

## **Cycling of the greenhouse gas methane in sea ice and sea water**

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### Abstract:

Besides carbon dioxide methane is one of the most important greenhouse gases in the atmosphere which contribute to climate warming. Most of the methane which is released to the atmosphere is produced in biological processes under the strict absence of oxygen. In the last years methane was observed in unexpectedly high concentrations in the Arctic Ocean surface waters despite the presence of oxygen. This phenomenon is called “methane paradox” and was first discovered in 1977 by scientists investigating methane in the subtropical North-Atlantic Ocean (Scranton and Brewer, 1977). It is likely that the methane is produced in the oxygen rich water by microorganisms, but the exact processes remain yet to be understood. This article explains the concept for methane production in oxygen rich waters in the sea ice covered central Arctic and highlights the ongoing research we performed during the research expedition TRANSARC II with the German Research icebreaker Polarstern in summer 2015.

### Methane and Microbes

Methane is a strong greenhouse gas among others that contributes significantly to the ongoing warming of the earth’s atmosphere. The concentration of methane in the atmosphere increases constantly and thus further amplifies global warming (Stoecker et al., 2013). Methane is produced by anaerobic *methanogens* a group of very small organisms (1/100 mm) which can only be seen under a microscope. They can make methane only under strictly anaerobic conditions - that means that oxygen must not be present. This process happens in many places, for example in soils on land, in rice fields in agriculture or in animal intestines and also in ocean sediments. Other microscopic organisms – the so called *methanotrophs* – can use the methane as food source, and thus reduce the amount of methane that is released to the atmosphere.

### Methane in the central Arctic

In the central Arctic methane is found in the oxygen rich water at the sea surface in high concentrations (Damm et al 2010). The concentrations are higher than what would be expected from dissolution of atmospheric methane into the ocean alone. But most of the seawater itself has too much oxygen to allow for anaerobic methane production to close the gap between observed and expected methane concentrations. Another potential source would be methane which is produced in the ocean sediments in the central Arctic by methanogens. But on its way to the surface this methane would dissolve in the deep ocean water or be used up by the methanotrophs. Also, due to the far distance of the central Arctic Ocean from land, introduction of the methane from soil sources (e.g. permafrost) is not likely.

This means that methane has to be produced in the oxygen rich surface water in opposite to what was previously thought. And indeed, in the recent years, researchers learned that methane could be produced by microorganisms even if oxygen is present in the environment. These organisms use substances with methyl groups (Figure 1) as food source and release methane in a process that is called methylotrophic methanogenesis. (Karl et al, 2008, Damm et al., 2010)

### The role of sea ice

Sea ice is the defining feature of the central Arctic Ocean that affects many physical, biological and chemical processes in the high latitudes. Sea ice is frozen seawater that differs from lake ice. While freshwater ice is a very compact structure, sea ice is porous due to brine that is constantly released in the freezing process. When sea water freezes only the water crystals build up a solid structure and the remaining brine with high salt content remains in pockets and pore spaces inside the ice matrix. Figure 2 A shows an ice core with a multitude of vertical brine channels. Due to the brine and air inclusions the ice is opaque and not transparent like an ice cube in a drink. Figure 2 B shows a “thick section”, a slice in vertical direction of the ice core, which also shows the porous structure and vertical channels. These pockets and pores are the living space of a multitude of small organisms. They can be bacteria and also microalgae or even small animals (Thomas and Dieckmann, 2002). Microalgae are microscopically small organisms that do

photosynthesis similar to land plants or macro algae. High numbers of these organisms can be found in sea ice, often enough to give the ice a brownish appearance. Figure 3 shows exemplary ice floes with a high bioactivity. However, since many organisms live at the bottom of the ice, they are only visible when floes are broken and turned over such as by a passing ice breaker.

Later in the year, when the water and atmosphere warms up during spring and summer, the sea ice starts to melt. The solid structure dissolves, the channels and pores get larger and all the liquid and particles that were previously enclosed in the ice drain into the ocean. Different chemical compounds, which are produced by the microalgae, are released to the sea water during this process. Two of them are dimethylsulfid and dimethylsulfoniopropionate, the so-called DMS and DMSP. Both compounds contain two methyl groups (figure 1; the name includes this property dimethyl). These methyl groups are one candidate for the production of methane by methylotrophic methanogens to produce methane. This process was first observed in the recent years and the importance for the methane cycle of the Arctic is currently an active field of research.

### Work during TRANSARC II

The expedition with the German research Icebreaker R/V Polarstern in late summer 2015 (TRANSARC II) provided the opportunity for us to study the processes described above, which lead to accumulation of methane in the aerobic surface water of the central Arctic Ocean. On board we sampled sea water and sea ice to analyze the concentrations of methane, DMS and DMSP. Sampling for gas analysis is a challenging task to obtain the needed accuracy: Water samples have to be filled very carefully into the sample containers, since bubbles and turbulences would lead to an exchange of the dissolved gasses in the water with those in the air. The gas content in the ice can only be measured, when the ice is melted because the gasses are trapped inside the pockets in gas bubbles or dissolved in the brine. Thus the ice cores have to be cut into smaller blocks in a freezer laboratory at a temperature of  $-20^{\circ}\text{C}$  and placed into gas tight bags or containers. Only then the ice is melted, to prevent any unwanted exchange of gases with the surrounding air. Figure 4 shows some of the sample containers and instruments we used during the expedition to analyze our samples.

