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**Draft**

1. **Abstract**

Unexpected methane peaks in a long-term Isotope measurement series and in a solar FTIR network measurement series in Hamburg were investigated in great detail. A Keeling analysis of the peaks indicates microbial methane production, pointing towards wetlands as emitters. The investigation into meteorological, water quality and water level data in Hamburg and the river Elbe showed a correlation between methane peaks and the river Elbe. A purpose-built time-reversed Gaussian Plume Transport showed the origin of the Methane peaks in the water bodies within and around the city, there include the port, channels and wetlands.

Previous research on the methane concentration in the Elbe showed that the river produces a significant amount of methane in the upper estuary where Hamburg is located. This concentration is enhanced with dropping in water level due to the tide. (### reference). Different research by (###reference) shows that fast-dropping water levels can cause spikes in methane emission to the atmosphere in water reservoirs.

It was concluded that the river Elbe emits a significant amount of methane in short bursts that can be observed from a distance of up to 5 km. The tidal cycle drives the methane release mechanism. A reduced water pressure during low water allows the methane bound in the water and sediments to bubble up and be released into the Atmosphere.

1. **Introduction**

* *Hinführen zum Thema*
* *allgemein -> speziell*
* *Ausgangspunkt der Arbeit, Ziele, Methoden*
* *Motivation und Bedeutung: warum dieses Thema? Warum diese Methoden? Alternative*
* *Methoden Stand der Forschung, Einbettung der eigenen Arbeit in den Stand der Forschung, was machen andere? Wichtige Literatur (evtl. als extra Kapitel, u.a. einschlägige Übersichtsartikel)*
* *Struktur der Arbeit / Inhaltsangabe*
* *ohne spezielle Vorkenntnisse lesbar, jeder Physiker/Chemiker sollte das (grob) verstehen können*

Methane 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 (reference: Global Warming Potential Values), making it 81 times more potent than CO\_2 for that time interval. *(Stocker and Qin (2013))*

Methane is released into that atmosphere in large quantities, estimations suggest 363 Mt annual emissions (reference <https://en.wikipedia.org/wiki/Methane_emissions>). Various sources produce methane and release it into the atmosphere, ranging from natural to anthropogenic. Natural methane emitters are considered ones where humane 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)) Anthropogenic sources are usually connected to using, transporting and treating fossil fuels, such as natural gas or oil. Fugitive releases from gas pipelines are known to significantly contribute to methane emissions (Schwietzke et al. (2014); McKain et al. (2015)). Together with other chemical industries and human infrastructure. This includes wastewater treatment, landfills, agriculture, and livestock. The methane present in the atmosphere is always a mixture of all the 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 rain in runaway emissions that can permanently harm the atmosphere's equilibrium.

Hamburg is the second-largest city in Germany, with a population of around 2.5 million. The city has diverse urban usage, including typical residential areas with high and low-density neighbourhoods alongside extensive indusial, 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 70 km inland. 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. Has a diverse system of methane emissions sources that contribute to the methane composition in the air.

It is known that the river Elbe is a significant methane emitter (reverence ###). The methane concentration in its water and release of methane into the atmosphere varies for the entire river. Its uneven distribution originates from many factors that will be discussed in further detail.

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 industrially used in the Czech Republic. The river is severely impounded in this section. The water has a very strong methane concentration due to pollution and few natural regeneration areas that form the feeding ground for good biotic methane oxidation.

The Third Section describes the Elbe as a lowland river flowing through Germany. Groynes only stabilize its banks, and the river is significantly naturalized with free-flowing characteristics. In this section, the biotic methane production is kept in check with its countering oxidation processes, resulting in a low methane concentration in the water and consequent low atmospheric diffusion rates.

Some heavily impounded human-made structures are present over the course of 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. While the oxidating mechanisms are repressed. The reason for the inability of oxidation is not fully understood yet and has most likely a multifactorial cause (reference ###).

The river Elbe estuary starting at the city of Hamburg, down to the North Sea into the Waddensea, experiences different environmental factors, and different mechanisms 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 from the saltwater of the Waddensea rivers to the very nutrient-rich freshwater occurs in the upper estuary due to insufficient mixing. (reference ###) The water in this region has a very 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 mechanism. High heterotrophic activity is related to remineralization processes of high loads of labile organic matter, and it has been shown by #### 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 marshland has 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. (reference ##) The low-temperature peak production occurs due to reduced methane oxidation at low temperatures. Marshlands system usually peaks in a 30 °C region in warmer climates. (reference###)

The water turnover time is significantly longer, providing good conditions for methane oxidation and greater methane diffusion into the atmosphere, resulting in a 10 times lower methane concentration than in the upper estuary (reference ###). 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 has a significant role in the methane cycle. For example, Methanotroph reduces CH4 Emissions from the sediments. As one can observe from tidal activities, resetting the sediments significantly increases methane production due to the reintroduction of biomass and ions to the sediments. (reference ###) The types of methane-producing bacteria can vary significantly due to the type of sediments and vary significantly over the course of 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. Reaching its peak at the lowest water level. ### 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 then causes the methane to form bubbles, which are released from the sediments and travel up to the surface and escape to the atmosphere. The reduced water column height can no longer oxidize most of this methane, releasing methane. 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.

