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The distribution of methane and hydrogen sulfide in basin sediments of the central and southern Baltic Sea

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SCHMALJOHANN, ROLF; PIKER, LEVENT; IMHOFF, JOHANNES F. 1998: The distribution of methane and hydrogen sulfide in basin sediments of the central and southern Baltic Sea. (Die Verteilung von Methan und Schwefelwasserstoff in Becken-Sedimenten der zentralen und südlichen Ostsee). – Meyniana, **50**, 191–211, 13 Fig., 2 Tab., Kiel.

The distribution of methane and hydrogen sulfide concentrations in sediments of various basins of the Baltic Sea was investigated during 4 cruises in 1995 and 1996. Significant differences in the concentrations of both compounds were recorded between the basins and also between different areas within the Gotland Deep. High-methane sediments with distinctly increasing concentrations from the surface to deeper layers were distinguished from low-methane sediments without a clear gradient. Methane concentrations exhibited a fair correlation with the sediment accumulation rate, determined by measuring the total thickness of the post-Ancylus Holocene sequence on echosounding profiles in the Gotland Deep. Only weak correlations were observed with the content of organic matter in the surface layers of the sediments. Hydrogen sulfide concentrations in the sediments showed a positive correlation with methane concentrations, but, in contrast to methane concentrations, were strongly influenced by the transition from oxic to anoxic conditions in the water column between 1995 and 1996. Sediments in the deepest part of the Gotland Basin (>237 m water depth), covering an area of approximately 35 km^2, were characterized by especially high accumulation rates (>70 cm/ka) and high methane and hydrogen sulfide contents. Concentrations of these compounds decreased rapidly towards the slope of the basin.

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Zusammenfassung

Die Verteilung von Methan- und Schwefelwasserstoff-Konzentrationen in Sedimenten verschiedener Ostsee-Becken wurde während 4 Schiffsreisen in den Jahren 1995 und 1996 untersucht. Zwischen den Becken und auch zwischen verschiedenen Bereichen des Gotlandtiefs wurden signifikante Konzentrationsunterschiede beider Verbindungen festgestellt. Sedimente mit hohem Methangehalt und deutlich zunehmenden Methankonzentrationen von der Oberfläche zu tieferen Schichten konnten unterschieden werden von Sedimenten mit niedrigem

Methangehalt, die im untersuchten Bereich keinen deutlichen Gradienten aufwiesen. Die Methankonzentrationen wiesen eine gute Korrelation mit der Sediment-Akkumulationsrate auf, welche durch Messung der Mächtigkeit der holozänen Ablagerungen seit dem Ancylus-Littorina-Übergang auf Echolot-Profilen im Gotlandtief bestimmt wurden. Die Menge organischen Materials in oberflächennahen Sedimentproben zeigte hingegen nur eine schwach positive Korrelation mit der Methankonzentration. Die Schwefelwasserstoff-Konzentrationen in den Sedimenten waren positiv korreliert mit dem Methangehalt, wurden jedoch im Gegensatz zu letzterem stark durch den Übergang von oxischen zu anoxischen Bedingungen in der Wassersäule zwischen 1995 und 1996 beeinflußt. Die Sedimente im tiefsten Teil des Gotlandbeckens (>237 m Wassertiefe) mit einer Fläche von ca. 35 km² waren durch besonders hohe Akkumulationsraten (>70 cm/ka) sowie hohe Gehalte an Methan und Schwefelwasserstoff gekennzeichnet. Die Konzentrationen dieser Verbindungen gingen zum Hang des Beckens hin deutlich zurück.

Introduction

The Baltic Sea, one of the largest land-bounded brackish water bodies of the world, consists of a series of basins with water depths ranging from 40 to 460 m. Due to only narrow connections with the open ocean and the establishment of permanent or seasonal thermo-/haloclines, there is little water exchange in the deep water of these basins. After depletion of oxygen, hydrogen sulfide and methane are found in the deeper parts of the water column (NEHRING *et al.* 1994). Sediments with intense sulfate reduction and methanogenesis are the source of these compounds (BANSEMIR & RHEINHEIMER 1974; PIKER *et al.* 1997) which penetrate the sediment surface as soon as oxygen becomes depleted, and aerobic oxidation of methane and sulfide can no longer occur within the sediment.

Though the Baltic Sea is a well-studied area, data on the occurrence of methane and sulfide in the sediments are scarce. Most publications are confined to coastal habitats (BANSEMIR & RHEINHEIMER 1974; BUSSMANN 1994; HEYER *et al.* 1990; SCHMALJOHANN 1996; WHITICAR 1982). Earlier investigations on the sulfur and carbon biogeochemistry of Baltic Sea basin sediments were carried out during a Russian cruise in summer 1978, covering several stations in the Arkona Basin, Eastern Gotland Basin, Gdansk Bight and Gulf of Riga (LEIN *et al.* 1981; LEIN 1983). A study of the methane distribution in the Southern Baltic Sea revealed high concentrations in sediments in and around pockmarks (GEODEKYAN *et al.* 1991). During 1993 to 1996, PIKER *et al.* (1997) carried out a detailed study of the sediments within the central deep part of the Gotland Deep, which showed the development of methane and sulfide concentrations during a transition period from oxic to anoxic conditions in the deep water.

The aim of the present investigations was to estimate the occurrence and significance of methane and sulfide in surface sediments of different basins in the Baltic Sea, and to determine some of the factors that are responsible for their heterogeneous distribution. For this reason, correlations between the concentrations of these compounds, organic matter, water depth and sedimentation rates were calculated. The Gotland Deep was selected for a more detailed study to delineate the area of highly reduced sediments, from which an export of methane and sulfide during periods of anoxic deep water can be expected.

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Material and methods

Sampling sites

Sediment sampling sites for the cruises in June 1995 and June 1996 were chosen so that they largely corresponded to the central basin stations selected by the Baltic Monitoring Program (BMP) of the Helsinki Commission (Helcom). Their numbers, geographical positions and water depths are given in Table 1 and Figure 1.

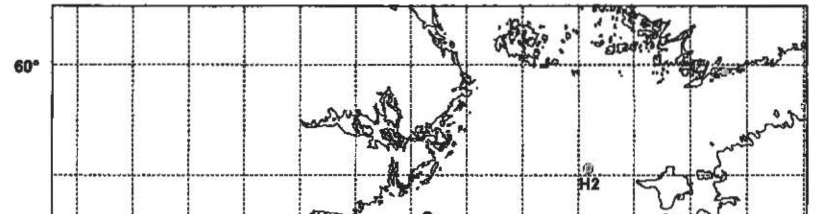

Fig. 1: Map of the Baltic Sea showing sampling stations.

