

Distribution of methane in the water column of the Baltic Sea

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[1] The distribution of dissolved methane in the water column of the Baltic Sea was extensively investigated. A strong correlation between the vertical density stratification, the distribution of oxygen, hydrogen sulfide, and methane has been identified. A widespread release of methane from the seafloor is indicated by increasing methane concentrations with water depth. The deep basins in the central Baltic Sea show the strongest methane enrichments in stagnant anoxic water bodies (max. 1086 nM and 504 nM, respectively), with a pronounced decrease towards the pelagic redoxcline and slightly elevated surface water concentrations (saturation values of 206% and 120%, respectively). In general the more limnic basins in the northern part of the Baltic are characterized by lower water column methane concentrations and surface water saturation values close to the atmospheric equilibrium (between 106% and 116%). In contrast, the shallow Western Baltic Sea is characterized by high saturation values up to 746%. Citation: Schmale, O., J. Schneider von Deimling, W. Gülzow, G. Nausch, J. J. Waniek, and G. Rehder (2010), Distribution of methane in the water column of the Baltic Sea, Geophys. Res. Lett., 37, L12604, doi:10.1029/2010GL043115.

1. Introduction

- [2] Methane (CH₄) is an important atmospheric trace gas influencing directly or indirectly the global climate. Compared to carbon dioxide (CO₂) the global warming potential (GWP) of methane is about 25 to 40 [Shindell et al., 2009] times higher on a 100 yr timescale. The atmospheric mole fraction has more than doubled since the beginning of the industrial era, but has been almost stagnant over the first 5 years of the new millennium. The reason for the observed renewed global increase of atmospheric methane since 2006 is still under debate.
- [3] Though aquatic systems constitute the largest natural source of atmospheric methane, the role of the marine environment is considered to be small [Bange et al., 1994]. Shelf regions comprise only 7.5% of the ocean's surface area, but seem to be of great importance for oceanic methane emission due to high methane production rates in the sediment and a fast ventilation of the relatively shallow water column.
- [4] The Baltic Sea is a European semi-enclosed marginal sea with an average water depth of 52 m and is connected to the North Sea and the Atlantic Ocean via the Skagerrak and Kattegat (insertion in Figure 1a). Including Belt Sea and Kattegat, the Baltic Sea covers an area of about 4.2×10^5 km²

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with a volume of about 22×10^3 km³. On the basis of the hydrographic and bathymetric conditions, the Baltic Sea can be divided into a series of basins separated by submarine sills (see insertion in Figure 1a). The Baltic Sea represents one of the largest brackish waters of the Earth with strong lateral variations in the salt content from near marine in the western to near limnic conditions in the northern part, i.e., the Bothnian Sea and Bothnian Bay. Water exchange with the open ocean is controlled by episodic inflow events of saline water from the North Sea. In the southern and central Baltic Sea these events, together with a positive freshwater balance, drive an estuarine circulation and result in a less saline surface layer and more saline deep and bottom water masses separated by a permanent halocline [Reissmann et al., 2009] (Figure 1a). Especially in the central deep basins, this diapycnal feature leads to strong water column stratification, limited vertical mixing, the development of a prominent redoxcline (oxic to sub- or anoxic conditions), and the formation of biogeochemical zonations [Nausch et al., 2008]. The resulting periods of deep water stagnation in these basins can only be interrupted by strong inflow events of saline oxygenated water from the North Sea. Due to the strong geochemical (e.g., oxygen distribution in different basins) and hydrographical (salt) gradients, the large geographical extension of the Baltic Sea over different climatic zones, and the episodic renewal of bottom waters in some of the silled basins, the Baltic Sea represents an ideal environment to study the effects of various settings on the aquatic methane cycle. Moreover, a stronger than global effect of global warming and a strong anthropogenic influence on nutrient supply and organic matter production (i.e., eutrophication) are likely to affect the production and migration pathways of methane in the Baltic (http://www. balticgas.net/).