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. During the campaign time period, high time-resolution mass spectrometer measurements were conducted, focusing on Deuterium (2^H) and Carbon 13 (13^C) isotopes. The measurement was stationary on the roof of the Geomatikum building owned by Hamburg University near the city centre, with a measurement inlet height of 83 m.

For the shorter time period of 27.07.2021 to 9.09.2021, a series of additional measurement approaches were conducted. 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 also 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 CH\_4, CO\_2 and H\_2 at a frequency of 0.3Hz and a Picarro model G4302 measured mole fractions of C\_2 H\_6, H\_2 O and CH\_4 at frequencies 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, mainly focusing 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 concentration of up to 4500 ppb, while the average background concentration was around 2100 ppb. The duration of the peaks was also very short, lasting for only around 0.5-2h.

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 emissions origination in the region of the city where the port, fleets, channels, and wetlands are located.

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. #### shows that the fast-dropping water level can trigger significant methane emissions into the atmosphere at freshwater reservoirs. Additionally, ### 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. This is also suggested by ####, in which the methane modelling is significantly improved by including the river in the inventory. While the fluctuations of methane release by rivers and wetlands due to tidal effects are not well investigated and understood yet. This thesis shows their observable effects and the conclusion linking methane concentrations in the air to the river Elbe while providing ideas for further research.

* *The current global mean surface dry air mole fraction of methane in the atmosphere is approximately 1906ppb (Lan et al. [2022], Figure 1.1). This attributes to a strongly increased concentration by 156 % compared to the year 1850 (Naik et al. [2021], Jackson et al. [2021])*
* *Bottum up and top down aproches…*
* *More about current researce*

1. **Method**

* verwendete Methoden (Prinzip, Literatur, experimentelle/theoretische Parameter)
* kein Lehrbuchwissen reproduzieren, nur Grundlagen relevant für diese Arbeit
* wichtige Details (insbesondere solche, die nicht in den Publikationen stehen) Nützliches für Nachfolger
  1. **The Campaign**
  2. **Mass Spectroscopy**

The commonly used analytical technique of mass spectroscopy offers an excellent tool for measuring ion mass to charge ratio. This allows for accurate measurement of the isotope ratios in a sample, giving great insight into the production mechanisms of molecules studied. By measuring and analysing the ratios of Hydrogen (H) to its heavier Deuterium (2^H) isotope and Carbon (12^C) to its heavier Carbon-13 (13^C) Isotope in methane, its origin can be estimated. Further detail on this analysis process will be given later in the section Keeling Analyse.

A mass spectrometer is able to measure the charge ratio of an uncharged molecule by ionising the molecule by electron impact. The ionised molecule now has an electric potential and can experience the effects of magnetic and electrostatic felts.

The ions are accelerated by using an electric potential, resulting in a similar Kinetic energy for all ions independent of their mass-to-charge ratio.

A magnetic field is then applied to the accelerated ions resulting in a Lorenz force experienced by the ions. Consequently, the trajectory of the Icons is bent towards a circle within the magnetic field. While equal charges with an equal velocity experience the same Lorenz force, they do not necessarily follow the same Circular trajectory. This is co-dependent on the mass of the charge, i.e. the ionised molecule. 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 contra part

Eq. 2.23

This generates a mass spectrum, a histogram of the isotope abundance/intensity versus its mass-to-charge ratio. By comparing the area of an isotope peak in the mass spectrum in the sample to a well-calibrated reference sample, the concentration can be calculated as follows

Eq 2.24

The Isotope ratio (delta) is noted Per mill and describes the Ratio of Heavy isotopes compared to the light isotope. This can be calculated with the Ratio R of a Standard reference and the sample.

Ep 2.25

The Isotope ratio is converted to the international Isotope scale by

Ep2.26

Pee Dee Belemnite (PDB) , VPDB Viana PDB.

<https://en.wikipedia.org/wiki/%CE%9413C>

Vienna Standard Mean Ocean Water VSMOW

https://de.wikipedia.org/wiki/Vienna\_Standard\_Mean\_Ocean\_Water

Continuous flow Isotopic Ratio Mass Spectrometer (IRMS)

* + 1. **Method of measurement**

Describe the instrument and the method!!

* 1. **Keeling Analyse**

It is essential to recognise that the model described by equations (1)– (3) involves two basic assumptions. First, we assume that a simple mixing of only two gas components is considered (a source S and the bulk background B). Second, we assume that the isotope ratio of these two components does not change over the course of the observation. It is rare for these two assumptions to hold true in a strict sense under natural field conditions. Rather, researchers have found appropriate points in time and space for which these assumptions are acceptable. Below we outline recommendations for minimizing error in the use of the Keeling plot for assessing the carbon isotope composition of respiration.

*The application and interpretation of Keeling plots in terrestrial carbon cycle research D. E. Pataki,1*

<https://reader.elsevier.com/reader/sd/pii/0016703758900334?token=0DBC685A3EE6237763F578EBF74EA09416F76D95982C2F26584893ED72DF7286314090AE33BF9CDFDD8A25F98C5C4152&originRegion=eu-west-1&originCreation=20230215125755>

* measured isotope ratio
  + δX = (R\_sample -R\_standard)/R\_standard
  + R ratio of light vs heavy isotope (C12/C13)
  + Δ in per mil
* In the isotope measurements the isotopic composition is rst determined relative to a reference gas (WS) of known isotopic composition. The isotopic ratio of the sample compared to the working standard δsample/WS is converted to the interna- tional isotope scale as follow:

δsample/IS = δWS/ISδsample/WS + δWS/IS + δsample/WS (2.26)

The isotope values are reported versus the international reference materials VPDB for δ13C and VSMOW for δ2H.