We also collected samples to investigate the microbial processes of methylotrophic methanogenesis and methane oxidation. Sea water was carefully filled into gas tight glass bottles

(shown in figure 4 D) and some of the bottles were fed with the substrate DMSP, to test if it would be used by the microbes to produce methane. The concentration of methane in the water was determined over a time period of ten days. First results showed an increase of methane in one experiment indicating a production of methane. In contrast in a second experiment the methane concentration decreased, indicating a larger impact of methanotrophs which consume methane in these experiments. These preliminary results show that the interactions between the different types of bacteria present in seawater are complex and need further investigation to distinguish between the different processes of methane production and consumption. Our next step regarding this question will be to analyze which types of bacteria were present in the different experiments. This will help us to learn which bacteria are important for the cycling of methane and how they influence the release of methane from the Arctic Ocean to the atmosphere.

#### Acknowledgements:

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Captions for figures:

Figure 1: Chemical structures of methane, dimethylsulfide (DMS) and dimethylsufoniopropionate (DMSP). Methyl groups in DMS and DMSP are indicated by the grey background.

Figure 2: Photographs of a sea ice core. (A) shows a section of an ice core of 9 cm diameter. Vertical brine channels are visible on the ice surface. (B) is a “thick section” of an ice core. A vertical slice of approximately 2 mm thickness is cut out from the ice core and shows channels and pores inside the solid ice matrix. The black bar indicates the vertical direction inside the ice core and a length of 5 cm. Photos courtesy of Stefan Hendricks.

Figure 3: Ice flow with high bioactivity. The brownish color is caused by a high density of microalgae inside the ice, which only become visible when the ice flow is turned over. Photo courtesy of Stefan Hendricks.

Figure 4: Laboratory equipment on board: (A) Ice samples in gas tight 20 mL vials for DMS and DMSP analysis. (B) Ice samples in gas tight bags for methane analysis. (C) Gas chromatographs in ships laboratory for analysis of methane, DMS and DMSP on board. (D) Gas tight bottles for incubation experiments.

Figure 1:

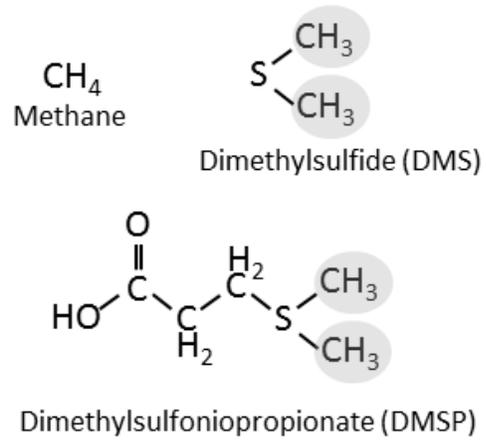


Figure 2:

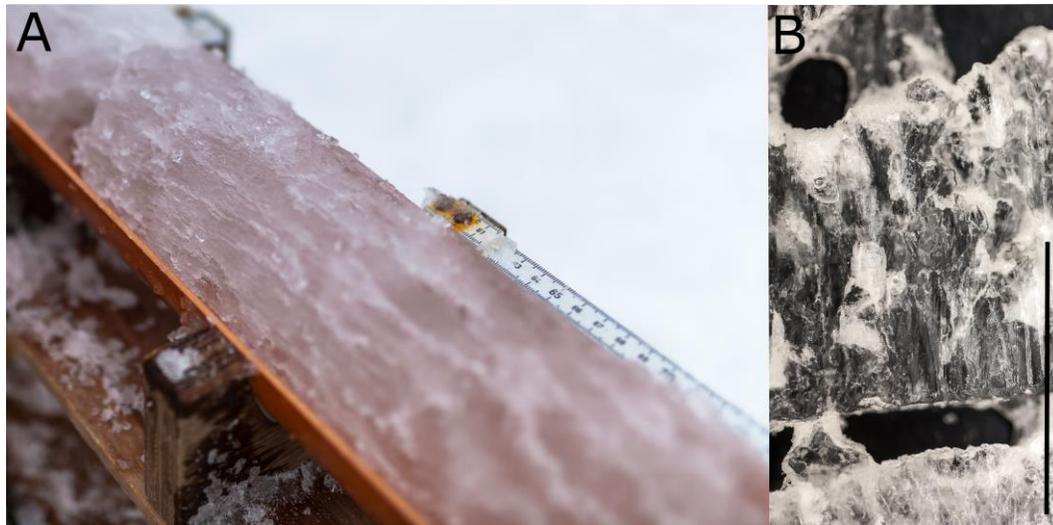


Figure 3:



Figure 4:

