures are equipped with a Michelson interferometer (Bruker, EM27/Sun). This spectrometer has an attached solar tracker that enables tracking the sun by redirecting the light rays with a set of electronically controlled gold-plated mirrors. The spectrome-

ter is housed in a weatherproof aluminium box to protect it and its auxiliary equipment, such as a computer, heating unit, control electronics, etc., from the elements. To enable an undisturbed light ray, the solar tracker sticks out the top of the box with an automatic cover that opens at favourable weather conditions and aligns itself with the solar tracker. To protect the tracker from precipitation, rain and cloud detection sensors are placed on top of the enclosure. They automatically initiate a closure of the cover when precipitation is detected, or cloud coverage is too great. The weatherproof enclosure and automated operation allow for autonomous data acquisition of a geographically extensive network with minimal staffing. Data collection during fluctuating weather conditions can be achieved as the measurement can be initiated and terminated quickly without lengthy setup times. A significant advantage of the FTIR approach to other in

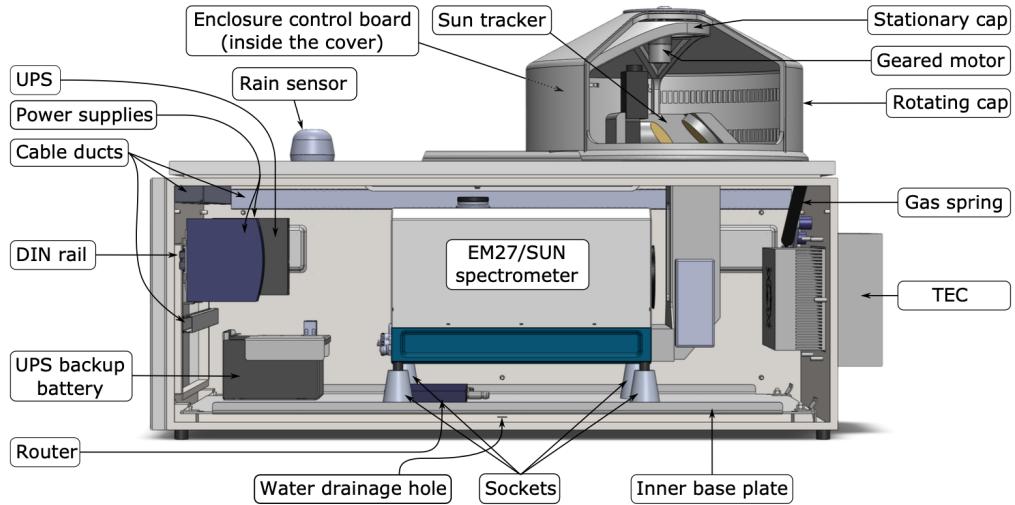


Figure 2.3: Schematics of the FTIR spectrometer enclosure (MUCCnet). [Heinle and Chen, 2018]

situ measurements lies in the total air column measurement of the atmosphere between the light emitter, i.e. the sun and the spectrometer. The spectral absorption by the methane can then be measured accurately for the entire atmosphere. Other approaches that measure concentration at the street level have the disadvantage that they can miss methane emission emitted above the instruments like high chimneys. The degree of mixing of the GHG with the background air highly depends on various airflow characteristics, topography, emission type, and location. A total column measurement can't negate all of them but provides a more reliable picture than simple in situ measurements.

2.3.1 Bayesian inversion modeling

By using the FTIR sensor network, differential total column measurements were performed, in which at least one sensor is always located upwind and one downwind of an

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emitter. The quantity of GHG released by an emitter can be estimated by comparing the concentration delta of the two columns.

A computational fluid dynamics (CFD) model is used to identify the emission location. This is aided by using a Bayesian inversion framework.

An inverse framework is a method where the effects of an event or condition are used to calculate the cause that leads to the observed effects. Here the methane concentration was measured in the atmosphere, and its emitter was calculated. In a forward method, the measured concentration in the air would be calculated from the known emitters.

To statistically improve the calculation of the cause, further prior information can be used. The TNO inventory, which has the highest spatial resolution of “known” emitters in Hamburg, is used in this case. This inventory is compiled by estimating emissions due to fossil fuel usage, density, type of emission, etc. When applying the Bayesian approach in the inversion, the TNO GHGco inventory was used as the prior estimation of the emissions.

The TNO GHGco inventory is a European database with spatially resolved emission data for CO₂, CH₄, CO, NO_x and NMVOCs. The spatial resolution is (1/60)° for longitude and (1/120)° for latitude [Super et al., 2020] [Super et al., 2019]. This inventory is Hamburg’s current highest resolution inventory, giving the best available prior emission estimation. Its limitation is that the bottom-up approach may not encounter all emission sources or does not yet account for relocated and sporadic emitters. To further improve the inventory, an additional layer that contained estimated emissions from the Elbe was added. For this, estimations of methane emissions from the separate sections of the Elbe [Matoušů et al., 2017] were added for each grid cell individually. Each grid cell was multiplied by the proportion of water coverage in this cell to account for the incomplete coverage of the Elbe by a coarse raster [Forstmaier et al., 2023].

In Bayes’s theorem, the posterior model is proportional to the prior model, which is the probability of the methane being emitted using previously acquired knowledge times the “likelihood of the data”. The likelihood of the data links the target model (the posterior of the measured variable) to the measured data. The likelihood is the probability of measuring a concentration given the emission from the Prior model.

$$\text{Posteriorprobability} = \frac{\text{Priorprobability} * \text{Likelihoodofthedata}}{\text{Normalizationconstant}} \quad (2.8)$$

$$P(A|B) = \frac{P(B|A)P(A)}{P(B)} \quad (2.9)$$

A Bayesian inversion can estimate the methane emission of a source by using prior knowledge of the source and updating this knowledge with measurements of the methane concentration in the air.

To identify the locations, the inversion also uses the ERA5 weather model. This model is additionally corrected for the boundary layer height and wind direction using a wind LiDAR. This corrected model is used to generate backward trajectory footprints with a Stochastic Time-Inverted Lagrangian Transport (STILT) model. The inversion is then able to use the STILT footprints for its identification of the emission location. For the

UNEP campaign, the existing framework developed by Jones et al., 2021 was adopted for Hamburg and used in the analysis.

2.4 Peak identification algorithm

The isotope ratio mass spectrometer measurements show a series of methane concentration peaks throughout the campaign time, with different magnitudes and duration. Hence the identification and characterisation of the peaks were of great importance. To achieve this goal, a peak finder algorithm was implemented that identifies the methane peaks over the entire time series. The output was the maximal concentration and time of the peak, as well as the concentration and time of the peak's start and end. The peak finding algorithm was tuneable in its identification criteria, allowing for separate investigations. With the peak identification, an automated tool was provided to be used later in the pipeline for isotope signature identification and correlation with other variables. In the analysis, two different identification criteria were consequently used. The first was the identification of all methane peaks that are distinct from the background concentration. The identification criteria defined by Menoud et al., 2021 were used as a reference. The following criteria were applied:

- A minimum enhancement above the background of 100 ppb.
- A minimum peak height of the lowest 10th percentile of the concentration-time series.
- The peak width contains at least three data points (approximately 60 min).
- The peak width is restricted to maximum ± 6 hours around the centre of the peak.

Figure fig. 3.1 shows an example of the peaks with the identified peak highlighted. The second peak identification criteria are designed to identify only the short and very prominent peaks. Those peaks are visually different from most others, and a different production mechanism was suspected. The peculiarity of those peaks was separately investigated to identify the mechanisms that govern those peaks. The criteria applied are as follows:

- High concentration of minimal 2100 ppb.
- Minimum three data points.
- Shorter maximal peak spared of 3 h.

An example of the identified peaks can be seen in fig. 3.2.

2.5 Methane and environmental data correlation analysis

2.5.1 Methane emissions with water level

At first inspection, the presence of the methane peaks in the concentration timeline occurs at random. Overlaying the methane concentration with the water level measurements at St. Pauli in Hamburg, performed by Wasserstraßen- und Schifffahrtsverwaltung des Bundes (WSV) and provided by Bundesanstalt für Gewässerkunde (BfG), indicates a correlation [Was, 5 01]. A pattern can be spotted in the Plot fig. 3.3, which is a section of the complete timeline. The dominant methane peaks occur around 1-3 h after the lowest water level.

While smaller peaks are visually more challenging to identify and correlate to the water level, the peak identification algorithm helps to highlight the smaller peaks. It further indicates a correlation with the water level of the river Elbe.

Pearson's correlation coefficient was used to prove a statistically meaningful correlation between the water level and the methane concentration. Unfortunately, the occurrence of elevated methane concentrations does not seem to be a single variable correlation. Hence, a simple correlation of the total water level and concentration yields no results. The wind direction must be considered to establish a correlation between water level and methane. This was done by separating the timeline in wind directions and speeds to be analysed separately by binning all methane and water level measurements in 10° wind directions and 1 m/s wind speed bins and followed by calculating the Pearson's correlation coefficient between the water level and methane concentration in the air for each bin.

A visual representation of the obtained results can be seen in fig. 3.4a. Each tile in this plot represents a wind data bin, with the colour representing Pearson's correlation coefficient.

To validate if the correlations are statistically meaningful, a p-value test has also been conducted with a value of $p < 0.05$. A plot visualizing the results can be seen in fig. 3.4b.

2.5.2 Methane concentration and water quality correlation

To investigate if the methane peaks and the methane concentration in the air are connected to the river Elbe, the water quality parameters of the Elbe have been correlated with the methane concentration time series.

It is well known that wetlands and water bodies can release significant amounts of methane into the atmosphere. [Matoušů et al., 2019] show that a high methane concentration in the water of the Elbe is present in the upper estuary of the city of Hamburg. The TNO GHGco inventory does not include emissions from the river Elbe, but [Forstmaier et al., 2023] shows that a correction including estimations of the river's emissions yields more reliable modelling results.

Water quality parameters are a good indicator of methane production, reduction and emission rates in the water [Wu et al., 2007]. A direct methane emission prediction cannot be made just from such water quality parameters due to the complexity of the

production mechanism and its strong dependence on local conditions and microbial composition of the water body. Nevertheless, a correlation between water quality parameters and methane production is observable in waterbodies such as the Elbe. This can help to provide further indication of alleviated methane concentration in the air due to mechanisms in the water of the river.

The water quality data measured at Elbe Seemannshöft provided by a Hamburg service were used for the investigation [IHUW, 5 01]. This data included the parameters: water temperature, oxygen concentration and saturation, pH, conductivity κ_{25} , turbidity, UV absorption, SAK, and algae concentration of different types. The data had a high temporal resolution of 10 min.

A Pearson's correlation coefficient analysis was conducted using the same correlation approach described before for the same wind direction and speed bins. An example can be seen in fig. 3.6.

2.5.3 Methane concentration and meteorological observation correlation

Data from the Deutsche Wetterdienst (DWD) was used to investigate a possible correlation between the methane concentration in the air and some meteorological parameters: air temperature at 2 m, dew point, humidity, precipitation, air pressure, and solar radiation intensity. The Deutscher Wetterdienst (DWD) provides weather and climate data through their Open Data Climate program [Deutschen Wetterdienst, 5 01], with an extensive array of measured parameters at different measurement time intervals for a large selection of weather stations. In Hamburg alone, there are two Stations and about five near the city. In this thesis, the data from the measurement station Hamburg-Fuhlsbüttel was used due to its proximity to the Geomatikum (2.3 km). This station provides highly standardised and quality-controlled measurement data, which were averaged every 10 min and every 1 h by the DWD [Kaspar et al., 2013].

The correlation investigation was performed in a similar manner as with the water quality and water level. A Pearson's correlation coefficient analysis and a P-value test for separate wind direction and speed bins were conducted. The resulting correlations were plotted in a tile plot for better visualisation.

2.6 Methane transport by wind

2.6.1 Methane emissions and wind measurements

The wind data were obtained from the DWD station Hamburg-Fuhlsbüttel and the Universität Hamburg. [Deutschen Wetterdienst, 5 01]

A significant advantage of using the data provided by the DWD is the standardization and quality control done by the DWD, providing considerable confidence in the measurements. Additionally, the wide array of measured parameters provided, including, for example, precipitation, soil and air temperature, solar radiation intensity, etc., enables comparison and correlation with many aspects of methane emission.

While this data adheres to strict standards, the wind measurements are performed only

2 m above ground. Measurements of this altitude are heavily influenced by surrounding topography. Time averaging improves in normalising the measurement. However, it impacts the temporal resolution of the measurements.

The Universität Hamburg provided three different sets of wind measurements at two locations [Lange and Universität Hamburg, 5 01]. The first location was at the Geomatikum itself, only a few metres from the CF-IRMS measurement inlet at 83 m height. At this height, the surface-level effects are mostly negated, although the Geomatikum building itself can potentially generate turbulences that influence the measurements. The Geomatikum is the highest building in the proximity by quite a margin, but disturbances from the surrounding cannot be completely out-ruled. The second location is at the weather mast in Hamburg Billbrook, approximately 17.3 km East of the Geomatikum. Measurements were taken at 50 m and 110m height. The measurement instruments were placed far from the support structure so that disturbances by the mast were minimised. Additionally, no high-rise buildings are located near the mast, aiding a mostly undisturbed measurement.

All four measurement data sets were time averaged over 10 min, and all were analysed and used in further modelling. The analysis in this thesis mainly focuses on the measurements at the Geomatikum as they showed to be the most reliable data set. The proximity to the isotope measurement inlet was the main contributor to the reliability, as small local wind patterns were picked up by both measurements simultaneously.

2.6.2 Methane emission distance modelling

In the methane concentration time series at the Geomatikum, the prominent peaks are very sharp, with a relatively short duration of 0.5 to 3 h and a very high methane concentration of up to 4000 ppb for a background concentration of 2000 ppb. This indicates an emitter located nearby with a relatively short emission time and a high amount of methane released.

The strong correlation between the methane concentration in the air and the tidal cycle of the Elbe was used to estimate the distance between the emitter and the measurement location. To achieve this, virtual tracks of wind particles were modelled using the wind data from the Geomatikum.

The tracks are modelled for the time between the maximal methane concentration of a peak and the lowest water level during the low water cycle of the Elbe before the methane peak. Tracks are backwards-modelled in time, originating at the Geomatikum. The particle follows the measured wind, with a time resolution of 10 min as dictated by the measurement. At each 10 min interval, the partial location is calculated using its previous location, the wind data and Bowring's ellipsoidal-surface formulae. This is repeated until the time when the lowest water level is reached. The total geodesics distance between the Geomatikum and the final location, i.e. the estimated emission location, is then calculated. The resulting distance for all peaks is plotted against its peak's maximal methane concentration in a scatterplot, shown in fig. 3.10.

2.6.3 Gaussian plume transport modelling for methane peaks

A transport model was constructed to locate the emission regions that cause prominent methane peaks. For this purpose, the temporally high-resolution wind data provided by DWD was used. The transport model uses the wind data to create Gaussian plumes with the measurement site as the particle emitter.

The emitted particles travel backwards in time; this allows the calculation of reversed particle tracks. To create Gaussian plumes at a specific emission time, many particles are emitted simultaneously at this time. The particle tracks are calculated using the wind direction and speed for each wind measurement interval so that the particle can follow changes in wind direction and speed over time. The direction and speed of each particle are randomised with a predetermined standard deviation at each interval for each particle. The degree of randomisation was taken from literature values for similar topography and wind speeds as in Hamburg (SD wind speed 0.5 m/s, SD wind direction = 20° [Farrugia and Micallef, 2017]). The standard deviation was calculated for each wind measurement data set using the rolling Yamartino method for the wind direction. A normal standard deviation for the wind speed showed similar values for all data sets. As a large number of particles are emitted, the randomisation on each individual particle yields a Gaussian distribution for the total particle distribution.

The transport model was used in tandem with the peak-finding algorithm to investigate the locations of the methane peak emitters. After the methane peaks were identified in the timeline, the lowest water level of the Elbe before the detected peaks within a 12 h period were identified. Around half an hour before the lowest water level, the majority of the shallow water regions of the Elbe were completely water-free, exposing the soil and sediments to the air. Those regions can be seen in fig. 2.4, showing a topographic map of the Elbe in Hamburg. The Regions that dry out during a low tide start from 0 m (yellow) to 2.7 m (red). It has to be noted that this survey does not include all connected channels and fleets surrounding the Elbe. Most are located in and around the city centre, and all of them are exposed during low tide. To account for all the sections of the river that dry out before the lowest water level is attained, half an hour before the lowest water level is calculated as it is estimated that at this time. The majority of the shallow regions are dry, but due to the change in the tidal range over a lunar cycle, this can vary substantially. The particle tracks are only calculated for the time between the maximum methane peak and the half hour before the lowest water level.

After all particle tracks for all selected emission times are completed, the particle distribution density is calculated. This is done by splitting the map into a 1000x1000 segment raster and calculating the density of particles in each segment. The raster is then normalised for the total domain. The transport model outputs a map with the rasterised particle density overlay as an interactive map fig. 3.11.