Within the Gotland Deep, a grid of 25 stations covering the deepest part (>235 m depth) was sampled, partly on a cruise in May 1996 and partly in October 1996. An area with a diameter of 4 nautical miles, including the HELCOM station BY 15A in its northwestern margin and the station AL 93 as the centre, was covered. The stations were arranged on axes extending from N to S, E to W, NW to SE, and SW to NE through the central station AL 93, at distances of 0.5, 1.0 and 2.0 nautical miles from the central station in each direction.

The investigated area in the Gotland Deep was additionally studied by echosounding. Using an 18 kHz echosounder (ELAC, Kiel), 10 survey lines trending E–W at intervals of 0.5 nautical miles as well as survey lines along the 4 axes connecting the sampling sites were carried out in order to obtain information on water depth and on the thickness of depositions since the Ancylus-Littorina transition, which is characterized as a well-marked change from acoustically transparent to dense sediment layers (NIEMESTÖ & VOIPIO 1974).

Table 1: Stations in the Baltic Sea basins that were sampled during June 1995 and June 1996.

Station no.	Position	Water depth	Area
K7	55°00.0'N; 13°18.0'E	46 m	western Arkona Basin
K4	55°02.0'N; 14°05.0'E	49 m	eastern Arkona Basin
K2	55°15.0'N; 15°59.0'E	94 m	central Bornholm Basin
H26	55°39.0'N; 16°14.0'E	71 m	northern Bornholm Basin
L1	54°50.0'N; 19°20.0'E	110 m	Gdansk Bight
K1	55°33.3'N; 18°24.0'E	91 m	southern Gotland Sea
I1	57°07.0'N; 17°40.0'E	110 m	Karlsö Deep
H3	58°35.0'N; 18°14.0'E	462 m	Landsort Deep
AL93	57°18.5'N; 20°06.9'E	240 m	Gotland Deep
Farö	58°05.2'N; 19°50.0'E	180 m	Farö Deep
H2	59°02.0'N; 21°05.0'E	166 m	northern Gotland Sea

Sediment sampling

Sediment cores were obtained with small gravity corers, fitted with 74 mm i.d. acryl glass liners (constructed by J. RUMOHR, Kiel) or with 50 mm i.d. liners (constructed by T. MEYER, Kiel). These handy gears were well suited to obtain cores with a minimum disturbance of the sediment surface, especially in the very soft sediment of the Gotland Deep. For subsampling, the cores were pushed out from the bottom and single horizons were sampled with cut-off syringes.

Analytic procedures

Porewater of different sediment horizons was obtained by filling centrifuge tubes completely with sediment, sealing with gas tight viton stoppers to minimize loss of hydrogen sulfide by oxidation, and centrifuging for 10 min.at 3500 g and 4°C. An aliquot of the porewater was fixed in 5% zinc acetate (w/v) immediately after centrifuging and hydrogen sulfide was determined by the colorimetric method following CLINE (1969). Sulfate concentrations in the porewater were analysed by ion chromatography as described by PIKER *et al.* (1997).

Sediment methane concentrations were measured by gas chromatography using a headspace technique combined with salting out of the gas (after PIKER *et al.* 1997). For this method it was important to take subsamples of the sediment cores quickly and within a short time (<2 h) after taking the cores on board of the ship. However, as methane concentrations (with a few exceptions) were not at saturation levels under atmospheric pressure, no degassing of the cores by bubble formation was observed. The accuracy of gas chromatographic measurements was better than ±1%.

The water content was measured by weighing sediment samples before and after heating for 24 h at 100°C. The organic matter content in the upper 5 cm of sediment was determined as loss on ignition of dried samples at 500°C for 24 h.

Results

A. Comparison of different Baltic Sea basin sediments.

Methane, sulfide and organic matter contents have been determined in the main basins of the southern and central Baltic Sea during two cruises in June 1995 and June 1996. Methane concentrations in the investigated basins varied within the upper 22 cm of sediments in a range of 3 orders of magnitude. Lowest concentrations in the range of several µmol dm^{-3} sediment were found in the western part of the area (Arkona and Bornholm Basin) and in the Farö-Deep, while the deep sediments of the central Baltic Sea (Gotland Basin and Gdansk Bight) were characterized by high concentrations (>50–2874 µmol dm^{-3}, Fig. 2).

At most of the stations the methane content was higher in 1996 than the year before. Two different patterns of vertical methane distributions were recognized in the sediments. The high-methane type (stations L1, K1, AL 93, I1, H2, H3) was clearly dominated by methane diffusion from deeper sediment layers, and showed distinct gradients from the surface to at least 22 cm depth (Fig. 3a). The low-methane type (stations K7, K4, K2, H26, Farö-Deep) generally did not show a distinct gradient at concentrations below

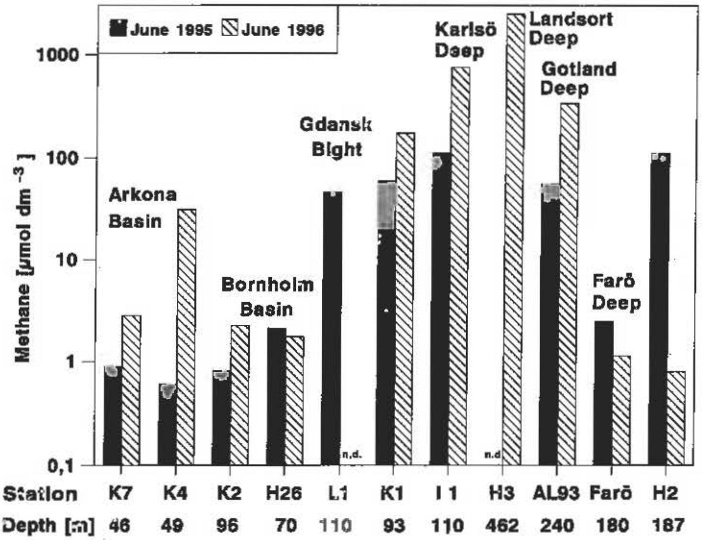

Fig. 2: Maximum methane concentrations in the upper 22 cm of Baltic Sea basin sediments, June 1995 and June 1996

3 µmol dm^{-3} (Fig. 3b). Only in of some of these low-methane sediments (stations K4, H26) increased methane concentrations in the upper 10 cm layer were measured in 1996, indicating active methanogenesis in these horizons that resulted in a reverse gradient with concentrations declining with depth (Fig. 3b). This phenomenon was also observed in the top 2 cm of high-methane sediments of the Gotland Deep during oxygen deficient conditions in the near-sediment water column (PIKER *et al.* 1997).

