Keeling Analyse

It is important 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

**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)**

**CHIMERE**

CHIMERE is a three-dimensional Eulerian limitedarea chemistry-transport model for the simulation of regional atmospheric concentrations of gas-phase and aerosol species.

Deutscher Wetterdienst (DWD) Data

The Deutscher Wetterdienst (DWD) Providers Weather and climate data for free with an extensive array of measured parameters with different time intervals for a large selection of weather stations. In Hamburg alone, there are two Stations and about five near the city. In the Thesis, primarily the data from the Fuhlsbüttel, Hamburg has been used due to the proximity to the Geomatikum, where the Isotope measurements and one of the Infrared total column stations have been located.

A significant advantage of using the data provided by the DWD is the standartification and quality control done by the DWD, providing considerable confidence in the measurements. Additionally, the wide arrange of parameters provided including precipitation, Soil and air temperature, solar radiation intensity etc. provided the ability to compare and correlate many aspects of Methane emission.

* <https://opendata.dwd.de/climate_environment/CDC/observations_germany/climate/>
* <https://wetterdienst.readthedocs.io/en/latest/data/coverage/dwd/observation/minute_10.html>
* <https://www.dwd.de/DE/leistungen/klimadatendeutschland/mnetzkarten/messnetz_mi.pdf;jsessionid=053DAD8C1C2781FF1086CA7986DFCD01.live11053?__blob=publicationFile&v=12>
* <https://www.dwd.de/DE/leistungen/klimadatendeutschland/klarchivtagmonat.html#buehneTop>

Bundesamt für Gewässerkunde (BfA)

The Water Level Data was provided by the Bundesamt für Gewässerkunde (BfA), and the data has been collected, checked and Quality controlled by the Wasserstraßen- und Schifffahrtsverwaltung des Bundes (WSV). The Data provided has a high temporal resolution of 1 min and high precision of 1 cm. The Location of the Station is St. Pauli which again was chosen for its proximity to the Geomatikum. The WSV provides many measurement stations, some stations provide data on chemical composition and pollution of the Water. Unfortunately, they don’t provide contentious timeline measurements so those measurements can only be used as a reference, but not in correlation to the methane emissions.

*Bitte benutzen Sie bei Publikationen die folgende Zitierweise:*

*Datenquelle:*

*Wasserstraßen- und Schifffahrtsverwaltung des Bundes (WSV), bereitgestellt durch die Bundesanstalt für Gewässerkunde (BfG). Dies gilt für Erst-, Zweit- und jedwede Nachnutzung.*

*Die übermittelten Datensätze entstammen der Pegeldatenbank der  
Wasserstraßen- und Schifffahrtsverwaltung des Bundes (WSV).  
Sie wurden durch die pegelbetreibenden Wasserstraßen- und Schifffahrtsämter geprüft und veröffentlicht.  
Trotzdem sind Datenfehler und Inkonsistenzen nicht vollständig auszuschließen. Eine Gewähr für die Richtigkeit und Vollständigkeit der Daten wird insofern weder durch die WSV noch durch die BfG übernommen.*

* <https://www.hamburg.de/clp/hu/seemannshoeft/clp1/>
* <https://www.pegelonline.wsv.de/webservices/files/Wasserstand+Rohdaten/ELBE/HAMBURG+ST.+PAULI>
* <https://undine.bafg.de/elbe/guetemessstellen/elbe_mst_seemannshoeft.html>
* <https://www.kuestendaten.de/Tideelbe/DE/dienste/karte?lang=de&topic=portal_tideelbe&bgLayer=bkg_open_farbig&E=564579.35&N=5930875.46&zoom=10.699999999999983&catalogNodes=13,8,104&layers=52583503286005e042812ad7d0d541c1&layers_visibility=5ce99fee0698d889f0cd2e0809f973dd>
* <https://www.bafg.de/DE/Home/homepage_node.html>

Wind Data by Hamburg Universität

The University of Hamburg conducts their own Independent Wind Measurements at multiple locations, two of them were of particular interest and have been used in this thesis. The First is at the Geomatikum, located very close to the Isotope measurement inlet. At a Hight of 86m. The Second location is the Weather tower at Billbrook, where wind measurements are performed at the height of 50m and 110m. While the Tower is located relatively far from the Geomatikum, it has the advantage of a very reliable measurement as disturbance from the Structure and the surrounding building is minimal. The Wind measurements the University provides are averaged for a 10-minute interval, enabling a good time resolution later. While all provided data has been used and analysed, it becomes apparent that the data measured at the Geomatikum provides the best results with further investigations.

* https://wettermast.uni-hamburg.de/frame.php?doc=MessanlageEng.htm

LIDAR by DLR

Not been used yet

* <https://www.vaisala.com/en/wind-lidars/wind-energy/windcube>
* <https://www.pa.op.dlr.de/DFWind_PA/lidar.html>

**Peak Identification Algorithm**

**Methane Emissions with Water level**

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. As seen in Plot *1\_CH4\_WL.png*, which is a Section of the complete timeline. Here, the dominant Methane Peaks occur around 1-3 h after the Lowest Water Level. The Smaller Peaks are visually more challenging to identify and correlate to the Water level. The Peak identification algorithm has been used to identify a correlation between the Peaks and the Water level, which yields the expected correlation to the Water level.

To prove a correlation, Pearson's correlation coefficient has been used. Unfortunately, the occurrence of Ellevated Methan 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.

To establish a correlation between water level and Methane, each wind direction and corresponding Velocity had to be analysed separately. This was done by binning all methane and Water level measurements in 10° Direction and 1m/s Velocity bins. 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 the 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 can be trusted, 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 rection can be pursued.

**Methan correlation with Water Quality**

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……..

Using the same correlation approach as before, a very 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 largest influence by the Tides. Further to the est, 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 strong indication the river Elbe is a large Methane emitter which is under the influence of multiple parameters that change over a daily, monthly and yearly cycle.

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

**Methane emission with meteorological observation**

Like the water level correlation, all other available meteorological observations have been investigated.

Most Meteorological Parameters don’t seem to have any correlation to methane emissions. Those include, for example, precipitation, air pleasure etc. Others do have a very strong correlation, while some seem to have a general correlation independent of the wind direction, like Dew Point ………. Of particular interest are other Meteorological parameters that show a very strong (negative) correlation to Methane emission, this includes Temperature, Solar radiation intensity. What is interesting is the significantly different Wind directions compared to the Water level correlation. 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.

……

**Methane Emissions with Wind**

As previously mentioned, dose the Wind plays a significant role in the measured methane concentration at the Geomatikum. Hence a detailed analysis of the observed wind is essential. 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 generally, Wind from all directions has been observed, four distinct directions 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 particular 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 that can be seen in the correlation plot with the Water level in the section *Methane Emissions with the Water level.* This is another strong indication that distinct emission regions are responsible for the methane peaks.

**Emission Distance**

The Sharpness of the Peaks, the relatively short duration of 1 to 3h and the very high methane concentration at the peaks indicate a location of the emitters relatively close to the measurement site. Together with the strong indications that the Methane Peaks correlate to the tidal cycle of the Elbe…

It is attempted to estimate the distance of the methane emission to the Measurement site at the Geomatikim. For this, a trek of a virtual Wind particle is modeled using the measured wind data at the Geomatikum. The Practical travel between the point of the max methan concentration per peak and the previeal Elbe river Low water Point. The totale distanze between the Geomatikum and the Esitmatet emission is than calculated.

The resulting distance ist plottet versus its Peakss Maxiam Methan concentration in a scatterplot seen below: *14\_Low\_WL\_to\_Peak\_dist\_new.png*

Here it can be observed that the Significant Peaks with a high concentration forme 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 obsert but with a significantlz lower concentation. When looking at the the Peks selected form with the Criteria dicribt above (Paper creteria) a corelation to concentration with distance can be seen. Schowing the thurther away the estimated sorce is the Lower the concentation. As one would expect. The Far away points are very likely less influenced directly by the Tidal cyle.

**Transport model**

It has been attempted to construct a Transport model to locate the emission region. 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 is emitted at each investigated emission time. Each partial direction and speed 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. 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 track 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 in close proximity to the city. So that the assumption of uniform wind in the region must be assumed.

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 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 is 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 max to half an hour before the Previous Low water.