* The keeling approach is a mass balance/mass Conservation approach.
* Methane Concentration in ambient air is ca
  + Sum of Methan concentration in background cb and sorce methan concentration cs
  + C\_a = c\_b + c\_s
* mass balance equation for heavy isotopes
  + δaca = δbcb + δscs
* Combining both equations:
  + δa =c\_b/c\_a (δb −δs)+δs
* δ = isotopic ratio
* c = concentration
* multiple possible sources δs is a source emissions weighted mean isotopic signature
* Equation is a linerare correlation of δa and 1/c\_a
* Y intersect is the isotopic signature of the source
* With knowledge of the isotopic content of methane of an air sample and its concentration it is possible to calculate the isotopic signature C13 and H2
  + Compare the signiture to literature and identify its sorce
* Plot:
  + orthogonal distance regression approach
  + signature for C13 and H2
  1. **Keeling for methane peaks**

To investigate if there is a difference in production mechanism between the background methane and the peaks the keeking analyse was profrmen by separating Peaks and Background. To achieve this the Peaks finder algorithm was integrated into the Keeling analyse. This allowed to identify the peaks with both criteria and produce Keeling plots for the Total measments, Background and both Peak criteria. With the use of previus Isotope investigations the results culd be copared an estimation of the emission mechanim could be made indifidualy.

* 1. **Keeling with wind**

By using the Keeling method for the background and peaks isotope measurement in combination with Wind measuments. It was attempted to identify any unisotropic behaviro in the methane production.

To achieve this the Isotope measurements where binned according to the averaged wind direction during the measument time. For this wind measuments at the Geomatikum provided by the Unversität Hamburg were used. As the wind measument were located very colsly to the Isotope measument inlet allowing for a high confidence in its accuracy.

The Isotope measurement bins were in 10° wind directions. For each bin a keeling analysis was performed separately. The results were than plotted in a ##### plot. In this plot the Y interesct of the keeling plot for the 2H and 13C were pottet on each axis. The location of the binned keeling analyse than gives an indecation of the methane production mechanim and emitter tipe when overlaying previus measument (data#### paper) provided by ####. A wide spread of the datapoints indicated different different methane production mechanimns. Wile closly spaced points indicated a homogenius emitter tyeds in all directions.

By additionally separating the Methane peaks from the background and repeating the wind sensible keeling analyse, it can be investigated if the peaks from different directions originate form different eimmitter tyes.

* 1. **Differential Colum Measurements**

A Fourier transform Infrared Spectrometer network has been deployed inside and around the city borders to investigate the urban greenhouse gas (GHG) emissions from the city region of Hamburg. Parts of he usually in Munich located sensor network MUCnet has been relocated to Hamburg and was deployed for a shorter time period between the 01.08.2021 to the 31.9.2021. The network consists of four fully autonomous and automated Enclosures. These were located about 20 km from the city centre to the east, North and West, with one enclosure in the city close to the city centre at the Geomatikum in close proximity to the mass spectrometer. The location can be seen in Figure #####.

Figure ####

The enclosures operate by measuring the solar spectrum with a high temporal resolution of 90 seconds, which is in the revival process, later on, averaged over a 10 min time period to accurately calculate the CH\_4, CO\_2….. concentration in the total air column.

The enclosures are equipped with a Michelson interferometer (Bruker EM27/Sun). This spectrometer has an attached solar tracker that enables the Tracking of the Sun by redirecting the light rays with a set of electronically controlled gold-plated mirrors. The spectrometer is housed in a weatherproof aluminium box to protect it and its auxiliary equipment, like 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 automated cover that opens at favourable weather conditions and aligns itself with the solar tracker. To protect the tracker from precipitation, a rain sensor and a cloud detection sensor are placed on top of the enclosure. They automatically initiate a closure of the cover when precipitation is detected or the cloud coverage is too great. The weatherprove 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.

The significant advantage of the FTIR approach to other in situ measurements lies in the total column measurement, which measures the total air column of the atmosphere between the light emitter, i.e. the sun and the spectrometer. The spectral absorption by the methane can then accurately be measured 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 is highly dependent on various airflow characteristics, Topography and Emission type and location. A total column measurement can’t negate all of them, but it gives a more reliable picture than simple in situ measurements.

A total column approach with solar spectroscopy has the added advantage of providing a reference for satellite measurements and vice versa.

The sensor network deployment achieves a differential total column measument, in which at least one sensor is always located upwind and one downwind of an 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 has been measured in the atmosphere, and it is attempted to calculate its emitters. 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 Basyan 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 that includes spatially resolved emission data for CO2, CH4, CO, NOx and NMVOCs, the spatial resolution is (1/60)◦ for longitude and (1/120)◦ for latitude” (Hamburg paper). This inventory is Hamburg's current highest resolution inventory, giving the best available prior emission estimation. Its limitation is the Bottom-up approach may not encounter all emission sources or does not yet account for relocated emitters and sporadic emitters.

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.

* Formal: Posterior probability = (Prior probability \* Likelihood of the data )/ Normalization constant

Text, letter

Description automatically generated

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

To identify the location, the inversion is also making use of the ###### weather model. This model is additionally corrected for the boundary layer height and wind direction by using a wind LIDAR. This corrected model is then 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.