Hydrogen sulfide concentrations also varied widely between the investigated sediments. Particularly high concentrations were found in the deep basins of the central Baltic Sea and the Gdansk Bight (stations K1, L1, I1, AL 93, H3) and also in the western part of the Arkona Basin (station K4), whereas the sediments of the eastern Arkona Basin and the Bornholm Basin (stations K2, H26) were characterized by low sulfide concentrations. Maximum concentrations from 12.5 µmol l^{-1} (Bornholm Basin) to 8.2 µmol l^{-1} (Gotland Deep) were measured within the uppermost 22 cm (Fig. 4). In most cases (with the exception of the stations in the Bornholm Basin, K2 and H26, and the northern Gotland Basin, H2) a significant increase of sulfide concentrations from 1995 to 1996 was observed, which coincided with the depletion of oxygen in the deep water of the Central Baltic Sea during this period (Piker *et al.* 1997).

The vertical distribution of hydrogen sulfide within these sediments followed at least 3 different patterns: i) At stations K7, K1, H3 and I1, a gradual increase from low concentrations in the 0–2 cm horizon to 700–800 µmol l^{-1}

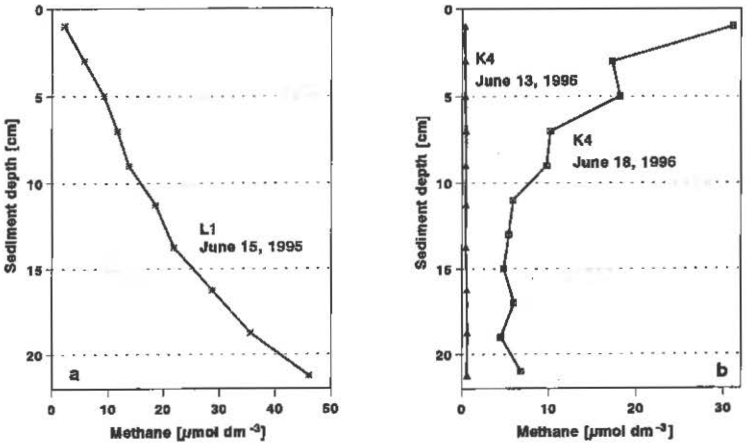

Fig. 3: Vertical distribution of methane in 2 typical Baltic Sea basin sediments in June 1995 and June 1996: a) L1, Gdańsk Bight, b) K4, eastern Arkona basin.

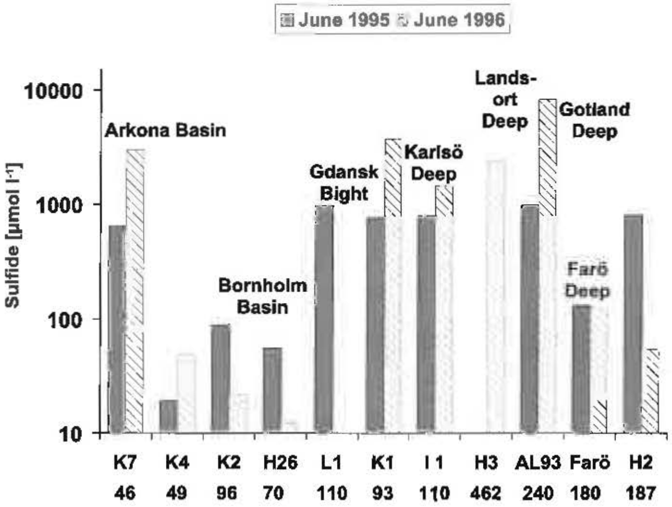

Fig. 4: Maximum sulfide concentrations in the upper 22 cm of Baltic Sea basin sediments, June 1995 and June 1996.

in 20–22 cm depth occurred (Fig. 5a). ii) At stations L1, AL 93 and H2, considerable amounts of sulfide were present in the surface layer, concentrations further increased steeply to a maximum between 3 to 7 cm and stayed at a high level below that depth (Fig. 5b). iii) In a third type, represented by stations K4, K2 and H26, in 1995 very low hydrogen sulfide concentrations at the surface increased slowly to a small maximum at 7 to 11 cm depth and decreased to non-detectable limits below. In 1996 these sedi-

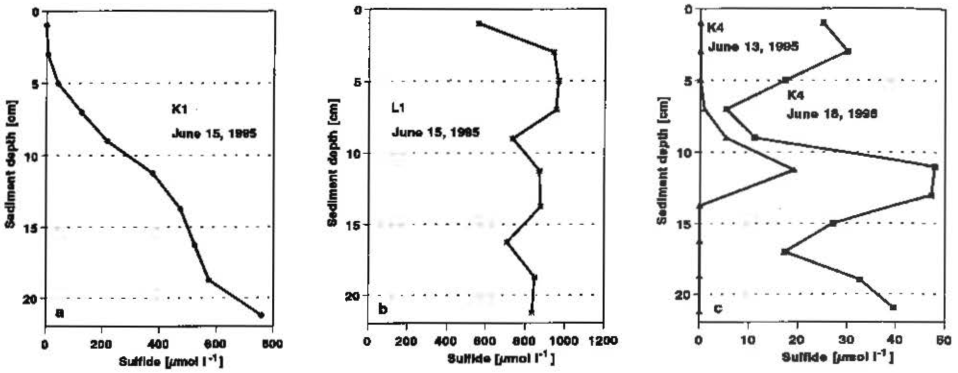

Fig. 5: Vertical distribution of sulfide in 3 typical Baltic Sea basin sediments: a) K1, southern Gotland Sea, b) L1, Gdansk Bight, c) K4, eastern Arkona Basin in June 1995 and 1996.

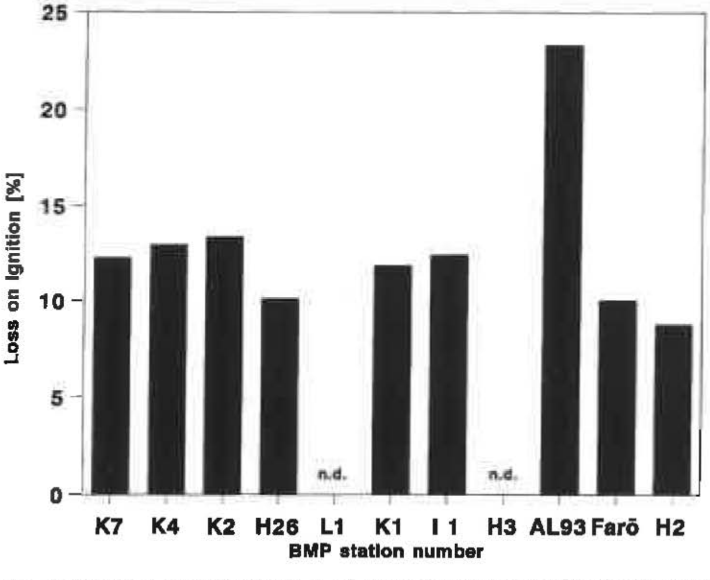

Fig. 6: Organic matter (loss on ignition) in % of dry weight in Baltic Sea basin sediments, June 1996.

ments showed increased concentrations within the top 4 cm, indicating sulfide production close to the sediment surface (Fig. 5c).

