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The Occurance of Methane in Marine and Freshwater Ecosystems and its Impact on Climate Change

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The Occurance of Methane in Marine and Freshwater Ecosystems and its Impact on Climate Change

Abstract

Actual effort to understand the global change encourage scientists to get more datas and expert knowledge about this worldwide problem. As a hydrosphere occupies almost two thirds of the Earth surface, it becomes an important part of current research. Greenhouse gases are slowly leaking from marine and freshwater ecosystems, and so I have decided to completely understand the potentional risk of escaping methane – an efficient greenhouse gas – from aquatic ecosystems.The purpose of such a research is to ascertain how important, hazardous and distant is sudden methane release danger. Whether the ocean reserves threaten our population and if there are other similar methane sources closer to us. This question follows the immense concern and focus on CO_2 emissions. According to the following text, seriousness of methane release situation is equally substantial. Not only, that CH_4 is twenty times more powerfull greenhouse gas than CO_2. It is furthermore an abundant component of our planet's habitats, hidden in the oceans and freshwater reservoirs. As my research shows, there are two main difficulties brought with methane emissions. First, it is a permanent and increasing leakage of methane gases from freshwater ecosystems. Second, there is a potential peril of a sudden masive release of methane from deeep ocean stores. Each case brings a significant risk on a global scale, besides, both have a positive effect on global warming. While comparing several aquatic habitats, such as oceans, lakes, rivers and streams, I discovered the magnitude and importance of methane emission issues. Nevertheless, despite the global warming theme is becoming more relevant and alarming, there is still a lack of information and scarcity of relevant data from methane release. Every cruical article or scientifical paper point out to this plain gaps and warn against the immense impact that lack of knowledge can bring.

Key words: Methane, Methane Hydrate, Methane Emission, Clathrates, Global Warming, Global Change, Marine ecosystems, Freshwater Ecosystems

CONTENT

Introduction 1

1 Methane and its characteristics 3

1.1 Basic properties 3

1.2 Origin and methanogenesis 4

1.3 Methane transport 5

1.4 Transformations and chemical reactions 6

1.4.1 Methane in the water column 6

1.4.2 Methane in the atmosphere 6

1.5 Methane hydrates 7

1.5.1 Structure I 7

1.5.2 Structure II 7

2 Global occurrence and quantity of methane in aquatic ecosystems 8

2.1 Methane deposits in marine ecosystems 8

2.1.1 Global occurrence 8

2.1.2 Global inventory abundance 9

2.2 Occurance and quantity of methane in freshwater ecosystems 9

2.2.1 Global occurrence 9

2.2.2 Global methane volume 9

3 Methane task in marine ecosystems and its impact on global change 11

3.1 Methane in the past 11

3.2 Present methane release and related risks 12

3.2.1 Warming ocean 12

3.2.2 Sudden methane inventory breakdown 13

3.2.3 Submarine slides and slumps 14

3.2.4 West Spicbergen measurements 14

3.3 Future perspective 15

4 Methane task in freshwater ecosystems and its impact on global change 16

4.1 Streams and rivers 16

4.1.1 Driving mechanisms 16

4.1.2 Measurements 18

4.1.3 Global fluvial methane emissions 18
4.2 Methane in lakes and reservoirs 19
4.2.1 Measurements 19
4.3 Anthropogenic influence 20
4.3.1 Damming 20
4.3.2 Land use 21
5 Measuring methods and methane as a potentional energy source 22
6.1 Measuring methods 22
6.1.1 Bottom Stimulating Reflector 22
6.1.2 Gas trapper 22
6.2 Methane as a potentional energy source 23
6 Discussion 25
7 Conclusion 26
8 References 27
9 Figures and tables 34

INTRODUCTION

Global change is an actual and cruical topic, discussed by many scientists, polititions and experts. We here about this theme in medias, read in news and magazines. We get cautionary messages almost every day. But what can an ordinary person do about that? I have decided to understand better at least a part of this immense global problem. Methane is a powerfull gas and its emissions or acculmulation can cause severe damages. Deeper knowledge and precise research of methane can prevent a potentional global risk.

The atmospheric methane concentrations began increasing since 1750s (IPCC, 2013). The exact rise has been about 150 % growth of CH_4 in the atmosphere, which makes 1834 ppb in contrast to previous 722 ppb (IPCC, 2016) According to the Nisbet□s research in 2014, only one third of actual emissions are consequences of natural processes. The rest is mainly powered by anthropogenic activities. (Nisbet et al., 2014). Due to high global warming potential of CH_4, it is necessary to observe the release and understand the process of loosening methane emissions into the atmosphere. (Delsontro el al., 2010) This gradual change influenced not only the atmosphere, but also other spheres, including aquatic ecosystems. (IPCC, 2013)

Eventually, actual annual total methane global emission extend to astounding 600 Tg of CH_4. (Ciais et al, 2013) Due to this fact, methane, as a strong greenhouse gas, is regularly discussed in cases of livestock, oceans, permafrost and also wetlands. But, *is methane deposited in oceans* or permafrost *seriously such a substantial danger?* Furthermore, *are other less explored places releasing methane less important?*

As generally known, freshwater ecosystems make 2-3 % of Earth□s surface and oceans cover approximately 70 %. But contrarily, lakes and rivers emit greater amount of methane to oceans. So why, according to previous numbers, are oceans such a disscussed theme, while freshwater ecosystems stay in the background? And on the other hand, how is it possible, that freshwater ecosystems emit roughly the same amount of CH_4, while the area of oceans is more then 20 times greater?

Methane in the ocean depths create methane hydrates, stable only in certain conditions. While the circumstances, such as high pressure and low temperature alter, stability weaken and methane release into the water column. (Archer, 2007) If the conditions would change rapidly, immense amount of methane would promptly loosen into the atmosphere and would cause a disaster. Nevertheless, thanks to an efficient methane oxidation in ocean waters, during slow stability changes, only a small part of methane really reach the atmosphere directly. (McGinnis et al., 2006).

Also water bodies, such as rivers, lakes, ponds or streams greatly participate as an important source of this greenhouse gas. (Bastviken et al, 2011) Due to a huge and fast organic matter income, fast transport and anoxic sediment conditions, methanogenesis is fast. Besides, urban areas, agriculture and sewage contribute to faster methane production and subsequently emissions. (Stanley et al, 2016)

In the next several pages, I have focused on research about methane release from aquatic ecosystems, such as oceans, rivers and lakes. I have attempted to *better understand the loosening mechanism* in each environs, *distinguish the main differences* and *subsequently determine the genuine peril that methane release can cause*, especially in case of global warming question. *How much aquatic methane emissions contribute* to the global change? And what are the main *anthropogenic activities that essentialy amplify the rapid increase of* CH_4 *emissions?*

Chapter 1

Methane and its characteristics

Methane, with its CH_4 formula is a simple alkane, the simpliest hydrocarbon and tetrahedral nonpolar molecule. Despite being a simple molecule, methane is a frequent and important chemical compound, with increasing magnitude in energy source and global change questions. (Docherty et al. 2006)

There are two types of methane. First one and most common is a *biogenic methane*. It is produced by methanogenic archaea, organisms, producing methane as a methabolic byproduct. The quantity is limited by the rate of bacteria methanogenesis and the supplies of organic material (Archer and Buffett, 2005) The other one, *thermogenic methane*, was discovered only on two places on Earth - Gulf of Mexico and the Caspian Sea. It is less common and of thermal origin (Kvenvolden, 1995). Methane from these regions is derived from a thermal decomposition of photosynthetically-produced organic material While the water temperature increases, to a worth of 110°C, methane is produced through the abiollogical way. Therefore is connected with oil, coal and other fossil forms of carbon (Archer, 2007).