* 1. **Peak Identification Algorithm**

The Isotope ratio mass spectrometer measurements show a series of methane concentration peaks throughout the campaign time, with different magnitudes and durations. Hence the identification and characterisation of the peaks were of great importance. To achieve this goal, a peak finder Agathism was implemented that identifies the methane peaks over the total time series. Outputting the maxim concentration and its time, together with the peaks start and end time and concentration. The peak finding algorithm was tuneable in its identification criteriums allowing for a separate investigation. 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 analyse, two different identification criteria were consequently used. The first was the identification of all methane peaks that are distinct from the background concentration. For this, the identification criteria defined by ### were used as a reference. This a described as follows:

* A minimum enhancement above the background of 100 ppb
* A minimum peak height of the lowest 10th percentile of the concentration-time series
* The width of the peak contains at least 3 data points (approximately 60min)
* The peak width is restricted to maximum ± 6 hours around the centre of the peak

An example of the peaks can be seen in Figure ## 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 other peaks, and a different production mechanism was suspected. The freak nature of those peaks was separately investigated to identify the mechanisms that govern those peaks The criteria applied are as follows:

* High concentration of min #### ppb
* Min 3 datapoints
* Shorter max peak spared of ## h

An example of the Identified peaks can be seen in Figure ### .

* 1. **Methane emissions with water level**

At first inspection, the presence of the methane peaks in the concentration timeline occurs at random. By overlaying the methane concentration with the water level measures at St. Pauli by #### indicates a correlation.

*~~On first visual inspection of the Methane emissions Peaks, they don’t seem to originate at completely random Times. In particular, a pattern can be observed when the Methane concentration Timeline is plotted together with the water level of the Elbe River.~~*

In Figure Plot *1\_CH4\_WL.png*, which is a Section of the complete timeline, a pattern can be spotted. The dominant Methane Peaks occur around 1-3 h after the Lowest Water Level.

While smaller Peaks are visually more challenging to identify and consequently correlate to the Water level. The peak identification algorithm helps to highlight the smaller peaks and gives further indications to a correlation with the water level of the river Elbe.

Pearson's correlation coefficient has been used to prove a statistically meaningful correlation between the water level and the Methane concentration. Unfortunately, the occurrence of elevated methane concentrations doesn’t seem to be a single variable correlation. So, a simple correlation of the Total water level and concentration yields practically no correlation. ~~As will discuss later, wind direction and velocity are major contributing factors~~.

The wind direction has to 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. This was done by binning all methane and Water level measurements in 10° Wind directions and 1m/s wind speed bins. Following 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 Plot *13\_CH4\_vs\_Waterlevel\_Correlation\_Geomatikum.png*. In this plot, each tile represents a wind data bin with the colour representing Pearson's correlation coefficient,

It can be seen that in three regions with particular directions and speeds, a strong correlation between methane and the water level is observed. ~~This indicated that three regions contribute to elevated methane emissions. The Suggested locations will be discussed later.~~

To validate if the correlation are statistically meaningful, a p-value test has also been conducted with a value of <(>)0.05. A plot visualizing the results can be seen in *13\_CH4\_vs\_Waterlevel\_P\_Value\_Geomatikum.png*.

Fortunately, the Regions of interest pass the test, while the regions that don’t show a correlation to the water level fail the test as expected.

~~With the correlation results indicating a significant dependence of the methane emission to the water level, further investigation in this region can be pursued.~~

* 1. **Methane Concentration in the air in correlation with the water quality of the Elbe**

It is well known that wetlands and waterbodies can release significant amounts of methane into the atmosphere. #### 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 inventory does not include emissions from the river Elbe, but a #### shows that a correction which includes estimations of the emissions from the river yields more reliable modelling results.

Water quality parameters are a good indicator of methane production, reduction and emission rates in the water. ###### reference. A direct methane emission prediction cannot be made just from such water quality parameters due to the complexity of the production mechanism and it strong dependence on local conditions and bacterial composition present in the water body. Nether the less, a correlation between water quality parameters and methane production has been observed (reference #####). This can help to provide further indication of alleviated methane concentration in the air due to mechanisms in the water of the river Elbe.

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

The water quality data measured at #### provided by #### were used for this. This data included the parameters ########, and had a high temporal resolution.

Using the same correlation approach described before, a Pearson's correlation coefficient analyse was made for the same wind direction and speed bin. An example can be seen in Figure ###

~~That the Elbe river seems to be the significant contributing factor to the methane peaks and generally to the composition of the Hamburg air composition can be seen when investigating the Water quality measurements provided by ####~~

* 1. **Methane Concentration in the Air in Correlation with the Meteorological Observations**

The release of methane into the Atmosphere by natural and anthropogenic mechanisms is highly dependent on environmental conditions. These include meteorological parameters such as temperature, perspiration, and solar intensity, …..

For natural methane emissions, methane production and, consequently release into the atmosphere is, for example, highly dependent on temperature, as different bacteria have a preferred temperature at which their methane production or reduction mechanisms peak. In general, higher temperatures are favourable for methane production. Another significant parameter is the amount of participation and consequent abundance of water on the surface. Some bacteria live in water or moist environments. An abundance of surface water aids the population growth of such bacteria. Additionally, water can help to flush organic material into the waterbody providing a plethora of nutrition for the bacteria, allowing for a large population and methane production.