The content of organic matter in the investigated Baltic Sea basin sediments (0–4 cm depth) typically was in the range between 9 and 13% of dry weight (Fig. 6). The sediment in the Gotland Deep (AL 93) was an exception, being approximately twice as rich in organic matter as the other basin sediments. More detailed data on this parameter in the Gotland Deep are presented in section B.

B. Gotland Deep sediments

During two cruises in May and October 1996 a survey of methane and sulfide concentrations as well as determinations of the organic matter content in sediments of the central part of the Gotland Deep were carried out. Areas with surprisingly large differences in the characteristics of sediments were found even in the central deepest part of this basin. Methane concentrations for a number of stations in the Gotland Deep are given in Table 2. As in other Baltic Sea basins, low-methane sediments with concentrations in the range of a few µmol dm^{-3} and without a pronounced gradient could be distinguished from high-methane sediments with continuously increasing concentrations (up to 1421 µmol dm^{-3} in 40–45 cm depth). The spatial distribution of methane concentrations in the Gotland Deep, based on pooled data of the 40–45 cm horizons in May and October 1996, is shown in Figure 7a. Data of this sediment layer were selected because they most reliably reflected the diffusion of methane from the deeper layers with active methanogenesis. Methane production in the top 40 cm in this habitat constitutes only a minor proportion of the amount of methane diffusing upward from the main zone of methanogenesis (Piker *et al.* 1997).

Low methane concentrations were found at the shallower stations at the southern, western and northwestern margins of the Gotland Deep and even in parts of the center, while high methane concentrations dominated in the deepest parts of the basin. The average methane concentrations in the different sediment layers of the Gotland Deep did not significantly increase from May to October 1996, and during both periods values were higher in the deeper layers and lower near the sediment surface (Fig. 8).

The spatial distribution of sulfide concentrations in the Gotland Deep in May and October 1996 is shown in Table 2 and Figure 7b. Due to a shift from oxic to anoxic conditions in the bottom water during this time period, sulfide concentrations within the sediments were much higher in October. Although the values of the two cruises were not at a comparable level, the selection of stations allowed a good comparison of the relative distribution of this parameter. The average sulfide concentrations of all stations increased from the sediment surface to deeper layers from 0.8 mM (5–10 cm in sediment) over 2.4 mM (20–25 cm) to 3.4 mM (40–45 cm) in May 1996 (Fig. 8). In October 1996, average sulfide concentrations in the 5–10 cm horizon were more than 10 times higher (8.8 mM) and decreased slightly towards deeper layers (7.1 and 7.4 mM in 15–20 cm and 40–45 cm depth). Sediments poor in sulfide were found at the slightly shallower stations which were situated 2 nautical miles or more south, west or northwest of the central station AL 93, while sulfide-rich sediments occurred in the central and deepest parts of the Gotland Deep (Fig. 7b).

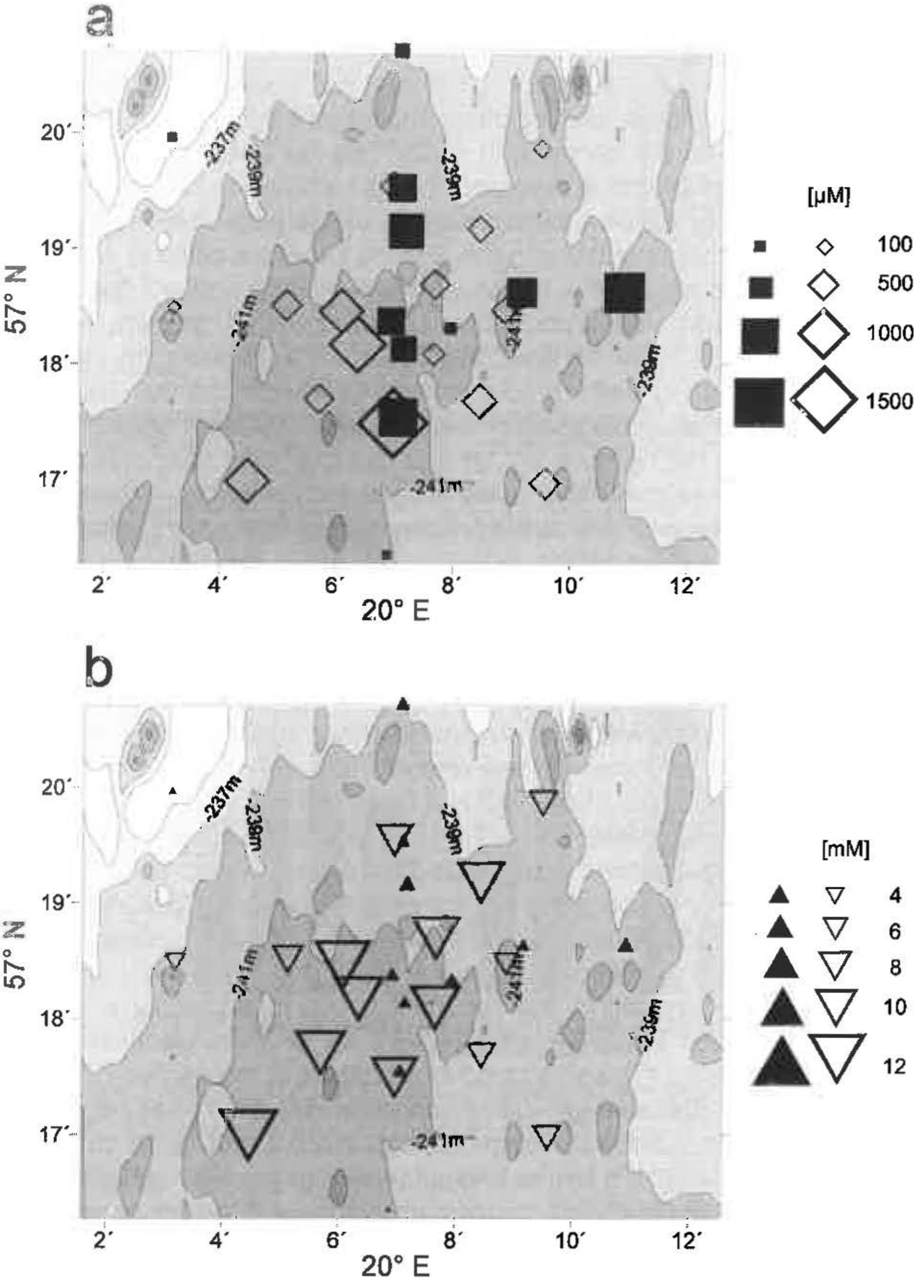

Fig. 7: Regional distribution of methane (a) and sulfide (b) concentrations in the Gotland Deep, May 1996 (closed symbols) and October 1996 (open symbols). Methane concentrations refer to the 40–45 cm horizon and sulfide concentrations are averages of 3 horizons: 5–10 cm, 15–20/20–25 cm, 40–45 cm. Bathymetric contours are shown.