1.1 Basic properties

At a room temperatures, methane has no colour, no smell. This plane alkane is lighter than the air. (Delsontro et al, 2010). As a part of the atmosphere, CH_4 is a strong, efficient and second most pletiful greenhouse gas. The amount of methane in the atmosphere raised more than three times since 1750 (table 1), and so the number of methane increased most rapidly. However it is not the most abundant gas, it is 28 times more effective in absorbing the IR radiation from the Earth than CO_2. (Blasing, 2016) Thanks to another characteristic, which is low solubility, methane create bubbles which occur in aquatic ecosystems, or freeze in frigid habitats. Methane hydrates, placed in ocean depths are also a special form of this „simple" alkane. (Delsontro et al 2010).

Table 1 - Preindustrial and recent concentrations of several substantial greenhouse gases and its global warming potential Since 1750, the amount of methane in the atmosphere raised from 722 ppb to 1834 ppb.

Greenhouse gas	Tropospheric concentration before 1750	Recent tropospheric concentration	GWP (100 year time horizon)
CO_2	280 ppm	399,5 ppm	1
CH_4	**722 ppb**	**1834 ppb**	**28**
N_2O	270 ppb	328 ppb	265

References: Blasing et al, 2016

Since the atmospheric concentrations of methane raised in 1750s, there is a substantial increase of methane in aquatic ecosystems. (IPCC, 2013) The exact rise has been about 150 % growth of CH_4 in the atmosphere, which makes 1834 ppb in contrast to previous 722 ppb (IPCC, 2016).

1.2 Origin and methanogenesis

Methanogenesis is a final process of decomposition of biomass in some environments (DeLong, 1992). It is performed by the organisms called methanogens. In unfavourable anoxic conditions, that is the only way how these organisms gain energy necessary for life. Uniquely, only they can produce methane as the metabolic by-product. (Thauer, 1998) The organic rain falling down on the seafloor goes through the organic decay. After the depletion of O_2, respirations of microorganisms carries on while utilizing NO_3^-, Mg^{2+}, Fe^{2+}, and eventually SO_4^{2-}. Once these electron acceptors are consumed, methanogenesis may start. (Archer, 2007) Whereas anaerobically decomposed, waste matter such as formic acid, acetic acid, methanol, carbon dioxide or hydrogen is released. Those are the electron donors, providing reduction of carbon dioxide to methane (1). (Thauer, 1998)

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2H_2O \qquad (1)$$

Methane in freshwaters is produced by oxidation of H_2 with CO_2 (1) as a terminal acceptor, or thanks to the decomposition of particularly acetate ($C_2H_3O_2^-$). (Bridgham et al 2013)

Group of microorganisms, releasing methane as a by-product of their metabolism activity in anoxic conditions is called *methanogens*. They belong to domain of archea, single-celled prokaryote. They occupy all kinds of environments, moreover archaea search for extreme conditions. (DeLong, 1992) While being a part of wetlands, hot springs, mammal s digestive system or wastewater treatment, methanogenic archaea occur in marine sediments and freshwater ecosystems, and produce methane. (Thauer, 1998)

1.3 Methane transport

Methane move between water and atmosphere, the same as within aquatic ecosystems. Understanding its shift helps to recognise methane origin and characteristics, and allows scientist to easily find measurement spots. (Delsontro et al, 2010)

The amount of CH_4 in aquatic ecosystems is an outcome of methane transfer between adjacent ecosystems (figure 1) - import and export (surface discharge, hyporheic exchange, groundwater discharge), caused by production and consumption of methane. An exchange between water and the atmosphere is called an *influx* (diffusion from atmosphere to water) and an *efflux* (diffusion from water to atmosphere). Methane can release from waters through four ways – ebullition, advection (via water plants), surface diffusion and exposition of deep water during mixing periods. *Diffusion* occurs mostly in the upper layer. It depends on the difference between methane concentration in the water and the atmosphere. (Stumm and Morgan, 1996)

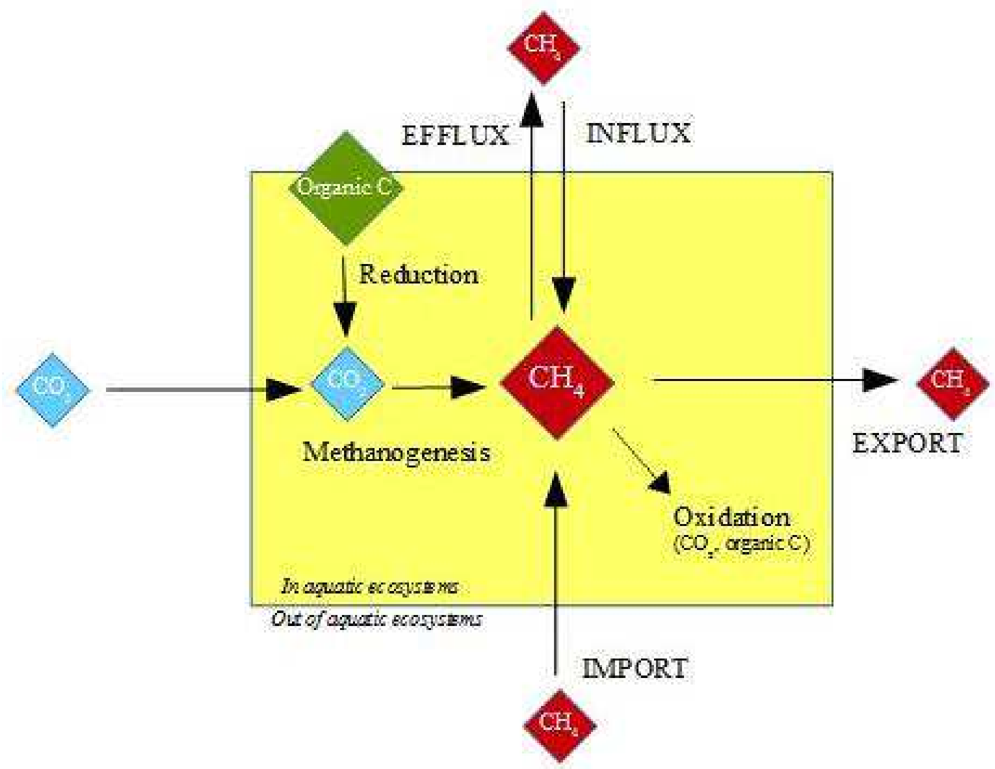

Figure 1 – Diagram showing methane transportation from aquatic ecosystems to land via import and export (discharge), influx and efflux (diffusion). The total amount of methane in the ecosystem is also controlled with a rate of methanogenesis (dependent on organic matter income) and methane oxidation. (Stanley et al, 2016)

Ebullition, a dominant way of methane transport, happens mostly in shallow waters. Bubbles ascend fast, getting over hydrostatic pressure, with a help of a minimum methane oxidation in the water column. (Fendiger et al, 1992) Bubbles usually have diameter about 2 – 8 mm. Due to low solubility of CH_4, methane in depth less than 50 m rather degas, than dissolve. According to the research made in 2010 in Lake Wohlen (Switzerland), about 30 % of methane bubbles dissolve in the water column, whilst almost 70 % achieve the atmosphere. (Delsontro et al 2010) Faster transport of bubbles into the atmosphere amplifies the amount of released methane, turbulent flow and shape of bubbles. Without these conditions, bubbles would split up and methane would dissolve prior to reaching the atmosphere. (Kvenvolden, 2007) On the other hand, we notice dissolution of methane during ascending in deep water with more than 50 metres depth (Ostrovsky et al, 2008) In these deep systems, bubbles rarely reach the atmosphere.

Diffusion occur mostly in the upper layer. It depends on the difference between methane concentration in the water and the atmosphere.

1.4 Transformation and chemical reactions

1.4.1. Methane in the water column

Free gas in the water column can dissolve, react or escape to the atmosphere. Besides, there is a free methane buoyant in the water column, floating through the sediment pores and through open water. (Archer, 2007).