Anthropogenic methane production is differently affected by meteorological parameters as the behaviour of humans mostly governs it. A well-observed example is the increase in fossil fuel consumption at colder temperatures. This is mainly well observed in an annual cycle. The methane is often released into the atmosphere through leaks in the infrastructure or incomplete combustion. Ther parameters also play also exist….

It was attempted to investigate a possible correlation between the methane concentration in the air and possibly the accordance of the methane peaks and some meteorological parameters. For this, the data provided by the Deutsche Wetteredienst was used. The measurement station #### was used due to its proximity to the Geomatikum. This Station provides highly standardised and quality-controlled measurement data, which were 10 min and 1 h Averaged by the DWD.

The measurement parameters investigated were #########.

The correlation investigation was performed like the previous water quality and level discus, with a Pearson's correlation coefficient analysis and a P-value test for separate Wind direction and speed bins.

* 1. **Methane Emissions with Wind**

As previously mentioned, the Wind plays a significant role in the measured methane concentration at the Geomatikum. Hence a detailed analysis of the observed wind is essential.

The wind data from the Deutsche Wetterdienst (DWD) and Universität Hamburg was used for this. The DWD provide data from its wetter station at ####; while this data adheres to strict standards, the measurement location is only 2m above ground. Measurements of this altitude are heavily influenced by surrounding topography. While time averaging helps in normalising the measurement, it dose impact the temporal resolution of the measurements. The Universität Hamburg provided three different sets of wind measurements at two locations. The first location was at the Geomatikum itself, only a few metres from the Isotope measurement inlet at the height of 83 m. At this height, the surface-level effects are mostly negated. But the Geomatikum building itself can potentially generate turbulences that influence the measurements. The Geomatikum was the highest building in the proximity by quite a margin, but disturbances from the surrounding can’t be completely out-ruled. The second location is at the weather mast in ### about ### km from the Geomatikum. Measurements there were made at the height of 50m and 110m. The measurement instruments are placed far from the support structure so that disturbances by the mast are minimised. Additionally, no high-rise buildings are located near the mast adding in 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 measurements at the Geomatikum proved to be the most reliable data set, and the analysis in this thesis mainly focuses on it. The Close 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.

* 1. **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 1 to 3h and a very high methane concentration above the background concentration. This indicates an emitter located close by with a relatively short emission time and a high amount of methane released.

To estimate the distance between the emitter and the measurement location,

the Strong correlation between the methane concentration in the air and the tidal cycle of the Elbe is used.

~~It is attempted to estimate the distance of the methane emission to the Measurement site at the Geomatikim.~~

To achieve this virtual trek of Windparticles are modelled using the wind data measured at 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. Treks 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 a geotracking algorithms. This is repeated until the time where the lowest water is reached. The total 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 versus its peaks maximal methane concentration in a scatterplot. This can be seen in figure ####: *14\_Low\_WL\_to\_Peak\_dist\_new.png*

*Here it can be observed that the highest concentration forms a peak at a distance from the Geomatikum of around 5 km. While most alleviated values are in the range of 1 to 13 km. Longer distances are observed but with a significantly lower concentration.*

*When looking at the peaks selected with the criteria described above (Paper creteria), a correlation between concentration and distance can be seen. Showing that the further away the estimated source is, the lower the concentration. As one would expect. The significant distance points are likely less influenced directly by the tidal cycle.*

* 1. **Gaussian plume transport modelling for methane peaks**

It has been attempted to construct a Transport model to locate the emission regions. For this purpose, the temporally high-resolution wind data provided by the University of Hamburg and The Deutsche Wetterdienst have been used. The transport model uses the wind data to create Gaussian Plums with the measurement site as a particle emitter. The emitted partials travel backwards in time; this allows the calculation of reversed particle tracks. To Create Gaussian Plums, form a single emission time, a large number of particles are emitted at each investigated emission time. The direction and speed of each particle is randomised with a predetermined Standard deviation for each particle trek segment. The degree of randomisation has been taken from literature values for similar topography and wind Speeds (values and reference). The methane emission location can be estimated by calculating the particles' density by geographical distribution.

Additionally, two separate approaches have been tied to investigate if the results are comparable. At first, the particle tracks are calculated using the wind direction and speed for each measurement interval. So that the particle can follow changes in wind direction and speed over time. The track is randomised at each interval. Using this approach, it can be observed that many particle tracks follow the path of the river Elbe quite closely. One limitation of this approach is that if a particle travels too far from the wind measurement location, it could experience a different wind system not detected at the measurement location. This is particularly interesting when the particles leave the city borders, as it is well known that a City's climate can differ quite largely from its surrounding due to Topography and temperature differences. Unfortunately, no weather station with the same degree of standardisations as seen from the DWD and Uni Hamburg is available near the city. So that the assumption of uniform wind in the region must be taken.

*In the second approach, the wind direction and speed measurement were averaged for the time of the investigation. (Standard deviation verwenden????). In particular, interest in the duration of a methane peak. The particle tracks are calculated for each minute, with the track randomisation at each interval. In this approach, the wind is assumed to be uniform for the region, but as the wind is averaged over a longer time, it can be assumed that the predominant wind direction expresses a larger influence than short fluctuations in speed and direction.*

The Transport model has been used in tandem with the peak finding algorithm to investigate the peak methane emission locations. *Here the First approach yields better results*. After the methane peaks are identified, the time of the lowest water level within the 12 hours before the Peaks are identified. As many regions of the Elbe River dry out sometime before the lowest water level is reached, half an hour before the low point is calculated. It is estimated that many riverbeds, fleets, and wetlands are already dry at this time. The Transport model estimates the tracks and distribution region from the methane peak maximum concentration to half an hour before the previous low water.

1. **Results**

**Resulte und Diskussion**

- Umfang ca 2/3 der Arbeit  
- trenne Resultate von Interpretation  
- wichtige Ergebnisse hervorheben  
- Argumentationskette ohne Lücken  
- Vergleichskapitel  
- nicht so relevante Details im Anhang

* 1. **Methane peaks**

With the aid of the methane peak identification tool, the peaks were investigated in detail. Figure #### and Figure ####, 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 selected according to literature criteria. The smaller peaks occur at a relatively high frequency with a substantial irregularity. The amount of peaks per day varies between 5 to 15 peaks. While during warmer months, August, September and October, the density/frequency of the peaks are lower than for the colder month, December, January and February.

Intermediate and prominent peaks occur at relatively regular intervals while they are never more than two peaks within a day, and their peak centres are never closer than 12 h apart.

In the second image, the Identification criteria are purposely designed to identify the prominent large and intermediate peaks and highlight the peaks well. Those peaks occur during the entire measurement campaign but with a higher frequency and concentration during the warmer months than the colder ones. The peaks are all quite sharp, i.e. with a short duration and high concentration compared to the background.

* 1. **The Water level and Quality**

**Water Level**

When the methane concentration timeline is overlayed with the water level of the Elbe River. It can be seen that the prominent methane peak occurs shortly after the low water of the river. This behaviour is observed throughout the measurement period. The peaks are, on average, 1-3 h after the low water. The overall methane concentration and presence of peaks are generally higher during periods when the Elbe experiences lower overall water levels. Visa verse, fewer methane peaks and a lower concentration are observed at high water periods. The variation in the water level for an extended amount of time is due to the Luna cycle in the tide and meteorological influences.

As the prominent methane peaks can’t be observed during every low water cycle of the River, additional factors seem to contribute to their production. But to establish a statistically meaningful correlation, the Per##### correlation coefficient between the water level and the methane concentration was investigated as previously described.

This correlation can be seen in Figure ##, here, the measurements are binned by Speed and direction using the Wind measurements made at the Geomatikum.

The plot shows a correlation and a negative correlation by colour. A Positive correlation indicates an elevated methane concentration with a high water level in the air. 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 Figure ### checks if the correlation is statistically meaningful, if the P-value is <>0.05 it passes the test and is indicated as such in the plot.

The correlation plot shows a negative correlation that also passes the p-value test for a wind direction 180° and 250° with a wind speed 1 m/s and 10 (15) m/s. With additional correlation regions at 140° to 160° (4 m/s and 6 m/s) and 300° to 330° (4 m/s and 6 m/s).

Following the direction of the wind leads to the port region of Hamburg. Where the water height measurement was performed by #### at St. Pauly.

In the other direction, significantly fewer water bodies are not freely flowingly connected to the Elbe and don’t experience the tidal effects.

Do the same with peak finder

While a perfect correlation was not observed, the correlation nether, the less gives a good indication pointing toward an amount of methane measured at the germanium originating from the Elbe river and correlates to its tidal movements.

**Water quality**

The influence of the Elbe can be seen in a particular Wind direction region and Wind Speeds. This region is around 180° to 300° for a Wind Speed between 1.5 m/s to 7 m/s. In this general direction to the Geomatikum the river is directed and has its most significant influence by the Tides. Further to the east, a series of Locks block the tide.

Apart from the water level of the Elbe, some water quality parameters also show a good correlation with the methane concentration.

Those include the Water temperature, Oxygen concentration, opacity, UV absorption and pH level. They are also in the same wind speed and direction (####° to ###° and ## m/s ) as with the water level.

Other water quality parameters, such as Electrical conductivity and Algy concentrations, don't show a correlation. As can be seen in figure ###

W~~hen looking at the correlation plots for Water temperature, Oxygen concentration, opacity and pH level. A very clear correlation can be observed~~.

The influence of the river Elbe on the Methane measurements can be seen on a short and long-term scale.

The correlated water quality parameters are not constant over time and experience cycles on short and lange scales.

This indicates that the river Elbe is a large Methane emitter under the influence of multiple parameters that change in daily, monthly and yearly cycles.

In the Literature (references) this is also strongly indicated…….

* 1. **Methane emission with meteorological observation**

The meteorological data measured by the DWD at ### has been investigated in the same manner as the Water parameters of the Elbe.

Here some parameters also correlate, those include air temperature, solar radiation, dewpoint and humidity. The Humidity and Dewpoint measurements have a general correlation for all wind directions and speeds, excluding the region 180° - 250° and (##m/s) where the Water parameters seem to dominate with their correlation.

The temperature and solar radiation correlate significantly with the methane concentration. The correlation is suitable in nearly all regions excluding the 180° - 250° and (##m/s) and has a clear correlation in the 330° to 130° at all wind speeds. The wind direction in this region point to the primarily residential regions of Hamburg and its surround. In this region, the river Elbe is not present, and no tidal-influenced waterbody exists.