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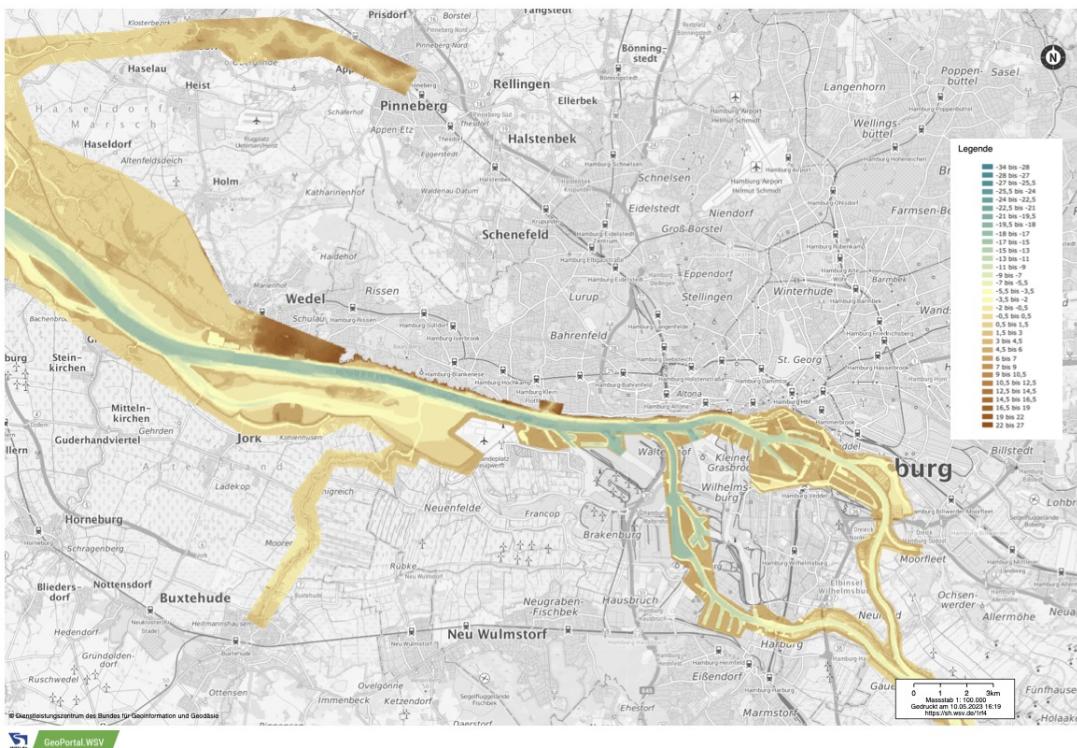


Figure 2.4: Topographic map of the Elbe River in the Hamburg region. Scale is in dm, 0 dm is at mean sea level. [ZDM GDWS, 2016]

Chapter 3

Results

3.1 Methane peaks

With the aid of the methane peak identification tool, the peaks were investigated in detail. In fig. 3.1 and fig. 3.2, a small segment of the total concentration timeline can be seen. Nearly all peaks are accounted for in the first image, where the peaks are

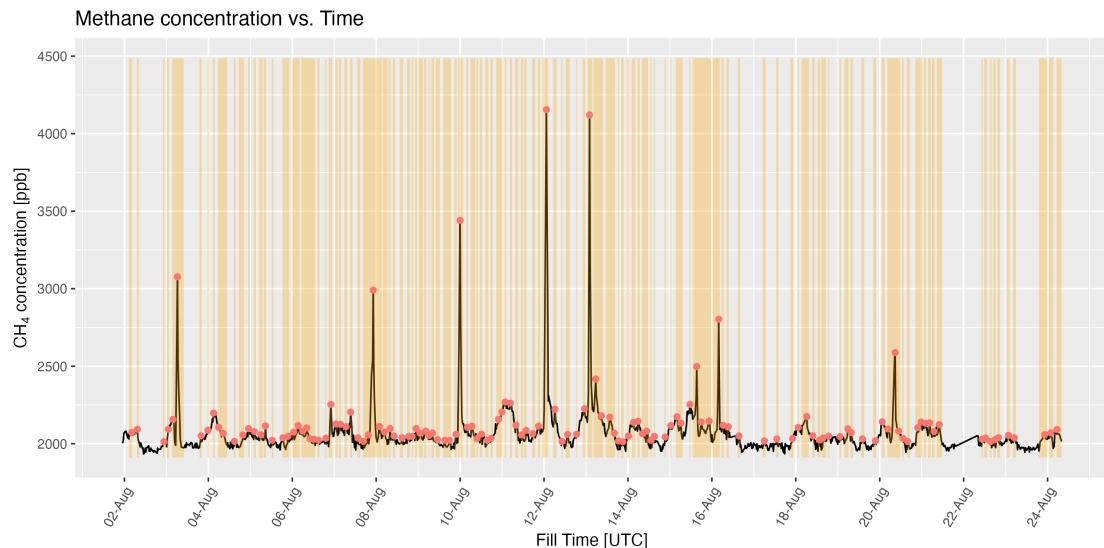


Figure 3.1: Section of CF-IRMS measurement showing the timeline of methane concentrations measured in Hamburg Geomatikum (83 m above ground) from 02.08.2021 to 24.08.2021. Peak identification criteria by Menoud et al., 2021. The red dots indicate the peak centres and the orange section highlights the peak width.

selected according to literature criteria. The smaller peaks occur at a relatively high frequency with a substantial irregularity. The number of peaks per day varies between 5 to 15 peaks, whereby the frequency of the peaks is lower during warmer months, August, September and October, than for the colder months, December, January, and February; see table 3.1. Intermediate and prominent peaks occur at relatively regular intervals, with a maximum of two peaks per day, and their peak centres are always at least 12

Chapter 3 Results

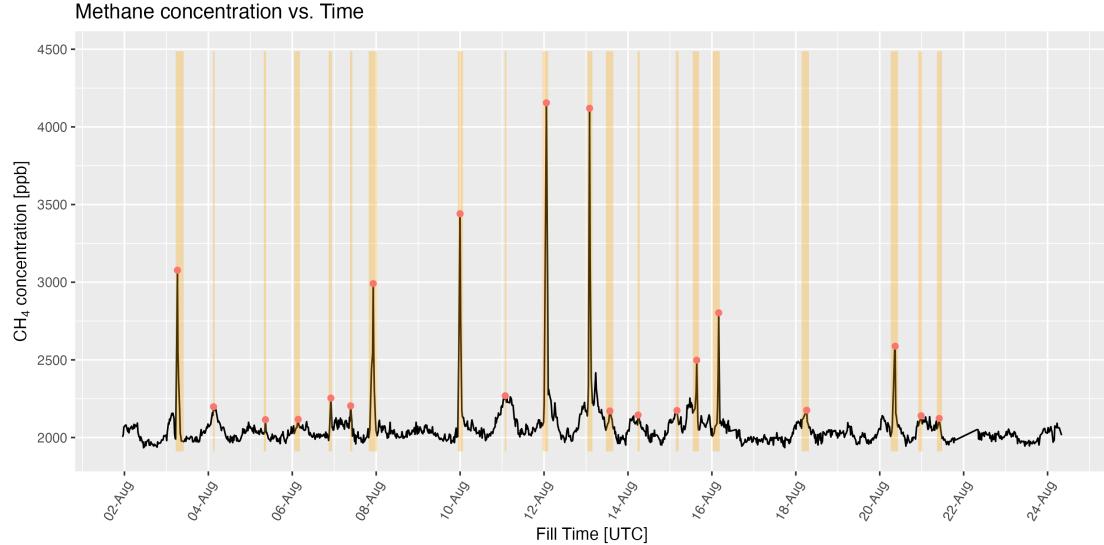


Figure 3.2: Section of CF-IRMS measurements showing the timeline of methane concentrations measured in Hamburg Geomatikum (83m above ground) from 02.08.2021 to 24.08.2021. Peak identification criteria are chosen for only prominent peaks. The red dots indicate the peak centres and the orange section highlights the peak width.

	Aug.	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
A:	164	182	195	185	205	174	145	190
B:	23	31	37	32	36	28	20	23

Table 3.1: Table of methane peaks per month using two different identification criteria. A: Selection criteria by Menoud et al., 2021. B: Strict criteria only selecting prominent peaks

hours apart.

In the second image, the identification criteria are intentionally designed to identify and emphasize the significant large and intermediate peaks, ensuring they are highlighted effectively. These peaks occur throughout the entire measurement campaign, although they are more frequent and concentrated during the warmer months compared to the colder ones. All of these peaks exhibit sharp characteristics, marked by short durations and higher concentrations when compared to the background levels.

3.2 Methane correlation analysis

3.2.1 Elbe water level methane correlation

The overlay of the methane concentration timeline with the water level of the Elbe is shown in fig. 3.3. It can be seen that the prominent methane peaks occur shortly, on average, 2 ± 1 h, after the low water of the river. This behaviour is observed throughout the measurement period. As the prominent methane peaks can not be observed

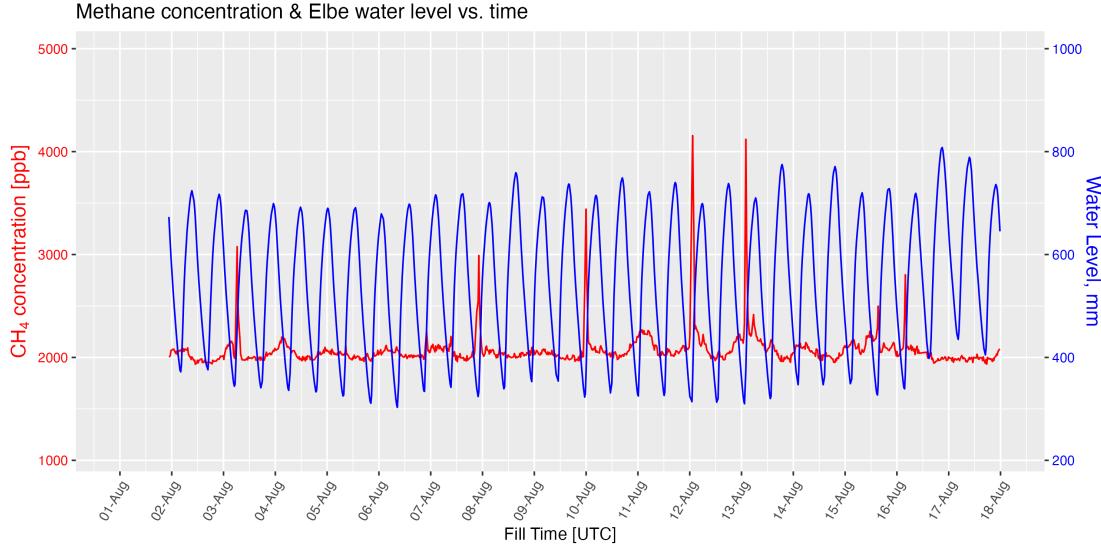


Figure 3.3: Section of the CH_4 concentration timeline measured with the CF-IRMS at the Geomatikum (Red). Overlayed with the water level timeline of the Elbe (blue). Measurements from 02.08.2021 to 18.08.2021 are shown.

during every low water cycle of the river, additional factors seem to contribute to their production. However, to establish a statistically significant correlation, the Pearson's correlation coefficient between the water level and the methane concentration was investigated as previously described. This correlation can be seen in fig. 3.4a. Here, the measurements are binned by speed and direction using the wind measurements made at the Geomatikum. The plot shows a positive correlation with a green colour and a negative correlation with a red colour. A positive correlation indicates an elevated methane concentration in the air with a high water level of the Elbe. In contrast, a negative correlation indicates a correlation between methane concentration in the air with a low water level of the Elbe. The P-value test in fig. 3.4b checks if the correlation is statistically meaningful with a P-value <0.05 indicating significance.

The correlation plot fig. 3.4b shows a negative correlation that passes the p-value test at a wind direction of 180° and 250° with wind speeds of 1 m/s and 7 m/s, respectively. Following the direction of the wind leads to the port region of Hamburg.

The remaining wind bins that include the wind directions East, North and West don't show reliable correlations between the water level and the methane concentration mea-

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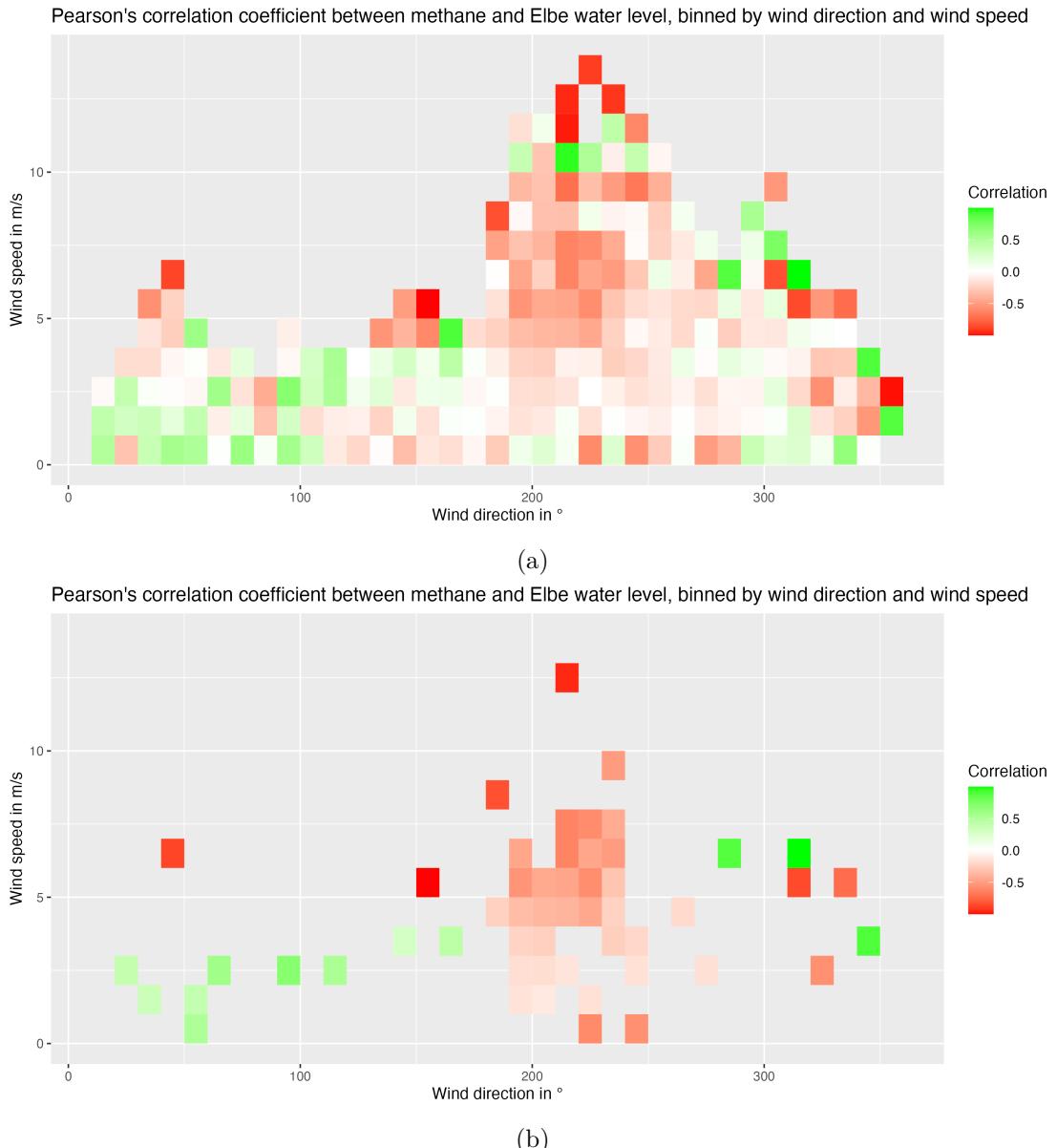


Figure 3.4: (a) Pearson's correlation coefficient between methane and Elbe water level, binned by wind direction and wind speed. Green shows a positive correlation (enhanced CH₄ at high water levels), and Red shows a negative correlation (enhanced CH₄ at low water levels). (b) Shows only the correlations which pass the 5 % P-value test for methane and Elbe water level, binned by wind direction and wind speed.

sured at the Geomatikum. From the Geomatikum to its East, North and West, significantly fewer water bodies are free-flowingly connected to the Elbe are present. Those water bodies do not experience tidal effects.