While methane in water column dissolves, it is oxidized by methane-oxidizing archea. This methane consumption happens either in oxic (2) or anoxic (3) (Knittel et al, 2009) conditions. The oxidation of methane comes about in locations with higher concentration of methane (Valentine et al., 2001). In deep waters, it might be about 90 % of total released methane, which never reach the atmosphere. (Bastviken et al, 2002)

Oxic conditions: $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ (2)

Anoxic conditions (mostly oceans): $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$ (3)

1.4.2. Methane after reaching the atmosphere

While methane from the ocean reach the air, it oxidizes to CO_2. This process takes about decades. (Archer, 2007) Released methane reacts with hydroxide anion and creates methane radical with water vapour (4). Newly emerged CH_3 is a reactive radical compound which subsequently merge with water vapour to eventually produce CO_2. Nevertheless, if there is no OH^- in the atmosphere (owing to the absence of sunlight), methane and O_2 can jointly exist for thousands of years. (Archer, 2007)

$CH_4 + OH^{\square} \rightarrow CH_3 + H_2O$ (4)

Nevertheless, according to the Buffet and Archer, slow and small escape of methane oxidize to $CaCO_3$ inside the sediments, while fast great release of methane can spill into the ocean and enhance the amount of CO_2 in the atmosphere. (Buffet, Archer, 2004)

1.5 Methane hydrates

Because of hydrophobic properties of methane, which implies low solubility, methane tends to connect instead of dissolve in water. (Docherty et al. 2006) *Methane hydrate* is a cristalline structure of methane and water (Buffet, 2000), which occurs in deep ocean along coastal margins and frigid area of arctic permafrost (Kvenvolden, 1993).

Under the specific conditions of high pressure and low temperature, methane generated from the organic matter in sediments or escaping from the underwater volcanoes, is trapped in cristalline cage. (Kvenvolden, 1993). Hydrates stability insist hydrostatic pressure more than 5 bars and simultaneously frigid temperatures lower than 7°C. (Haq, 2009)

Gas hydrates occur in polar regions all over the world. It is a frozen crystalline structure, made of gas, especially methane, captured in frigid water. The form of a crystal differs from hexagonal form of ice (Kvenvolden, 1993). Gas hydrates crystallize in the izometric crystal system. (Sundquist, 1985)

1.5.1 Structure I

There are two structures of isometric (cubic) lattice. The first one, most common, is *structure I*. Hydrogen-bonded water molecules each capture a methane molecule. In addition, these frigid water molecules are big enough to carry methane, but also ethane, carbon dioxide or hydrogen sulfide (Kvenvolden, 1993). Each hydrate contains two dodecahedral and six tetradecahedral water cages in one unit cell. (Steven et al., 2006) This type of hydrate, which occurs in 90% of all methane clathrates, is found in deep marine sediments, made of microbially created methane. Because methane is isotopically light, ($\delta^{13}C < -60‰$) it is discovered that the origin of hydrates come from a microbial reduction of CO_2. Furthermore, fresh waters icebound in permafrost or continental shelves may connect with methane and create clathrates also. Besides, methane clathrate stability is substantially higher in fresh waters. (Kvenvolden, 1995)

1.5.2 Structure II

Talking about methane hydrate structures, there is another, less common type - *structure II.* Simply one percent of methane is created this way. This structure can hold methane and ethane, but on top of that, it contains some large cages which can carry longer-chained hydrocarbons, such as propane and isobutane. (Kvenvolden, 1993). Carbon is isotopically heavier ($\delta^{13}C$ is −29 to −57 ‰) and so the origin of carbon comes from the ocean depth, where the thermal deposition of organic matter from sediments forms methane. (Kvenvolden, 1995)

Chapter 2

Global occurrence and quantity of methane in aquatic ecosystems

2.1 Methane deposits in marine ecosystems

2.1.1 Global occurrence

Global occurrence of methane clathrates depends on special conditions - temperature less than 7°C and pressure higher than 5 bars. Due to need of organic matter to iniciate methanogenesis, methane is created only in spots rich on organic matter or volcanic activity, in the depths less than 1000 m. That is why methane deposit close to the continental slopes (figure 2) and never store in the abyss. (Buffet, Archer, 2004) We can find huge supplies way closer to the surface (below 250m depth) in high latitudes, in contrast, below 530 m depth in low latitudes. (Haq, 2009)

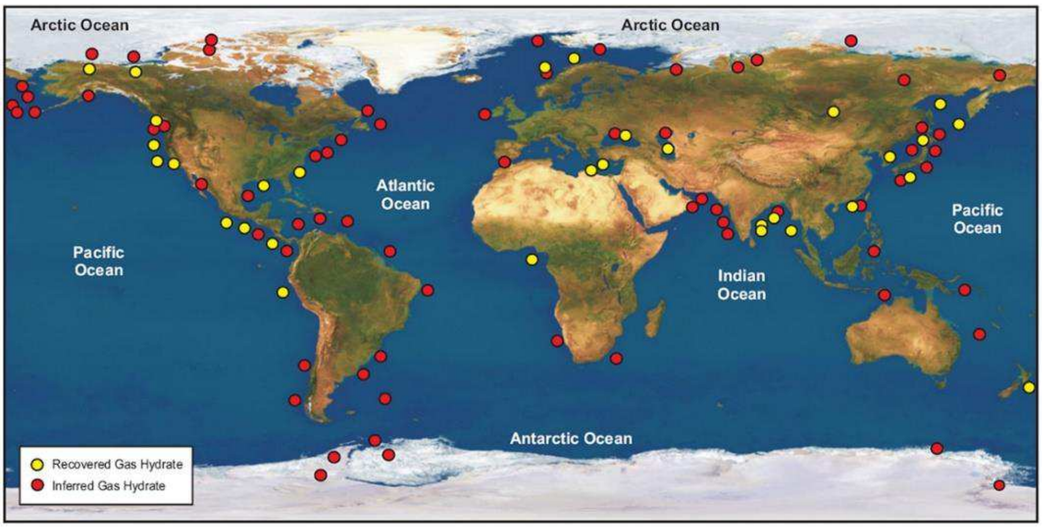

Figure 2 – Global methane occurrence, with data taken from Kvenvolden and Rogers, 2005. Yellow points indicate explored methane hydrate supplies, whilst red points show estimated hydrate deposits. (Krey, 2009)

But why do the methane deposits occur only near the continental slopes? Microbially generated methane deposits on places with intensified benthic flux. The presence of organic matter in deep waters is located in near-shore sediments (Buffet, Archer, 2004). Also shallow waters are close to the shorelines. (Buffet, Archer, 2004). Besides, *thermogenic methane*, was discovered only on two places on Earth - Gulf of Mexico and the Caspian Sea. (Kvenvolden, 1995). Furthermore, the huge methane hydrate supplies in the ocean depths, it also occurs in frozen permafrost and great lakes. (Krey, 2009)

2.1.2 Global inventory abundance

Mistakes made thanks to the imperfection in measuring make a huge scale in global methane clathrates inventory. According to Kvenvolden, the clathrate supplies are comparable to the fossil fuel carbon inventory, with the amount of methane estimated from 3000 – 15000 Gton C (Kvenvolden, 1993). By Valker Krey□s opinion, a certain number of 1000 Gton C may exceed into uncertain supplies between 1000 – 10 000 Gton C, which is equal to 2000 – 20000 trillion cubic meters of natural gas (Krey, 2009). Anyway, new measurements and estimates determine methane hydrates supplies as 1800 – 2300 Gt C ,and at the same time denote the previous rough estimates as overestimated. (Ruppel, 2017) Despite the fact, that the estimates differ and are not accurate, the assessments equal to the potentional fosil fuel carbon inventory. (MacDonald, 1990). That makes methane hydrates be a potential energy source, however, this makes it to also be a global danger if released suddenly and rapidly. (Mienert, 2009)

2.2 Occurrence and quantity of methane in freshwater ecosystems

2.2.1 Global occurrence

In a historical period of time, the amount of CH_4 in freshwater was rare. The fact, that fresh aquatic ecosystems are sufficiently aerated, cause methane be valuable (Zaiss et al, 1982). Nevertheless, since the atmospheric concentrations of methane raised in 1750s, there is a substantial increase of methane in freshwater ecosystems. (IPCC, 2013) These measurements show, that majority of streams, rivers and lakes are sources of CH_4 to the atmosphere (Stanley et al., 2016).

But what areas are globally favourable to methane production? There are no differences found out due to the size of water stream or river, however there is a significant contrast between biomes and land cover units. For example, we can observe high methane concentrations in taiga, temperate grasslands or tropical forests. In contrast, temperate coniferous forests emit only low concentrations. Nevertheless, the highest concentrations are recorded in wetlands and agricultural or urban areas, where the coexistence of dissolved organic matter, NH^{4+} ammonium and CH_4 is evident. (Zaiss et al. 1982).

2.2.2 Global methane volume

The previous scientific papers give *freshwater rivers and streams* small value in a global scale, according to many researchers, maximum one percent of global C escape. Unfortunately, these calculations are all underrated. Calculations do not pay attention to ebullition or gaseous fluxes, or do not include enough datas. And so, according to the estimates from Stanley et al in 2016, the total number of globally released methane from freshwater rivers and streams is 26.8 Tg CH_4 per year. In contrast to Bastviken estimates in 2013, with 1.5 CH_4 Tg per year, these numbers are almost 18 times higher and also more cautionary. Well, their reckoning is based on the calculations of median diffusive fluxes from their database, multiplied by the total global stream and rivers area from Raymond et al., 2013. (Stanley et al, 2016)

Eventually, rough results shows, how important streams and rivers are in case of CH_4 release into the atmosphere in global scale. Even it is hard to prove precisely, due to such a dissimilar methane release estimates, freshwater also play a significant role in world methane circle. Concerning the flow rate, high-current periods distinguish by low concentrations of methane, thanks to the heavy precipitation and snowmelt dilution. On the other hand, maximum methane concentrations are detected in flooded periods, while the wetlands, sediments and agricultural areas are connected to the stream or river. The concentrations might rise up to 600 times (Stanley et al, 2016)

Globally, *freshwater* lakes and reservoirs release a significant amount of methane emissions. The number differs amongst 100 – 148 Tg of methane per year (Bastviken et al, 2004) (Lima et al, 2008)

Chapter 3

Methane task in marine ecosystems and its impact on global change

3.1 Methane in the past

It took a several million years to create huge methane hydrate supplies (Archer, Buffet, 2005) In late *Cretaceous* (100-66 Ma years), methane clathrates could have existed, but only with a very slim layer. Because of the warmer ocean water temperatures, they would be deeper and out of the sedimentary column. *Paleocene* bottom waters (66-56 Ma years) had about 22°C. This unfavourable factor could not allow the methane to accumulate. And so, the best proportious conditions occured in *Eocene*, aproximatelly 40 Ma years. By that time, the ocean got cold bottom waters and there was an organic matter income by the continental slopes. (Haq, 2009)

Anyway, there is an assumption, that the methane clathrate colapse caused a huge temperature increase in the Paleocene-Eocene period (10 kyr). According to the studies on the sediment core, the results showed, that the carbon-isotopic shift took place in about few thousand years. This fact points on the methane release effect. (Archer, Buffet, 2005)

Glaciation, launched by the Milankovitch cycles, comes slowly and easily with the decrease of greenhouse gases. In contrast, deglaciation is a fast process, related with fast increase of carbon dioxide and methane, which last only for decades or centuries. After the sea level rises again, the remaining gas hydrates get stable and create new inventory if methane clathrates. (Raynaud et al., 2000)

Which means, that sudden methane release can be a natural terminator of the glaciation period. Alongside with the glaciation, the sea level drops and loosen great mass of methane. As a greenhouse gas, it gives a negative feedback to the glaciation. Moreover, the warming enhances another warming. The permafrost and other methane trapped in the ocean hydrates melt simultaneously with the increasing temperature. This is believed to happen in Younger Dryas (10000 years, extremely cold climate oscillation in last glacial maximum). (Haq, 2009)

3.2 Present methane release and related risks

Clathrates are stored in the sediment pores and create hydrate stability zone. Thickness of this zone depends on the pleasant conditions. Below, there is a zone of free gas, which is escaping with the controle of gas solubility (figure 3). (Haq, 2009) There is only 2 – 9 Tg of methane gas releasing to the atmosphere annually. Nevertheless, the risk of sudden release of immense methane hydrates supplies is eminent and actual. (Ciais, 2013)

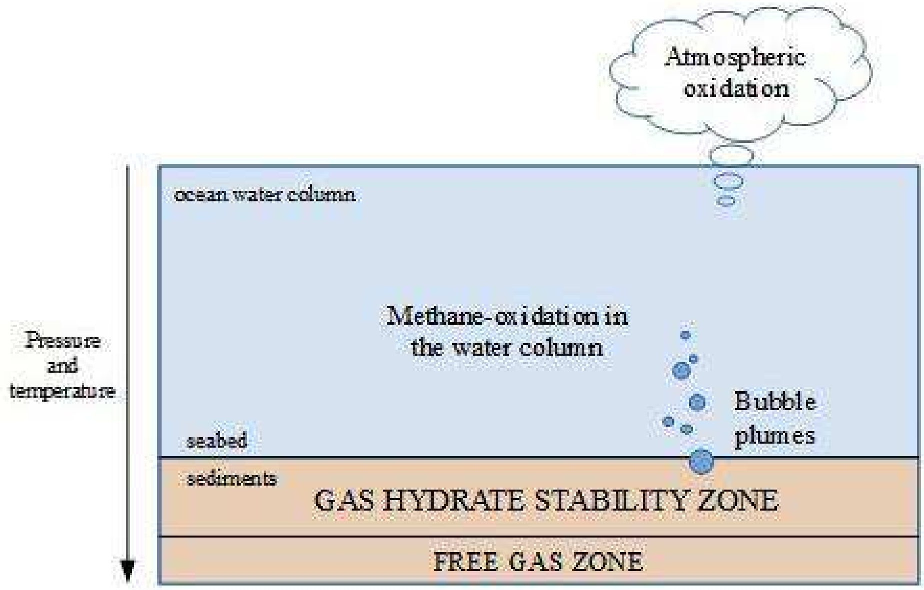

Figure 3 – Ocean methane hydrate supplies scheme. Gas hydrates create stability zone with free gas beneath. Bubbles of methane are slowly escaping to the water column, where part oxidize and the rest reach the atmosphere. (Kvenvolden, 1993)

3.2.1 Warming ocean

The anthropogenic rise of CO_2, caused mainly by burning the fossil fuel hydrocarbons or modification in land use, has grown into 400 ppm amount of CO_2 in the atmosphere nowadays. This number completely differs from the previous preindustrial value of 280 ppm. And it is the ocean, absorbing about 90 % of the energy. (Balmaseda et al., 2013). If not, the volume would be 520 ppm of CO_2. (Rogelj et al., 2011).

