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EXPERIMENTAL ARTICLES

Sulfate Reduction, Methanogenesis, and Methane Oxidation in the Holocene Sediments of the Vyborg Bay, Baltic Sea

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Abstract—Methane content and the rates of microbial processes of the carbon and sulfur cycles were determined for the sediments of the Vyborg Bay, Baltic Sea. Formation of the gas-bearing surface sediments in the Vyborg Bay was found to depend on the activity of the modern microbial processes of the transformation of organic matter, resulting in production of significant amounts of reduced gases (methane and hydrogen sulfide). Rapid consumption of sulfate in the course of sulfate reduction coupled to organic matter decomposition both suppressed anaerobic oxidation of methane and promoted microbial methanogenesis. The gas-bearing sediments of this area therefore become a source of methane, and methane concentration in the near-bottom water increases significantly.

Keywords: pockmark, gas-bearing sediments, sulfate reduction, methanogenesis, anaerobic oxidation of methane, Vyborg Bay, Baltic Sea.

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The Baltic Sea, due to its geographic location, hampered water exchange, and abundant continental flow, is a highly productive marine environment, with the average primary production of ~190 g C m^{-2} per year and the values for some regions (Danish straits, Gulf of Riga, or the Russian sector of the southeastern Baltic) exceeding 200 g C m^{-2} per year [1]. Both the high productivity of the Baltic waters and significant inflow of the allochthonous organic matter (OM) favor intense processes of OM decomposition in the sediments. Under anoxic conditions, the terminal phase of OM decomposition, involving sulfate reducers and methanogens, results in the formation of great amounts of biogases (methane and hydrogen sulfide). Elevated concentrations of these gases have been reported for many Baltic sites [2, 3]. The first large-scale measurements of the rates of the key microbial processes (sulfate reduction, methanogenesis, and methane oxidation) in reduced sediments of the open sea, in the Gulf of Riga, and in the silts of the Arkona and Gotland Deeps have been carried out in the 1970s–1980s [4]. The highest rates of sulfate reduction (up to 5–6.6 mg S dm^{-3} day^{-1}) were found in the upper sediment horizons (0–20 cm). Deeper in the Holocene sediments, this rate was usually 1–2 orders of magnitude lower. In the silts investigated, methane was produced mainly via CO_2 reduction, with the highest rates of methanogenesis found in the shallow sediments of the Gulf of Riga.

The anomalies in methane distribution in the near-bottom water and bottom sediments of the Baltic Sea, which were discovered in the early 1970s by researchers from the Shirshov Institute of Oceanology, Russian Academy of Sciences, result from discharge of gas-bearing fluids. Their localization is associated with the specific geomorphology of the bottom (depressions, craters, etc.). Similar methane craters (pockmarks), with gas-saturated sediments and elevated methane levels in the near-bottom water, were subsequently found in a number of sites within the Gdansk, Arkona, and Gotland Deeps [5,6].

The craterlike structures (pockmarks) found in the Eckerförde Bay (Germany) at the depth of ~20 m were associated with the discharge of groundwater, rather than with gas emission. However, the rates of sulfate reduction and methane oxidation in the sediments of these pockmarks were higher than at the background stations in the bay [7,8].

The continuous seismoacoustic profiling (CSP) studies of the Vyborg Bay carried out in the 1990s by researchers from Karpisky Russian Geological Research Institute (VSEGEI) revealed the strata of the Holocene aleuro-loamy silts, where scattering of the acoustic signal occurred [9]. Such acoustic anomalies were usually associated with high saturation of the sediments with gases. Local funnel-shaped structures, both reaching the bottom surface and buried in the

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sediment layer, were also revealed. Oval and rounded structures up to 25 m in diameter were subsequently observed in the Vyborg Bay area by the workers of Petrotrans Ltd. These craterlike structures were investigated by VSEGEI in 2007–2009 using side-looking sonar echosounding (SLSE) [9]. Microbiological and biogeochemical investigation of this part of the Baltic Sea had never been carried out.

The goal of the present work was a comprehensive investigation of the microbiological and biogeochemical processes in the gas-bearing sediments and pockmarks of the Vyborg Bay, Baltic Sea.

MATERIALS AND METHODS

The water and bottom sediments were sampled in July 2009 from RV *Ladoga* (90 t) bearing the equipment for geophysical, geologo-geochemical, and microbiological research.

