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EXPERIMENTAL ARTICLES

Sulfate Reduction, Methanogenesis, and Methane Oxidation in the Upper Sediments of the Vistula and Curonian Lagoons, Baltic Sea

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Abstract—Microbiological, biogeochemical, and isotope geochemical investigations of the upper sediments of the Vistula and Curonian lagoons, Baltic Sea, were carried out. High content of organic matter in the sediments was responsible for the high numbers (over 10^{10} cells cm^{-3}) and activity of heterotrophic microorganisms. The calculated integral rates of dark CO_2 assimilation for the upper 30 cm of the sediments varied 12.5 to 38.8 mmol m^{-2} day^{-1} and were somewhat higher in the Curonian Lagoon than in the Vistula Lagoon. Integral rates of sulfate reduction were higher in the more saline Vistula Lagoon. Rapid consumption of sulfates of the pore water resulted in intensified methanogenesis, with significantly higher rates detected in the silts of the Curonian Lagoon. High rates of methanogenesis in the Curonian Lagoon correlated with higher methane levels in its upper sediments and near-bottom water. The highest rates of methane oxidation were detected in the uppermost sediment horizons (oxidized or slightly reduced), which was an indication of the barrier role of aerobic methanotrophic bacteria. The calculated methane flows from the sediments into the water column were 0.45 and 0.007 mmol m^{-2} day^{-1} for the Vistula and Curonian Lagoons, respectively. Low methane flow from the sediments of the Curonian Lagoon resulted probably from the specific weather (wind) conditions during sampling. The near-stormy conditions in the Curonian Lagoon caused sediment detachment, resulting in methane release into the water column.

Keywords: sulfate reduction, methanogenesis, methane oxidation, Vistula and Curonian lagoons, Baltic Sea

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The Curonian and Vistula lagoons are shallow (average depths 3.8 and 2.7 m, respectively), freshwater-to-brackish gulfs, which are separated from the southeastern Baltic Sea by the Curonian and Vistula spits. These lagoons, interacting with the open sea via narrow straits, are a kind of running-water intermediate mud traps receiving liquid and suspended drains from the land [1]. The ratios of fresh and brackish water arriving yearly to the Vistula and Curonian lagoons is 1 : 5 and 4 : 1, respectively, marking them as lagoons affected predominantly by the sea or by the rivers. The average salinity of the Vistula Lagoon is 3.8‰, while the investigated southern part of the Curonian Lagoon was freshwater. To the Curonian Lagoon terrigenous organic material arrived mostly with the river flow (87%), with seawater responsible for only 1.6%. In the case of the Vistula Lagoon, 25% of terrigenous material arrived from the sea and 58% originated from river flow. Variations in the degree of the influence of the river and marine flow affect the amount of the sediment accumulated in these lagoons. In the Curonian Lagoon basin, especially in its southern part, 74% of the sedimentary material is precipitated, with only 26% is carried out [2]. At the bottom of the Vistula Lagoon, 16% of the terrigenous material is accumulated, while most of it (84%) is carried out into the sea. Thus, at the present stage of sediment formation, the sedimentary material is mostly carried out from the Vistula Lagoon and mostly accumulated in the Curonian Lagoon. The resulting rate of sediment formation in the Curonian Lagoon is 3.5 times that of the Vistula Lagoon [3].

Geological and geochemical investigation of the Curonian and Vistula lagoons was carried out by E.M. Emelyanov and his school [4, 5]. The bottom sediments of both lagoons were found to exhibit the concentric “circumcontinental” distribution of the types of bottom sediments, with the silts in the center (in the deepest regions) and the sands along the outer boundary of the lagoons. This pattern was especially pronounced in the Curonian Lagoon [6]. In both lagoons, significant areas were occupied by dirty sands

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Table 1. Sampling stations in the Vistula and Curonian lagoons, Baltic Sea, July 2011

Station no.	Coordinates	Depth, m	Salinity of near-bottom water, ‰	Temperature of near-bottom water, °C
		Vistula Lagoon		
1	54°38.9′; 20°02.6′	4.0	5.5	20
2	54°37.0′; 20°06.5′	4.1	5.5	19
3	54°30.8′; 19°51.5′	4.6	5.5	19
4	54°27.9′; 19°41.4′	2.3	5.0	20
		Curonian Lagoon		
5	54°57.0′; 20°56.0′	4.0	0.1	19
7	55°05.0′; 20°56.0′	5.0	0.1	19
8	55°00.0′; 20°55.0′	5.0	0.1	19

and aleuro-pelitic silts with relatively high C_{org} content. The average C_{org} content in the Curonian Lagoon precipitates was (1.7–2.4%), with the highest values (over 7%) in its southern part reflecting the high rate of sediment formation and high production of organic matter (OM). In the Vistula Lagoon deposits C_{org} content was significantly lower, seldom exceeding 2% even in the uppermost sediment layers. Long-term monitoring of the levels of chlorophyll, biogenic elements, and planktonic biomass, as well as of the primary production and OM mineralization in the Curonian and Vistula lagoons, supported their classification as a hypereutrophic and an eutrophic lagoon, respectively [7]. According to a number of criteria, eutrophication of the Vistula Lagoon did not reach the critical level, while it exceeded the acceptable level in the Curonian Lagoon.