The ocean is a great reservoir of water, carbon and also heat, and is an important part of global climate regulation. Suitable properties of water, such as high density and specific heat allow oceans to store a great amount of warmth, approximately 4000 times more than the air. Moreover, the ocean has already absorbed nearly 93 % of anthropogenic global warming heat, from the beginning of year 1971. (Wijffels et al., 2016). According to the Intergovernmental Panel on Climate Change, this huge amount of energy input comes from the intensified anthropogenic greenhouse gases. (IPCC, 2013) The models show, that the ocean temperature warms about 0.106°C in 10 years. Anyway, in high latitudes, the ocean warming is much faster. The estimates are 0.4°C. (Koch et al., 2014) On the other hand, the distribution of ocean water warming vary. The depths warm slower. For example, in 1 km depths the temperature might rise of 0.5 – 1.5°C till the end of 21th century (Gleckler et al., 2016)

3.2.2 Sudden methane inventory breakdown

Major factor in the stability of methane is temperature and pressure. If either one of these is disrupted, the zone of hydrate stability may alter. It means, if the global temperature decreases, the sea level drops simultaneously with the hydrostatic pressure. Or, the temperature on the surface rises, it warms water in depth, which later thickness the stability zone (figure 4). (Archer, 2007) Both, pressure decrease or temperature increase might be the reason why methane hydrate splits up into a mixture of sediments, water and free gas. (Mienert, 2009)) Additionally, it might be an earthquake or another disturbance, which can break the stability zone of methane clathrates and loosen some bubbles from the free gas zone. This can cause fast release of methane to the atmosphere, together with submatirine slides or slumps. (Mousis, 2015)

Changes in pressure transform hydrate stability zone. For examaple, while the glacial period cause sea level fall, the methane hydrate stability zone thickness. Anyway, these changes cause only small differences in stability zone. For example, 100 m level drop bring about 10 m thickness of the stability zone. (Buffet and Archer, 2004)

Also *changes in temperature* destabilize zone of hydrates. While the temperature increase, the stability zone of clathrates lowers and the inventory reduce. For example, if the water warms about 3°C, the methane inventory falls to 15 %. (Buffet and Archer, 2004) The increase of temperatures is more likely an instrument, which will destabilize the methane hydrate stability zone, but on the other hand, warming inflicts the sea level rise and the hydrostatic pressure increase. (Haq, 2009)

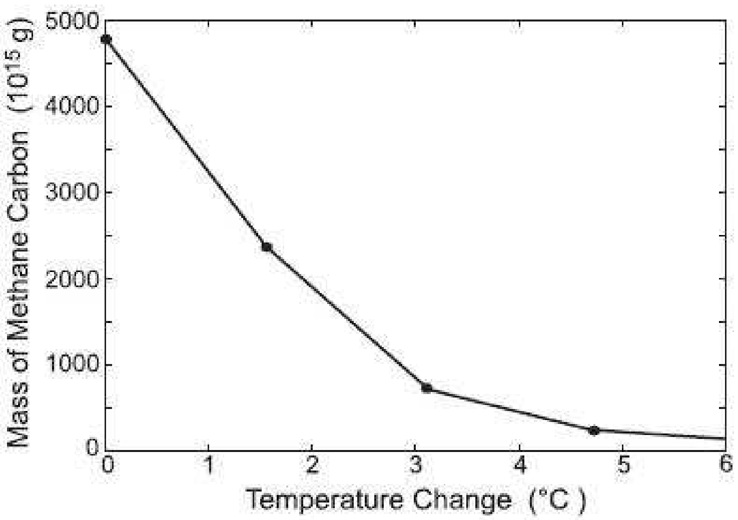

Figure 4 – Methane supplies transformation, dependent on a small seafloor water temperature change in 1 km water depth. (Buffet and Archer, 2004)

A sudden collapse of methane hidden in the oceans can cause huge climate changes. The fact, that methane hydrate stability relies on the specific temperature and pressure conditions, implies that only a small change can disrupt the stability. For example, if the sea level drops during the glacial periods, the deep ocean pressure changes and cause the methane release. Moreover, this can also inflict submarine slides (Mienert, 2009)). Therefore, the great amount of energy stored in clathrate inventory can cause positive and negative effects. Either, the energy can possibly be gained from the sediments as a source of energy (Docherty, 2006). Or, after changes in the clathrate stability, the negative feedback might amplify global warming and additionally cause undersea slumps and slides and slope instability (Kvenvolden, 1993).

3.2.3 Submarine slides and slumpes

Submarine slope movements can be initiated by earthquakes, volcanic activities or sediment sliding on steep slopes. Nevertheless, there are also submarine slides, not caused by any of these impulses. (Mienert, 2009)

Thanks to the facts, that these slides take place on slopes with very low angles, and during sea level maximum but also minimum, it is suggested that release of methane hydrates is the trigger of these movements. While methane clathrates dissociate, water and gas is loosen. Then, the instability create zone of weakness and cause the slope failure. (Mountjoy et al., 2014)

Vast quantities of methane clathrates form the continental margins and seafloor. If the stability is disrupted, the gravity helps to generate sediment slumping or sliding. These movements can achieve not only few kilometres, but also hundreds of kilometres square. (Mienert, 2009)

3.2.4 West Spicbergen measurements

According to the Westbrook s research in 2008, there were about 250 methane bubble plumes in the area of West Spitspbergen. Thanks to the warming of West Spitsbergen current, about 1°C in last thirty years, the bubbles occurred in maximum 400 metres depth, on the upper hydrate stability zone. (Westbrook, 2009)

The bubbles were detected with a fishfinder sonar. It was discovered, that the speed of bubble s movement differs from 0.08 – 0.25 m/s. And escapes out in several minute periods. (Westbrook, 2009)

If the measurements are proper, than the potential annual release in the West Spicbergen area (22 300 km^2) reaches up to 20 Tg of methane per year. Furthermore, increasing temperature in the future would amplify the methane escape into many tens of teragrams a day. (Westbrook, 2009) Still, only a small part would reach the atmosphere directly. (McGinnis et al., 2006). As visible on sonar record, only a few plumes reach the surface. The rest dissolves in the ocean, oxidizing into CO_2. Anyway, CO_2 acidify the surroundings and consequently lowers the amount of oxygen, essential for life. (Valentine et al., 2001) Subsequent research points out, that in three hundred years, 5.3 – 29 Gt per year might be released in the area of west Svalbard (Marín-Moreno et al., 2013).

3.3 Future perspective

Due to a Kretschmer study in 2016, the climatic model shows future methane hydrates changes. In next 100 years, the impact of warming will fall on shelf regions in Arctic, Australia, Indonesia and Nova Scotia. There, the shallow regions (in depths from 300 – 1500 m) will warm about 3°C, and so affect the methane hydrate stability zone. Globally, this will cause 0,6 % methane release in next century. Deep waters in oceans will be left unchanged over the next century. But in a longer time scale of thousands of years, also deep oceans will be affected. (Kretschmer et al, 2015) Nevertheless, continuous warming cause faster CO_2 and CH_4 decomposition and simultaneously release into the atmosphere. (McGinnis et al., 2006).

Chapter 4

Methane task in freshwater ecosystems and its impact on global change

Human activity, such as discharge of sewage, liquid waste and fine-grained sedimentary deposits daily wash out to fresh waters and cause water quality decline. This knowledge enhance scientists to search more and understand better, what is the role of CH_4 in rivers and lakes in a global methane balance (Zaiss et al. 1982). Another driving force to know more came from oceanographers, seeking for the source of methane in estuarine and pelagic waters. The last push was obviously the global climate change issue, which raised the CO_2 and simultaneously CH_4 data research to a power. (Stanley et al, 2016) In general, there were two significant studies in 2007 and 2011, which pointed out the relevance and thread of methane in the freshwater rivers and streams. First paper, published by Cole et al. in 2007, brought out how relevant the freshwaters are in the global C cycle. (Cole et al, 2007) And few years later, Bastviken and his group came out in 2011 with an unexpected results. According to their measurements, methane released from rivers, lakes and freshwater reservoirs equals, in case of global warming threat potential, to the continental C sink. (Bastviken et al, 2011)

4.1 Streams and rivers

Thanks to a microbial respiration, streams and rivers can transfer an incoming organic matter from the inland. Even though CO_2 is an end-product of respiration, CH_4 also occur in these ecosystems, nevertheless, methanogenesis demand anoxic conditions. Regardless this fact, CH_4 is an eminent component in streams and rivers, loosening about 26,8 Tg of methane per year. This equals to 15% - 40% of wetlands and lake discharge. (Stanley et al., 2016)

4.1.1 Driving mechanism

Actually, there are two groups of driving mechanisms (figure 5). First sites with an effect on CH_4 is temperature, organic matter used for respiration, nutrients supporting methanogens growing, and terminal electron acceptors leading redox status. These are so called *proximate drivers*, influencing methanogenesis in streams and waters directly. (Stanley et al., 2016)

Organic matter work as a fuel for respiration. It is an important component to determine if methanogenesis can even happen in stream or river. Organic matter also lead respiration process to the point where methanogenesis is the only possible result. Obviously, the amount of OM in fluvial ecosystem is essential for methane production. (Thauer, 1998) *Temperature* has an effect on CH_4, connected to other impulses. Most methane emissions are detected during summer. (Silvennoinen et al. 2008). The occurrence of more *terminal electron acceptors* (O_2, NO_2^-, and SO_4^{-2}) can repress CH_4 output. (Gauci et al 2004) It is considered that under the influence of *nutrients* - phosphor and nitrate - CH_4 might generate also under aerobic conditions. Eutrophication cause large exhaustion of oxygen and so create habitats, where the oxygen is depleted. This finally inflicts methane production. (Harrison et al. 2005)

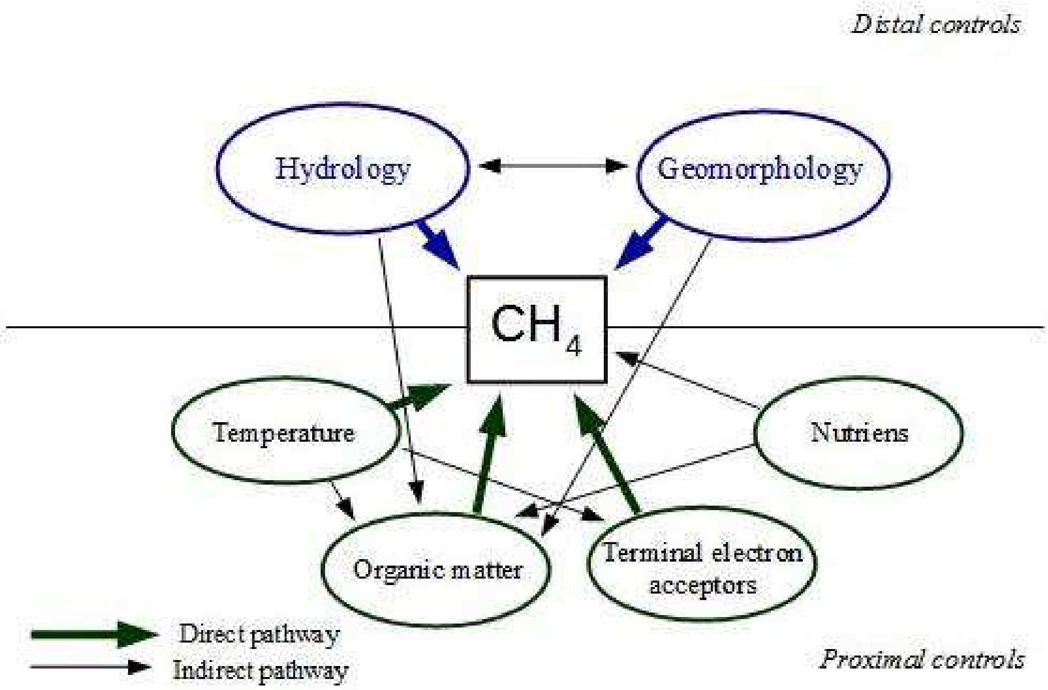

Figure 5 – Scheme of drivers, influencing methane production and shift. Thick arrows point out the major pathways of impact, in contrast to thin arrows, showing the indirect pathways of influence. (Stanley et al, 2016)

The other set is hydrology and geomorphology, also named *distal controls.* The water movements and flows distribute CH_4 within rivers and streams. It brings methane from shallow waters with saturated soils and peat sediments. Also water flowing through sediments, groundwater inputs and adjoining marshlands. (Stanley et al, 2016)

In case of *geomorphology*, there are two main facts, influencing and regulating methane distribution. First, the form of a channel define, how methane delivers in streams. Second, a sediments bedrock determine if methanogenesis is being boosted. Methanogenesis and also ebullition are most efficient and supported on fine organic matter rich sediments (Sanders et al

2007). For example in habitats transformed by beavers into dammed organic rich ecosystem. (Hertwich, 2013).

4.1.2 Measurements

Solubility of methane in water is relatively low and in contrast, gas changing quite high. This results that supersaturated methane degas from stream or river in a short time. And so, it is easy to detect the local point of CH_4 production or inputs. (Billett and Harvey, 2013)

First way, how to get the knowledge about methane importance is to study CH_4 and CO_2 ratios. Because methanogenesis is a part of total ecosystem respiratory, it is possible to determine methane production. High ratios $CH_4 : CO_2$ were mostly observed in freshwaters situated in human modified areas, such as rivers by the agricultural sites, places by the organic-rich industrial liquid waste. And on the other hand, low CH_4:CO_2 ratio was measured in waters located in natural boreal and temperate forests (Beaulieu, 2007).

4.1.3 Global fluvial methane emissions

Nevertheless, there is an important research from Stanley and his group, made in 2016. All approachable datas of methane in streams and rivers were gathered with all necessary information, published until September 2015. (Stanley et al., 2015)

Using these average data, Stanley and his group reckoned a total global methane emissions from streams and rivers. They counted the average methane emission volume as 4,23 mmol · m^{-2} per day. (Stanley et al, 2016) Consequently, they multiplied mean figure with a total overall stream and river area. This total area, computed as 3,001,009 km^2 was taken from Raymond's research (Raymond et al, 2013) *Final result was counted as 26.8 Tg of CH_4 global annual emissions*. (Stanley et al 2016) Eventually, this fact showed, that methane fluvial emissions are of the same magnitude such as wildfires, methane hydrates and permafrost (cca 21 Tg CH_4 per year), or equals to the terrestrial methane absorption (cca 28 Tg CH_4 per year). (Kirschke et al 2013) This new knowledge, distinct from others underrated studies highlighted the importance and magnitude of streams and rivers methane emissions. (Stanley et al 2016)

Stanley's research pointed out, that majority of fluvial ecosystems are sources of CH_4 to the atmosphere (Stanley et al., 2016). There were no differences found out due to the size of water stream or river, however there is a significant contrast between biomes and land cover units. For example, we can observe high methane concentrations in taiga, temperate grasslands or tropical forests. In contrast, temperate coniferous forests emit only low concentrations. Nevertheless, *the highest concentrations were recorded in wetlands and agricultural or urban areas*, where the coexistence of dissolved organic matter, NH_4^+ ammonium and CH_4 was evident. (Zaiss et al. 1982)

4.2 Methane in lakes and reservoirs

Globally, freshwater lakes take about 2-3% of land, but release a significant amount of methane emissions. The number differs amongst 8 – 48 Tg of methane per year, which is 6 – 16 % of global natural emissions and thus more than released methane from marine ecosystems (Bastviken et al, 2004) Contrarily, artificial water reservoirs loosen about 100 Tg CH_4 annually. (Lima et al, 2008)

Lakes possess their own methane storage, which generates every year during non-mixing periods. Anoxic conditions allow a significant methane production, which begin to release when stratified lakes start to mingle. It means in spring and autumn. Generated methane in anoxic sediments later release via ebullition or diffusion (figure 6). While methane escapes, majority oxidize in the water column (depending on water depth). The rest reach the atmosphere through diffusive export, caused by methane concentration variance in water and atmosphere. (Bastviken et al, 2002) In the other way around, ebullition leads methane bubbles directly to the atmosphere and so limit oxidation in water column. (Fendinger et al., 1992)