[5] Only a few studies are dealing with the distribution of methane in the water column of the Baltic Sea [Bange, 2006, and references therein]. These investigations have been conducted on a regional scale (most of them offshore Denmark and Germany) and show that the release of methane from the sediment into the water column is a widespread phenomenon. Especially in the center of the basins, geochemical pore water investigations and seismoacoustic studies of the seabed reveal large areas with high dissolved methane concentrations [Thießen et al., 2006] and free gas occurring [Laier and Jensen, 2007] within an organic-rich postglacial sediment layer known as the "Holocene mud" of the Littorina facies. Biological investigations in the Baltic Sea could show that the microbial oxidation of methane within the sediment and water column represents an effective process which restricts the direct transfer of methane into the surface waters and the atmosphere [Piker et al., 1998; Abril and Iversen, 2002]. Nevertheless,

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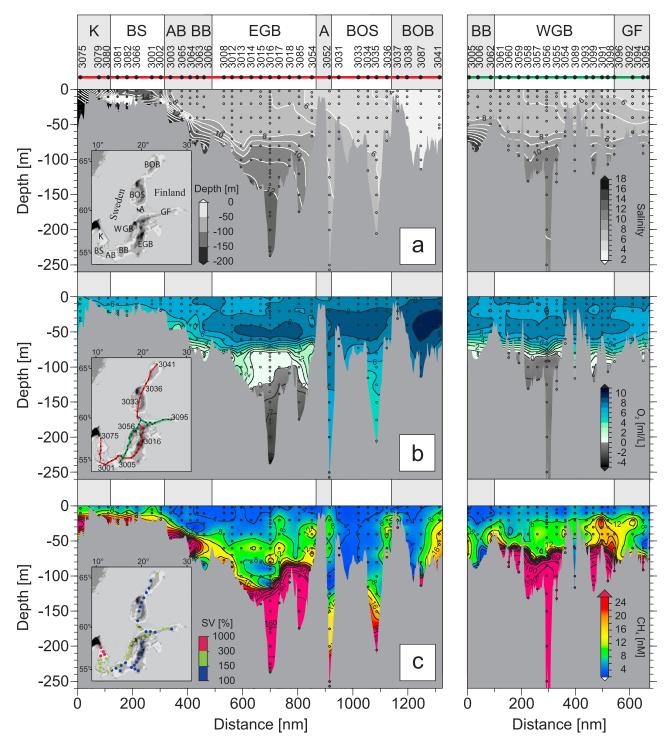


Figure 1. Contour plot of (a) salinity, (b) oxygen and (c) methane concentration along two transects across the Baltic Sea. Hydrogen sulfide was converted into negative oxygen equivalents. The insertion in Figure 1a shows the bathymetry of the Baltic Sea and the location of the main basins (K, Kattegat; BS, Belt Sea; AB, Arkona Basin; BB, Bornholm Basin; WGB, Western Gotland Basin; EGB, Eastern Gotland Basin; A, Åland Sea; BOS, Bothnian Sea; BOB, Bothnian Bay; GF, Gulf of Finland). The extension of the individual basins is also indicated at the top of the salinity section (Figure 1a). The course of the two transects (marked with red and green lines) is displayed in the insertion in Figure 1b together with selected station names to provide better orientation. The data obtained from the red (station 3075 to 3041) and green transect (station 3005 to 3095) are displayed on the left and right side in Figure 1, with the stations labeled at the top of Figure 1a. The insertion in Figure 1c shows the saturation values of surface water samples (depth interval 0–5 meter below sea surface).

Bange et al. [1994, 1998] could demonstrate that the surface waters of the Baltic Sea are considerably methane-oversaturated with respect to the atmospheric equilibrium, and that the concentrations show strong seasonal and regional variations. In the present study we show a comprehensive methane concentration dataset covering the entire Baltic Sea from the sea surface to the deepest basins.

2. Sampling and Methods

[6] Our data were gathered in summer 2008 on the German research vessel Maria S. Merian (MSM 08/3) between June 18th and July 18th. The dataset includes 63 water stations carried out with a rosette water sampler equipped with 24 10-liter Hydrobios-Freeflow bottles. For continuous CTD profiling a Seabird sbe911+ system was attached to the underwater unit. The oxygen distribution was measured according to Winkler's method, hydrogen sulfide in the deep waters was analysed colorimetrically with the methylene blue method [*Grasshoff et al.*, 1983]. Dissolved methane was extracted from the water sample by the use of a vacuum degassing method and its mole fraction was determined with a gas chromatograph equipped with a flame ionization detector [*Keir et al.*, 2009]. Surface water saturation is given following the equation

$$SV[\%] = C_w / C_{equi} * 100$$
 (1)

where SV is the saturation value, $C_{\rm w}$ is the measured concentration in seawater and $C_{\rm equi}$ the concentration in equilibrium with the atmosphere calculated using an atmospheric mole fraction of 1.89 (annual mean 2008, available from NOAA global sampling networks, sampling station: Baltic Sea, BAL, Poland, http://www.esrl.noaa.gov/) and the solubility coefficient given by *Wiesenburg et al.* [1979].