The sampling stations were selected based on the results of continuous seismoacoustic probfiling (CSP) and side-looking sonar echosounding (SLSE).

CSP was carried out using a GEONT-HRP specialized digital complex (Spektr–Geofizika Ltd., Russia). A high-frequency electrodynamic boomer was used as the source of acoustic signals. The band center of the radiation was at 2000 Hz, and the measured level of acoustic noise made it possible to use the 220–3000 Hz bandwidth for reception. The complex included a high-voltage storage system (up to 200 J), a 2-m device to receive the boomer signals, an amplifier (30–10000 Hz) with a set of high- and low-frequency filters, a multichannel analog-digital converter, a digital control unit, and a notebook computer. A special, small catamaran was used to tow the boomer. This complex was used for the search of the zones of gas-bearing sediments with determination of the location of their upper rim (roof). Typically, on the seismograms of such zones the reflective borders immediately below gas-saturated sediments are partially or completely lost.

For detection of craterlike structures on the sediment surface, a CM2 side-looking sonar (C-MAX Ltd., United Kingdom) was used. The swath was chosen so as to obtain a detailed picture of the bottom surface. For the SLSE profiling, the operating frequency of 325 kHz was used, with the swath of up to 150 m. For detailed profiling of selected sites, the operating frequency of 780 kHz was used, with the overall swath from 25 to 50 m. The antenna was towed behind the stern. The data were processed using the dedicated software packages (Octopus Marine Systems Ltd.) and MaxView.

Bottom sediments were sampled with a Niemistö-type hermetic corer and a 4-m direct-flow tube. Geological description of the profiles of the cores on board the vessel made it possible to determine the major lithological and stratigraphic horizons related to the stages of the Baltic Sea development. Water samples were collected with a 5-l plastic bathometer.

For enumeration of microbial cells, the sediment samples were fixed on board with glutaraldehyde (0.5 mL of the 25% solution per 5 mL sediment). The samples were then transported to the laboratory and sonicated in an UZDN-2 device for 2–10 s in pulse mode (22 kHz, 0.015 A). Water solution of acridine orange was used for staining [10]. Bacterial cells were counted under a Zeiss Axioplan Imager fluorescence microscope (Germany).

The rates of microbial processes were determined by the radioisotope method with ^{14}C- and ^{35}S-labeled substrates. Immediately after hauling the samples onboard, aliquots of sediments (3 mL) from the relevant horizons were placed in cut-off 5-mL plastic syringes and sealed with gas-tight butyl rubber stoppers. The labeled substrate (0.2 mL) was injected through the stopper, and the samples were incubated for 1–2 days at 5–7°C. The samples were then fixed with 0.5 mL of 2 N KOH. Subsequent treatment of the samples was carried out in the laboratory as described earlier [11,12]. To determine the rate of methane oxidation (MO), ^{14}C-labeled methane was dissolved in gas-free distilled water and 1 μCi of ^{14}C-methane was added to the sample. The rates of sulfate reduction (SR) and methanogenesis (MG) were determined with ^{35}S-labeled sulfate and ^{14}C-labeled bicarbonate or methyl-labeled ^{14}C-acetate (10 μCi per sample), respectively. The alkali-fixed samples incubated in a refrigerator for 6 h prior to injection of the labeled substrate were used as the controls.

Methane content in the water and sediment samples was determined by the headspace method (phase equilibrium degassing) [13]. The water samples were dispensed into 30-mL penicillin vials and fixed with KOH to suppress microbial processes. A known volume of water was then removed, and the vials were sealed with gas-tight butyl rubber stoppers. The sediment samples collected with a cut-off 2-mL plastic syringe were placed into penicillin vials, filled with degassed water, and after removal of a known volume of water, sealed with butyl rubber stoppers. Methane content in the gas phase was measured on a Kristall 2000 gas chromatograph (Russia) equipped with a flame ionization detector.

Pore water was obtained by 10-min centrifugation of the sediments at 8000 rpm in a TsUM-1 centrifuge (Russia). Alkalinity was determined by titration using the standard reagent kit (Merck, Germany). Sulfate content in silt water was measured on a Staier ion chromatographer (Russia).