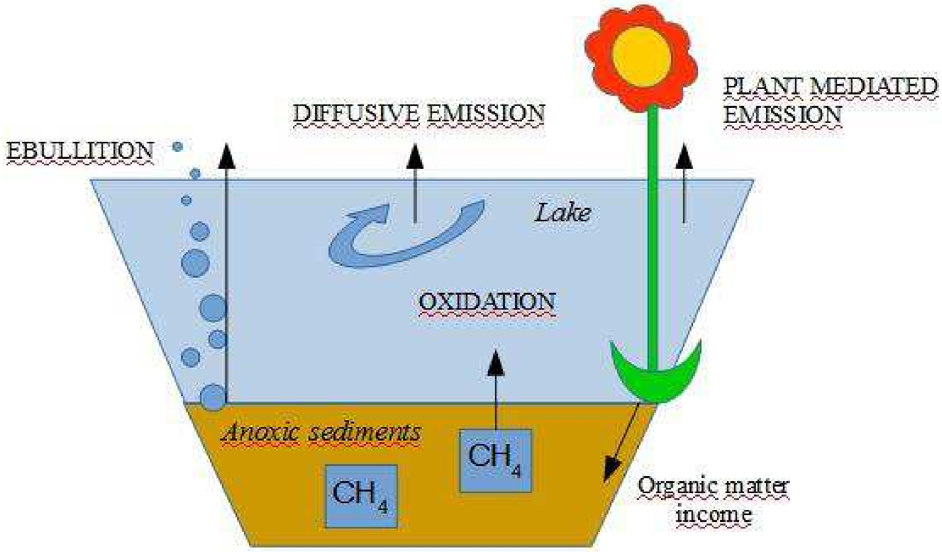

Figure 6 – Methane production and shift pathways in lakes and water reservoirs. (Bastviken, 2004)

4.2.1 Measurements in Lake Wohlen

Lake Wohlen is situated in Switzerland. With its average depths of 10 m is placed in temperate zone, with water temperatures extent from 5°C to 20°C. It gets relatively rich organic input, and due to permanent water mixing, it holds oxic conditions. (Delsontro et al, 2010)

Exact measurements in hydropower reservoir in 2010 showed several results, referring to a slight connection between CH_4 emissions and temperature. These measurements pointed out, that the amount of methane collected in the upstream sampling station were lowest, unlike the highest methane production occurred at flooded side of the dam. In addition, bubbles containing 100 % CH_4 rose to the surface. While ascending, about 30 % of methane dissolved in water, but almost 70 % reached the atmosphere. Besides, the connection between temperature and methane emissions was confirmed. As the temperature rise, the number of emissions increase. Methane emissions rise with increasing temperature exponentially (figure 7), which confirm low CH_4 emissions during winter season. These measurement show the importance and significance of temperate water reservoirs in case of methane emissions. (Delsontro et al, 2010)

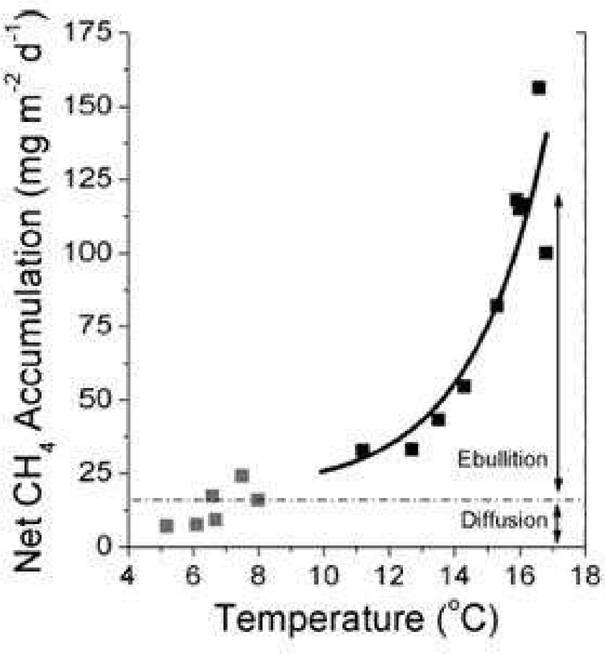

Figure 7 – Methane emissions dependency on temperature change. The amount of methane releasing from water reserviors rise with increasing temperature exponentially. (Bastviken, 2004)

4.3. Anthropogenic influence

Water ecosystems are changing rapidly due to diverse human activities. As generally known, streams and rivers are the most and fastest transformed and degraded ecosystems in the world. (Carpenter et al. 2011). Any changes in distal or proximate controls affect methane distribution. Let s now consider two important transformations in freshwater ecosystems.

4.3.1 Damming

First is *anthropogenic damming*. Same as beavers damming, these places with great amount of organic matter, dammed and separated lentic and lotic waters are suitable for proper methanogenesis. After that, how important in methane emissions must be a huge hydroelectric power stations. It is only a question of time, to ascertain what a big source of greenhouse gas damming is. (Hertwich, 2013) So, why is damming a problem? At first, reducing flow rate inflicts sediment accumulation. This creates layers with anoxic conditions and support methanogenesis. Second problem enhancing methane production is the dam enclosure, which can cause floods in adjacent lands and bring more organic matter. (Matthews et al, 2005). At the beginning of reservoir inundating, the terrestrial material decompose and cause very high values of CH_4 and CO_2 emissions. After a time, the emissions decrease. (Hertwich, 2013). Besides, especially small impoundments age and fill with sediments and transform into organic-rich wetland-like ecosystem, which starts to produce more methane again. (Powers et al 2013)

4.3.2 Land use

Following impact on methane production and distribution has an *agricultural land use*. More than one third of global land is being used for agricultural utilization (Foley et al 2011). Such a vast area is fertilized and transformed with anthropogenic forces, and brings enormous impacts (not only) to freshwater ecosystems. As a consequence, streams and rivers are supplemented with nutrients and sediments (Stanley et al, 2012) As mentioned before, nutrients and sediments both support methanogenesis. For example, as human use the land for agriculture, soils movements become more common and the fine sediments decompose in valleys and channels. These spots are subsequently susceptible to become anoxic and therefore turn to be suitable for methane production. (Sanders et al 2007)

But not only these two ways of anthropogenic changes influence CH_4 production. There is also another few interventions such as logging, urbanization, restoration and pollution. Furthermore, freshwater warming cause sedimentation and eutrophication, both enhancing methanogenesis. (Kaushal et al, 2010)

Chapter 5

Examples of measuring methods and methane as a potentional energy source

5.1 Measuring methods

For better knowledge and understanding of methane marine and freshwater emissoins, it is necessary to use, improve and develop measuring methods and instrument. Here is an exmaple of each marine and freshwater data collecotor, mostly use in case of methane emissions research. ...