The overall methane concentration and presence of peaks are generally higher when the Elbe experiences lower overall water levels. Visa versa, fewer methane peaks and a lower concentration are observed at high water periods. The variation in the water levels for an extended amount of time is due to changes in meteorological influences over an annual cycle and the lunar cycle influences in the tide. This can be seen in fig. 3.5. The plot shows the total measurement campaign with a rolling average of one month for the water level as well as the methane concentration measured at the Geomatikum. While a

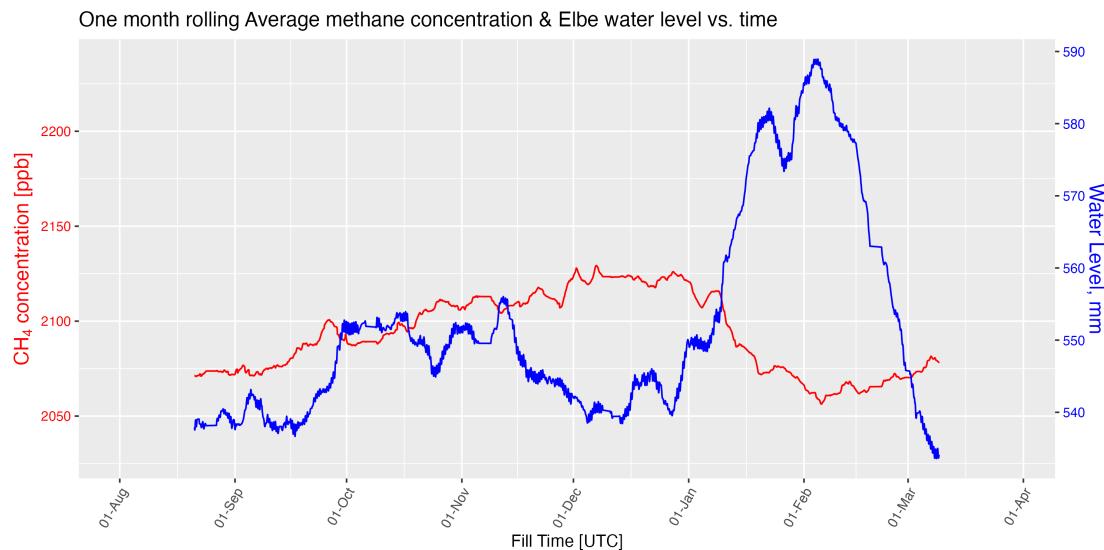


Figure 3.5: Rolling average timeline plot of CH₄ concentration measured with the CF-IRMS at the Geomatikum (Red) overlaid by the water level timeline of the river Elbe (blue).

perfect linear correlation between the water level and the methane concentration was not observed when not regarding the wind direction and speed. The correlations that were observed, for particular wind directions and speeds, indicate that a significant amount of methane measured at the Geomatikum originates from the Elbe that also correlates to its tidal movements.

3.2.2 Elbe water quality methane correlation

Water quality parameters measured at Elbe Seemannshöft provided by Hamburg Service were used [IHUW, 5 01] and as well investigated using the Pearson's correlation coefficient and the P-value test. The influence of the Elbe can be seen in a particular region of wind direction and wind speeds in the resulting binned correlation plots fig. 3.6. This region is around 180° to 300° for a wind speed between 1.5 m/s to 7 m/s and is

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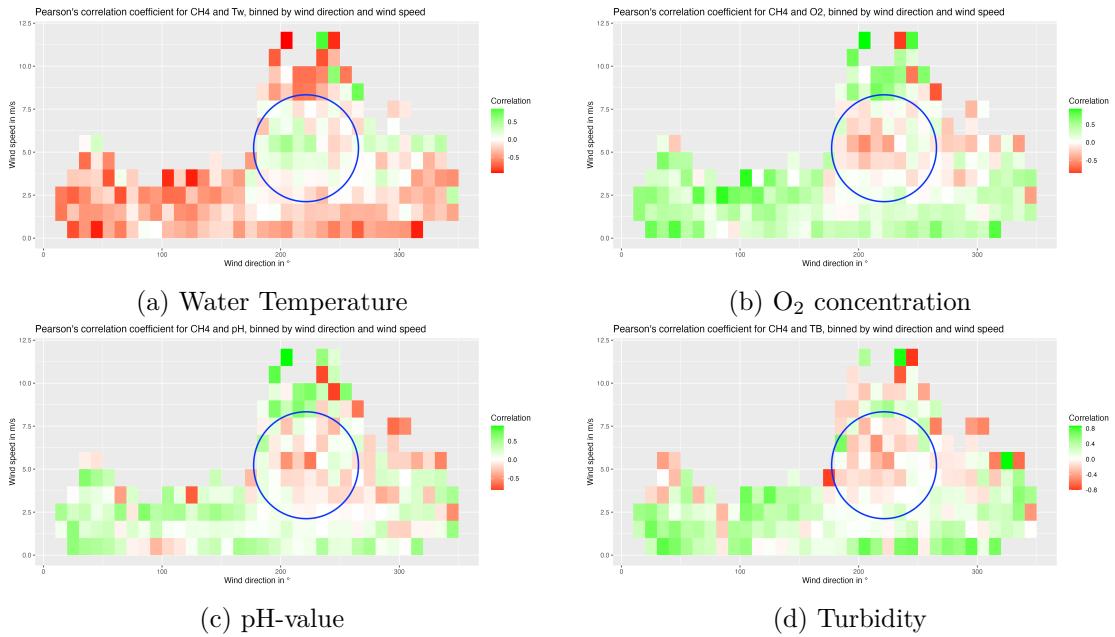


Figure 3.6: Pearson's correlation coefficient between methane-air concentration and Elbe water quality parameters, binned by wind direction and wind speed. Green shows a positive correlation (enhanced CH₄ at high values), and red shows a negative correlation (enhanced CH₄ at low values). The blue circles indicate the wind direction and speed where the Elbe has a strong influence.

highlighted by blue circles in the plots. In this general direction from the Geomatikum, the river is located and is most drastically influenced by the tides. Further to the east, a series of locks blocks the tide in the river, while to the west, the Elbe is significantly wider and more naturalised. [Matouš et al., 2019] has shown a 10 times lower methane concentration in the Elbe in this section.

Apart from the water level of the Elbe discussed previously, some water quality parameters also show a good correlation with the methane concentration in the air measured at the Geomatikum.

Those include the water temperature, oxygen concentration and saturation, turbidity, UV absorption and pH level. The water temperature is the only parameter that shows a positive correlation with the methane concentration measured at the Geomatikum; all other parameters show a negative correlation with the methane concentration. All previously listed parameters pass the P-value test in the blue highlighted region that represents the general direction of the Elbe. Other water quality parameters, such as electrical conductivity and algae concentrations (chlorophyll concentration of various different species), do not show a correlation with the measured methane concentration. Those parameters do not seem to influence the microbial performance in the Elbe significantly enough to influence their methane production and reduction mechanisms substantially.

3.2.3 Meteorological observation and methane correlation

The meteorological data measured by the DWD at Hamburg-Fuhlsbüttel [Deutschen Wetterdienst, 5 01] was investigated in the same manner as the water parameters of the Elbe. The Pearson's correlation coefficient and P-value tests for the meteorological parameter with the methane concentration in the air show some correlations between them. Those include air temperature, solar radiation, dew point and humidity.

The humidity and dewpoint measurements have a general correlation for all wind directions and speeds, excluding the region $180^\circ - 300^\circ$ and (0.5 to 3.5 m/s). In this region, no significant correlation can be observed. This can be seen in fig. 3.7a and fig. 3.7b, where the black circle indicates this region. Following these wind directions and considering the low wind speeds leads to the densely urbanised city centre, where very few natural areas such as parks and gardens are present.

The temperature and solar radiation correlate significantly with the methane concentration. A negative correlation is observed in nearly all regions, only excluding the $180^\circ - 250^\circ$ (1.5 to 7 m/s) region. In this wind direction, the Elbe is located, and the methane emissions from the Elbe seem to dominate in this region. In fig. 3.7c and fig. 3.7d, this region is indicated by blue circles. The remaining region shows a significant negative correlation of the temperature and solar radiation with the methane concentration in the air. In particular, wind directions from 330° to 130° show a very strong negative correlation at all wind speeds. The wind direction in this region point to the primarily residential regions of Hamburg. The Elbe is not present in this region, and no tidal-influenced water bodies exist there. The Keeling plot analyses with regards to wind direction, which will be discussed later, indicates a strong influence of anthropogenic methane production from, for example, fossil fuel combustion. This is also confirmed by Maazallahi et al., 2020, who found numerous gas infrastructure leakages and a generally high anthropogenic methane mixture in this region using street-level mobile measurements. Other meteorological parameters were investigated, such as precipitation and air pressure, etc. For those parameters, no correlation with the methane concentration in the air measured at the Geomatikum could be observed.

3.2.4 Wind analysis and methane correlation

By analysing and implementing the wind measurements provided from the DWD and Hamburg Universitat, the data measured at the Geomatikum proved to yield the most reliable results. The measurements by the DWD at Hamburg-Fuhlsbüttel suffered from high variability due to the low measurement altitude and presences of high disturbances in the topography, fig. B.5. In contrast, the measurements at the weather mast in Hamburg Billbrook showed good, turbulent-free results. However, the 17 km distance between the CF-IRMS measurement location and the weather mast, the analysis showed a temporal mismatch between of the two measurement series. Consequently, the measurements at the Geomatikum proved the most reliable due to the proximity to the CF-IRMS measurement and the relatively low disturbance resulting from the height of the measurement device being 83 m. In the modelling discussed later on, the measure-

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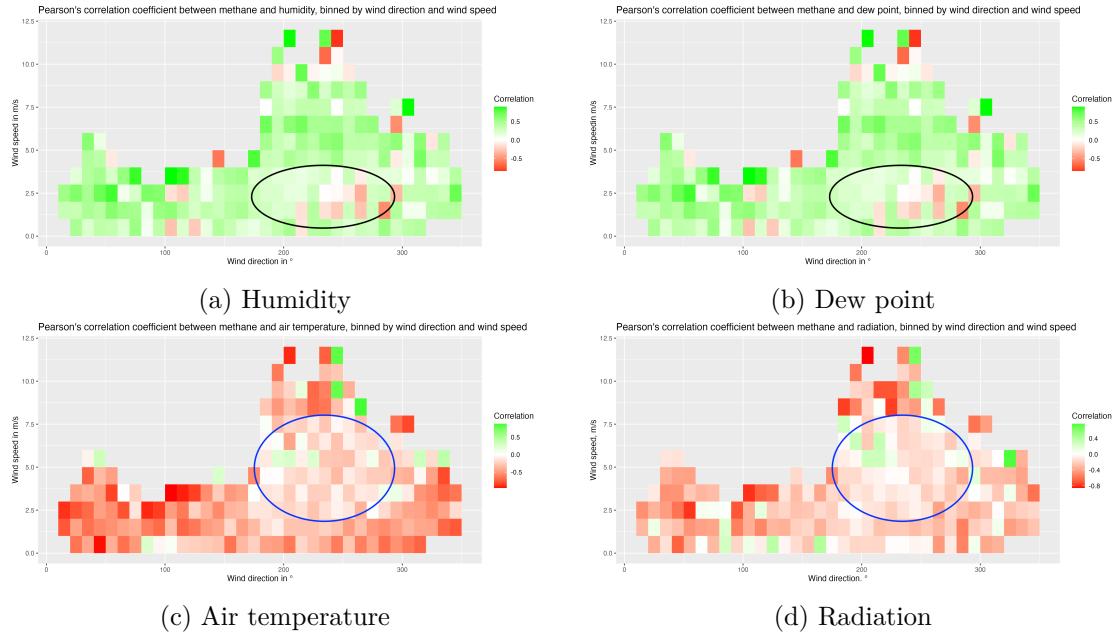


Figure 3.7: Pearson's correlation coefficient between methane-air concentration and meteorological data, binned by wind direction and wind speed. Green shows a positive correlation (enhanced CH₄ at high values), and red shows a negative correlation (enhanced CH₄ at low values). The black circles indicate a region with no correlation, potentially the city centre of Hamburg. The blue circles indicate the region where the Elbe is located.

ments at the Geomatikum also showed the best results.

The total measurement series from 01.08.21 to 01.4.2022 showed that dominant wind direction could be observed from the South-West with generally medium wind speeds. The Windrose Plot fig. 3.8 shows this average wind direction from South-West rather well. While wind from all directions has generally been observed, four distinct patterns were observed, indicating some reoccurring and distinguished weather patterns in Hamburg, most likely, the westerly winds, high-pressure regions over the mainland and transitions of cyclones into central Europe. By additionally using the methane measurements in a pollution rose plot, one can see that methane can be observed from every direction. This indicates the background methane concentration has no clear emission direction. The highest concentrations in the pollution rose plot is observed most often in the South-South-Western wind direction. When applying the Peak finding algorithm with the strict identification criteria to the wind measurement data, the wind rose distribution changes substantially fig. 3.9. Measurements from the northern wind directions are observed very rarely. Generally, only wind measurements between the South and West are observed regularly. The wind speed is also significantly slower, where most measurements have a speed of 2-4 m/s.

The pollution rose plot fig. 3.9b, in particular, shows that the peaks, especially the high

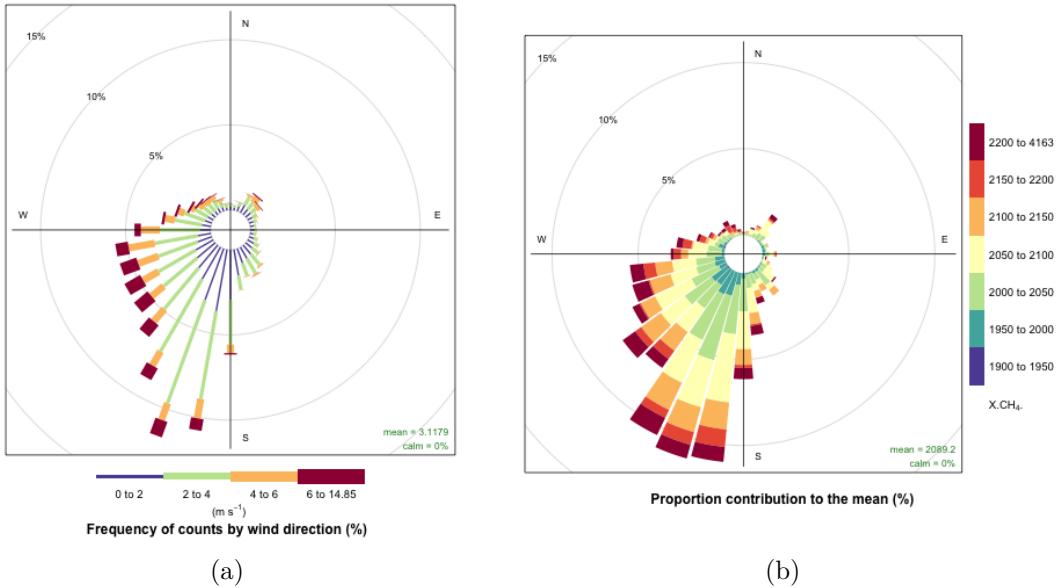


Figure 3.8: (a) Wind rose for the total campaign measured at the Geomatikum. (b) Pollution rose with wind data measured and CH₄ concentration measured at Geomatikum in ppb.

concentration ones, occur in three distinct directions, South-West, South-South-West and South-South-East. The highest methane concentration peaks of over 2600 ppm occurred in wind directions of South-South-West. In this direction, the Elbe is in closest proximity to the Geomatikum. In the South-South-East to the Geomatikum, the city centre with its numerous channels, fleets and small ports is located. The water body in this region strongly experiences the effect of the tide.

The directions observed in the pollution rose plots are the same as the ones observed in the correlation plot in section 3.2.1, correlating the water level and quality with the methane concentration in the air. This is another indication that the methane observed at the Geomatikum originates at the Elbe.

3.3 Methane transport modeling

3.3.1 Source distance estimation

With the use of the distance estimation model, the distance between the methane peak emission location and the Geomatikum was modelled. The resulting plot can be seen in fig. 3.10. In this plot, each point represents an individual methane peak with its methane concentration measured at the Geomatikum versus the estimated distance between the emitter and measurement location. The blue line represents a local regression with its standard errors highlighted in dark grey. For this plot, strict peak identification criteria are used. A plot with the identification criteria as described by Menoud et al., 2021 can

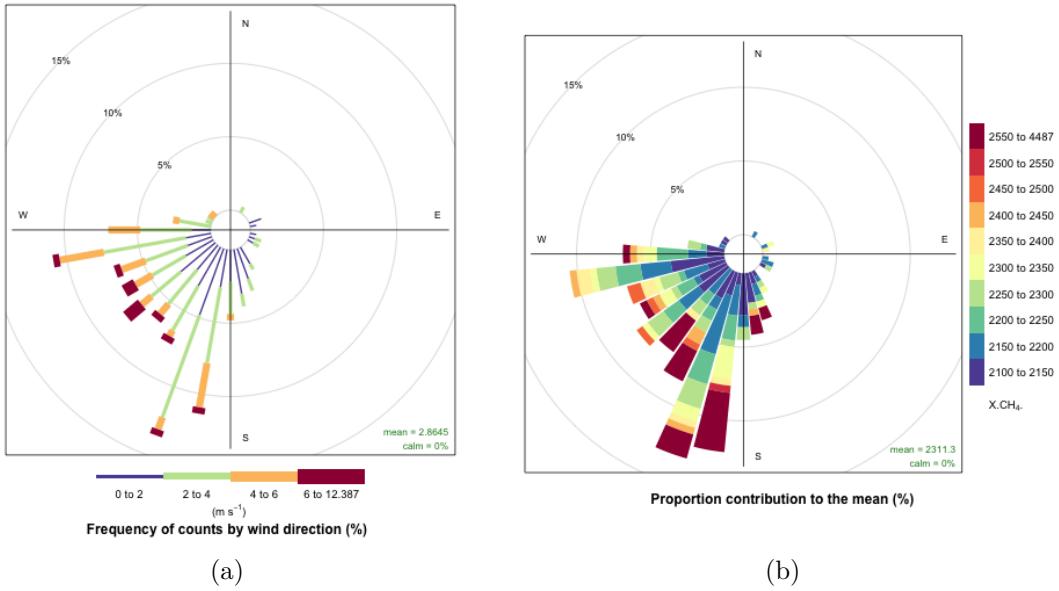


Figure 3.9: (a) Wind rose during CH₄ peaks identified with strict criteria measured at the Geomatikum. (b) Pollution rose for the CH₄ peaks with wind data measured and CH₄ concentration measured at Geomatikum

be seen in fig. B.6. A few details can be observed from the plot. The highest density of peaks is seen between 2 and 10 km distance form the Geomatikum, with rapidly decreasing density with increasing distance. A couple of peaks show large distances of up to 60 km away. The distance estimation for those points is most likely not correct as the distance travelled is substantial, and the plume of a strong and localized methane emitter would most likely spread considerably over this distance. A geographically large emitter such as the Waddensea is in the 60 km range, and large emissions from this region could, at favourable wind conditions, result in an elevated methane concentration in the air. A possible distance overestimation due to strong winds for a close-by emitter is also possible.

When considering the local regression line, a peak at a distance of 5 km can be observed. The curve also shows that the peaks estimated to originate further away have a decreasingly lower methane concentration. This curve indicates that the emission location responsible for the high concentration peaks is located at a distance of around 5 ± 3 km from the Geomatikum. In a 5 km radius of the Geomatikum, most of the Hamburg port, the channels fleets etc., are located, while a 10 km radius includes most of the water bodies located in Hamburg.

3.3.2 Emitter location modelling

Methane transport has been modelled and is shown in fig. 3.11. In this plot, only the methane peaks identified with the strict identification criteria are modelled. The density

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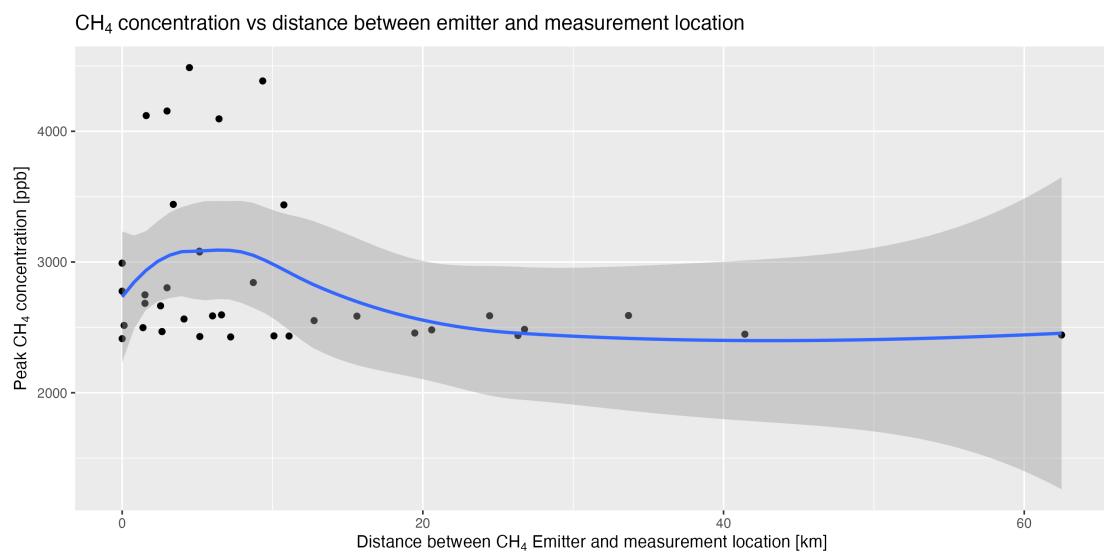


Figure 3.10: Scatter plot of modelled distance between the estimated emission location and the measurement location at the Geomatikum, against the methane concentration observed by the CF-IRMS at the measured Geomatikum. A local regression line is fitted to the plot (blue), showing the highest concentration peaks to be emitted at a distance of 5 ± 3 km. The standard error of the line is shown in dark grey. The peaks were identified using the strict identification criteria.

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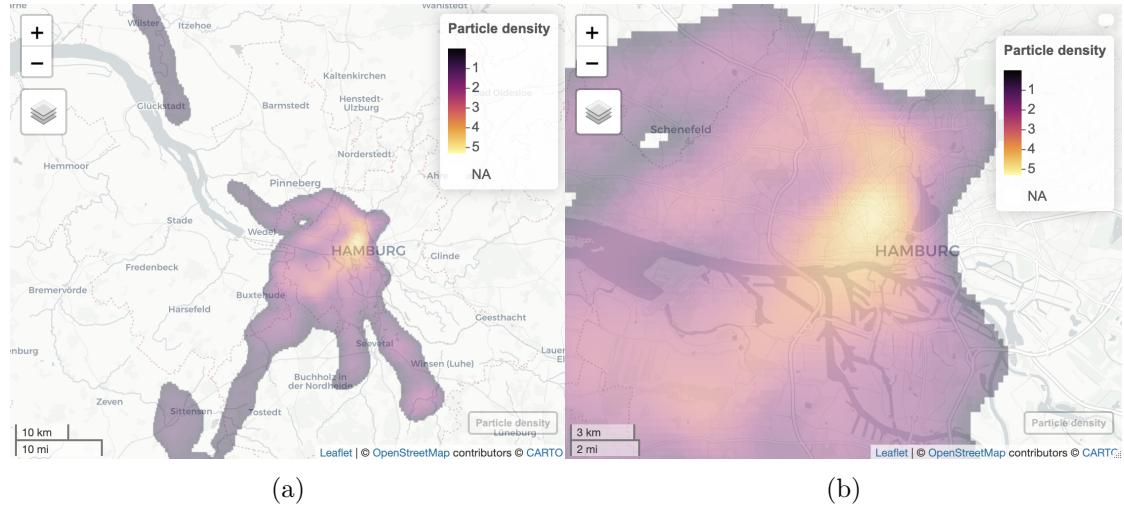


Figure 3.11: (a)Map of the partial density for the time-reversed Gaussian plume model. Strict methane peak identification criteria were used to select only prominent methane peaks. Wind data was measured at the Geomatikum with 10 min time-averaged values. 1000 particles were released per methane peak with standard deviations of 0.5 m/s and 20°. The heat map overlay represents the particle density at each segment using a logarithmic scale. Figure (b) is zoomed into the Hamburg city region.

distribution represents the probability of the methane emission locations and is depicted as a heat map overlay in the figure. The plot shows an exceptionally high density in certain inner-city regions. The first is in the historic city centre, where the Alster joins the Elbe. The Alster is a large, sweet, and relatively shallow water lake located in this region of the city. [Maazallahi et al., 2020] and the mobile measurements during the UNEP campaign consistently observed an elevated methane concentration around the Alster. While the enhancements were low in magnitude, they were spread out over a large area around the lake.

The second region is the south of Hamburg, where the Hamburg port is located. The region includes a vast network of channels, contributing rivers, small harbours and some small wetlands.

Locks in this region partly control the river and its tidal cycle. Still, most of it is free-flowing and experiences significant water level changes and even running dry in certain areas.

The last region of higher density is on the western side. Notably, many tracks follow the Elbe downstream towards the Waddensea. This region experiences the effects of the tide very strongly, with large regions that run dry during low tide, most notably, some wetland regions outside of the city border.

This indicates that the origin of methane peaks can be quite far away. Still, methane accumulation in the air along the river's entire length is possible, and high methane

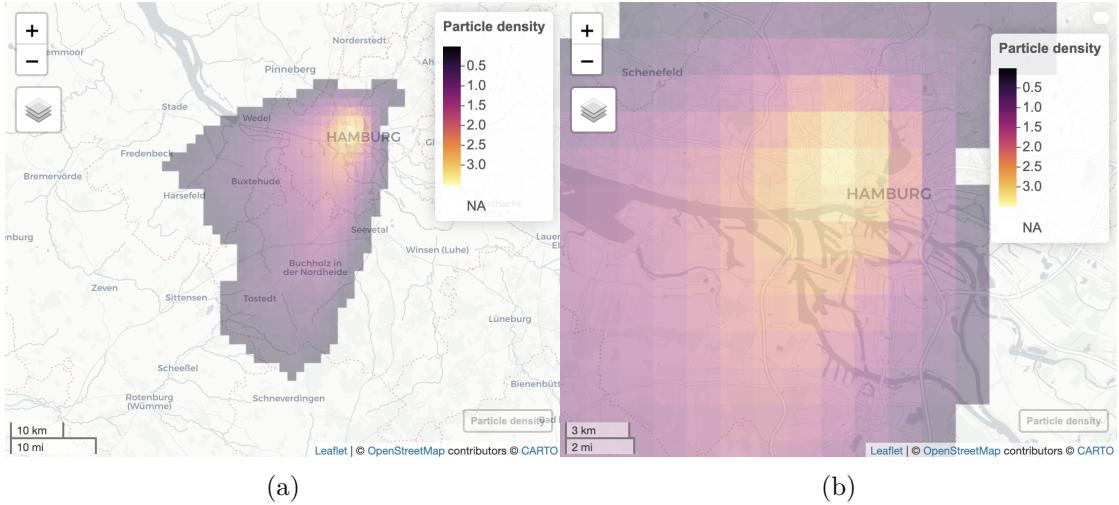


Figure 3.12: Map of the partial density for the time-reversed Gaussian plume model. Using methane peak identification criteria by Menoud et al., 2021. Wind data was measured at the Geomatikum with 10 min time-averaged values. 100 Particles released per methane peak with standard deviations of 0.5 m/s and 20°. Heat map overlay representing the particle density at each segment with a logarithmic scale.

concentrations in the city can occur when wind conditions are favourable. One can also notice that a higher density occurs North of the Geomatikum. A further investigation of the tracks shows that at those peaks, the wind speed is relatively slow, and the wind direction is turning. The tracks also lead to a large wetland region on the Elbe just outside the city bordered on the south-west side of the city.

When applying the peak identification criteria by Menoud et al., 2021, identification of a distinct emission region is much more difficult. This is due to the wide range of peak types that are detected with this method. As will be discussed in section 3.4, significantly more Anthropogenic emitters contribute to the smaller peaks. fig. 3.12 shows that the origin of those peaks, including ones from anthropogenic emitters, is less localised. The region around the Geomatikum shows a high density, with a generally high density in the Hamburg port region to the South and South-West of the Geomatikum. Coincidentally this is also the dominant wind direction, as can be seen in fig. 3.8. The area covered by the tracks and the distance travelled by the particle is generally larger and more uniformly spread in every direction. This probably originates from the more random nature of the peaks occurring at unpredictable times and wind conditions.

3.4 Isotope signature analysis

3.4.1 Keeling plot analysis

Using the Keeling method, the methane origin sources were investigated. The complete timeline of the $\delta^{13}\text{C}$ and δD CF-IRMS measurements together with the CH_4 concentration is shown in fig. 3.13. By using this complete timeline, the Keeling plot approach

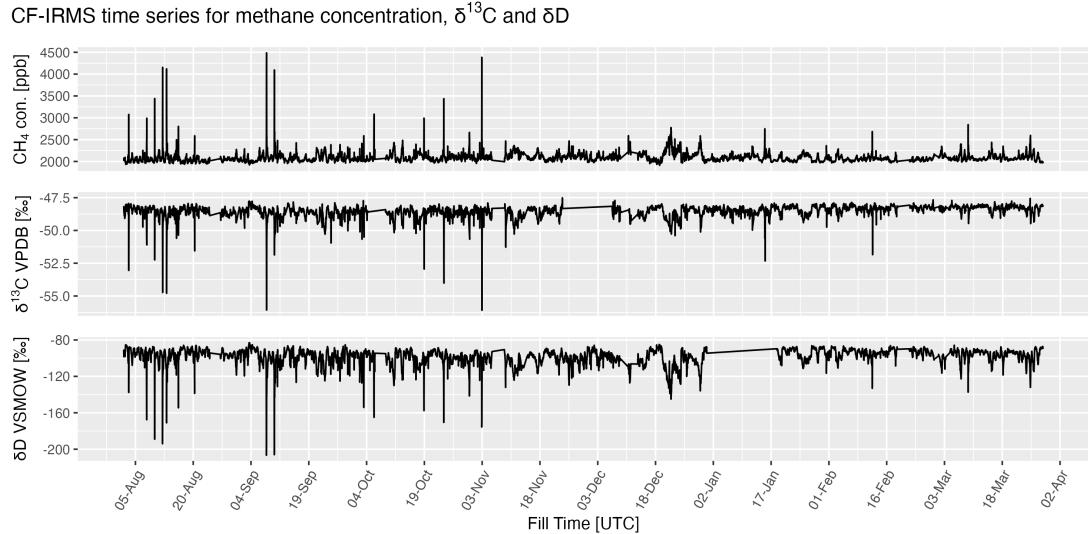


Figure 3.13: Complete timeline of the $\delta^{13}\text{C}$, δD and CH_4 concentration measured by CF-IRMS at Geomatikum from 1.08.2021 to 1.04.2022

was deployed, and the resulting plots are shown in fig. 3.14. The isotopic signature for Carbon-13 was calculated to be $\delta^{13}\text{C} = -57.7 \pm 0.1\text{\textperthousand}$ and for Deuterium to be $\delta\text{D} = -290.5 \pm 0.8\text{\textperthousand}$. Comparing those results to the database values show that the dominant methane production mechanisms during the total campaign time in Hamburg were thermogenic and microbial CO_2 reduction. In particular, wetland, agriculture, and waste. Fossil fuel and other anthropogenic sources play a minor role in the composition of the methane mixture. This is surprising as Hamburg has a significant amount of heavy industry, including fossil fuel refinery, chemical industry, shipping, energy production etc. On the other hand, this is expected, as the surrounding countryside has significant ecological use, including cattle farms and large wetland and marshland areas nearby. This also includes the vast Waddensea of the German bight near the city. This Waddensea region lay upwind in the dominant wind direction to the west.

By applying the peak finding algorithms to the methane measurements data exclusively, the methane peaks were investigated. Here it is focused on the strict identification criteria. The Keeling plots for the identified peaks are shown in fig. 3.15. The Keeling method shows isotopic signature for Carbon-13 to be $\delta^{13}\text{C} = -60.3 \pm 0.2\text{\textperthousand}$ and for Deuterium to be $\delta\text{D} = -298 \pm 2\text{\textperthousand}$. This indicates methane production mechanisms are much more evident in the microbial CO_2 reduction region and less in the thermogenic, shifting

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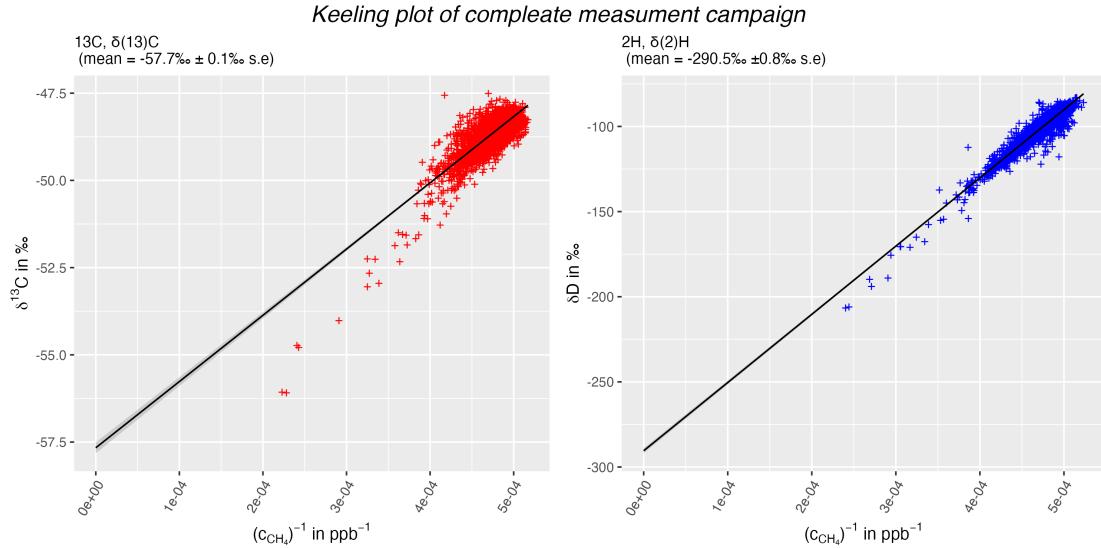


Figure 3.14: Keeling Plots of Carbon-13 and Deuterium in methane measured at the Geomatikum from 1.08.2021 to 1.04.2022. The resulting isotopic signatures $\delta^{13}\text{C} = -57.7 \pm 0.1\text{\textperthousand}$ and $\delta\text{D} = -290.5 \pm 0.8\text{\textperthousand}$

this more clearly into the wetland region, while less likely to originate from waste and agriculture. The Keeling method points toward the origin of the methane peaks due to biogenic mechanisms in the Elbe, its contributors and the wetlands at its riverbanks. Using the wind direction makes it possible to take an even closer look at the methane emission type depending on its estimated origin location. This is done in the dual isotope plot seen in fig. 3.16. Here a Keeling analysis for every wind direction is done within 10° bins. Each point has an error bar corresponding to its standard deviation. The point colour indicates the wind direction in regard to the North (blue) and South (red) wind directions. The wind directions, West and East are not considered in this plot for simplification. The highlighted coloured areas indicate the fundamental methane production method (microbial CO_2 reduction (yellow); microbial fermentation (pink); thermogenic (dark green) and abiotic (light blue)). The coloured boxes show particular emitter types (fossil fuels and non-industrial combustion (red); agriculture (green); waste (purple); other anthropogenic sources (dark blue); natural wetlands (black)). The reference database used in this dual isotope plot for the highlighted segments is from [Menoud et al., 2021].

