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**Draft**

1. **Abstract**
2. **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 in the Atmosphere. It is ### times more potent than CO2 and is released into that atmosphere in large quantities. Estimations vary from ### to ### t per year. A great variety of sources produce methane and release it into the atmosphere, ranging from Natural to anthropogenic. Natural methane emitters are usually considered ones where humane influence is not directly involved, such as biotic decomposition of organic materials, release by livestock such as cattle or bound Methane releases in permafrost deposits due to temperature rise. Anthropogenic sources are usually connected to the use, transport and treatment of fossil fuels, such as Natural Gas or Oil. Together with other Chemical industries and human infrastructure structures. 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.

The ##### 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 inverters currently available.

The Campaign was conducted between the 01.08.2021 and the 01.04.2022, with a short maintenance break between the #### and the #####. During the campaign time period, high time-resolution mass spectrometer measurements were conducted focusing on Deuterium and Carbon 13 isotopes. The measurement was stationary on the roof of a Hamburg University building (Geomatikum) near the city centre, with an inlet height of 83 m.

For the shorter time period of the 01.08.2021 to 31.09.2021, a series of additional measurement approaches were conducted. These include a solar Fourier Transform Infrared Spectrometer (FTIR) Network with four EMS27/Sun spectrometers located in and around Hamburg. Using the Bayesian inverse modelling approach, this network enabled a differential total column measurement. A wind LIDAR (Windcube) was also deployed to improve the transport modelling by correcting the atmosphere Boundary layer height and the Wind direction of the wind model. Mobile Methane and Enthan measurements by car and Boat were also conducted to validate and improve the inventory for the uses as Priory in the Bayesian inverse modelling. The mobile measurements mainly focused on the Industrial and Port region in the north, filling the gaps left by a previous measurement campaign with the same approach, which mainly focused on the residential areas to the South.

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 ### ppb, while the average background concentration was around #### ppb. The duration of the peaks where also very short lasting, for around 0.5-2h.

By carefully investigating the chemical composition of the gases by a Keeling analyse during the peaks, it was concluded that emission sources were due to natural 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, docks, fleets and canals are located. By correlating the meteorological data, water level and water quality data (#####). These regions experience strong water level fluctuations due to tidal effects. The occurrence of the peaks has been successfully correlated to the Water level. It is known from #### that the fast-dropping water level can trigger significant methane emissions into the atmosphere at freshwater reservoirs, while ### 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 the Methane inventory. This is also suggested by #### and ####. While the fluctuations of methane release by rivers, wetlands etc., due to tidal effects are not well investigated and understood. This Thesis shows their observable effects and the conclusion drawn linking it to the River Elbe while providing ideas for further research.

1. **The Campaign**
2. **Methoden**

* 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. **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**
  2. **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. **Theory**
   1. **Keeling Method**
   2. **Transport Model**
   3. **Peak Identification Algorithm**
2. **Results**
   1. **Identification of Peaks**
   2. **The Water level and Quality**

Water quality

A clear 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.

When looking at the correlation plots for Water temperature, Oxygen concentration, opacity and pH level. A very clear correlation can be observed. This strongly 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. **The Meteorological data**
  2. **The wind**
     1. **The distance**
  3. **The Transport model.**
  4. **The Keeling method**

1. **Discussion**
2. **Conclusion**
3. **Acknowledgement**

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