[7] The sampling strategy for the MSM 08/3 cruise was to gather a comprehensive dataset of the entire Baltic Sea (insertion in Figure 1b). Sampling stations were preferentially chosen offshore in a quasi-equidistant manner to horizontally and vertically trace various geochemical parameters from all basins of the Baltic Sea.

3. Results and Discussion

[8] The vertical water column stratification was very stable during the cruise with a pronounced halocline (Figure 1a) and a thermocline within the upper 30 m. The prevailing wind during the sampling campaign was on average low (mean 7.2 m/s +/- 3.6 m/s) leading to a mean Ekman depth of 25 m. Overall, the distribution of oxygen, hydrogen sulfide and methane is strongly controlled by the vertical density stratification (dominated by the salt distribution; Figure 1a). Below the prominent halocline oxygen is decreasing with depth, whereas hydrogen sulfide and methane show enhanced concentrations in the more saline deep and bottom water (Figures 1b and 1c). The conspicuous increase of methane with increasing water depth points to a widespread release of methane from the sediment into the water column [Thießen et al., 2006; Laier and Jensen, 2007]. In this context the main basins in the southern and central Baltic Sea seem to be of great importance. These stratified basins are characterized by high transport rates of organic matter (originated from primary production and

onshore erosion) into the deep water where it is partly mineralized and thus lowers the oxygen concentration in the water [Reissmann et al., 2009]. The sub- or anoxic conditions in the deep water support an efficient burial of organic matter and thus favor microbial methane production in the sediment. Apart from that, local input of methane by rivers and submarine groundwater discharge represent additional sources [Bange et al., 1994]. Subsurface production of methane in microenvironments, like fecal pellets and zooplankton guts or under phosphate limiting conditions [Karl et al., 2008], is also postulated to take place in the Baltic Sea [Bange et al., 1994] and may lead to an unknown source term of atmospheric methane.

[9] In the following, the results from the main basins of the Baltic Sea (insertion in Figure 1a) are presented and the spatial distribution of methane is discussed for the individual regions.

3.1. Kattegat

[10] Shallow gas and gas bubble releasing seep sites were reported to occur in this region [Dando et al., 1994; Laier and Jensen, 2007]. Rapid vertical gas-bubble transport through the water column can transport a large fraction of methane from the seafloor into the atmosphere [Schmale et al., 2010]. Though the Kattegat is stratified to a large extent due to the general circulation pattern, boundary and turbulent mixing can still transfer dissolved methane upwards as well. Our methane data in Figure 1c show that a plume of dissolved methane spreads unaffected from the pronounced water column stratification (Figure 1a) from the seafloor up to the sea surface. This results in the highest surface saturation of all regions investigated during this survey, with values between 197% (station 3080) and 746% (station 3075, insertion in Figure 1c). This is consistent with high saturation of methane in the Skagerrak and the eastern part of the North Sea at about 58°N, which have been suggested to originate from the westward transport of surface waters enriched in methane in the Kattegat and Skagerrak [Rehder et al., 1998].

3.2. Belt Sea

[11] Seismo-acoustic and geochemical investigations in Århus Bay [Jensen and Bennike, 2009], Eckernförde-[Wever et al., 2006] and Mecklenburg Bay [Laier and Jensen, 2007] demonstrate that free shallow gas is a frequent phenomenon. The release of methane gas bubbles and the groundwater discharge of methane-enriched fluids into the water column are known from some of these regions. Both, the depth of the free gas zone and the release of sedimentary methane into the water column were reported to depend on hydrostatic pressure [Wever et al., 2006] and bottom water temperature [Thießen et al., 2006] changes. Moreover, the input of fresh organic matter in surface sediments affects the microbial methane production rates [Bange et al., 1998]. An additional seasonal factor influencing the methane concentrations in these regions is given by varying input rates of methane-enriched river water [Bange et al., 1998]. Because of the shallow average water depth in this region the sedimentary methane source strength reacts highly sensitive to seasonal or long-term air temperature changes. In addition, the transport and current regime in this bottleneck between North Sea and Baltic is highly