As seen in figure *10\_Emission\_Distribution\_with\_Changing\_Measured\_Wind.png* the Density is exceptionally high in certain Inner-city regions. Firstly, in the Historic city centre where the river Alster joins the Elbe (Paper high concentration measurements). This Part of the city has a large, still sweet water Lake, the Alster lake, which is relatively Shallow. Additionally, a large amount of interconnected small Fleets, Historic harbours, and channels are present in this region, most of them completely dry out for some amount of time during the tide cycle. Exposing 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.

The Last region of higher density is on the western side. Notably, a significant amount of 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. Indicating that the origin of the methane peak can be quite far away, but the accumulation of methane along the entire length of the river in the air 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 quite 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.

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.

Keeling Analyse

Using the Keeling Methode, the Methan 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. It can clearly be seen that fossil fuel and other Anthropogenic sources play a minor role in the composition of the Methan mixture. This is surprising as Hamburg has a significant amount of Heavy industry, including Fasile fuel refinery, chemical, Shipping, energy production etc. On the other hand, this is expected, as the surrounding Countryside has significant agocalural 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 even more clearly into the Wetland region, while less likely to originate from waste and angragulure. The Keeling method clearly points toward the origin of the methane peaks due to biogenic mechanisms in the river Elbe, its contributors and the wetlands at its riverbanks.

By using the Wind direction, it is 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 in this region, considerably fewer wetlands are present, and many residential areas lay there, one can assume that this shifts the methane mixture towards the 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 Methan mixture.

For the southern and western directions, the Methan signature is quite strong in the microbial CO2 reduction region, pointing out that the largest contributors to this Methan 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 agraguluraly use of the region. What is rather surprising is the seemingly neglegtebal effect of anthropogenic sources, like fossil fuel and industry, as this region is also heavily used in that regard.

The same analyses have been done for the methane peaks, as seen in the dual isotope plot, *12\_Keeling\_Peaks\_Wind.png.* hier, it has to be noted that not all wind directions had sufficient peaks to create a statistically meaningful keeling analyse. For the remaining wind directions, the dual isotope plot indicates a wetland and agricultural origin. Point again toward a biogenic origin in the river Elbe and its wetlands.

**Thesis Structure**

1. Abstract
2. Introduction
3. The Campain
4. Theory
   1. Mass Spectroscopy
      1. Method of measurement
   2. Keeling Method
   3. FTIS
   4. Inversion model
   5. MuccNet
   6. Transport Model
   7. Peak Identification Algorithm
5. Results
   1. Identification of Peaks
   2. The Water level and Quality
   3. The Meteorological data
   4. The wind
      1. The distance
   5. The Transport model.
   6. The Keeling method
6. Discussion
7. Conclusion

**The Elbe River; Methane emissions**

* The Elbe River is a strong Methane emitter.
* The Methan concentration in the Water and in the atmosphere are very different, different region of the elbe.
  + Methane originates form Hotspotrs along the river, rather then contenius supply by sediments
  + highest methane concentrations were found in human-altered riverine habitats, i.e., in a harbor, in a lock and weirs, and in general in the whole “impounded” river segment
    - High Methane Production, no Oxidation
    - Why no oxidation ist unknown
  + methane oxidation rate was more efficient in the “natural” segment
    - Best natural Barriar for Methane beening reliesd
      * Not happening in inpoundet rivveres
* Very High Methan Concentration in Hamburg habor
  + High concentration in other Habors upstream.
  + High Methane concentration due to Methane influx from freschwarter influx
  + Short remaning time. i.e. low Methane oxidation
  + High Polution
  + High Biomass
  + No Methane froam wadden sea, as waters don’t mix suficently
* Lowe estury has Lower methane concentration in water
  + Methane from Upper dose not reach the lower estuary
  + Longer particle remaining time
  + More oxidation
  + More time to defuse into atmosphere
  + 10 times lower than in houbur
  + (In Marshlands) Methanogenic bacteria were found in oxic as well as in anoxic soil layers
  + The highest methane production rates were measured at 10°C and 20°C
  + Usualy at high temeratures around 30°C, at elbe Different Bactreia produce methane at low temperature, 10°C
* Waddensea very high methan production
  + Most of methan influxe in water due to Tide in Wadden sea
* Mathan in Water i.e. emissins to atmosphere du to Micibial production and oxidation
  + Temperature dependet
    - High methan oxidation in summer, low oxidation in winter
    - Methanotroph reduces CH4 Emissions from sediments
    - (for total river) Low Waterlevel and high temperatures enhances microbial activity and thus decreases oxygen levels
  + No Clear relation to Suspendet particular metter
    - But turnover dose increase Methan production in seliments
      * Due to introduction of ions…
      * Tidal strams increase “reset” or “mixing up” in particular with low waterlevels
* Waterlevels changes influences the methane concentration in the Water and release into atmosphere
  + We found that when the water level was **dropping** the higher CH 4 concentrations were observed (r 2 = 0.86, n = 10) in the upper estuary, but no correlation was found in the lower estuary.
    - Watercolume hight changes the methan release due to preasure changes.
      * More Buble released due do drop in Hydro statik preasure
    - Thick Selimantes layeres can store a large amount of Methame
      * They can suddenly increase realease due to pressure drope (like in tides)
    - Kone ́ et al. 2010; Upstill-Goddard and Barnes 2016
    - minimiesed Oxidation of Methane in water collum (Less water to oxidice the methane)
    - The sensitivity of reservoirs to drawdowns is likely to be a function of sediment characteristics (e.g., sediment cohesiveness and, especially, organic matter content 13 ), reservoir average depth, the frequency of draw-downs, rates of methanogenesis, and CH 4 oxidation, and is a topic meriting further attention in future work
* Methane Concentration correlates with BOD-7 (measure of the bioavailability of degraded organic matter)
* high heterotrophic activity related to remineralization processes of high loads of labile organic matter
* Despite active methane oxidation, the microbial filter was estimated to be responsible for 5–41 % of the methane total loss. The other part was attributed to methane diffusion into the atmosphere

It is known that the river Elbe is a significant methane emitter. The methane concentration in its water and consequent release to the atmosphere varies for the entire river. ~~Showing significant differences over its entire course~~. 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 noch impact by human influences. In this region, the river has no significant methane emissions as the Natural methane oxidation mechanisms are in balance with its Production and influx mechanisms. In the second section, the river is heavily industrially used in the Czech Republic. The river is heavily 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. In the Third Section, Elbe is described as a Lowland river. Its banks are only stabilized groynes, and in the German regions, the river is significantly renaturalised with free-flowing characteristics. In this section, the biotic methane production is kept in check with ist countering oxidation processes, resulting in a low methane concentration in the water and consequent low defusion rates to the atmosphere.

During the course of the river, some heavily impounded human-made structures are present, including harbour, locks, and weirs. These sections form methane hotspots, as Methane production is rampant due to the disturbed flow of the river and strong 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.

The river elbe estuary starting at the city of Hamburg down to the Nothsea into the Waddensea experiences different environmental factors, and different mechanisms drive its methane production and reduction mechanism. The Upper estuary is defined by the heavily impounded region around Hamburg, including its port. The upper estuary experiences large 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 here due to insufficient mixing. The water in this region has a very short turnover time, with a very high Methan concentration, similar to other harbours and Humand 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 in pollutants and biomass significantly enhances the Methan 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 a large network of connected marchlands. 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. the low-temperature peak production occurs due to the reduced methane Oxidation at low temperatures. Marshlands system usually peaks in a 30°C region in warmer climates.

The water turnover time is significantly longer, providing good conditions for methane oxidation and a larger defusion of methane into the atmosphere, resulting in a 10 times lower methane concentration than in the upper estuary. 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 clear 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 the Methande production in the sediments due to the reintroduction of Biomass and Ions to the sediments. 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 oxidise the methane due to its lower water collum height over the sediments. In the Elbe estuary, the Methan concentration in the water is correlated to the Falling of its water levels due to the Tide. Reaching its peak at the lowest water level. Studies have shown that the fast reduction of the water level increases the methane concentration and, consequently, its emission to the atmosphere. This can be explained as 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 that are released from the sediments and travel up to the surface and escape to the atmosphere. The reduced water column height cannot oxidize the majority of this methane anymore, resulting in the release of methane. The exact condition required for such a surge in methane emission is not yet understood in detail and 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 the methane diffusion.