Determination of C_{org} content in the sediments was carried out using a TOC-Vcph analyzer (Shimadzu, Japan) equipped with an SSM-5000A device in the Laboratory of Ocean Chemistry, Institute of Oceanology, Russian Academy of Sciences.

For mass spectral analysis ($\delta^{13}C$), methane from the sediments was collected as follows. A 250-mL glass vial was half-filled with the sediment, concentrated salt solution was added to 230 mL, and the vial was hermetically sealed with a rubber stopper and stirred vigorously. In the laboratory, the gas phase was collected with a syringe by replacing the volume with the salt solution and stored under the salt seal. The $\delta^{13}C$ value of methane was measured on a TRACE GC gas chromatograph (Germany) coupled with a Delta plus mass spectrometer (Thermo Electron Corporation, Germany).

Mass spectral measurement of the $\delta^{13}C$ for the carbonate minerals in pore water was carried out with gaseous CO_2 as a working gas. Pore water carbonates were converted to $BaCO_3$, and CO_2 was obtained by the fusion of barium carbonates and tin salts at 560°C. The $\delta^{13}C-CO_2$ value was measured on a Delta Plus mass spectrometer and calculated using the known equation:

$$\delta^{13}C = ([^{13}C]/[^{12}C])_{sample}/([^{13}C]/[^{12}C])_{st} - 1) \times 1000‰,$$

where $([^{13}C]/[^{12}C])_{sample}$ and $([^{13}C]/[^{12}C])_{st}$ are the ratios of ^{12}C and ^{13}C abundance in the sample and standard, respectively. The international PDB standard was used with the $[^{13}C]/[^{12}C]$ of 0,001172. The error of $\delta^{13}C$ measurements did not exceed ±0.1‰.

RESULTS

The stations for detailed investigation were determined according to the results of echosounding and acoustic profiling. The samples of the bottom sediments and near-bottom water were collected at three stations (Fig. 1a) west of Primorsk in the Gulf of Finland, Baltic Sea. Station 1 was located close to a pronounced oval funnel-shaped bottom structure 7–10 m in diameter (Fig. 1b), somewhat resembling the gas craters (pockmarks) known in the other Baltic Sea sites. Its depth relative to the bottom surface was 2–4 m. The upper 15–17 cm of the sediment of the core formed a layer of unsorted greenish-gray sands with admixtures of aleuro-pelitic material and dark inclusions of disperse organic matter. This layer of oxidized or weakly reduced sediments was evidently formed in the Holocene during the littorina and post-littorina stages of the Baltic Sea development. The sand layer was located above gray clays (17–55 cm) with numerous black contractions of amorphous iron sulfides (hydrotroilite); their presence is a diagnostic feature characteristic of the Acilic Lake deposits. The deeper layer (55–205 cm) consisted of the Baltic Ice Lake sediments, represented by gray clays with lens-shaped interlayers of aleuro-pelitic material. Below 100 cm, Eh of the sediments was positive, from 20 to 145 mV. The alkalinity, reflecting the content of carbonate ions in the pore water, varied slightly along the profile, from 1.8 to 2.5 mg-eq L^{-1} (Table 1). The profile of methane content was unusual for coastal shallow sediments. The highest methane content (48 μmol dm^{-3}) was found in the upper subsurface horizons, at 5–20 cm. Below this layer, methane content decreased to 0.6–1.4 μmol dm^{-3}. Sulfate content changed insignificantly along the profile, varying from 4.6 to 5.5 mmol dm^{-3}, with its highest content in the surface horizon. C_{org} content in the sediments was low, 0.16 to 0.22 % (Table 1).