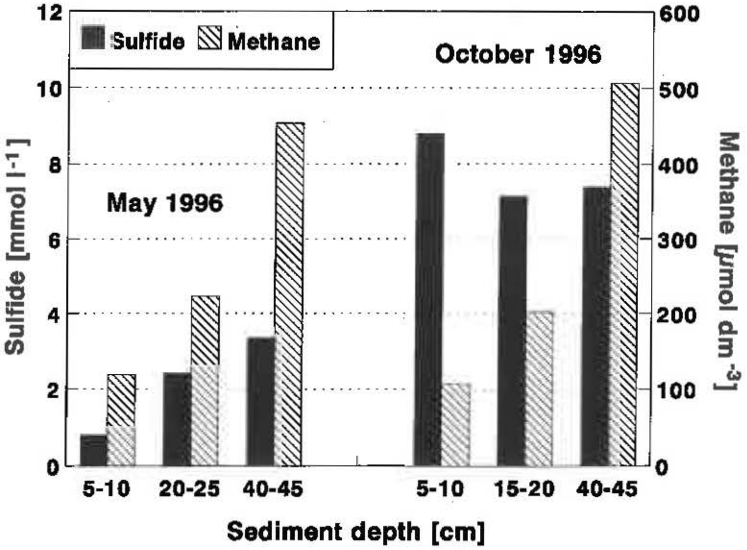

Fig. 8: Comparison of average methane and sulfide concentrations in single sediment horizons (Gotland Deep, all stations) in May 1996 and October 1996.

The areas with high methane and sulfide concentrations in the sediment were roughly identical for both compounds, extending over approximately 35 km^2 in water depths >237 m. Low concentrations of methane and sulfide were also present in sediments of additional stations at the eastern and southern slope of the Gotland Deep in 140 m, 200 m, and 220 m depth (data not shown).

The organic matter content, determined as loss on ignition, varied between 20.3 and 28.9% of sediment dry weight in the top 5 cm of the investigated sediments in the Gotland Deep (Tab. 2). This is approximately twice as high as in other Baltic Sea basin sediments (Fig. 6). The station BY 15A at the northwestern margin of the Gotland Deep contains between 18 and 22% of organic matter, as is known from cruises in the years 1994 and 1995 (data not shown). Considering a mean carbonate proportion of dry weight of 5% in surface sediments of the Gotland Deep (U. STEINER, Univ. Hamburg, August 1996, pers. comm.) and a carbon proportion of organic matter of 50%, carbon contents of 6.5 to 12.0% of sediment dry weight were estimated for the investigated area of the Gotland Deep. The thickness of the sediment layer which represents sedimentation since the transition between the Ancylus and the Littorina stages of the Baltic Sea (7000 years before today), based on echosounding data, varied between 4.75 and 6.1 m in this area, with one exception (3.6 m) at the western margin of the basin (Tab. 2). An echogram of a profile from the westernmost station W 2.0

Table 2: Geochemical data at Gotland Deep profiles. Station names show direction and distance from the central station AL 93 (e.g. N 0.5 means 0.5 sea miles north of AL 93). Mean values of H_2S-concentrations were from 3 sediment horizons at 5–10 cm, 15–20/ /20–25 cm, 40–45 cm. Loss on ignition was determined at 0–5 cm depth.

Station	Water depth (m)	Post-Ancylus deposits (m)	H_2S (mM) mean value 3 horizons		CH_4 (μmol dm^{-3}) 40–45 cm horizon		Loss on ignition (%)
			May 96	Oct.96	May 96	Oct. 96	Oct. 96
AL 93	240.5	5.4	2.47		614	320	28.9
N 0.5	240.2	5.7	3.05		883		
N 1.0	239.8	5.4	2.29	7.00	670	381	23.9
N 2.0	238.0	4.6	2.43		183		
NE 0.5	240.1	5.0		9.30		423	25.7
NE 1.0	238.7	4.6		9.15		318	22.3
NE 2.0	237.5	5.0		5.39		134	25.1
E 0.5	239.8	4.6	3.06		85		
E 1.0	239.0	5.0	2.08	4.53	714	349	24.7
E 2.0	238.1	6.1	2.93		1063		
SE 0.5	240.0	5.3		9.82		240	20.3
SE 1.0	240.0	6.0		5.48		539	23.9
SE 2.0	239.2	5.3		5.24		457	21.9
S 0.5	240.7	5.4	2.04		578		
S 1.0	241.0	6.1	2.61	9.02	1007	1421	25.7
S 2.0	240.2	5.4	0.05		1		
SW 0.5	241.0	6.1		9.81		1092	24.1
SW 1.0	240.7	5.4		9.86		406	27.3
SW 2.0	240.1	5.4		11.44		790	26.4
W 0.5	240.6	5.7		11.03		790	24.8
W 1.0	240.2	5.0		5.96		441	25.7
W 2.0	238.5	3.6		3.56		2	22.4
BY 15A	236.0	4.7		0.60	2		

through the central station AL 93 to the easternmost station E 2.0 revealed the varying thickness of this sediment layer characterized by its dark color in contrast to the acoustically transparent layers below (Fig. 9). Generally the thickness of this layer decreased from the center of the basin to the slopes, but there was no strong correlation with the water depth.

Two representative stations have been compared in detail. The vertical distribution of methane, sulfide, water content, and organic matter in 1 m sediment cores of the central station AL 93 (240 m water depth) and at station BY 15A (236 m deep) approx. 2 nautical miles distant is shown in Figures 10 and 11.

Sediment cores of both sites were optically distinguishable through different color and layering. While cores of site AL 93 were characterized by dark greyish to black colors in the top 30 cm, cores of site BY 15A were lighter