5.1.1 Bottom Stimulating Reflector

The amount of methane hydrates is hardly estimated with the help of bottom simulating reflectors (BSR). BSR is an indirect evidence of the presence of gas hydrates. The seismic signals differ in the velocity – low velocity zone of free gas zone below the high velocity zone of the solid hydrate. The contrast causes the BSR detection phase-reversed, while the usual are in equivalent phase to the seafloor. (Mosher, 2008)

This is the instrument which allows scientists to mimic the seafloor, moreover spot the hydrate supplies. Unfortunately, the low abundance of hydrates in some places is not visible for the BSR. Which subsequently inflicts the lack of exact and relevant information about the methane hydrate supplies. (Carcione et al, 2000)

5.1.2 Gas trapper

Measuring gas bubbles escaping through the water column is essential for further and better understanding of methane releasing process. Gas trapper (figure 8) is an instrument that helps scinetist measure ebullition fluxes precisely. A collection chamber is connected to a pipe, terminated by a cone. While the cone is being submerged to collect bubbles, collection chamber measures pressure created by gas bubbles acumulation in the chamber. Whereas datas are collected continuously, the results are measured every 5 or 10 minutes. (Varadharajan et al, 2010) Bubble dissolution and emisson is subsequently estimated with help of dissolution model. (Delsontro et al, 2010)

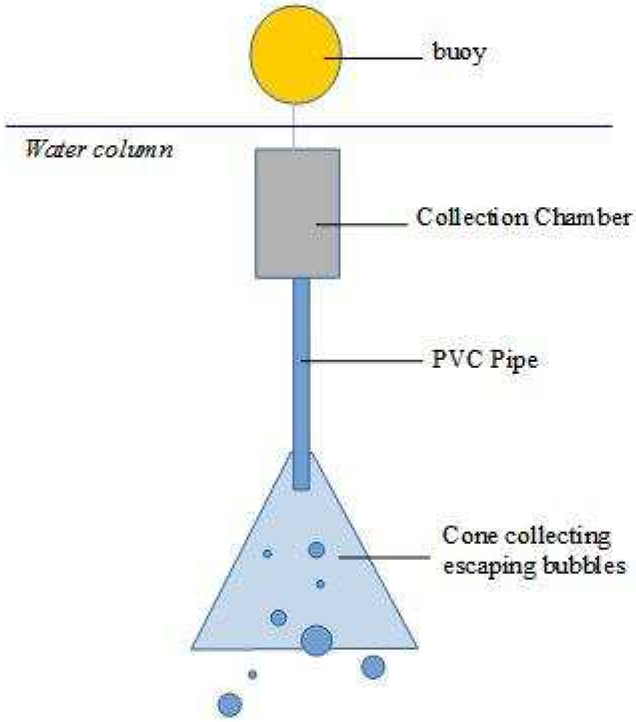

Figure 8 – Gas trapper scheme. Instrument measuring ebullition consists of cone, collectiong escaping bubbles. PVC pipe, collection chamber measiuring pressure. And eventually buoy, preventing gas trapper from immerse. (Varadharajan et al, 2010)

5.2 Methane as a potentional energy source

The global oil inventories are beiing exhausted. Due to that fact, there are efforts to find another energy source. And so it is believed, that methane hydrate, hidden in the ocean or permafrost, can replace the fossil fuel energy. Moreover, the global supplies are expected to be two times larger than present petroleum sources. Many countries are involved in gas hydrate developement. Japan, United States, Canada, China, Taiwan and India. (Lee and Holder, 2001)

There are three techniques, enabling to free the gas, buried in hydrate. Because methane is trapped in a cage of ice (thanks to van der Waals forces), it is neccessary to dissolve hydrates in situ. Methods discovered up to now are thermal stimulation, depressurization and inhibitor injection. (Chong et al., 2016)

Thermal stimulation - This methode uses heating to disturb the stability zone. The natural gas is heated by the hot water injection in situ. Released gas from the methane decomposition is subsequently catched and piped away to the surface. (Chong et al., 2016)

Depressurization - Lowering the pressure below the hydrate pressure equilibrium disturb the methane hydrates stability. Without changing the local temperature, this method is less demanding on the energy consumption, however much slower than the previous method. (Chong et al., 2016)

Inhibitor injection - This method, less studied, is supposed to change the equilibrium to the higher pressure and lower temperature. This way, the natural gas would be destabilized in the local and natural conditions. The inhibitor injections used are thermodynamic (methanol, ethylen glycol) and kinetic inhibitors. Methanol and ethylen glycol are being used to raise gas production, in contrast, kinetic inhibitors slow down gas decomposition. (Chong et al., 2016)

DISCUSSION

It is essential to believe that freshwater ecosystems, including rivers, streams and lakes are important in question of methane release. That all together, its emissions equals to weighty wetland s global emissions. Besides, anthropogenic activities, such as agriculture, damming, fertilizing and contamination attribute to freshwater eutrophication and sedimentation. Enhancing these ecosystems to create advantageous conditions for methanogenesis.

It is necessary to stop reshaping natural environment. Anthropogenic damming, land use and lodging create conditions supporting methanogenesis in water ecosystems. Also, the population must reduce greenhouse gas emissions, besides every other warming boost another warming and eventually can cause a huge and sudden marine methane breakdown.

Furthermore, future studies must obtain more data, especially in case of ebullition, which seems to be relevant to CH_4 emissions (DelSontro et al 2015). The lack of measurements, and the imperfection of measuring instruments is an important problem in methane release research. Insufficient quantity and quality of data cause inaccurate results and understanding. As obvious from this research, the estimates of methane hydrate supplies or methane emissions differ from research to research.

After all, there is a fundamental question of future methane mining. Is that a correct step to future? Are methane hydrates another step forward, switching places with oil and creating a new source of energy? While breaking into the inventories, people can disturb the stability of methane hydrate supplies. There might be a risk of sudden inventories breakdown.

CONCLUSION

Methane is a simple alkane, but powerful gas. Its global annual emission raised more than three times since the year 1750. As one of the most spreading greenhouse gas, it is necessary to control methane production and better understand the releasing process.

In this research, I concentrated on methane occurrence in aquatic ecosystems, such as oceans, rivers, streams and lakes. Actual global methane emissions are determined as 500 – 600 Tg CH_4 per year. But only 30 – 50 % comes from natural sources. (Ciais et al, 2013) Not mentioned in this research, natural wetlands are the biggest source of these emissions. Its volume range from 80 – 280 Tg CH_4 yr^{-1} (Bridgham et al, 2013).

Concerning freshwater ecosystems, lakes emit insignificant amount of methane, ranging from 20 – 70 Tg CH_4 yr^{-1} (Bastviken et al, 2011). Artificial water reservoirs loosen 100 Tg CH_4 to the atmosphere (Lima et al, 2008) Streams and rivers were surprisingly discovered also as important methane source, with its 26,8 Tg CH_4 yr^{-1}. Eventually, this fact showed, that methane fluvial emissions are of the same magnitude such as wildfires, methane hydrates and permafrost (approximately 21 Tg CH_4 per year), or equals to the terrestrial methane absorption (cca 28 Tg CH_4 per year). (Kirschke et al 2013) This new knowledge, distinct from others underrated studies, highlighted the importance and magnitude of streams and rivers methane emissions (Stanley et al 2016).

Eventually, global methane emissions from the ocean are slight compare to all freshwater emissions. Marine waters, covering over 70 % of Earth´s surface, emit into the atmosphere only 2 – 9 Tg CH_4 annually (approximately 3 % of total CH_4 emissions) (Ciais, 2013). This number is tiny compared to substantial freshwater emissions.

Despite the fact, that there are no significant methane emissions, oceans bring an immense peril to the question of global warming. As long as ocean store huge amount of global energy (carbon, heat), it creates its own carbon supplies and ocean water temperature is increasing. Methane generated or absorbed by marine waters accumulates in sediments as methane hydrates. As mentioned in this research, increasing temperatures of ocean water may result a huge collapse of these deposited hydrates supplies. Bringing large amount of released methane, further warming and creating submarine slides and slumps. Fortunately, there is no close prospect anticipating such a crisis in next hundred years.

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LIST OF FIGURES AND TABLES

Tab. 1 Preindustrial and recent concentrations of several substantial greenhouse 4

Fig. 1 Diagram showing methane transportation from aquatic ecosystems to land 5

Fig. 2 Global methane occurrence 8

Fig. 3 Ocean methane hydrate supplies scheme 12

Fig. 4 Methane supplies transformation, dependent on a seafloor water temperature 13

Fig. 5 Scheme of drivers, influencing methane production and shift 17

Fig. 6 Methane production and shift pathways in lakes and water reservoirs 19

Fig. 7 Methane emissions dependency on temperature change 20

Fig. 8 Gas trapper scheme 23