The sediments of stations 2 and 3, from the region where acoustic anomalies were revealed by probing, were significantly different from those of station 1 (Fig 1c). At these stations, the 1.5-m sediment cores consisted of littorina–postlittorina marine deposits. Along all the core length, the deposits consisted of greenish-gray water-saturated fluid clayish aleurites with a small admixture of sand grains. In the 25–100 cm layer, the smell of sulfide was observed, together with the evidence for gas saturation (the core cracked and fell apart on board the ship). The oxidized layer was almost absent at station 3, while the layer of brown oxidized warp at station 2 was ~1 cm thick. At station 3, reduced sediments with negative Eh values were found to the depth of 1 m. At station 2, only the upper 20 cm of the sediments were strongly reduced. Unlike station 1, the alkalinity of the sediments from stations 2 and 3 increased with depth, reaching 14–18 mg-eq L^{-1} below 1m (Table 1, Fig. 2). Methane content in the sediments of these stations was also significantly higher. At station 2, methane content increased with depth from 0.24–0.64 mmol dm^{-3} in the upper 15 cm to 4.10–4.30 mmol dm^{-3} at the depth of 1–1.5 m. At station 3, methane content was even higher, 0.52–3.01 mmol dm^{-3} in the upper horizon (0–12 cm) and 4.50–4.60 mmol dm^{-3} in the 20–70 cm layer. In deeper layers (100–150 cm), methane concentration decreased to 3.16–3.60 mmol dm^{-3}. Elevated methane concentrations were found in the near-bottom water of stations 2 and 3.

At stations 2 and 3, along with increase of methane levels with depth, a drastic decrease in sulfate concentrations was detected in pore water, indicating high rates of sulfate reduction in the upper sediment horizons (Table 1, Fig. 2).

The highest total microbial numbers (TMN) at stations 2 and 3 (Fig. 3), which were found in the near-surface layers (to 5 cm), reached $3.6–4.6 \times 10^9$ cells g^{-1} silt. In the same horizon, the highest diversity of microorganisms was found, while rod-shaped cells predominated. At station 3, filamentous microorganisms constituted up to 10% of the TMN in the 0–3 cm layer. These organisms were usually thin (~0.5 μm), segmented or multicellular. The filamentous forms of the Vyborg Bay sediments differed from *Beggiatoa*-like sulfur bacteria, which are common in OM-enriched marine sediments [14], having significantly thinner cells. At station 1, TMN was 3 to 4 times lower, not

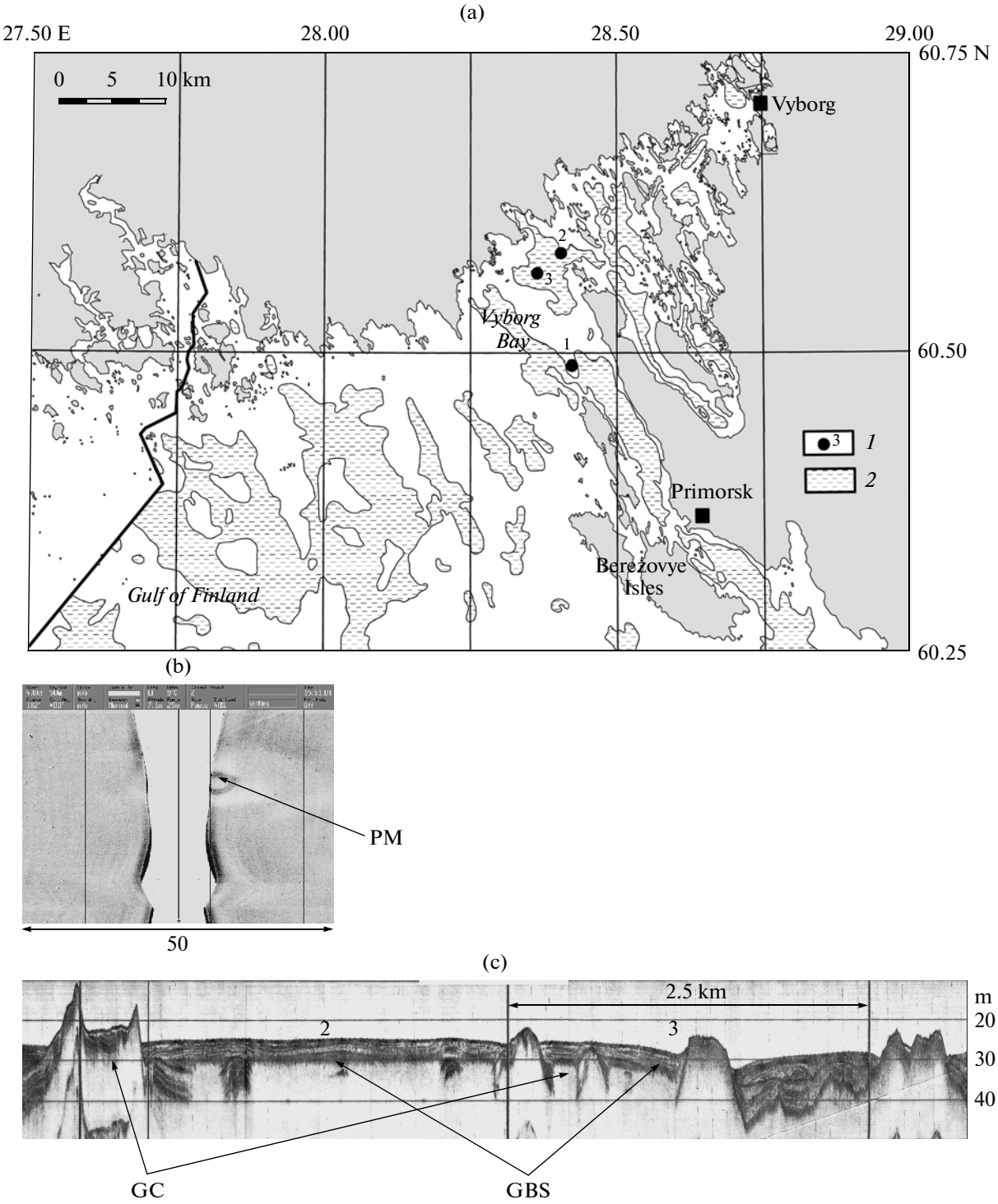

Fig. 1. Investigated polygon in the Vyborg Bay, Baltic Sea. (a): sampling stations (1) and zones of accumulation of modern clayish silts (2). (b): the pockmark-like geomorphological structure (PM) at the site of station 1 revealed by the side-looking sonar. (c): gas-bearing sediments (GBS) according to seismoacoustic probing. GC stands for the glacial complex, 2 and 3 mark the location of the sampling stations.

Table 1. Physocochemical characteristics of the sediments of the Vyborg Bay, Baltic Sea

Station no., depth, coordinates	Horizon, cm	Sediment type	Humidity, %	Eh, mV	Alkalinity, mg-eq L^{-1}	CH_4, mmol dm^{-3} wet silt	SO_4^{2-}, mmol L^{-1} pore water	C_{org}, %	$\delta^{13}C$, ‰	
									CH_4	HCO_3^-
St 1, 26.8 m, 60°29.335 N 28°25.469 E	2–17	Littorina and postlittorina marine deposits	30.0	180	1.8	0.048	5.522	0.22		
	17–25	Acilic Lake	27.4	–38	2.0	0.022	4.474	0.19		
	38–55		27.7	–75	2.0	0.001	4.409	0.18		
	100–110	Baltic Ice Lake	40.0	100	2.0	0.001	4.628	0.19		
	160–170		42.4	20	2.0	0.001	4.912			
	195–200		38.4	145	2.0	0.001	4.989	0.16		
St 2, 25.8 m, 60°33.880 N 28°21.863 E	0–5	Littorina and postlittorina marine deposits	77.1	–190	3.5	0.239	2.918	1.32		–19.8
	10–15		76.3	–250	9.5	0.638	0.408	1.07		
	15–20		73.3	–140	10.0	1.790	0.178			–12.8
	40–50		69.1	–10	12.0	3.161	0.010	2.75	–65.1	–9.7
	100–105		65.5	–10	15.5	4.308	0.010	4.23		0.8
	140–150		65.9	–100	18.0	4.112	0.100	4.17	–63.5	3.2
St 3, 29.5 m, 60°34.970 N 28°24.050 E	0–3	Littorina and postlittorina marine deposits	85.85	–188	6.6	0.522	1.758	4.22		–20.9
	3–8		84.49	–190	6.8	1.741	1.130	5.72		–9.8
	8–12		86.65	–222	7.9	3.014	0.071	6.38		–2.0
	12–18		82.24	–225	9.0	4.037	0.249		–65.5	–1.9
	18–24		83.31	–228	12.5	4.033	0.237	4.80	–63.6	0.7
	24–30		81.53	–217	15.0	4.472	0.021			3.1
	30–35		81.14	–209	13.0	4.527	0.077	4.56	–66.0	5.0
	45–50		77.00	–205	12.5	4.592	0.069	2.23		5.1
	65–70		71.93	–150	14.0	4.156	0.059	3.15	–69.7	4.1
	85–90		68.76	–150	13.5	4.399	0.010			
	100–105		67.16	115	14.0	3.607	0.010	2.80		
	140–150		64.19	–15	14.5	3.158	0.010	3.80	–76.6	