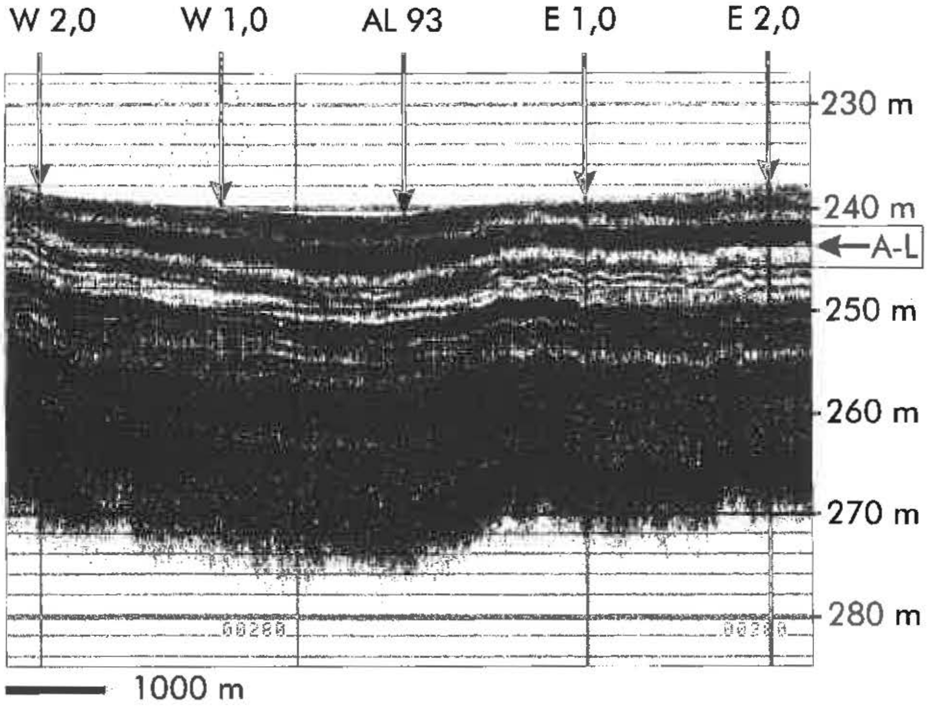

Fig. 9: East-West 18 kHz-profile through the deepest part of the Gotland Deep. Note the distinct transition between Ancylus and Littorina depositions (A-L) and thickness variations of the post Ancylus sediments.

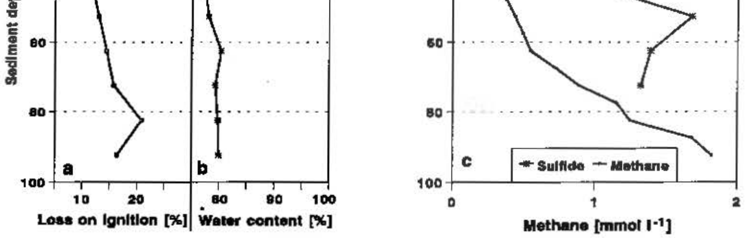

Fig. 10: Loss on ignition (a), water content (b), methane and sulfide concentrations (c) in the porewater of station AL 93, May 3, 1996.

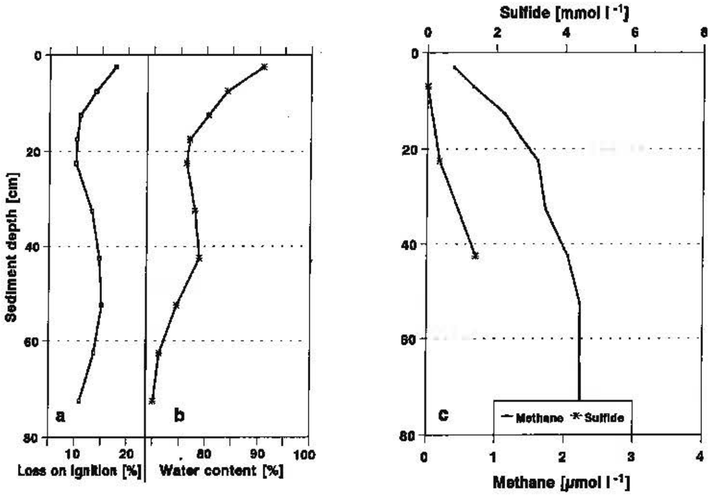

Fig. 11: Loss on ignition (a), water content (b), methane and sulfide concentrations (c) in the porewater of station BY 15A, May 3, 1996. Note different scale (µmol l^{-1}) for methane in contrast to Fig. 10

grey and showed a more distinct fine layering in the upper centimeters. Both sediments were very soft and covered by a fluffy layer with high water content (>90%) and high proportion of organic matter. This layer was between 15 and 20 cm thick at AL 93 but less than 5 cm at BY 15A (Fig. 10b, 11b). The loss on ignition in the top 5 cm was between 23 and 29% of dry weight at AL 93 and 18–22 % at BY 15A, decreasing at both sites to 11–14% at 20–30 cm depth (Fig. 10a, 11a). Below 50 cm increasing concentrations of organic matter were recorded at station AL 93, in contrast to BY 15A.

While methane concentrations increased continuously from several µM at the surface to 2 mM at 1 m depth at AL 93, concentrations remained below 3 µM at BY 15A without a pronounced gradient (Fig. 10c, 11c). Also concentrations of sulfide were significantly higher in the porewater of AL 93, showing distinct maxima between 10 and 20 cm and below 50 cm sediment depth, whereas at BY 15A only a minor increase from the surface to deeper layers was observed (Fig. 10c, 11c). This was due to different intensities of sulfate reduction and was also reflected by the distribution of sulfate in the sediments: Sulfate concentrations at site AL 93 decreased due to intense sulfate reduction from 8 to 12 mM at the surface to <1 mM at 60 cm depth, while in the same depth interval at site BY 15A lower sulfate reduction rates were measured and sulfate concentrations decreased from approx. 11 mM to values of 7 mM (PIKER *et al.* 1997; DREWS, April 1997, pers. comm.).

C. Correlations between the measured parameters

In an attempt to understand the widely varying concentrations of sulfide and methane in the Gotland Deep and other Baltic Sea sediments, correlations between these two parameters as well as with the content of organic matter and accumulation rates were analyzed. Regarding the different basins this is complicated by the fact that many factors influence the distribution of methane and sulfide. For example different physicochemical qualities of the sediment (e.g. iron content), sedimented plankton blooms or different oxygen conditions in the water column can affect both parameters. It was therefore important to evaluate data from a restricted area like the Gotland Deep, where overall conditions can be expected to be similar, with the possible exception of varying accumulation rates and water depths.

Figure 12 shows correlations between methane and sulfide concentrations and between me-thane concentrations and organic matter content in different basins of the Baltic Sea. Low methane concentrations (<3 µmol dm^{-3}) were in most cases correlated with low sulfide concentrations (<100 µmol l^{-1}), and high methane concentrations (>50 µmol dm^{-3}) coincided with sulfide concentrations of more than 500 µmol l^{-1} (Fig.12b). If methane concentrations are compared with organic matter content in the surface layers, a wide scattering of data points is seen (Fig. 12a). Average values of organic matter between 12 and 13% in the surface layer did not correlate well with methane concentrations varying between 2 and 900 µmol dm^{-3}.

Similarly, in the Gotland Deep the high proportions of organic matter at the sediment surface were not correlated with the methane concentrations (Fig. 13a). The same is true for the correlation between methane and sulfide concentrations (Fig. 13b) and between methane concentrations and water depth (Fig. 13c) in this area. A fair linear correlation ($r = 0.78$) was found between methane concentrations and accumulation rates (thickness of post-Ancylus deposits) in the investigated area (Fig. 13d). The loss on ignition, as well as the thickness of post-Ancylus deposits, do not seem to be closely connected to the amount of sulfide in the porewater.