Other meteorological Parameters don’t seem to have any correlation to methane concentration. Those include precipitation and air pleasure, etc. ~~The general region of the emissions is North-West to East-South-East, which points inland where the River Elbe is not present and is more agriculturally used. The p-value test shows that the correlations pass the test for the regions of most interest.~~

……

* 1. **The wind**

By analysing the wind measurements, a dominant wind direction could be observed with generally medium wind speeds during the entire measurement campaign. The Windrose Plot *WindRose\_Total.png* show rather well an average wind direction of South-West. While wind from all directions has generally been observed, four distinct directions/patterns have been observed, indicating some reoccurring and distinguished weather patterns in Hamburg. Most likely, the westerly winds, High-pressure regions over the main and transitions of cyclones into central Europe. By additionally using the Methane measurements, one can see in a Pollutionrose that the methane emission dose comes from every direction with a distribution closely reassembling the direction distribution. This shows us that the background methane concentration has no clear emission direction. Hence no strong emitter nearby influences the Background. (find Average for direction)

When now only considering the methane peaks identified with the Peak finding algorithm, the distribution changes substantially. In plot *WindRose\_Peaks.png* and *PollutionRose\_Peaks.png*. The Pollution rose plot, in particular, shows that the peaks, especially the high concentration ones, have three distinct directions, South-west, South-South-West and North-North-West. The directions observed are the same as seen in the correlation plot with the water level and quality in the section *Methane Emissions with the Water level.* This strongly indicates that distinct emission regions are responsible for the methane peaks.

* + 1. **The distance**

The estimated distance of the methane emission resulting in peaks from the measurement location at the Geomatikum can be seen in Figures ## and ## plots. Here both peak identification criteria have been used to illustrate the differences.

A couple of details can be observed when looking at the strict peaks identification criteria that selected only the prominent peaks. The distribution of the distance from the measurement Location is relatively close, with most points located under 20 km away. A couple of very distant points exist up to 60 km away. The distance estimation is most likely not correct for them, as the distance travelled is substantial, a possible distance overestimation due to strong winds is possible, or a different origin for the peaks might be the cause.

The methane concentration measured decreases with the distance travelled. When potting a smoothed curve, a peak at a distance of 5 km can be observed. This peak represents the high concentration points between 2 to 12 km from the measurement location. The curve also indicates that peaks which are estimated to originate further away also have a lower methane concentration.

The distribution changes sustainably when applying the peak identification criteria described in the literature by ###.

While most peaks are estimated relatively close to the measurement location, a high concentration can be measured at a distance of up to 100 km. Some outlier peaks have an estimation of 370 km. The Concentration dose again decreases with the distance, with the highest concentration being under 20 km.

Using this plot, it has to be assumed that the peak identification criteria identified many peaks that don’t seem to originate from the Elbe and have a different production mechanism.

The plot nether the less helps us to define a boundary for the transport modelling of maximal 60 km from the measurement location. A greater distance would be subject to too many variables….

* 1. **The Transport model**

The transport of the methane has been modelled and is shown in figure *10\_Emission\_Distribution\_with\_Changing\_Measured\_Wind.png,* the density distribution represents the probability of the methane emission locations, which is shown as a heatmap 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 river Alster joins the Elbe (Paper high concentration measurements). This Part of the city has a large, sweet water lake, the Alster Lake, which is relatively Shallow. The Lake and river join the Elbe by locks and controlled water management systems. Additionally, this region 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 Second region is the south of Hamburg. The Hamburg Port is located in this region, which includes a vast network of channels, contributing rivers, small harbours and some small wetlands. This region also shows an elevated density following the river Elbe upstream land inward. 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 regions.

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

This indicates that the origin of the methane peak can be quite far away. Still, the accumulation of methane along the river's entire length in the air is possible. It can produce a high methane concentration in the city with favourable wind conditions. One can also notice that a higher density occurs north of the Geomatikum. But further investigation of the track shows that the wind at those peaks is relatively slow and shows a turning wind direction. The tracks also lead to a large wetland region on the Elbe just outside the city bordered on the west side of the city.

* 1. **The Keeling method**

Using the Keeling method, the methane origin sources have been estimated. While investigating the entire timeline. The indicated production mechanisms of methane are thermogenic and microbial CO2 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 ecocultural use, including cattle farmers and large wetland and marshland areas nearby. This also includes the vast Wadden Sea of the German bight near the city. This Wadden Sea region lay upwind in the dominant wind direction to the west.

When applying the Peak finding algorithms to the methane measurements data. The Keeling method indicates methane production mechanisms much clearer in the Microbial CO2 reduction region and less in the Thermogenic, shifting 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 river 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/direction. In the dual isotope plot *12\_Keeling\_Wind.png,* one can identify a difference in isotope signature and origin type by the wind direction. For the total 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. Probably unburned methane from heating and cooking, leakage in the Gas grid and energy generation plays a significant role in the composition of the methane mixture.

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. While waste can be more or less eliminated 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 strongly agriculturally use of the region. What is surprising is the neglectable 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, *12\_Keeling\_Peaks\_Wind.png.* here, it has to be noted that not all wind directions had sufficient peaks to create a statistically meaningful keeling analyse. The dual isotope plot indicates a wetland and agricultural origin for the remaining wind directions. Point again toward a biogenic origin in the river Elbe and its wetlands.