Thus, the earlier geochemical, hydrological, and biological investigation suggests active microbial processes of OM decomposition in the sediments of the Vistula and Curonian lagoons. Microbiological and gas–geochemical investigation of the sediments of the Russian parts of these lagoons has not been previously carried out. The goal of the present work was therefore to obtain quantitative data on the rates of microbial processes of OM decomposition and on the role of microorganisms during the early stages of digenesis of the upper sediments in the Curonian and Vistula lagoons.

MATERIALS AND METHODS

The water and sediment samples were collected in the Vistula and Curonian lagoons in July 2011 from small-size vessels of the Atlantic Branch of Shirshov Institute of Oceanology, Russian Academy of Sciences (AB IO RAS) (Table 1, Fig. 1) using a limnological stratometer and a low-depth corer developed in AB IO RAS.

To determine the total numbers of microorganisms (TNM), water samples were fixed with formalin (final concentration in the sample 2.5%), while silt samples (1 cm^3) were diluted 1 : 15 with the filtered lagoon water and fixed with 1.5 mL of 25% glutaraldehyde. The samples were then transferred to the laboratory of the Winogradsky Institute of Microbiology (INMI RAS), where the cells were desorbed by sonication (UZV-2/150-TN-RELTEK, 22 kHz, 2 min) and filtered through Osmonics membranes (0.2 μm). The filters were stained with Sybr Green, and the cells were counted under an Olympus BX 41 epifluorescence microscope using the Image Scope Color M software package.

The rates of microbial processes were determined by the radioisotope method with ^{14}C- and ^{35}S-labeled substrates. Immediately after heaving the geological corer onboard, the sediment samples (3 mL) from the relevant horizons were collected into cut-off 5-mL plastic syringes and sealed with butyl rubber stoppers. The labeled substrate (0.2 mL) was injected through the stopper, and the samples were incubated for 1–2 days at 16–18°C. The incubation temperature corresponded to the temperature of the upper sediment layers determined by a submerged thermometer at the time of sampling. After incubation, the samples were fixed with 1 mL of 2 N KOH and transported to the laboratory. The samples were then treated as described previously [8, 9]. The rate of methane oxidation (MO) was determined with 1 μCi of ^{14}C-methane dissolved in degassed distilled water. The rate of sulfate reduction (SR) was determined using ^{35}S-sulfate (10 μCi per sample). The rate of methanogenesis (MG) was determined with ^{14}C-bicarbonate and methyl-labeled ^{14}C-acetate (10 μCi per sample). The samples fixed with alkali and incubated in a refrigerator for 6 h prior to addition of a labeled substrate were used as the controls.

Methane content in the water column and bottom sediments was determined by headspace analysis [10]. Water samples in 30-mL penicillin vials were treated with 2 N KOH (0.1 mL) to suppress microbial processes. A known volume of water was then removed and the vials were sealed with gas-tight butyl rubber

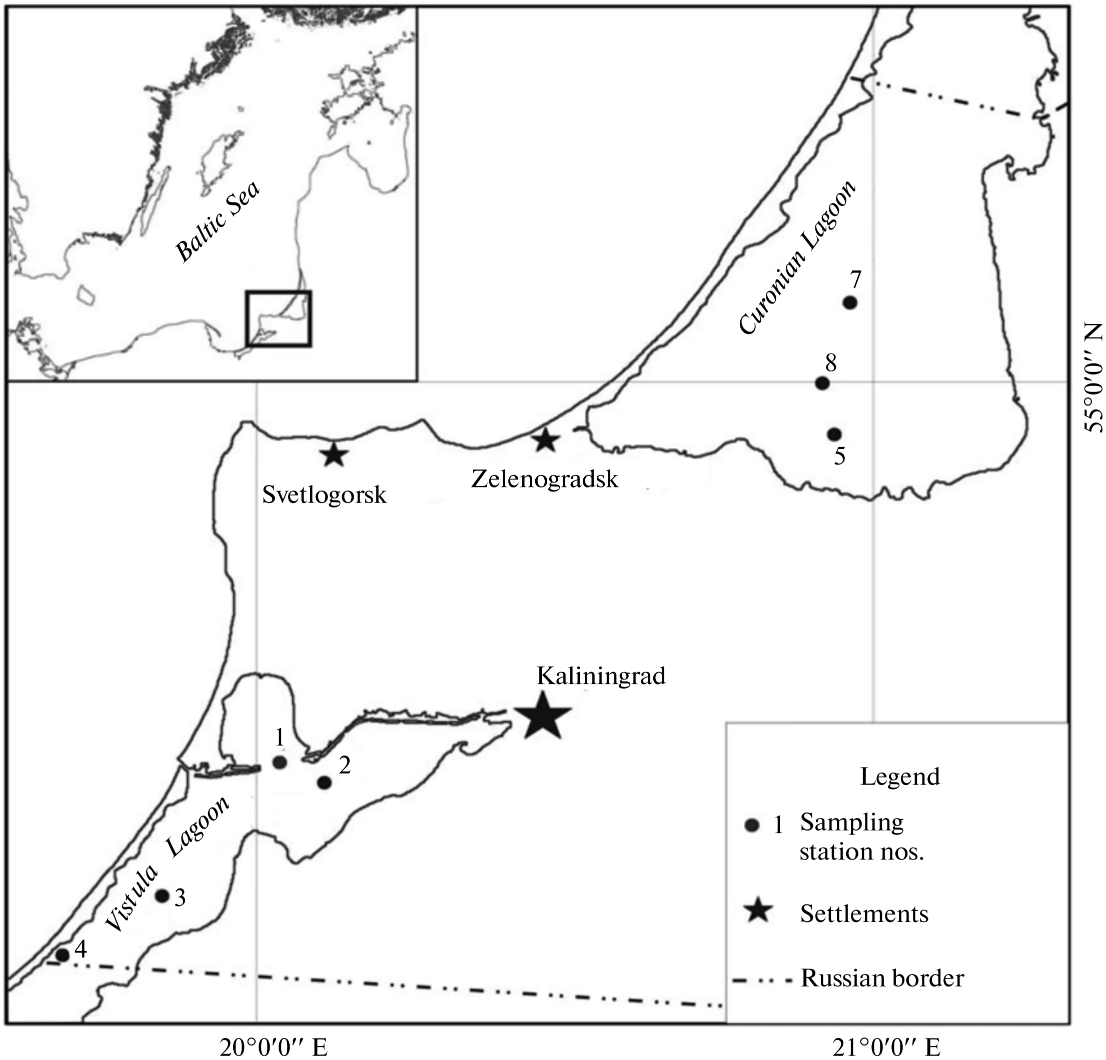

Fig. 1. Location and designations of the sampling stations in the Vistula and Curonian lagoons, Baltic Sea.

stoppers. Sediment samples were collected with cut-off 2-mL syringes, transferred into penicillin vials, and filled to capacity with degassed water. After removal of a known volume of water, the vials were sealed with butyl rubber stoppers. Methane content in the gas phase was determined on a Kristall 2000 gas chromatograph (Russia) equipped with a flame ionization detector.

Pore water was obtained by centrifugation of the sediments for 10 min at 8000 rpm in a TsUM-1 centrifuge (Russia). Total alkalinity was determined by titration using the standard reagent kit (Merck, Germany). Sulfate ion in pore water was determined on a Staier ion chromatograph (Russia).

Content of C_{org} in the sediments was determined on an AN-7560 express analyzer in the analytical laboratory of Shirshov Institute of Oceanology, Russian Academy of Sciences.

Mass spectral analysis of methane carbon of the sediments ($\delta^{13}C$) was carried out as follows. A 250-mL glass vial was filled to half-capacity with the sediment, supplemented with the concentrated salt solution to 230 mL, sealed hermetically with a rubber stopper, and stirred vigorously. In the laboratory, the gas phase was collected with a syringe by displacement with a volume of the salt solution, and the gas was stored above the same solution. The $\delta^{13}C$ value for methane was determined of a TRACE GC gas chromatograph (Germany) coupled to a Delta plus mass spectrometer (Germany).

Mass spectral determination of $\delta^{13}C$ of pore water carbonates was determined with CO_2 as a carrier gas according to the previously described procedure [11]. The error of $\delta^{13}C$ measurements did not exceed ±0.1‰.

The weight porosity (water content of the sample) was determined by heating the wet sediment [12]. Methane flow into the water column from the upper sediment horizon (0–5 cm) was calculated according to the previously described procedure using the data on weight porosity and temperature of the near-bottom water [13]. The temperature of near-bottom water was measured using a submerged mercury thermometer.

RESULTS

The cores of the Vistula Lagoon sediments consisted of terrigenous aleuro–pelitic silts. At station 1, the upper oxidized yellowish-gray later was 0.5 to 1 cm, with greenish-gray reduced sediments (Eh from –10 to –80 mV) containing characteristic contractions of amorphous iron sulfides (hydrotroilite) in the 5–12 cm interval and with a weak smell of sulfide below 12 cm. Lithologically, the sediments of stations 2 and 3 were similar to those of st. 1, but with a 3–5-cm upper oxidized layer. Hydrotroilite-rich, black or grayish-black aleuro-pelitic silts were found below 3 cm in the shallowest part of the lagoon close to the Polish border (st. 4). The sediments of the Curonian Lagoon were also aleuro-pelitic silts with shell rock admixtures. The upper yellowish-gray oxidized layer was ~3 cm at st. 5 and 7 and 5–7 cm at st. 8. Slightly reduced greenish-gray silts with infrequent darker layers containing hydrotroilite inclusions were located at greater depths.

Physicochemical characterization of the bottom sediments (Table 2) revealed the patterns of total alkalinity and sulfate content in pore waters which were typical of shallow-water sediments. In all the cores, total alkalinity of the pore water increased with depth, while sulfate content decreased. At st. 4, which was most distant from the strait near Baltiisk, where seawater arrives into the lagoon, the lowest sulfate concentration in the upper sediment horizon was found (1.32 mmol dm^{-3}).

The lagoons differed significantly in porosity of the silts. While the upper (0–5 cm) sediments of the Vistula Lagoon had porosity of 0.90–0.94, which was comparable to the values for gas-bearing sediments of the Gdansk Deep, Baltic Sea [14], the Curonian Lagoon silts had porosity of ~0.7.

In the sediments of the Vistula Lagoon, C_{org} values (Table 2) were within the range reported previously (1.11 to 1.58%) [6], except for st. 1 (2.70 and 3.44% in the 5–10 and 27–32 cm horizons, respectively) and the upper horizon of st. 4 (2.11%). The sediment cores from the Russian sector of the Curonian Lagoon had significantly higher C_{org} content (up to 8.44% at st. 5), which agreed with the results of earlier studies [4–6].

Methane content in the Vistula Lagoon sediments varied significantly from station to station (Table 2). The highest CH_4 concentrations were found in the silts of st. 1 (242–372 μmol dm^{-3}) and 4 (up to 528 μmol dm^{-3}), while methane content along the core of st. 3 varied from 17.5 to 19.2 μmol dm^{-3}. In the reduced sediments of the Curonian Lagoon methane levels were generally higher than in the Vistula Lagoon; a rapid increase in methane content to 250–877 μmol dm^{-3} occurred at all stations below 5 cm. Methane concentrations in the near-bottom water at all Curonian Lagoon stations were also higher than in the Vistula Lagoon (Fig. 2).

Among the samples of the Vistula Lagoon sediments, the highest TNM values were observed at st. 1. In the upper 0–5 cm horizon it was 3–4 times higher than at other stations and reached 21×10^{10} cells cm^{-3}. While in the 5–10 cm horizon TNM decreased to 4.3×10^{10} cells cm^{-3}, it was twice as high in deeper layers (17–27 cm) and remained at the level of 3.3×10^{10} cells cm^{-3} at the depth of 27–32 cm. At other stations, TNM values for the upper 0–3 cm varied insignificantly (5.1×10^{10} –6.2×10^{10} cells cm^{-3}). TNM usually decreased with depth (Table 3).

In the Curonian Lagoon (for two sampling stations), TNM values were somewhat lower, 1.3×10^{10}–3.2×10^{10} cells cm^{-3}. At st. 5, TNM decreased with depth to 0.6×10^{10}–0.8×10^{10} cells cm^{-3}. At st. 8, TNM in the 12–22 cm horizon was somewhat higher than in the surface horizon, although it decreased in deeper layers.

Small coccoid cells (cell volume 0.02–0.03 μm^3) predominated in the microbial benthos. The surface layers were characterized by close association of microbial cells with silt particles. Over 80% of the cells remained attached to the particles even after sonication (Fig. 3). Organo-mineral suspended material probably prevailed in the upper layers, immobilizing microbial cells.

In OM-enriched sediments, dark CO_2 assimilation is a known measure of the net heterotrophic activity of microbial communities. The measured rates of this process in the sediments of the Vistula and Curonian lagoons are presented in Table 3. At all stations, the highest rates of dark CO_2 assimilation were detected in the uppermost layer of the sediments. The rate of this process decreased gradually with depth.

Sulfate reduction rates generally followed the same depth profile. In the Vistula Lagoon, the highest SR rates were observed in the 10–15 cm layer. In this horizon, SR rates varied from 5.5 to 42 μmol dm^3 day^{-1}. Deeper in the sediments, SR rates decreased significantly (Table 3). The Curonian Lagoon sediments followed a similar pattern, although SR rates in the upper horizons were somewhat lower and varied from 3 to 24 μmol dm^3 day^{-1}.

Unlike the rates of SR and CO_2 assimilation, methanogenesis rates in the sediments of these shallow lagoons increased with depth (Table 3). The highest rates of methanogenesis (over 700 nmol dm^{-3} day^{-1}) were recorded in reduced sediments of st. 4 (Vistula Lagoon) and st. 5 (Curonian Lagoon). Unlike MG,

Table 2. Physicochemical parameters of the sediments of the Vistula and Curonian lagoons in July 2011

Station no./depth, m/horizon, cm	Eh, mV	Porosity	CH_4, µmol dm^{-3}	SO_4^{2-}, mmol dm^{-3}	Alk, µmol dm^{-3}	C_{org}, %
Vistula Lagoon						
1/4.0						
0–5	–10	0.94	242	2.92	3.0	1.21
5–10	–20		357	2.85	3.1	2.70
17–22	–10		372	1.83	4.5	
22–27	+10		361	1.67	5.0	
27–32	+30		332	1.15	5.6	3.43
2/4.1						
0–3	+20		93.2	2.40	3.7	
3–8	+10	0.9	95.9	2.38	4.1	
8–12	–15		95.2	1.71	4.9	1.18
15–20	–45		106	1.43	6.1	1.16
20–25	–35		111	1.11	6.6	
3/4.6						
0–3	+160	0.9	17.5	2.83	3.9	
3–8	+10		18.6	2.96	4.3	1.45
8–12	–80		18.3	1.86	4.7	
12–17	–75		18.0	1.46	5.0	1.57
17–23	–75		19.2	0.66	5.3	1.41
4/2.3						
0–3	+60	0.9	50.2	1.32	5.4	2.11
3–8	–75		51.6	0.98	6.2	1.59
8–12	–120		127	0.64	7.0	
15–20	–110		179	0.11	7.6	1.45
30–40	–90		213	0.03	7.8	1.41
40–50	–55		528	0.02	8.4	1.15
Curonian Lagoon						
5/4.0						
0–3	+170	0.71	81.1	0.146	3.4	6.12
3–10	–60		352	0.037	5.0	5.01
12–17	–20		256	0.011	4.6	8.44
20–25	–10		252	0.009	4.3	
25–30	+10		359	0.007	4.1	7.91
7/5.0						
0–3	+180	0.7	3.06	0.740	2.3	4.97
5–12	–30		543	0.229	3.9	4.28
12–19	–10		586	0.021	3.9	2.86
19–27	+15		401	0.027	4.0	2.61
8/5.0						
0–5	+170	0.68	1.64	0.302	2.7	5.77
5–12	+20		210	0.146	3.4	5.53
12–22	–35		486	0.027	4.7	4.11
20–30	+15		667	0.015	4.9	4.42
50–60	+15		877	0.005	5.2	4.77

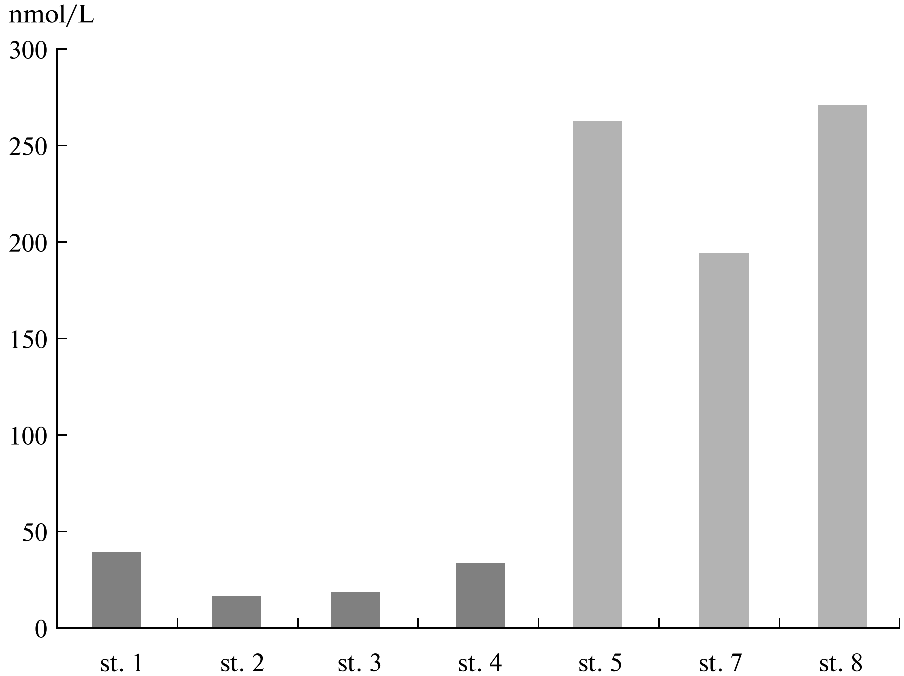

Fig. 2. Methane content in the near-bottom horizons of the Vistula (st. 1–4) and Curonian (st. 5–8) lagoons of the Baltic Sea.

the highest MO rates were found in the upper 10 cm of the sediment (Table 3). The rate of methane oxidation decreased with depth and usually did not exceed 0.5 μmol dm^3 day^{-1}.

The carbon isotopic composition of methane ($\delta^{13}C$) measured at the stations in the Vistula and Curonian lagoons with the highest methane levels indicated the biogenic origin of CH_4. The $\delta^{13}C$ values for methane varied from –77.3–63.3‰ (Table 4).

Increased rates of methanogenesis in deeper sediment horizons correlate with the isotopic composition of carbonate carbon in pore water (Table 4). In the Vistula Lagoon, fractionation of the carbon isotopes of pore water carbonates was most pronounced at st. 4, where sulfate consumption and a significant increase in MG rates was observed below 15 cm. Pore water carbonates were found to become heavier with depth at all stations of the Curonian Lagoon.

DISCUSSION

High content of organic matter in the studied lagoons was responsible for high numbers of microorganisms revealed in the bottom sediments. At most stations TNM in the upper sediments exceeded 10^{10} cells cm^{-3}. In the Vyborg Bay, TNM in summer did not exceed 10^9 cells cm^{-3} [11], while in the Gdansk Deep (even at the pockmark sites) it was still lower, to 10^8 cells cm^{-3}. The TNM data correlated with the results on dark CO_2 assimilation. Its rate calculated for the upper 30 cm of the sediment exceeded 10 mmol m^{-2} day^{-1} at all the stations, indicating high activity of heterotrophic microorganisms. Importantly, the net rate of dark CO_2 assimilation in the sediments was higher in the Curonian Lagoon than in the Vistula Lagoon (Table 5). This may result from the higher C_{org} content in the silts of the Curonian Lagoon. Apart from arrival of the terrigenous OM with river flow, this

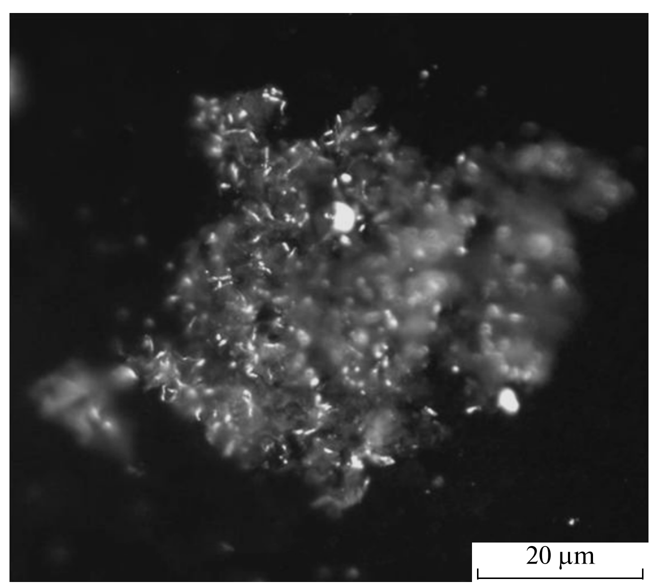

Fig. 3. Microbial cells on the particles of the upper silt sediments.

Table 3. Total numbers of microorganisms (TNM) and rates of microbial processes in the sediments of the Vistula and Curonian lagoons, Baltic Sea, July 2011

Station no.; horizon, cm	TNM, $\times 10^{10}$ cells cm^{-3}	Rates of microbial processes			
		Dark CO_2 assimilation, μmol C dm^{-3} day^{-1}	CH_4 oxidation, μmol dm^{-3} day^{-1}	CH_4 formation, nmol dm^{-3} day^{-1}	Sulfate reduction, μmol dm^{-3} day^{-1}
Vistula Lagoon					
1					
0–5	21	92.5	1.21	ND*	31.4
5–10	4.3	91.3	0.76	0.01	8.19
17–22	9.3	25.7	0.18	2.4	0.16
22–27	8.8	36.3	0.13	21.0	0.29
27–32	3.3	29.8	0.65	112	2.72
2					
0–3	5.4	128	0.75	ND	36.5
3–8	1.5	51.2	0.68	0.93	12.9
8–12	1.1	32.9	0.12	11.5	5.46
15–20	1.0	34.2	0.07	27.9	1.17
20–25	0.9	28.3	0.13	18.3	1.20
3					
0–3	6.2	104	0.67	ND	9.13
3–8	2.1	102	0.22	1.14	39.2
8–12	1.7	46.8	0.35	2.77	24.3
12–17	1.4	19.1	0.11	17.4	7.33
17–23	1.6	10.8	0.09	123	9.96
4					
0–3	5.1	274	1.32	0.04	18.1
3–8	2.4	116	0.12	0.07	42.3
8–12	3.2	42.7	0.34	52	14.4
15–20	1.1	37.0	0.39	343	6.58
30–40	0.5	21.2	0.25	524	3.31
40–50	2.2	12.1	0.17	797	0.41
Curonian Lagoon					
5					
0–3	3.2	297	1.21	0.01	11.68
3–10	1.7	132	1.07	12.0	3.05
12–17	0.6	20.7	0.58	515	1.01
20–25	0.8	–	0.14	780	0.23
25–30	0.8	16.9	0.23	278	0.29
7					
0–3	–	288	2.89	0.03	24.1
5–12	–	225	0.49	179	16.0
12–19	–	72.4	0.12	387	0.36
19–27	–	27.0	0.07	294	0.26
8					
0–5	1.3	464	1.19	0.01	8.41
5–12	2.1	170	0.99	79	12.1
12–22	2.5	33.7	0.10	396	2.59
20–30	1.8	10.5	0.21	643	1.03
50–60	0.9	7.82	0.09	415	0.32

* ND stands for not detected.

higher C_{org} level resulted also from higher primary production in the Curonian Lagoon [7].

Analysis of the physicochemical parameters and of the rates of microbial processes (SR, MG, and MO) (Table 5) showed that sulfate content in pore waters was the most important factor affecting the rates of microbial processes in the studied sediments. Due to higher (compared to the Curonian Lagoon) sulfate content in the Vistula Lagoon, sulfate reducers played the major part in terminal decomposition of organic matter in the upper 30-cm layer. Certain differences observed in sulfate concentration of the pore waters from different sites within the Vistula Lagoon resulted from their different distance from the strait connecting the lagoon with the open sea. At st. 1 and 2, which were the closest ones to Baltiisk, higher sulfate levels were associated with the lowest rates of methanogenesis. This is not surprising, since sulfate is energetically preferable to carbonate as an electron acceptor, and SR usually predominates when sufficient amounts of sulfate are present in the pore water [15]. At st. 4, which was most distant from the strait, rapid consumption of sulfate was observed in the upper 15 cm of the sediment, and the integral MG rate was consequently higher (Table 5). In the sediments of the Curonian Lagoon, sulfate content did not exceed 0.03 μmol dm^{-3} already at 10–12 cm, and methane content in the upper sediments was therefore higher than in the Vistula Lagoon.

Consumption of organic carbon in the course of SR and MG in the sediments may be calculated from the generalized equations of these processes [16]. The stoichiometry of C_{org} utilization for formation of reduced sulfur compounds and methane during SR and MG, respectively (2 : 1), together with our data on SR and MG rates (Table 5) were used to calculate consumption of organic carbon for sulfate and carbonate reduction in the sediments of the Curonian and Vistula lagoons. The daily C_{org} consumption for sulfate reduction in the Vistula Lagoon sediments varied from 4.5 to 9.7 mmol m^{-2} day^{-1}, while methane formation by microbial methanogenesis resulted in consumption of only 8.64–248 μmol m^{-2} day^{-1} C_{org}. Unsurprisingly, the highest contribution of methanogenic archaea to OM decomposition in the Vistula Lagoon was observed at the least saline st. 4.

Although MG rates and C_{org} consumption for carbonate reduction in the Curonian Lagoon were higher than in the Vistula Lagoon, bacterial SR remained the main terminal process of OM mineralization, responsible for the oxidation of 1.4–4.6 mmol C_{org} m^{-2} day^{-1} (Table 5). Thus the relatively low sulfate concentration in pore water of the Curonian Lagoon sediments (<0.31 mmol dm^{-3}) was sufficient for the functioning of a highly active community of sulfate-reducing bacteria, which plays the dominant role in OM mineralization.

Table 4. Carbon isotopic composition ($\delta^{13}C$) of dissolved methane, organic matter (C_{org}), and carbonates (C_{min}) of pore water from the sediments of the Vistula and Curonian lagoons, Baltic Sea, July 2011

Station no.	Horizon, cm	($\delta^{13}C$), ‰		
		CH_4	C_{org}	C_{min}
Vistula Lagoon				
1	0–10			−11.30
	17–27			−12.90
	27–32			−11.56
2	0–3		−26.54	
	3–8		−26.65	−12.92
	8–12		−26.99	−14.41
	15–20		−27.19	
	25–30		−27.46	−14.05
3	0–3			−12.78
	8–12			−14.86
	30–40	−73.61		−11.32
4	0–8		−26.40	−13.48
	8–12		−26.43	−12.89
	12–20	−76.71	−26.41	−10.44
	30–40		−26.11	−8.17
	40–50	−77.32	−25.72	−3.31
Curonian Lagoon				
5	0–10			−7.21
	20–30	−63.29		−5.41
7	0–4		−29.07	
	5–12		−28.86	−10.63
	12–19		−28.08	−5.79
	27–34		−28.33	
8	0–5		−29.14	
	5–12		−28.96	−8.93
	30–40	−72.36	−29.22	−0.91