Discussion

The analysis of methane and sulfide concentrations and their distribution in sediments of Baltic Sea basins revealed a high variation between the basins as well as between different areas within the Gotland Deep. Probably varying accumulation rates and hydrographic conditions were among the most important factors that govern the microbial processes leading to the formation of methane and sulfide in these sediments. Although the Gotland Deep could be expected to be a comparatively homogeneous environment due to low currents and a relatively smooth bottom morphology at its

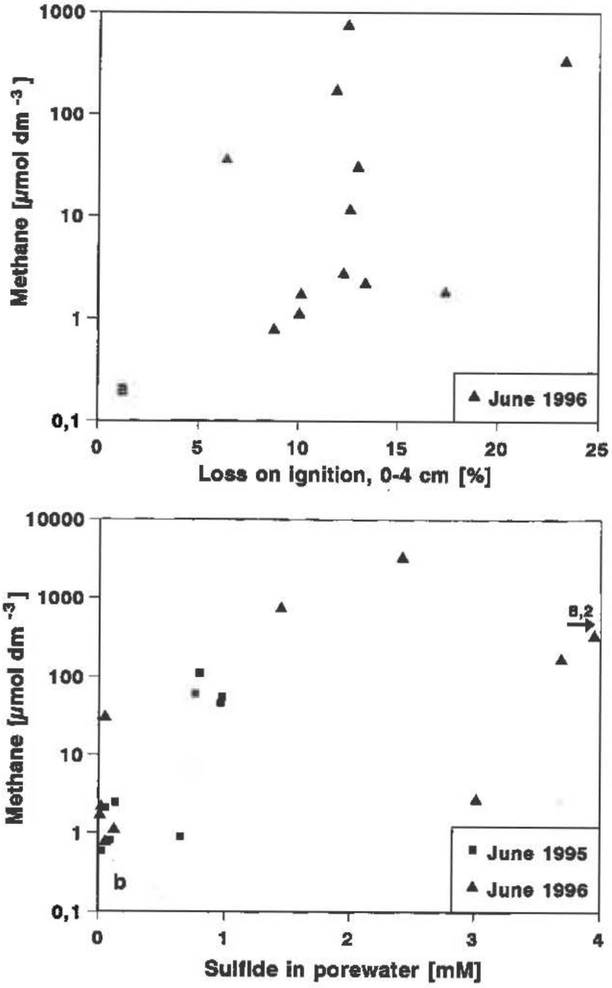

Fig. 12: Correlations between methane and organic matter (a) and between methane and sulfide (b) in sediments of different Baltic Sea basins.

deepest part, considerable differences in the sediment accumulation rate were recorded in different areas. According to a bathymetric map by Hollan (1973), the central area with a depth of more than 235 m is approximately 100 km^2 in size. Only approx. 35 km^2 of this area are covered by sediments with high methane and sulfide concentrations, as demonstrated in this study. The observation by Ignatius *et al.* (1971), that the thickness of the layer representing post-Ancylus sedimentation (from 7000 a B.P.) varies locally between 5 and 7 m, was confirmed in this investigation, where corresponding values between 3.6 and 6.1 m were obtained. In another study by Seifert *et al.* (1996) the age of a 4.3 m deep core section from the site AL 93

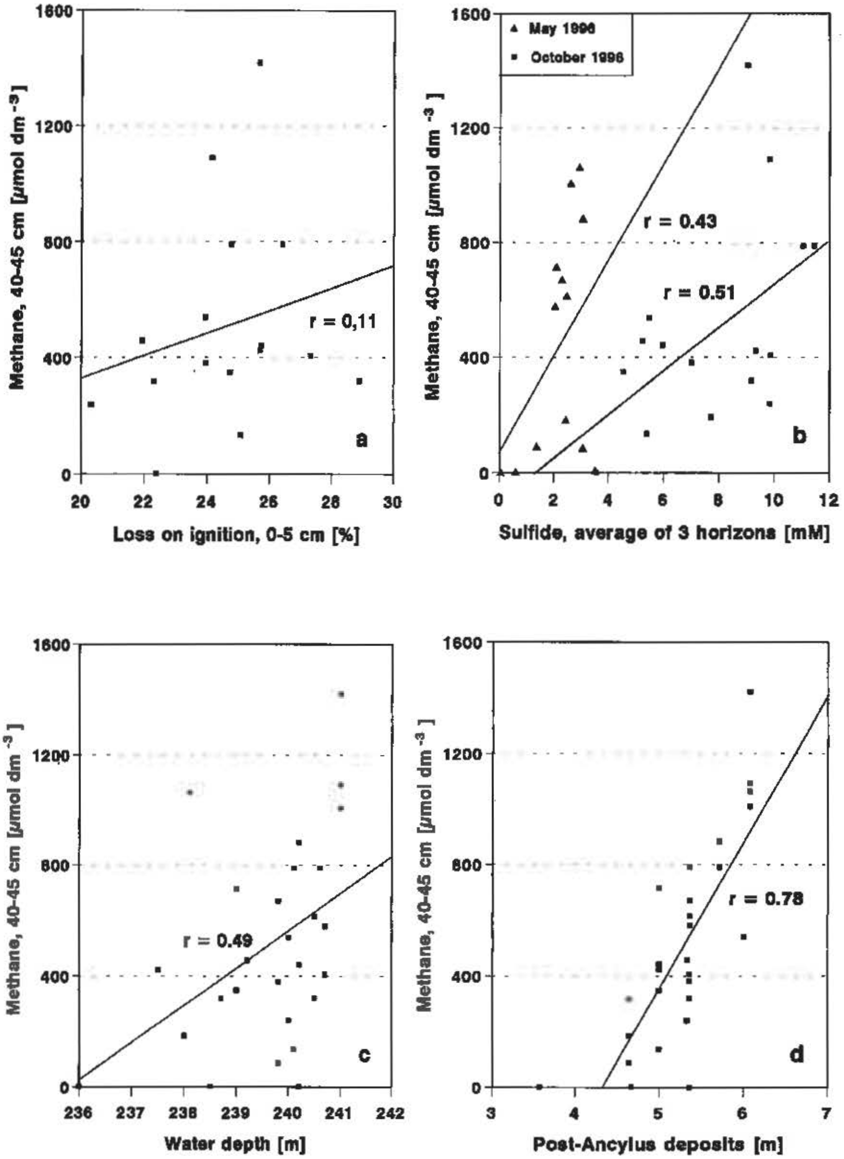

Fig. 13: Correlations between methane and other parameters as organic matter (a), sulfide (b), water depth (c) and post-Ancylus depositions (d) in the Gotland Deep.

was determined with 6650 years, which is in the same range as our echo-sounding data. Accumulation rates in this area thus can be estimated to range between 0.7 and 1.0 mm y^{-1}. Differences in these rates were attributed to local differences in the hydrodynamic processes near the bottom, such as an uneven, tongue-like penetration of new water (VOIPIO & MÄLKKI 1972).