1. **Conclusion**

This investigation indicates an elevated methane emission originating from the Water system and its surrounding in Hamburg and its outskirts. The first instinct is to conclude that the river is the main contributor to methane. Nevertheless, other contributing locations must be investigated. The first is the obvious presence of industry along the river. Example of those includes fossil fuel refineries, chemical production, Shipping etc. They are all heavily dependent on the river Elbe, and many of them have to follow the tidal cycle for their operation. But as seen by (Paper) the emission from these sources has been investigated and seems to be only a relatively small emission source. Additionally, as discussed later, the isotopic signature is not typical for Anthropogenic sources. So that this aspect is not a plausible explanation for the methane peaks.

The Second possible contributor in the Hamburg Port region is the presence of civil infersurture, which includes waste water treatment, garbage processing, etc. Those locations have also been investigated closely with drive-by measurements using a boat and a car. This is described in more detail in (Paper). No elevated concentrations have been observed near those locations. Further questioning of the facility's operators revealed that the facilities operate completely sealed from the environment, and Methane produced by the process is collected and introduced to the local gas grid. Additionally, it was ensured that no venting of the feasibility occurs at any time, eliminating the possibility of the Methane peaks occurring due to short methane venting events during their operation.

In the inner-city regions, no such infrastructure and industry are present. Only residential and business zones are located in this region.

1. **Discussion**

The long-term high temporal Isotope measurement showed high-concentration methane peaks. Those peaks were observed for the total measurement campaign ## months. This was also observable for FTIR measurement performed over a shorter time period. Additional measurement limitations prohibited a contentious measurement, prohibiting a direct comparison to the Isotope measurements.

A keeling analysis showed the difference in the isotope composition of the methane between the background and the methane peaks using the peak identification criteria provided by####. The peaks showed a more substantial influence by Anthropogenic sources, like fossil fuel combustion. While the background shows a generally strongly influenced methane composition by natural production mechanisms such as ####.

A keeling analysis considering the wind direction showed an anisotropic methane production distribution. Indicating a solid anthropogenic methane production in the northern regions of Hamburg, where primarily residential areas are located. A further indication of this hypothesis was shown by the correlation of methane concentration in the air with temperature in this wind direction. It is suggested that the alleviated methane concentration originated from increased fossil fuel consumption during colder temperatures, heating and electricity production and increased private automotive transportation during that time.

The keeling analyses from the southern wind suggested a strong methane production from natural mechanisms. This region hosted an industrial section in the Hamburg port region, with water infrastructure and wetlands.

The methane peaks measured during the southern wind also suggested natural production methods. A difference between the smaller peaks' generally more anthropogenic composition of the smaller peaks and Biotic wetland-produced methane from prominent methane peaks could be observed by applying stricter peak identification criteria.

This indicated that the extremely high concentration and sporadic methane peaks originate from the Elbe River and its connecting water bodies.

A correlation of water quality parameters such as oxygen,#### and the methane concentration at specific wind directions gave further indications pointing to the Elbe River as responsible for the prominent methane peaks.

A purpose build Gaussian plume time reversed transport model showed that the most likely origin of the methane peaks lay in the waterbody within and around the city of 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.

The occurrence of methane peaks could also be linked to the dropping of the water level in the Elbe due to the Tidal cycle. As shown by ####, dropping the water level increases the methane concentration dissolved in the Elbe river water. ### showed that the dropping in water level in water reservoirs with high sediments and pollution causes a significant release of methane into the atmosphere due to the hydrostatic water pressure reduction due to the drop of the water column height. ### and ### showed that the Elbe River forms methane production hotspots in heavily human-altered and impoundment sections of the river, including the region of Hamburg.

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

A complex interplay of many factors enables this behaviour. The river is fertile for methane production, mainly when high pollution and low water quality are observed ~~while the oxidation processes are disrupted~~. The methane can accumulate in the sediments over time, as natural methane reduction methods are disturbed due to the heavy impoundment within the city region. The tidal cycle of the Elbe is quite large for a river due to its connection to the Wadden Sea and the North Sea. While methane-rich water from the Wadden sea is also flushed upstream by the tides. The fast drop in the water level that even allows for the river to run dry in certain regions is the main catalyst for releasing methane into the atmosphere. The low water level reduces the pressure allowing bubbles to form and travel to the surface, while the short water column height doesn’t allow for sufficient methane oxidation. The regions where the sediments are exposed to the air may also release significant methane. While the resetting of the sediments due to the suddenly accelerated water flow over the sediments due to the low water may also reintroduce organic matter to the sediments, which is known to accelerate methane production (reference #####).

The suddenly released methane is then transported away from the Elbe by the wind. Depending on the directions and speed, this can produce a very sharp and high methane concentration in the city's air. It is assumed that the Geomatikm 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.

That the river Elbe is an unaccounted methane emitter has also been shown by the Inverse Bayesian modelling for the FTIR measurement. As ### demonstrates, the modelling could significantly be improved when the Elbe is accounted for in the Prior. The tidal cycle and its resulting variation in methane emission from the Elbe are unfortunately not accounted for in this correction. This could further improve the model.

1. **Further investigation ideas**

* Contenius measuments close to the Water body. Located downwind.
* Methane emmisin to the athmospere measuments using the funal methode.
* Contenius methan concentration measuments in the water
* Soli investigation from the port regions.

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