The ratio between integral rates of MG and MO shows predomination of methane oxidation in the upper sediment horizons at most of the stations. At two Vistula Lagoon stations, MO rate exceeded the MG rate by more than an order of magnitude. For the sediments of st. 3 and 4, integral rates of MO and MG differed 1.8- and 3.7-fold. While MO dominated in the Curonian Lagoon sediments as well, the ration of MO and MG rates varied from 1.5 to 2.3. Higher MO rates indicated that the biogenic methane formed in deep sediment layers was oxidized in the upper 30 cm of the sediments of these Baltic lagoons. The tendency of MG rates to increase with depth supports this conclusion. Importantly, the highest MO rate was restricted to the uppermost, oxidized, or weakly reduced horizons. Thus, unlike the bas-bearing silts of

Table 5. Methane flow from the sediment surface into the water column and integral rates of microbial processes calculated for the upper 30 cm of the sediments of the Vistula and Curonian lagoons, Baltic Sea

Station no.	CH_4 flow from the sediment surface into the water, mmol m^{-2} day^{-1}	Dark CO_2 assimilation, mmol m^{-2} day^{-1}	Sulfate reduction, mmol m^{-2} day^{-1}	CH_4 formation, μmol m^{-2} day^{-1}	CH_4 oxidation, μmol m^{-2} day^{-1}	C_{org} consumption for microbial processe	
						Sulfate reduction, mmol m^{-2} day^{-1}	Methanogenesis, μmol m^{-2} day^{-1}
				Vistula Lagoon			
1	0.93/1.15*	16.6	2.30	4.64	161	4.60	9.28
2	0.50/0.51	13.3	2.24	4.32	80.7	4.48	8.64
3	0.10/0.10	12.5	4.87	17.0	62.3	9.74	34.0
4	0.27/0.28	27.1	4.25	68.7	124	8.50	248
				Curonian Lagoon			
5	0.01/0.66	21.9	0.68	121	181	1.36	242
7	0.01/0.81	37.6	2.30	72.0	171	4.60	144
8	0.00/0.20	38.8	1.58	102	158	3.16	204

* The first value corresponds to the flow calculated using methane concentrations in the upper sediment layer (Table 2). The second value was calculated using the averaged CH_4 concentration in the 0–10 cm sediment layer.

the Gdansk Deep, where we observed high rates of anaerobic methane oxidation [17], aerobic methanotrophic bacteria probably play a major part as a barrier for methane migrating from the sediments to the near-bottom water.

The difference in methane concentrations in the upper (0–5 cm) sediments and the near-bottom water (Table 2, Fig. 2) leads to development of methane flow from the sediment, in spite of active microbial methane oxidation. The calculated values of methane diffusion flow for the studied lagoons varied significantly (Table 5). In the Vistula Lagoon, the flow varied from 0.1 to 0.93 mmol m^{-2} day^{-1} with the average at 0.45 mmol m^{-2} day^{-1}. In the Curonian Lagoon, the flows varied from 0.00 to 0.01 mmol m^{-2} day^{-1} with the average (for three stations) at 0.007 mmol m^{-2} day^{-1}. The average values of methane flow from the Vistula Lagoon silts were comparable to the average values for gas-bearing sediments and pockmarks of the Gdansk Deep (0.8 and 0.1 mmol m^{-2} day^{-1}, respectively) [13].

The low values of methane flow from the sediments of the Curonian Lagoon probably resulted from the specific weather (wind) conditions during sampling. The near-stormy conditions in the Curonian Lagoon caused sediment detachment, resulting in methane release into the water column. This suggestion is supported by two findings. Methane concentration in the near-bottom water at all the sampling stations was relatively high (an order of magnitude higher than in the Vistula Lagoon). Moreover, recalculation of the methane flow using the methane concentration averaged for 0–10 cm of the sediment (Table 5) yielded comparable values for the Vistula and Curonian lagoons (0.51 and 0.57 mmol m^{-2} day^{-1}, respectively). Thus, detachment of the upper sediment layers in stormy weather may result in methane release into the water, causing elevated methane concentrations in the near-bottom water. Under temperate winds, methane is probably accumulating in the sediment, so that its flows in both lagoons become identical.

It should be noted that in shallow basins, due to diurnal variations in temperature, higher methane flows at the sediment–water boundary were observed at daytime [18–20]. Thus, the calculated average daily methane flow may be an overestimate. The authors, however, calculated only the diffusion flow, not considering gas seepage by bubble formation, which results in higher overall flow through the sediment–water boundary. Our results are in the first stage of investigation of methane flows in the sediments of the Vistula and Curonian lagoons. Such isolated measurements are insufficient for establishing the methane budget in these basins. The latter task requires year-round monitoring.

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