sensitive to the meteorological conditions, leading to large variations of the water mass characteristics at individual sites. The sensitivity of this region to seasonal and meteorological fluctuations is reflected by the highest variability of surface water methane concentrations reported by *Bange et al.* [1994] for the southern Belt Sea (area weighted mean saturation values between 113% (winter) and 395% (summer) and maximum values in the southern Belt Sea of 15040% during the summertime). The strong source strength of the near-shore shallow regions is characterized by high methane concentrations up to 6.71 nM (station 3081) and high saturation values at all surface water samples (saturation values between 171% (station 3002) and 246% (station 3081; Figure 1c).

3.3. Arkona Sea and Bornholm Sea

[12] Large fractions of the areas of the Arkona- and Bornholm Basin show free shallow gas within an organicrich Holocene mud [Thießen et al., 2006]. In the central parts of the Arkona and Bornholm Basins, a distinct plume of elevated methane arises laterally from the seabed at stations 3003, 3065, 3064, and 3063. Here, a permanent halocline at 35-40 m water depth separates the surface water from the deep water [Reissmann et al., 2009]. Obviously, the pronounced halocline hampers diapycnal eddy-diffusive methane transport into the well ventilated upper mixed layer (Figures 1a and 1c). Given the sharp gradient and low concentration in the upper layer, gas bubble transport as reported for the Skagerrak and Kattegat is unlikely to play an important role here in regard to vertical methane transport. The Arkona Basin and Bornholm Basin, silled to both sides, but with more frequent bottom water renewal, stronger mixing processes, and less pronounced oxygen deficiency than the Gotland Basins, provide excellent study areas for some aspects of the marine methane cycle. Over the term of stagnation periods, the water gets less oxygenated due to organic matter degradation, fresher due to vertical mixing, and presumably successively more enriched in methane.

3.4. Gotland Sea and Gulf of Finland

[13] Examinations of the methane cycle are rare for the Eastern Gotland Basin [Bange et al., 1994; Piker et al., 1998], and - to our knowledge - completely lacking for the Western Gotland Basin. For the Eastern Gotland Basin Piker et al. [1998] could demonstrate that dissolved methane diffuses from the deep sedimentary strata into the water column. Hydrographical studies show that the surface water is separated from the deep stagnant water by a permanent halocline in about 70–90 m depth (Figure 1a) [Reissmann et al., 2009].

[14] The deep water body of both basins is characterized by the presence of hydrogen sulfide (Figure 1b) and the highest concentrations of methane found in our water column studies (1086 nM in the western basin (station 3056) and 504 nM in the eastern basin (station 3016; Figure 1c). These methane values are some hundred times elevated compared with the sea surface concentrations in the Gotland Sea (average Western Gotland Basin 5 nM and Eastern Gotland Basin 3 nM), which are near atmospheric equilibrium (average saturation values Western Gotland Basin 206% and Eastern Gotland Basin 120%, insertion in

Figure 1c). Decreasing methane concentrations within the suboxic part (conc. O₂ <2 ml/l) of the redoxcline (depth range between 80 and 120 m, e.g. station 3016) indicate microbial oxidation and thus transport limitation from the deep methane pool as already reported for similar oceanic settings like the Black Sea [Schmale et al., 2010]. An interesting finding of our water column study in the Gotland Sea is a distinct methane elevation in about 40–100 m water depth in the eastern basin (methane concentrations between 8 and 12 nM; Figure 1c). The most likely reason for the observed feature is a baroclinic inflow entering the basin from the southwest and carrying a low methane signature (see Reissmann et al. [2009] for a hydrographic overview). These inflows take place during the summer time and carrying a warm and saline hydrographic signature (indicated in our vertical CTD profiles in the central part of the basin by temperature anomalies in a depth range between 100 and 120 m water depth, data not shown). This specific process leads to an entrainment and ventilation of the affected water body [Reissmann et al., 2009]. In the Western Gotland Basin a comparable feature could not be detected in our hydrochemical and hydrographical dataset (Figure 1). This part of the Baltic Sea is characterized by a very stable chemical and physical stratification of the water column. However, elevated methane concentrations >8 nM are observed in the water column up to depth levels of 20–30 m in most of the Western Gotland Basin and the Gulf of Finland. This shallow methane elevation is also reflected in the surface methane concentrations in these regions (see saturation values in Figure 1c). The Gulf of Finland and the Western Gotland Basin appear elongated and narrow compared to the Eastern Gotland Basin. The larger importance of boundary wall shear might be the reason for a less confined salt gradient (except for the very deep part of the Western Gotland Basin), enabling better upward transport of deep methane-enriched waters. The proximity to the basin flanks allows a fast isopycnical transport of sedimentary methane into the basin interior, which is also likely to contribute to the elevated methane concentrations to these shallower depths levels. Especially high methane values in the Gulf of Finland and easternmost part of the Western Gotland Deep are again related to the stagnant (salt stratified; Figure 1a) deep water in the depressions (station 3094, 3096, 3098, 3099).