In the dual isotope plot considering the total measurement time series fig. 3.16a, one can identify a difference in isotope signature and origin type by the wind direction. For the entire measurement series, one can see that the signature shifts to the abiotic production type for general northern wind directions, hence towards fossil fuels and other anthropogenic sources. As considerably fewer wetlands are present in this region, and many residential areas lay there, one can assume that this shifts the methane mixture towards fossil fuels. Moreover, unburned methane from heating and cooking, leakages in the gas

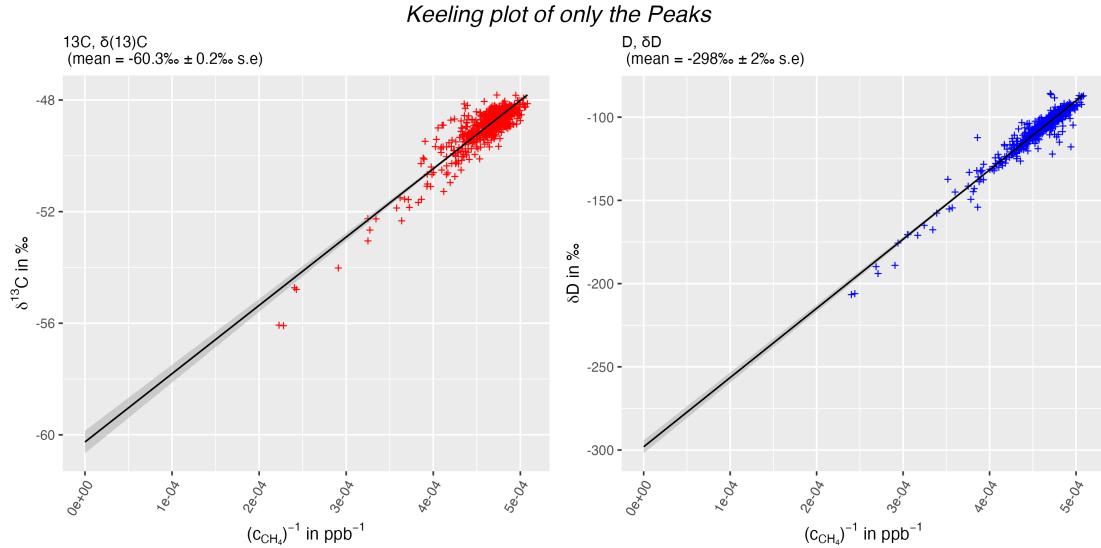


Figure 3.15: Keeling Plots of Carbon-13 and deuterium in methane peaks measured at the Geomatikum from 1.08.2021 to 1.04.2022. Strict peak identification criteria that only selected the prominent methane peaks were used. The resulting isotopic signatures $\delta^{13}\text{C} = -60.3 \pm 0.2\text{\textperthousand}$ and $\delta\text{D} = -298 \pm 2\text{\textperthousand}$

grid, and energy generation plays a significant role in the composition of the methane mixture [Lebel et al., 2022], [Dietrich et al., 2023]. This finding confirms observations made by Maazallahi et al., 2020, who focused on ground-based mobile measurements in the northern region of Hamburg by identifying numerous methane leaks in the gas grid. For the southern and western directions, the methane signature is quite strong in the microbial CO₂ reduction region, pointing out that the most significant contributors to this methane mixture are wetlands, agriculture and waste. At the same time, waste can be discarded due to the absence of large landfills in the region. As mentioned previously, this is expected due to its geographical and biological features, together with the strong agricultural use of the region. What is surprising is the minor effect of anthropogenic sources, like fossil fuel and industry, as this region is heavily used.

The same analyses have been done for the methane peaks, as seen in the dual isotope plot, fig. 3.16b. Here, it has to be noted that not all wind directions had sufficient peaks to create a statistically meaningful Keeling analysis. The dual isotope plot indicates a wetland and agricultural origin for the remaining wind directions. Pointing again toward a biogenic origin in the Elbe and its wetlands.

3.5 FTIR total column analyse

The FTIR measurements suffered from technical limitations that restricted the measurement time of the sensor network. In addition to the inability to measure during the night, the weather severely disturbed the analysis. During the relatively short period

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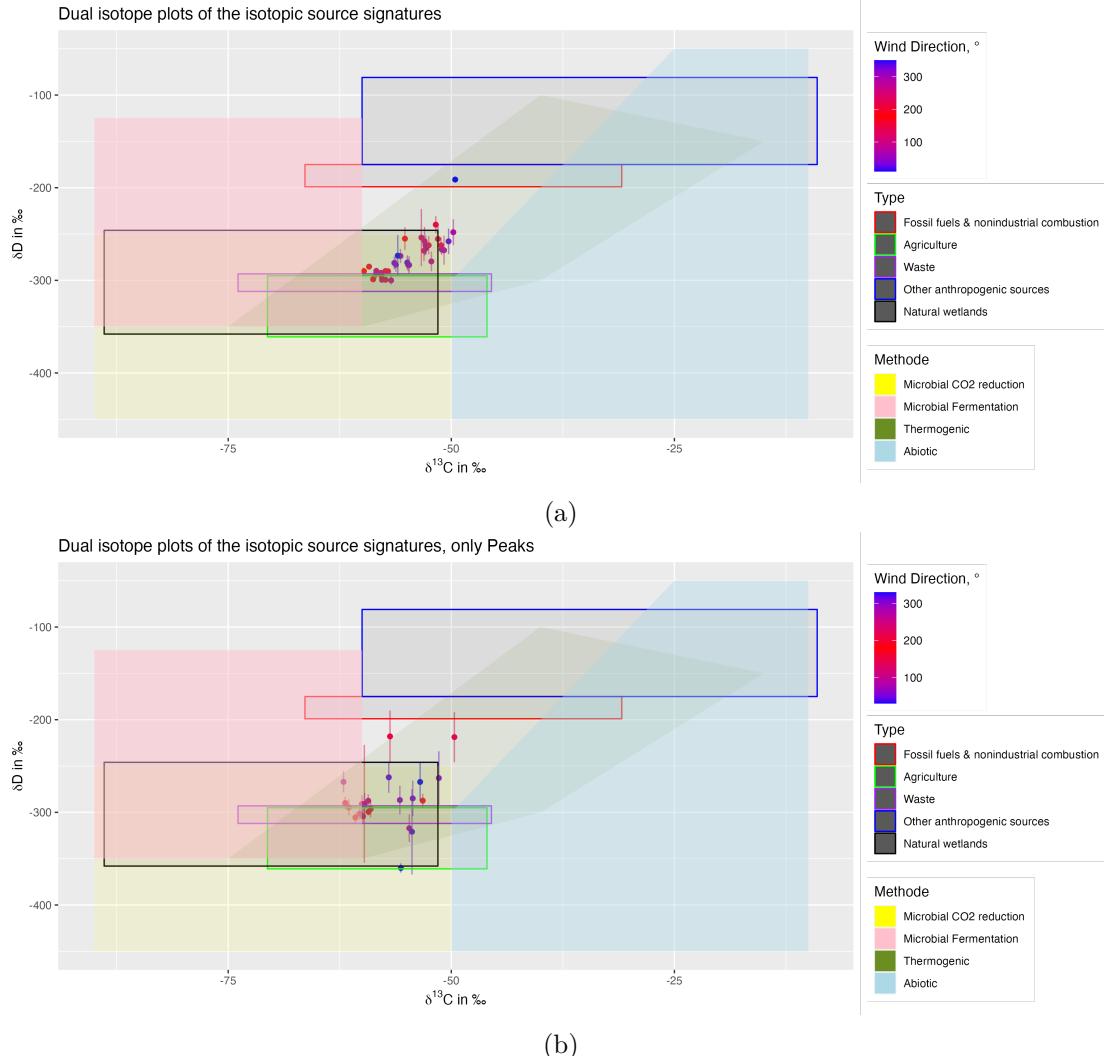


Figure 3.16: Dual isotope plot for CF-IRMS measurement for 10° wind direction represented as point colour (blue towards North, red toward South) with highlighted production mechanism (coloured highlight) and source type (coloured boxes). Error bars indicated the standard deviation. fig. 3.16a shows total time series, fig. 3.16b shows only peaks selected with strict identification criteria

between 27.07.2021 and 09.09.2021, much precipitation and consistent cloud cover were observed. For the Bayesian inversion to work, at least two stations must operate uninterrupted for an extended time. To find good days for the inversion, the following series of pre-filters was applied:

1. Physical properties of the measurements
 - Solar elevation
 - Absolute solar intensity
 - Solar intensity variation during an FTIR scan
2. Statistical removal of outliers and measurement periods with too few data points
 - At least two stations measured at the same time
 - More than 5 h per day per station
3. Measurements are averaged using a 10-min moving average

This resulted in only nine usable days out of a 43-day campaign.

The inversion model estimated a total annual emission for the uncorrected TNO GHGco inventory and the mobile measurement updated inventory. The emissions sources were also segmented into natural and anthropogenic. With the TNO GHGco inventory, the natural (including the river) and anthropogenic emission summed up to $6300 \pm 3500 \text{ kg h}^{-1}$, and with the updated inventory to $6300 \pm 4100 \text{ kg h}^{-1}$ for the total modelling domain. This domain included a significant area surrounding the city and can be seen in fig. 3.17. For the natural sources, which include the Elbe, the model estimated hourly an emission of $1900 \pm 1000 \text{ kg h}^{-1}$ for the TNO GHGco inventory and $1900 \pm 1000 \text{ kg h}^{-1}$ for the updated inventory [Forstmaier et al., 2023]. This is a significant amount of the total emissions in the domain. A considerable amount of the modelled methane emissions can be attributed to the Elbe, riverbanks, marshland and wetland surrounding the river.

3.5.1 Total column methane peaks

To identify methane peaks that can be linked to the tidal cycle of the Elbe, individual sensor stations needed to measure uninterrupted for an extended amount of time. A low water cycle also needed to align with this measurement window. As with the CR-IRMS measurement, the wind conditions also needed to be favourable to transport a plume to the observation column.

Multiple peaks that appear to originate from the water level dropping in the Elbe could be identified by manually filtering the total column and the water level measurements. For those peaks, the transport model showed that the wind direction and speed were favourable for emission from the river and its surroundings to be observed at the sensor locations.

Peaks suggested to originate from the Elbe were mainly observed from the stations at the Geomatikum (North (me)) and Jork (West (mc)). The Geomatikum (North (me))

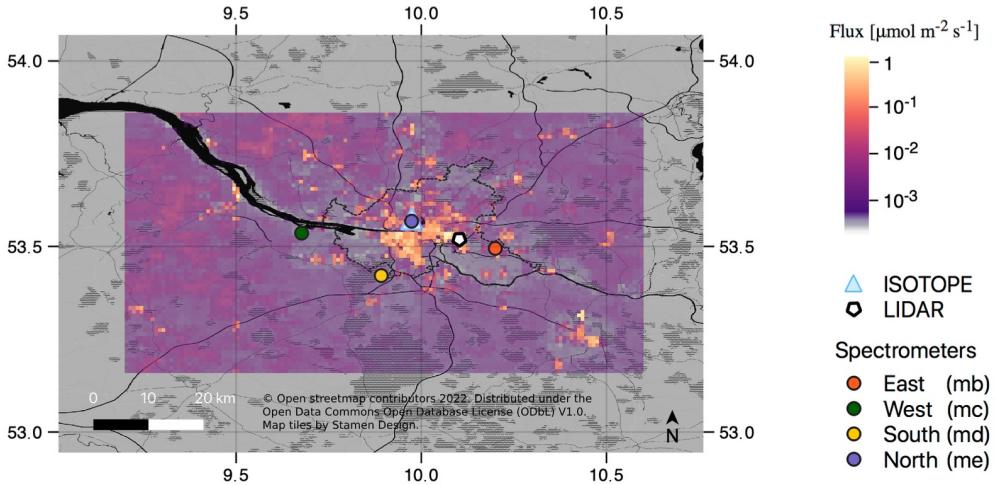


Figure 3.17: Modeling domain used in the Bayesian inversion with the prior TNO GHGco emission inventory. No corrections for the mobile measurements and the Elbe. The locations of the FTIR Spectrometers, wind LiDAR and CF-IRMS during the campaign are shown. The city borders of Hamburg are marked in black. [Forstmaier et al., 2023]

station showed that the concentration and occurrence of methane peaks measured by the FTIR spectrometer were relatable to the CR-IRMS measurements.

The Jork (West (mc)) station was located relatively close and South to the Elbe, which is upwind of Hamburg's dominant wind direction. Methane peaks, likely originating from the Elbe were still observed occasionally at wind directions from the North fig. B.7a. The remaining stations at Rosengraten (South (md)) and Bergedorf (East (mb)) were quite far from the Elbe, both in opposite directions from the predominant wind direction. At favourable wind directions, elevated concentrations could be observed fig. B.7b, but a clear link to the Elbe could not be made due to the strong influence of the city and the large distances to the Elbe.

An example of a methane peak that is assumed to originate from the dropping water level of the Elbe is seen in fig. 3.18. The measurement was performed at the Geomatikum on 06.08.2021. The wind conditions at the Geomatikum were suitable for a plume to be transported to the measurement location. The peak reaches its maximum at the lowest water level of the Elbe. When comparing the FTIR measurements to the CF-IRMS measurements, the same methane peak can be observed with both measurement techniques. A clear distinction between the two measurements is the measured concentration. While the FTIR measurement shows a peak of 1903 ppb from an 1896 ppb background, the CR-IRMS measurements show a peak of 2120 ppb against a 1995 ppb background. The lower peak concentration in the FTIR measurement is due to the averaging over the total air column instead of a surface-level in situ measurement.

Similar peak observations were detected over the short FTIR measurement campaign.

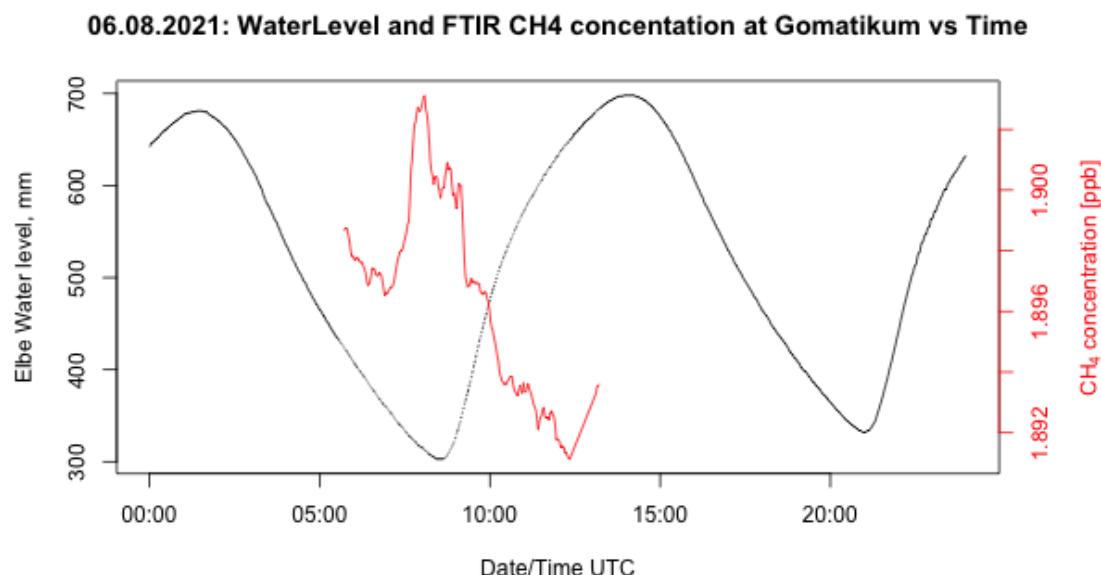


Figure 3.18: Plot of the total column methane concentration measured at the Geomatikum (Red line), overlayed with the Elbe water level measured at St. Pauli (black line). The measurements were performed on 06.08.2021.

Generally, no significantly larger peaks were observed with the FTIR approach, as seen in the CR-IRMS timeline, where peaks reached a concentration over 4000 ppb. The FTIR network could not measure simultaneously during those large peaks due to sunlight availability or weather conditions. Reliable statistical correlations, as can be seen with the CF-IRMS measurements, could not be observed with the FTIR approach. The spotty measurement intervals don't allow for reliable peak identification, and the few continuous measurements are insufficient for a reliable statistical correlation.

