**Methane distribution and methane oxidation in the water column**

**of the Elbe estuary, Germany**

* Hamburg to Cuxhafen
* High Methan Concentration In Hamburg Habour
* 10 Times Lower in lower estury.
* No Clear relation to Suspendet particular metter
* Correlation with Methan in water and temperature
* High methan oxidation in summer, low oxidation in winter
* Methanotroph reduces CH4 Emissions from sediments
* „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.“
* We found significantly higher CH 4 concentrations at   
  falling water levels in the upper estuary. Grunwald et al.  
  (2009) suggested that CH 4 concentrations usually peaked   
  during low tide, probably due to the CH 4 -rich freshwater   
  input and that, conversely, low values may be caused by   
  dilution with CH 4 -poor marine water and degassing pro-  
  cesses. This was revealed and postulated also by others   
  (Kone ́ et al. 2010; Upstill-Goddard and Barnes 2016).   
  However, we did not find a correlation to water gauge/   
  level, like Grunwald, but with the ‘‘falling water level’’.  
  We assume that our sampling strategy from a moving boat   
  versus fixed stations biased this effect. For the North Sea   
  the tidal flat have been shown to be a methane source (Wu   
  et al. 2015), and we assume that the strong surge at falling   
  water levels results in the release of methane into the river/   
  estuary.
* Methane in the whole estuary but more specifically in its   
  upper part is positively correlated with the BOD-7, which   
  represents a measure of the bioavailability of degraded   
  organic matter. The high CH 4 concentrations in the upper

part of the Elbe estuary likely result from the high het-  
erotrophic activity related to remineralization processes of   
high loads of labile organic matter.

* Turnover and temperature is improtent
* Upper esury, methane due to the river (pollution , biomas etc.)
* Lower Methane due to Wadden see
* Methane from Upper duse not reach the lower estury
* Despite active methane oxidation, the microbial filter was esti-  
  mated to be responsible for 5–41 % of the methane total   
  loss. The other part was attributed to methane diffusion   
  into the atmosphere

Sediment methane dynamics along the Elbe River

* Biological methane -> wet anoxix soils and sediments
* Frequently observed inverse relationship between discharge and CH4   
  concentration is most probably given either by dilution (Kone et al.,   
  2010; Anthony et al., 2012) or by higher temperature during low water   
  periods. Increased temperature further enhances microbial activity and   
  thus decreases oxygen levels (Borges et al., 2018).
* (Teodoru et al., 2015; Barbosa et al., 2016)
* This implies that the CH 4 input into the water   
  column may originate in some hot-spots of CH4 production rather than   
  a continuous supply from the sediment.
* Alles nicht so nützlich….

**Methane dynamics in a large river: a case study of the Elbe River**

* The highest methane concentrations were found in human-altered riverine habitats, i.e., in a harbor (1,888 nmol L−1 ), in a lock and weirs (1409 ± 1545 nmol L −1 ), and in general in the whole “impounded” river segment (383 ± 215 nmol L −1 )
* The methane oxidation rate was more efficient in the “natural” segment (71 ± 113 nmol L −1 day −1 , which means a turnover time of 49 ± 83 day −1 ) than in the “lowland” segment (4 ± 3 nmol L −1 day −1 , which means   
  a turnover time of 39 ± 45 day −1)
* Methane emissions from the surface water into the atmosphere ranged from 0.4 to 11.9 mg   
  m −2 day −1 (mean 2.1 ± 0.6 mg m −2 day −1 ) with the highest CH 4 emissions at the Meissen harbor (94 kg CH 4 year −1 )
* Such human-altered riverine habitats (i.e., harbors and similar) have not been taken into consideration in the CH 4 budget before, despite them being part of the river ecosystems, they may be significant CH 4 hot-spots
* The aerobic CH 4 consumption (methanotrophy) by   
  methane-oxidizing bacteria (MOB) is, so far, the best   
  known process providing a natural barrier of CH 4 being   
  released from different ecosystems into the atmosphere.
  + Not happening in impunded riveres
* On the other hand, in the water col-  
  umns of rivers, microbial CH 4 oxidation is believed to be   
  much less efficient (Zaiss et al. 1982)
* Many authors pro-  
  pose that river impoundments (weirs, locks, dams, reser-  
  voirs) represent the hot-spots CH 4 emissions due to high   
  CH 4 production in these man-made habitats (e.g., Guérin   
  and Abril 2007; Hertwich 2013; Maeck et al. 2013).
* However, the reason for the   
  inhibition of CH 4 oxidation in these habitats still remains   
  unexplained and so needs further research
* Nevertheless, our data show   
  that both damming of the river as in the “impounded” seg-  
  ment of the Elbe and the occurrence of CH 4 hot-spots (e.g.,   
  harbors), may promote CH 4 emissions and contribute to the   
  high variations of CH 4 fluxes at the river scale

**Two temperature optima of methane production in a typical soil of the Elbe river marshland**

* 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
* Moore and Roulet [32] showed that methane production in peat-  
  land soils decreased in relation to a lowered water   
  table.
* Different Bactreia produce methane at low temperature 10°C…

**Reservoir Water-Level Drawdowns Accelerate and Amplify Methane Emission**

* Water-level fluctuations due to reservoir management could substantially affect the timing and magnitude of reservoir methane (CH 4 ) fluxes to the atmosphere
* Reduction in Waterlevel invreases methande flux to atmosphere due to minimiesed Oxidation of Methane in water collum
* In fact, a recent review of nine lakes   
  with both CH 4 production and oxidation measurements   
  conservatively estimated that methanotrophs consume 50−  
  95% (median: 90%) of all CH 4 produced in lakes and an even   
  greater fraction of the nonebullitive CH 4 flux
* More Buble released due do drop in Hydro statik preasure
* With Lots of seliment , the seliment can store lots of methan and release it by low water event
* Increases methan wenn seliments are “reset” or mixed up.
* 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 emissions from Mexican freshwater bodies:   
correlations with water pollution**

* Polution generates more methane emission

**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
  1. **The river Elbe (summery in Thesis)**

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.