3.5. Aland Sea, Bothnian Sea, and Bothnian Bay

[15] The Åland Sea and the large northern basins (Bothnian Sea and Bothnian Bay) are separated from the Baltic Proper and against each other by shallow sills. Together with a pronounced positive freshwater balance, this results in fresher, not permanently stratified, and well ventilated water within these basins. Only very few methane-related studies exist [Hutri and Kotilainen, 2007] for the northern basins. These studies could identify seafloor structures like pockmarks and mud volcanoes that are often related to gas or groundwater seepage. However, the present activity of these structures and the corresponding methane flux remain unknown. Generally, our methane concentration dataset in the northeastern areas shows increasing concentrations towards the seafloor (e.g., station 3041, 3087, 3036 and 3035), again documenting an active emission of methane from the sediments into the water column (Figure 1c).

[16] In the Åland Sea an elevated shallow water methane signal was observed at station 3052, similar to the situation in the Gulf of Finland and Western Gotland Basin. Further north, the methane concentration significantly drops in the area of the Bothnian Sea. Except for locations very deep and close to the seafloor or land (stations 3035, 3036) the methane concentrations over large areas appear homogeneously low with surface water concentrations close to the atmospheric equilibrium (stations 3031, 3033, 3034, corresponding to saturation values between 106% (station 3033) and 116% (station 3034)). The noticeable methane pattern in the water column reflects the sediment characteristics with spatially limited mud accumulations apparently representing the main methane source in the other basins. The stations sampled in the Bothnian Sea and Bothnian bay during the cruise were located away from these mud areas in regions characterized by hard sediments [Al-Hamdani and Reker, 2007]. The low methane concentrations in the Bothnian Sea extend into the Bothnian Bay until the very end of the profile. Here, a pronounced methane signal throughout the water column was observed (station 3041).

4. Conclusions and Outlook

[17] The present methane dataset indicates that the sediments release methane into the water column over large areas of the Baltic Sea. Methane concentrations are highest in the central deep basins of the Gotland Sea and lowest in the Bothnian Sea and Bay, despite the higher freshwater fraction in the north. Highest concentrations are restricted to suboxic to anoxic regions. The surface water represents an atmospheric source of methane with strong oversaturations in the northwestern and southwestern regions and decreasing values towards the central and northeastern basins. In the central basins the path of methane from the deep water towards the sea surface seems to be controlled by oxidation at the redoxcline and restricted vertical transport and mixing due to density stratification.

[18] Our dataset presents a comprehensive overview and orientation. Nevertheless, to understand the sources and sinks of methane in the Baltic Sea, more detailed studies are needed. So far, no information of microbial mechanisms mediating the oxidation of methane at the redoxcline in the water column of the central Baltic is published. Seasonal studies could be used to evaluate the climatic influence on the methane source strength (i.e., impact on methane production rates in the sediment and water column, gas transport mechanisms between sediment and water column like gas bubble seepage, hydrographic changes like deep water ventilation). Future studies should also address the impact of eutrophication on methane production rates in the sediment and its influence on the water methane cycle (http://www. balticgas.net/). The strong salinity and redox gradients, the natural perturbation-relaxation experiments resulting from the alteration of deep water renewal and stagnant periods on different time-scales, and the straightforward understanding of the expected response to global change in the area make the Baltic Sea a unique environment for process studies addressing the methane cycle, which could be transferred to other high productivity and silled estuary settings worldwide.

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