Chapter 4

Conclusion and discussion

Methane is one of the most important greenhouse gas and contributor to global warming. While a substantial amount is released through natural processes, anthropogenic sources highly contribute to the emission of methane into the atmosphere. In this study, the methane budget of Hamburg and its surrounding was monitored and deciphered with an array of different approaches. The thesis focuses on the methane emissions originating from the Elbe, which showed to be an unexpectedly strong emitter which is able to release large amounts of methane in short bursts.

The long-term high temporal resolution CF-IRMS measurements showed high-concentration methane peaks with an in situ concentration of up to 4500 ppb. Those peaks were observed for the total measurement campaign over eight months and also at favourable weather conditions, with the FTIR network measurements performed for a shorter time period of two months.

By using a peak identification algorithm and peak selected criteria provided by Menoud et al. 2021, the observed methane peaks were investigated in more detail. With the use of the Keeling plot method, a difference in methane isotope composition between the background and the methane peaks was observed. The peaks indicate a more substantial contribution of anthropogenic sources, like fossil fuel combustion, while the background methane composition is generally less influenced by anthropogenic sources. This indicates that the origin of the peaks is from methane plumes produced by anthropogenic sources near the measurement site. Those emitters are likely related to fossil fuel combustion and leakages in the city's gas infrastructure. Heavy industry and fossil fuel refining in and around the city may also play a significant role.

Previous studies in the Hamburg region demonstrate the presence of high methane enrichment with numerous plumes, most likely originating from natural gas infrastructure leakages [Maazallahi et al., 2020]. An extension of this work by this study, adopting the same approach, confirmed those results [Forstmaier et al., 2023] showing numerous previously unaccounted anthropogenic methane emitters in the Hamburg area.

The CF-IRMS measurement timeline also showed very prominent methane peaks that were distinct from the majority of the previously identified peaks. They showed a much higher methane concentration, a shorter duration and were always separated by at least 12 h. By adjusting the Peak identification criteria in the peak identification algorithm, those peaks were investigated separately. The investigation of the isotope signature of those prominent peaks showed an isotopic signature of $\delta^{13}\text{C} = -60.3\text{\textperthousand}$ and $\delta\text{D} = -298\text{\textperthousand}$, indicating firmly a natural methane source with a microbial production mechanism, most

likely by wetlands and water bodies.

This observation indicates that the exceptionally high dry air mole fraction of methane peaks, reaching levels of up to 4500 ppb, can be attributed to the Elbe River and its associated water bodies, including the nearby riverbanks and wetlands. These natural features are likely significant sources of methane emissions, contributing to the observed peaks in the measurements.

But additional possible emitters in the Hamburg region have to be considered that may be responsible for the prominent peaks, as, for example, in the port region, there is a significant presence of civil infrastructure. These include wastewater treatment and garbage processing. Surrounding the city, the agricultural industry is also present, including, for example, cattle farms. Closer investigations of these locations were conducted using mobile drive-by measurements, utilizing both a boat and a car. This approach allowed for detailed data collection and analysis of the target areas.

By this method, no significantly elevated methane concentrations have been observed near the civil infrastructure locations [Forstmaier et al., 2023]. Upon further questioning of the facility operators, it was disclosed that the facilities operate completely sealed, effectively isolating them from the surrounding environment. Methane generated during the process is carefully captured and introduced into the local gas grid. Furthermore, measures have been implemented to prevent any methane venting from the facilities at any point.

The mobile measurements also targeted the surrounding rural areas and investigated cattle farms that showed elevated methane concentrations in the air. Those locations show to be small emitters that could not produce an enhancement significant enough to be observable in the city. Those sources can henceforth be disregarded to be responsible for the prominent methane peaks observed by the CF-IRMS and FTIR measurements.

A Keeling plot analysis of the entire CF-IRMS time series showed an isotopic signature of the methane strongly influenced by natural emitters. By analysing the isotopic signature with regard to the wind direction measured simultaneously. It was attempted to identify a dependence of source type with wind direction. Thereby, measurements conducted during northern wind directions shifted towards emission types associated with anthropogenic sources. Most residential areas are located north of the measurement site at the Geomatikum, with little surface water and agriculture present.

Furthermore, a negative correlation between the measured methane concentration with the CF-IRMS measurements and the air temperature was identified for this residential region. This further indicates that a substantial amount of methane originating from this region is released from anthropogenic sources such as fossil fuel burning. The consumption of those fuels for heating and private transport increases at colder temperatures, resulting in elevated methane releases to the atmosphere from incomplete combustion of natural gas and leakages from consumer products [Lebel et al., 2022].

CF-IRMS measurements performed at wind directions from the south were observed to have an isotope composition stronger influenced by microbial CO₂ reduction emitters, such as wetlands, waste treatment and agriculture. Those emitter types can be found in the southern region of Hamburg and its surrounding, while the heavily industrialised region of the Hamburg port is also located there.

The isotope analysis also shows that the large Hamburg port, with its associated industrial park, probably plays a smaller role in the methane composition than expected. On the one hand, this can result from the potentially strong natural emitters dominating the methane composition and, on the other hand, a result of a possible overestimation in emissions from the industry located in the port.

The findings align with research at comparable rivers such as the Themse in London by [Zazzeri et al., 2017], which demonstrated that the methane emissions of a river could significantly contribute to the isotope signature in large cities' air.

By establishing a correlation between certain water quality parameters measured at the Elbe, such as water temperature, oxygen concentration and saturation, turbidity, UV absorption, pH, and the methane concentration in the air during specific wind directions, additional evidence emerged, further implicating the Elbe as the source of the notable methane peaks. These findings suggest a connection between the measured water quality parameters and the methane concentrations, reinforcing the association between the Elbe and the observed methane emissions.

A correlation between the water quality of a river and its methane emission has been observed before [Wu et al., 2007] and in particular in the Elbe where it is shown that the Elbe forms methane production hotspots in heavily human-altered and impounded river sections [Matoušů et al., 2019]. The estuary of the river where Hamburg is located has not yet been studied in detail regarding the pollution. A correlation between the amount of methane released into the atmosphere and the water quality is very likely, and probably an important reason for the large methane concentration that can be observed in the water of the upper estuary of the Elbe [Matoušů et al., 2017].

The occurrence of methane peaks could also be linked to the dropping of the water level in the Elbe due to the tidal cycle. This was achieved by correlating the occurrence of the prominent methane peaks and methane concentration in the air with the measured water level of the Elbe during suitable wind directions. It was also observed that the prominent methane peaks were always measured during falling water levels and during the lowered water level.

As shown by Matousu et al. 2017, a decreasing water level increases the methane concentration dissolved in the Elbe water. Harrison et al., 2017 showed that the dropping in water level, particularly in water reservoirs with high sediments and pollution, causes a significant release of methane into the atmosphere due to the hydrostatic water pressure reduction with the drop of the water column height. To further investigate the emission location leading to the prominent methane peaks, a purpose build Gaussian plume time reversed transport model demonstrated that the origin of the methane peaks lay in a 5 to 12 km radius West to South-East of the Geomatikum. The transport model revealed that the emission most likely stems from water bodies in and around Hamburg. Those include the wetlands to the South-West, the port in the south and the channels, fleets, and harbours in the historic city centre. It must be considered that the transport model cannot pinpoint an exact emission location but rather shows a probability arising from the density distribution of the particle tracks.

The transport model also has the limitation that only the wind data from one of the four locations in Hamburg is used. If a particle travels too far from the wind measurement

location during the modelling, it could experience a different wind system not detected at the measurement location. This is particularly interesting when the particles leave the city borders. It is well known that a city's climate can differ largely from its surrounding due to topography and temperature differences. Unfortunately, no weather station with the same degree of standardisation as seen from the DWD and Uni Hamburg is available near the city. Therefore, the assumption of uniform wind in the region was taken. This limits the reliability of the transport model for large distances that exceed the city borders and its direct surroundings.

Another limitation arises from using wind data measured in a single location, as the degree of randomization in the particle tracks has to be estimated. This is difficult to achieve with only a single measurement location and a large modelling domain with varying topographies. For this purpose, the standard deviation of the different data sets was calculated and used as a reference in the setting of the randomisation parameters together with literature values for similar topographies and wind velocities.

Due to limitations in which the FTIR sensor network is able to operate, a continuous measurement was not possible, excluding measurements during the night and in cloudy conditions. This resulted in only very few instances where methane peaks could be observed with both measurement approaches simultaneously, prohibiting a detailed direct comparison between the two approaches.

The FTIR network observed methane peaks at three of its four locations, likely originating from the Elbe due to its tidal fluctuation in the water level. As only nine measurement days provided continuous measurements over multiple hours for individual enclosures, it was not possible to provide a statistically meaningful correlation between the water level and the measured methane concentration in the total air column. For a successful measurement of the methane peaks using the FTIR network, the tidal cycle had to align with favourable wind conditions, together with low cloud cover and significantly high sun azimuth angle. Unfortunately, this was really observed during the 45-day FTIR measurement campaign. The FTIR measurement data was used in a Bayesian inversion modelling approach. With the help of this modelling, it was determined that the Elbe is a significant emitter of methane in the Hamburg urban region and is underrepresented in Methane inventories. Specifically, it was estimated that the Elbe emits approximately 1900 ± 1000 kg of methane per hour [Forstmaier et al., 2023].

With the acquired correlations and modelling together with the resources found in the literature, it can be concluded that the methane peaks observed in the city centre of Hamburg originate from the Elbe.

A complex interplay of many factors causes this behaviour. The river is fertile for methane production, mainly when high pollution and low water quality are observed. The methane can accumulate in the sediments over time, as natural methane reduction methods are disturbed by the heavy impounding and pollution within the city region. The tidal cycle of the Elbe is quite large for a river due to its connection to the Waddensea and the North Sea. By the tides, methane-rich water from the Waddensea is also flushed upstream. The fast drop in the water level that even allows for the river to run dry in certain regions was found to be most likely the main catalyst for the methane release to the atmosphere. The water pressure decreases due to the low water levels,

which allows for the formation of bubbles that travel to the surface. At the same time, the shorter water column height does not allow for sufficient methane oxidation, causing a higher methane release.

In regions where sediments are exposed to the air, there is a considerable potential for significant methane release. The resetting sediments, caused by the sudden acceleration of water flow over the sediment surface due to low water levels, can reintroduce organic matter to the sediments. It is recognised that the reintroduction of organic matter and ions in sediments can accelerate methane production [Bednářík et al., 2019].

The suddenly released methane is then transported away from the Elbe by the wind. Depending on the directions and speed of the wind, this can produce a very sudden and high methane concentration peak in the city's air. It is assumed that the Geomatikum is located conveniently to observe such peaks. At the same time, a measurement location closer to the river would probably result in more regularly sized and frequent peaks.

The inverse Bayesian modelling for the FTIR measurement has also shown that the Elbe is an underrepresented methane emitter. As [Forstmaier et al., 2023] demonstrates, the modelling could significantly be improved when the Elbe is accounted for in the Prior. Unfortunately, this correction does not account for the tidal cycle and its resulting variation in methane emission from the Elbe. This could further improve the modelling. The findings of this thesis underline the importance of methane monitoring in urban regions to ensure air quality and accurate estimation of unexpected methane emission sources. Future studies should focus on improving the measurement of methane emissions of the Elbe and the accurate modelling of the released methane by the Elbe and the location of the release hot spots.

To further investigate the emissions by the Elbe in the Hamburg city region, it would be recommended to perform a continuous long-term in situ measurement at a more convenient location closer to the Elbe. This could eliminate the uncertainty arising from the transport of methane through the atmosphere. For this, a cavity ring-down spectrometer would most likely be sufficient to estimate the methane concentration in the air accurately. An isotope ratio mass spectrometer survey using sample bags during low water cycles would also improve the confidence of the methane originating from the Elbe and its wetlands. These results can also be compared with the isotope signatures obtained in this study.

To understand the methane production mechanisms in the water of the Elbe in detail, a continuous methane concentration in the water at a fixed location (buoy or floating dock) similar to the approach taken by Matousu et al. 2017 would be beneficial. An integration with preexisting water quality measurement stations from the BAFG would be beneficial for comparison with standardised long-term data.

To estimate the methane release from the Elbe to the atmosphere via diffusion most accurately, a measurement approach similar to the one described by Harrison et al., 2017 would most likely yield the best results. In this approach, methane bubbles are released from the water and sediments are collected in the water using a funnel and gas trap system. The volume and composition of the collected gas can consequently be analysed in great detail with an isotope ratio mass spectrometer.

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Appendix A

Supporting material for chapter 2, Method

A.1 Codebase and data

The modelling and data analysed for this thesis were done in the R programming language. The complete codebase created for this thesis and the required raw data to execute the code are available via GitHub.

https://github.com/tum-esm/Hamburg_Methane_Peaks.git

Some basic instructions on running the code are provided in the ReadMe and comment sections. For further questions, please contact via email at: juan.bettinelli@tum.de or bettinelli.jb@googlemail.com

A.2 Figures App. ch.2

Appendix A Supporting material for chapter 2, Method

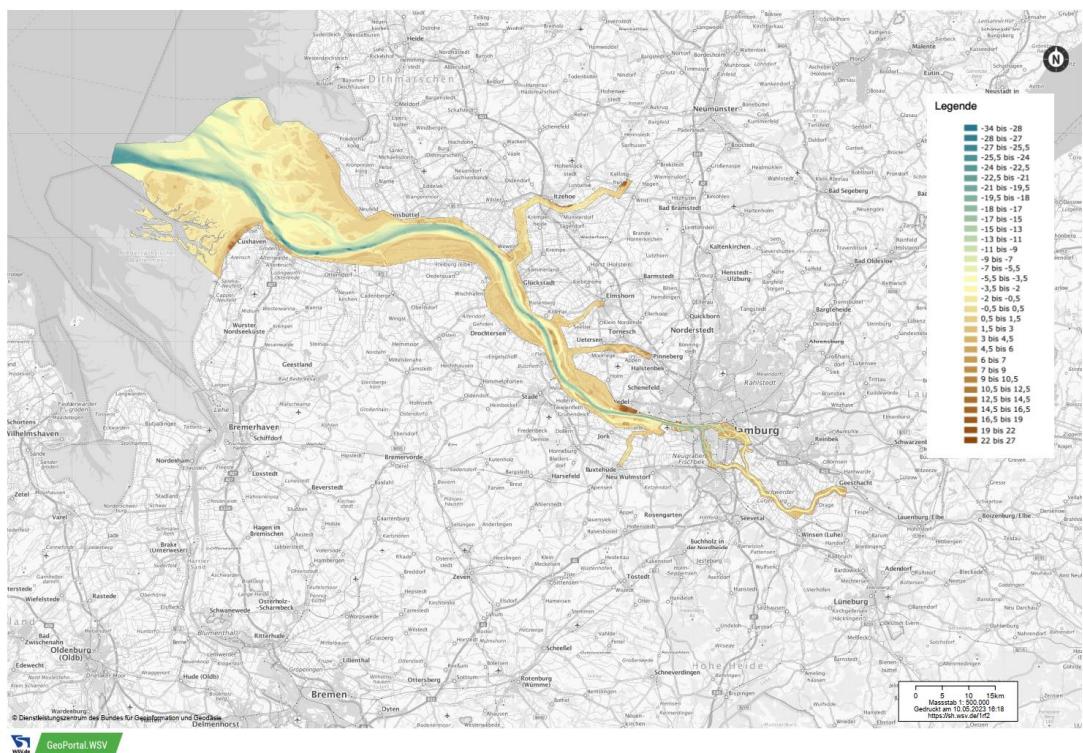
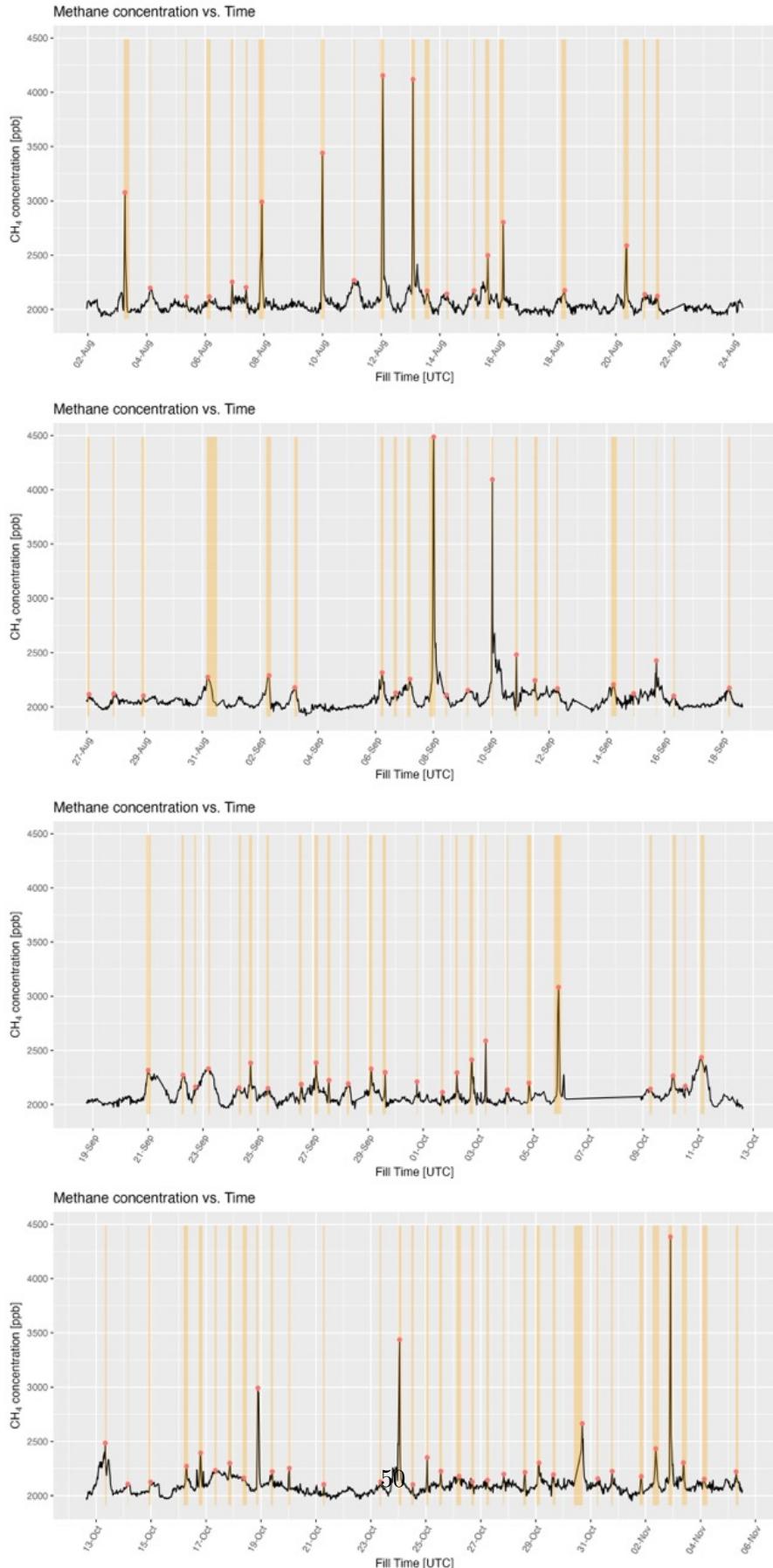


Figure A.1: Topographic map of the estuary of Elbe. From the Hamburg region to the Waddensea. Scale is in dm, 0 dm is at mean sea level. [ZDM GDWS, 2016]

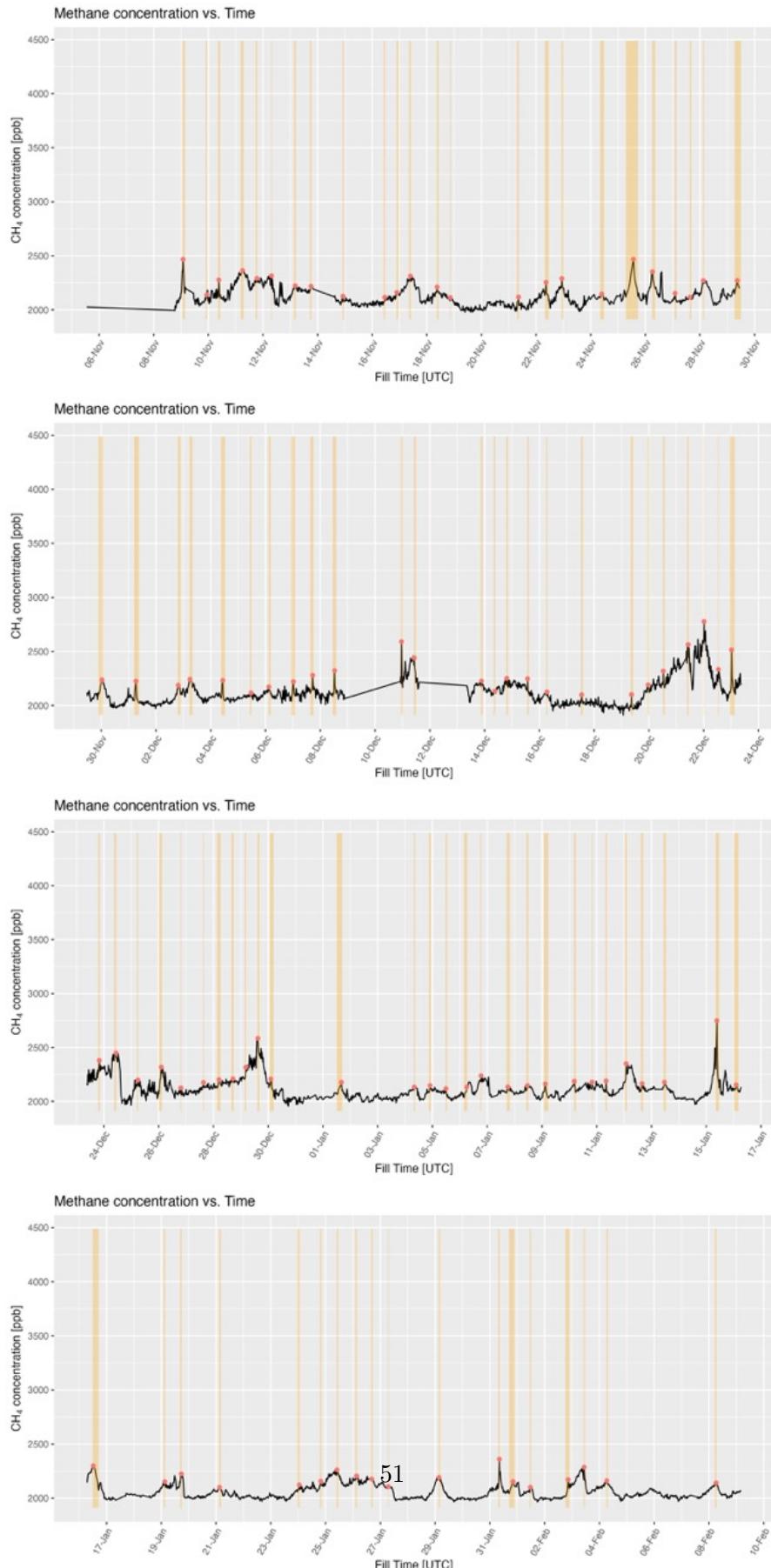
Appendix B

Supporting material for chapter 3, Results

Appendix B Supporting material for chapter 3, Results



Appendix B Supporting material for chapter 3, Results



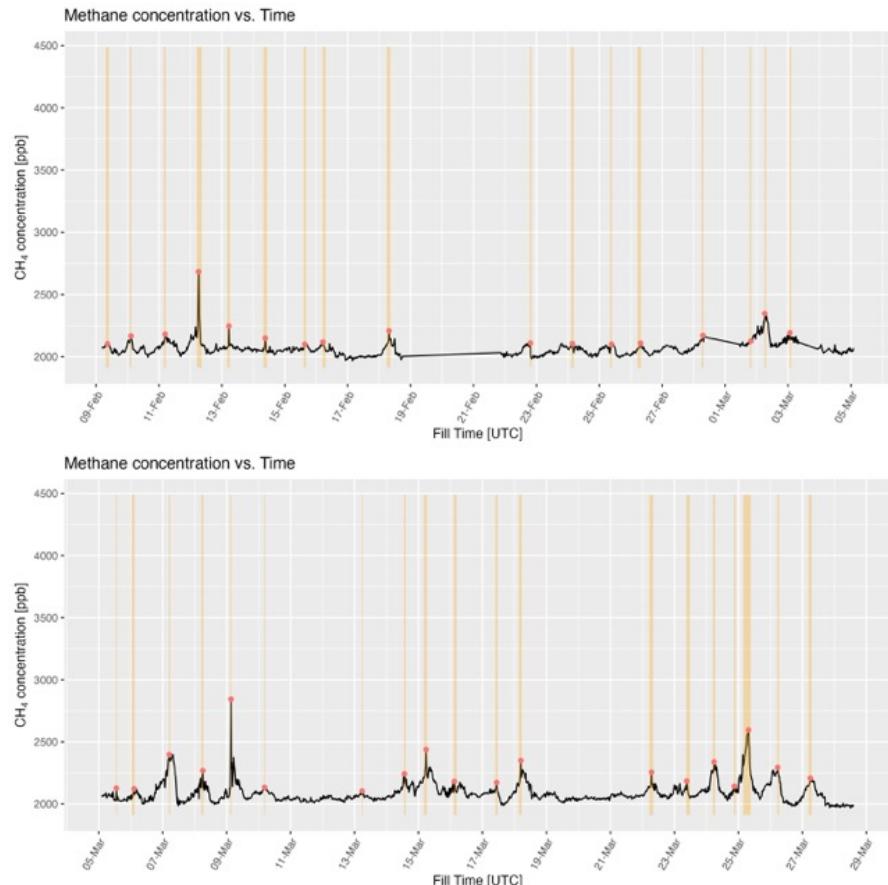


Figure B.1: Complete CF-IRMS measurement time-line, measured at the Geomatikum at an altitude of 83m above street level. Measurements from 02.08.2021 to 29.03.2021 are shown. Prominent peaks are identified and highlighted. Red dot for peak centre and orange highlight box for peak width.

W. Direction	$\delta^{13}\text{C}$	SE $\delta^{13}\text{C}$	δD	SE δD
10	-49.	8.0	-191	2.5
20	-50.	1.9	-257	13.
30	-52.	0.6	-265	6.9
40	-51.	1.0	-266	5.7
50	-52.	0.85	-261	10.
60	-50.	1.1	-267	15.
70	-49.	1.2	-248	13.
80	-52.	0.99	-279	10.
90	-53.	1.3	-2	15.
100	-53.	1.5	-253	30.
110	-51.	1.6	-255	14.
120	-53.	1.2	-268	10.
130	-52.	1.1	-262	9
140	-51.	0.90	-262	8.5
150	-51.	0.9	-239	9.0
160	-55.	0.91	-255	12.
170	-54	0.	-283	6.
180	-59	0.27	-290	3.7
190	-58.	0.23	-298	2.3
200	-57.	0.2	-290	1.9
210	-59.	0.22	-285	2.4
220	-5	0.26	-294	2.0
230	-57.	0.3	-289	3.1
240	-57.	0.32	-299	2.7
250	-57.	0.32	-299	2.8
260	-57.	0.28	-291	2.7
270	-58	0.33	-289	2.8
280	-56.	0.51	-30	4.3
290	-58.	0.43	-29	5.2
300	-56.	0.68	-283	7.5
310	-55.	0.96	-273	7.2
320	-54.	0.75	-283	9.4
330	-56.	0.74	-281	6.6
340	-54.	1.0	-28	7.6
350	-55.	3.2	-273	22.

Table B.1: Table of isotopic signature of $\delta^{13}\text{C}$ and δD by Keeling analyse for the total CF-IRMS measurement at the Geomatikum, 01.08.2022 to 01.03.2022, separated in wind directions during the measurement.

Appendix B Supporting material for chapter 3, Results

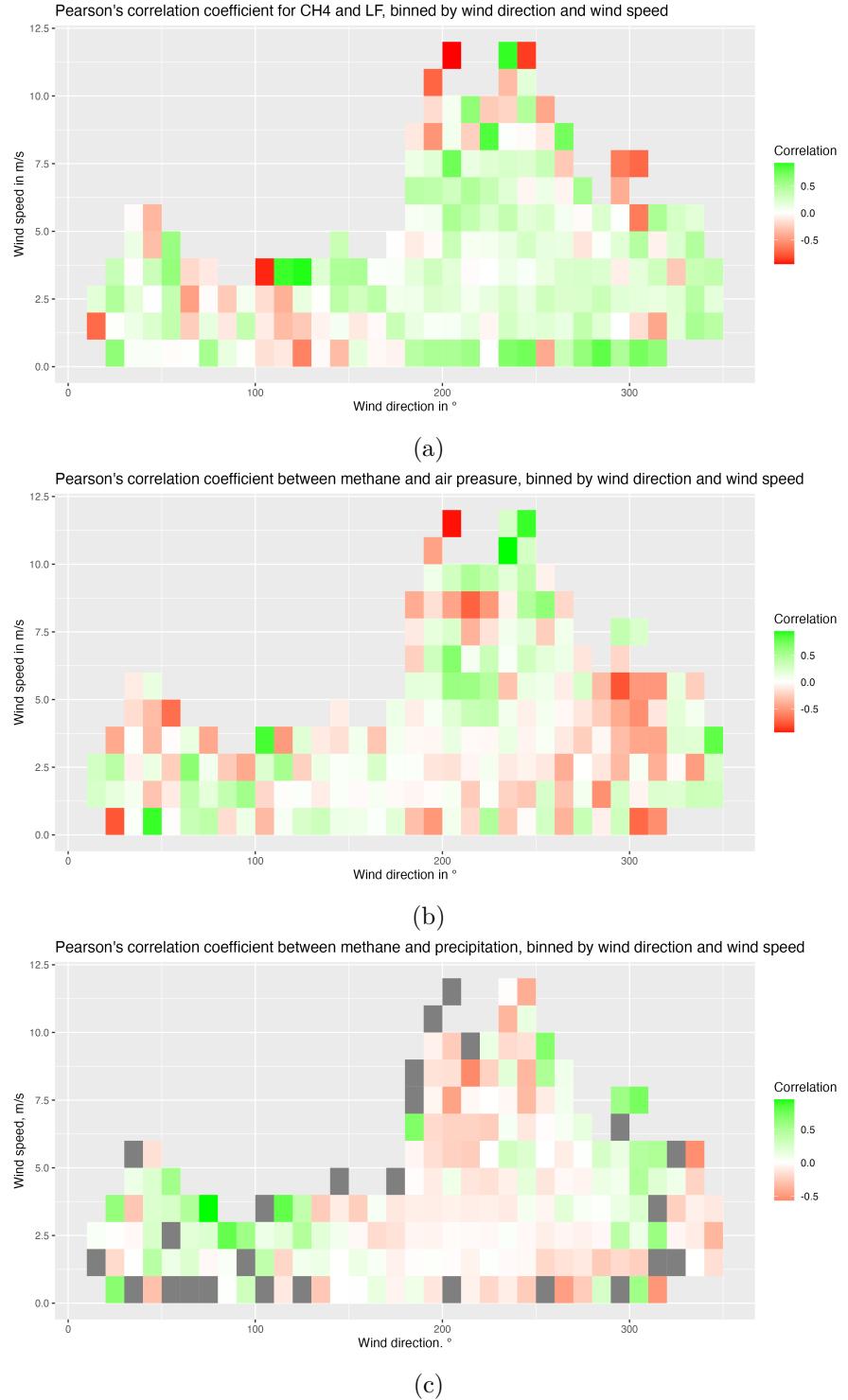


Figure B.2: Pearson's correlation coefficient between methane-air concentration and meteorological/water quality data, binned by wind direction and wind speed. Green shows a positive correlation (enhanced CH₄ at high values), and Red shows a negative correlation (enhanced CH₄ at low values). (a) Correlation between methane concentration and electrical conductivity in the Elbe water, (b) Correlation between methane concentration and air pressure, (c) Correlation between methane concentration and precipitation height

Appendix B Supporting material for chapter 3, Results

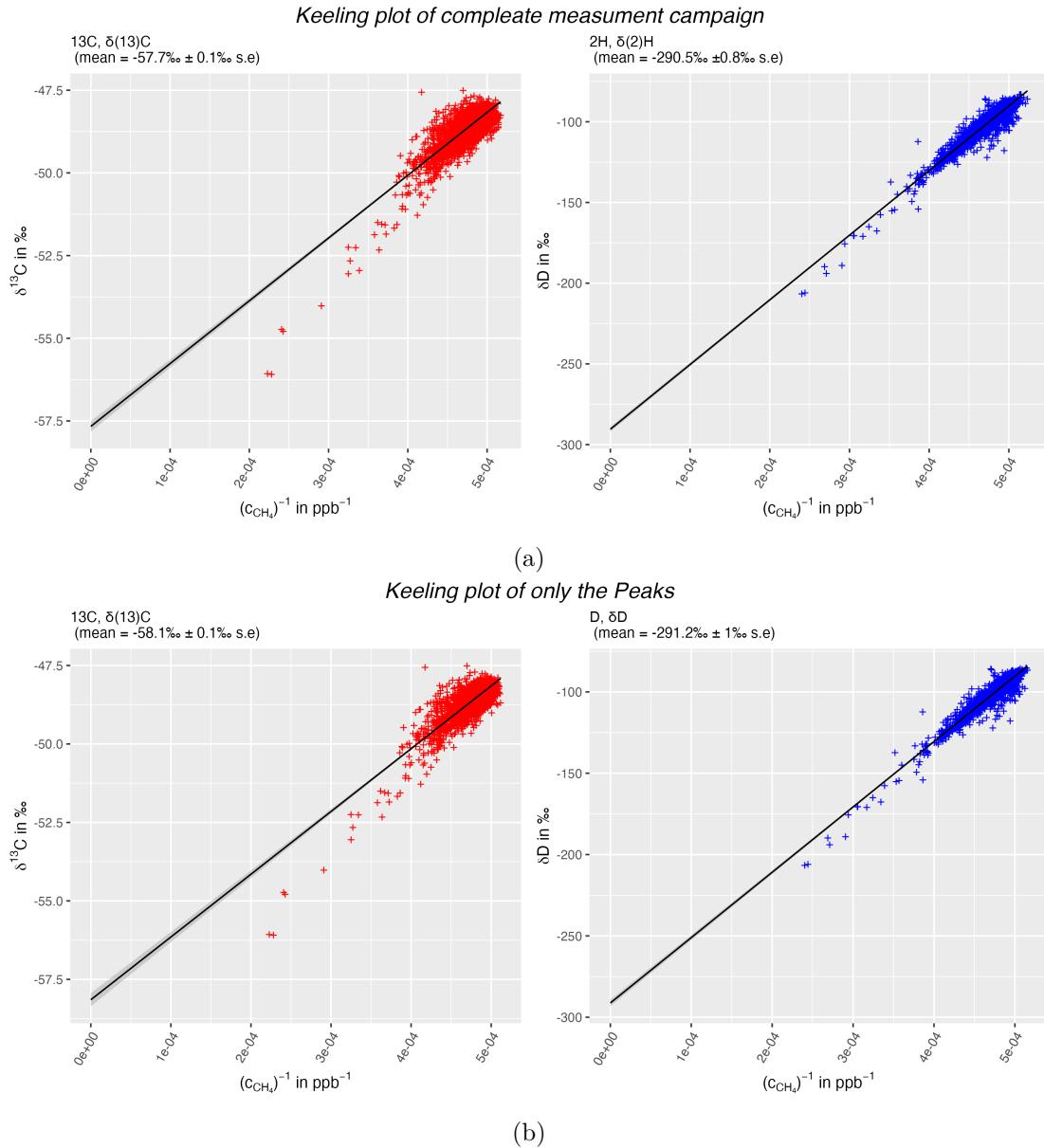


Figure B.3: Keeling Plots of Carbon-13 and Deuterium in methane peaks measured at the Geomatikum from 1.08.2021 to 1.04.2022. (a) total timeseries with resulting isotopic signatures $\delta^{13}\text{C} = -57.7\text{\textperthousand}$ and $\delta\text{D} = -200.5\text{\textperthousand}$. (b) peak identification criteria by [Menoud et al., 2021]. The resulting isotopic signatures $\delta^{13}\text{C} = -58.1\text{\textperthousand}$ and $\delta\text{D} = -291.2\text{\textperthousand}$

Appendix B Supporting material for chapter 3, Results

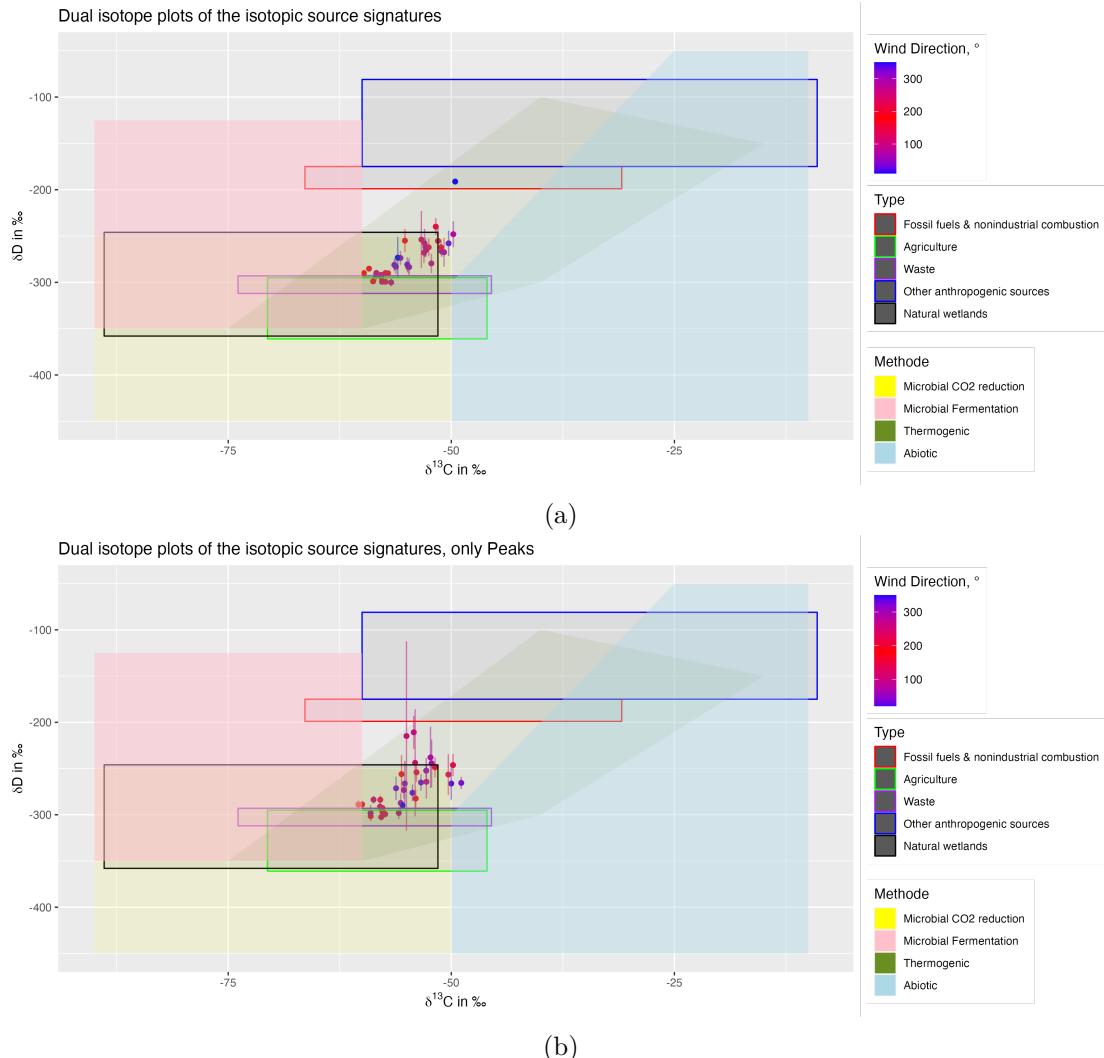


Figure B.4: Dual isotope plot for CF-IRMS measurement for 10° wind direction represented as point colour(blue towards North, red toward South) with highlighted production mechanism (coloured highlight) and source type (coloured boxes). Error bars show one SD. (a) shows total time series, (b) shows only peaks selected with identification criteria by [Menoud et al., 2021]

Appendix B Supporting material for chapter 3, Results

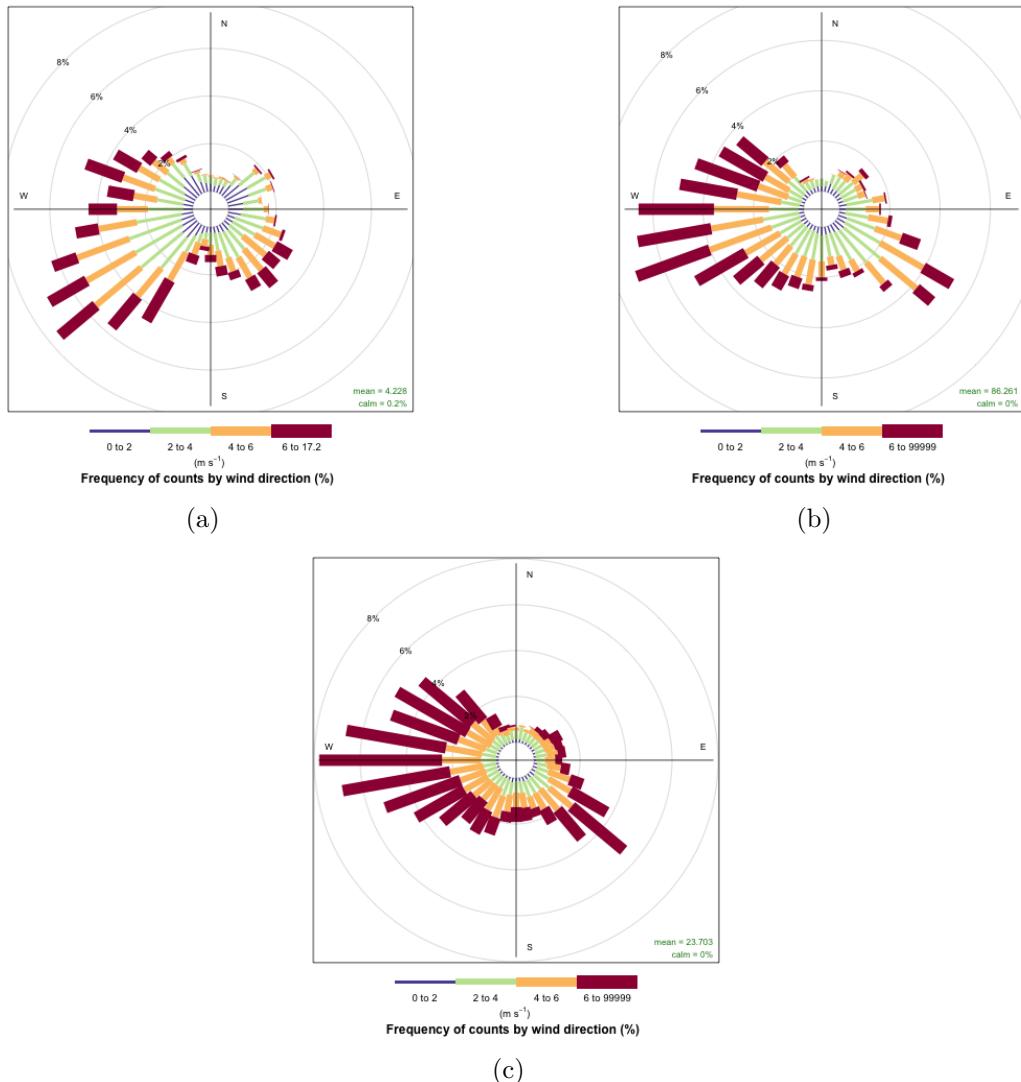


Figure B.5: Windrose plots with data from (a) Deutscher Wetterdienst (DWD) ([Deutschen Wetterdienst, 5 01]) at Fuhlsbüttel, Hamburg and Universität Hamburg [Lange and Universität Hamburg, 5 01] with wind measurements at (b) 50 m and (c) 110m

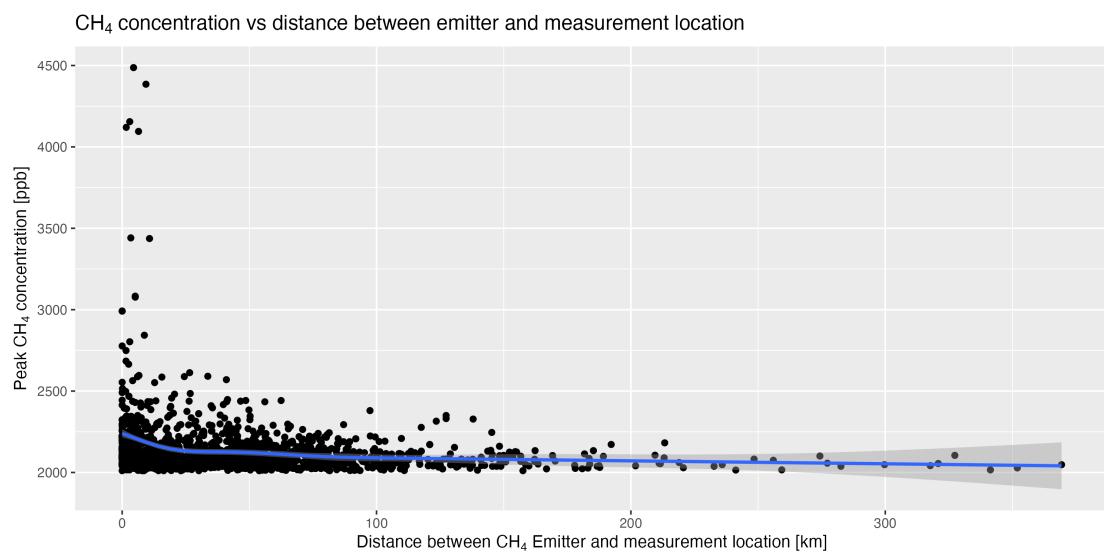
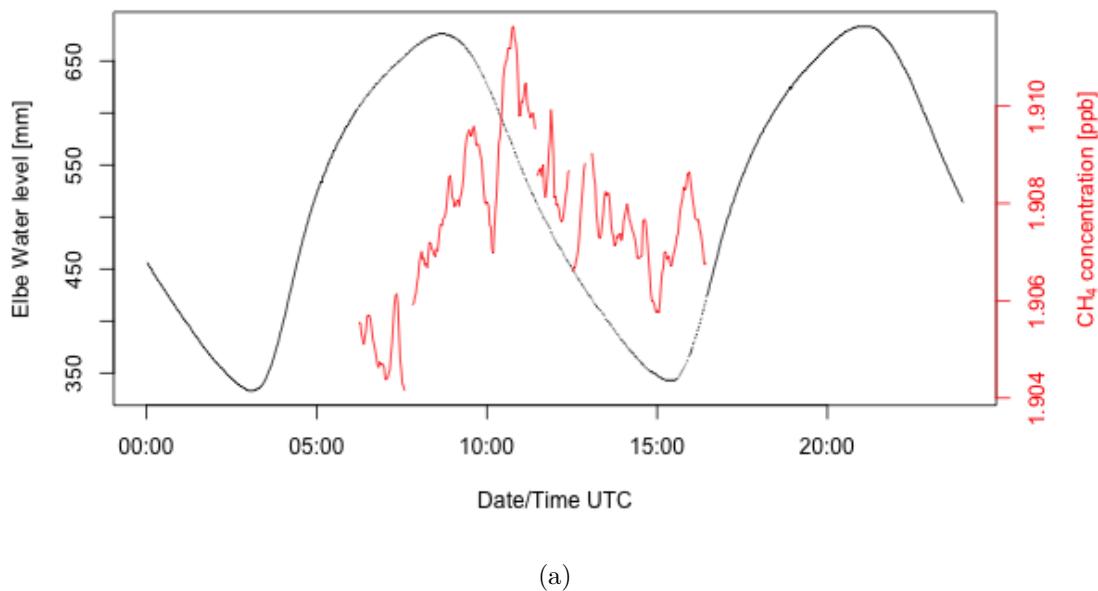


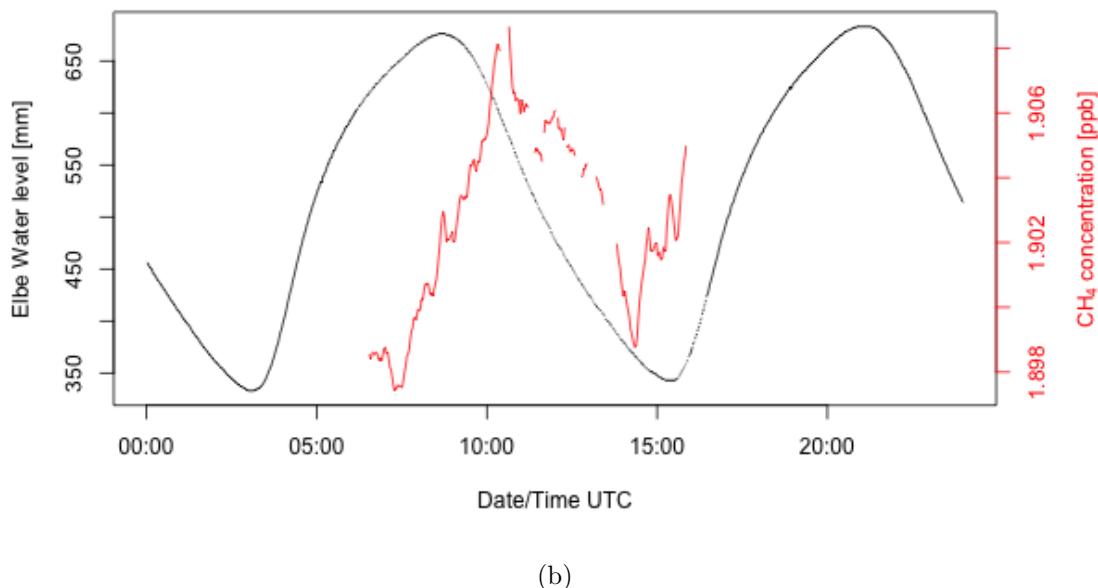
Figure B.6: Scatter plot of modelled Distance between the estimated emission location and the measurement location at the Geomatikum, against the methane concentration observed at the Geomatikum measured by the CF-IRMS. A local regression line is fitted to the plot (Blue). The standard error of the line is shown in dark grey. The peaks were identified using the identification criteria by [Menoud et al., 2021]

31.08.2021: Water level and FTIR CH₄ concentration at Jork vs Time



(a)

31.08.2021: Water level and FTIR CH₄ concentration at Rosengarten vs Time



(b)

Figure B.7: Plot of the total column methane concentration measured (Red line) overlaid with the Elbe water level measured at St. Pauli (Black line). The measurements were performed on 31.08.2021. (a) measured at Jork, (b) measured at Rosengarten. A low water methane peak can be seen at 16:00 UTC.

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