A fair correlation between methane concentrations and thickness of post-Ancylus sediment depositions was documented in this study. The comparison of two different sites (AL 93 and BY 15A) showed that high accumulation (site AL 93) was concomitant with high methane production in deeper sediment layers, but low accumulation (site BY 15A) with minor methane concentrations in the sediments. The inclusion of a greater number of sites revealed that the two sites represented two major, significantly different areas of the Gotland Deep. High accumulation rates may favour methanogenesis by reducing the proportion of aerobic decomposition of organic matter and accelerating burial of freshly sedimentated material to anoxic sediment layers. This can result in a higher concentration of compounds utilizable for methanogenesis in deeper layers.

In contrast, the proportion of organic material in the top sediment layer, determined as loss on ignition, was not closely correlated to methane concentrations in Gotland Deep and other basin sediments. At first sight, this is surprising since it has been shown that a higher input of organic material generally favours methanogenesis in freshwater and marine sediments (KELLY & CHYNOWETH 1981; HEYER 1990). It could be argued that the distribution of recently deposited organic material in the surface layer is not necessarily a measure for the organic substrates in the actual horizon of methanogenesis in deeper layers, which consist of material more than 1000 years old. However, if we assume, that the sedimentation regime in the Gotland Basin in former times was comparable to that of today, then the actual spatial distribution of organic matter should not differ much from its relative spatial abundance in former times. This is shown by the fact that the difference in loss on ignition between the stations BY 15A and AL 93 is comparably distinct in the surface layer as well as in the 70–75 cm layer. It is more probable that either the unusually high proportion of organic matter in the Gotland Deep, resulting in substrate saturation, is the reason for the lacking correlation with methane concentrations, or that the quality of the organic material is more important than its quantity. In this respect it is interesting to note that during investigations in the Gdansk depression (CHERNOVA & BAGAEVA 1991), no clear correlation between the content of organic matter and methane concentrations were found, and sediments with virtually equal amounts of organic matter could contain either high (30–150 cm^3/kg mud) or low methane concentrations (0.025–0.030 cm^3/kg). However, there was a correlation with the qualitiy of organic matter, as high methane contents were found in sediments of coprogeneous composition with an admixture of humic components, while those with organic matter of primarily aline nature showed always low methane concentrations.

High accumulation rates should have a similarly positive effect on the production of sulfide as on the production of methane (via a smaller proportion of aerobically decomposed organic material and intense sulfate reduction in near-surface horizons, rich in organic substrates). A comparison between the stations BY 15A and AL 93 shows that the sediment with higher accumulation rates (AL 93) is also characterized by higher sulfate reduction rates and higher sulfide concentrations. However, regarding the survey of the 23 stations in the Gotland Deep, the situation is more complicated and variations are higher, though a weak positive correlation between accumulation rates and sulfide concentrations was found. While methane concentrations in the investigated sediment layers (5–45 cm) are determined by a constant diffusion of methane from deeper layers and anaerobic microbial oxidation at the methane/sulfate transition, and are not subject to chemical modification or recent sedimentation events, the situation is different for sulfide. This is produced in layers close to the sediment surface and may be modified by a variety of chemical and microbial processes. The depletion of oxygen in the deep water must have a significant effect on sulfide concentrations in the porewater (PIKER *et al.* 1997) as was confirmed by a comparison of data from the Gotland Deep from May and October 1996 (Fig. 10). Other factors influencing sulfide concentrations in the porewater are anaerobic oxidation (SCHNEIDER & IMHOFF 1996) or precipitation as pyrite (BOESEN & POSTMA 1988).

Water depth in the Gotland Deep is connected directly to the duration of the exposure of the sediment surface to oxic or anoxic bottom water and hence may influence anaerobic processes there. In periods of transition from oxic to anoxic conditions anoxia generally spreads from the deepest sites resulting in a chemocline rising from the sediment surface into the water column. On the other hand the deepest sites, exhibiting the highest salinity, are the first to receive "new", oxygen-containing water during saltwater intrusions, which irregularly occur, at a small scale also during generally anoxic periods. Furthermore the absolute water depth is relativated by morphological factors, e.g. slight depressions. These considerations may explain, why the correlation of methane concentrations to water depth is not as close as to accumulation rates.

The data obtained on methane and sulfide concentrations in sediments of the Gotland Deep allow an estimation of the amount of these compounds, which is released from the sediment into the water column during periods of anoxic deep water. If it is assumed that during these periods no aerobic oxidation of methane occurs at the sediment surface, then the methane flux rates within the top sediment layers should equal the amount of methane, that diffuses into the water column. Comparing the methane concentration data of Table 2, it becomes evident that the station AL 93 is representative for the methane-rich central part of the Gotland Deep. The values for this station (614 and 320 µmol CH_4 dm^{-3} in May and October 1996) are well within the range of the other high-methane stations (579±338 µmol dm^{-3}). Surface methane flux rates in the top 25 cm at station AL 93 were measured repeatedly during 1993 to 1996 and varied between 41.0 and 55.4 µmol m^{-2} d^{-1} (PIKER *et al.* 1997). Thus an area of 35 km^2 would produce between 1435 and 1939 moles of methane per day, which is sufficient to account for the major part of methane in the deep water of the Gotland Deep. The low-methane sediments occurring around the deepest part of the basin exhibit surface methane flux rates >3 orders of magnitude lower than in the centre (SCHMALJOHANN, unpublished data) and will not significantly contribute to the water column methane budget.

In conclusion, methane concentrations in high-methane sediments of the Baltic Sea basins are basically dependent on the production of methane in deeper sediment layers and on the proportion oxidized anaerobically during diffusion to the sediment surface. These processes are independent from seasonal aspects and from the oxygen regime in the deep water. Methane concentrations are correlated to the accumulation rates of the sediments, but do not correlate to the proportions of organic matter in the top sediment layers. Nevertheless, transfer of methane into the water column is significantly influenced by the presence of oxygen at the sediment surface, which enables and stimulates the aerobic oxidation of methane within the sediment.

In general, sediments with high concentrations of methane also exhibit high rates of sulfate reduction and high concentrations of sulfide. However, sulfate reduction is most active in layers between 3 to 20 cm, and the processes of the sulfur cycle (reductive and oxidative part as well) are strongly influenced by seasonal aspects and by the presence of oxygen in the deep water. Sulfate reduction is stimulated after a period of oxic bottom water, and oxidation of sulfide is greatly reduced after oxygen depletion and subsequent consumption of other possible electron acceptors in the sediment, allowing a tremendous increase of the sulfide concentrations in sediments after prolonged exposure to anoxic conditions.

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