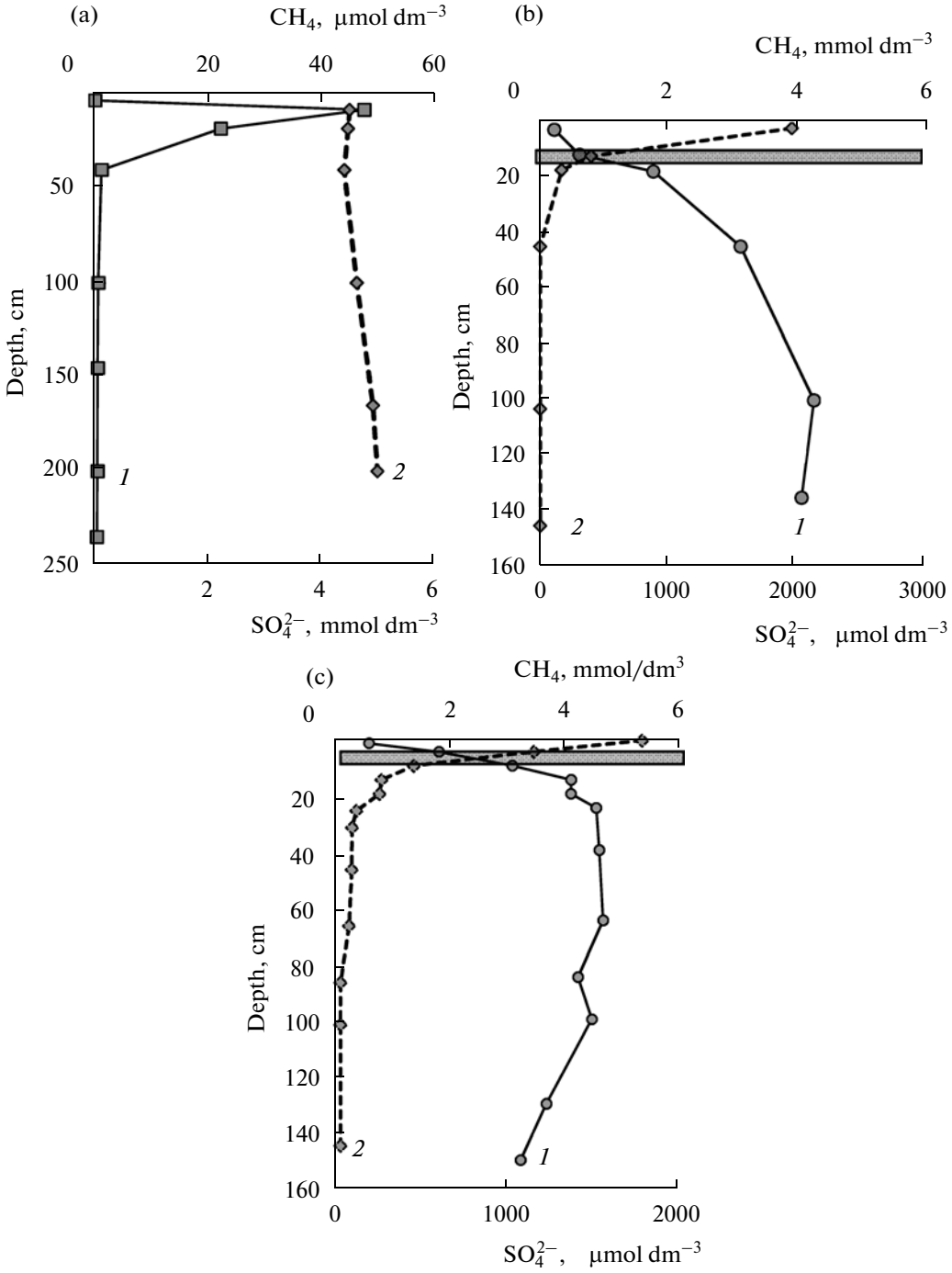

Fig. 2. Profiles of methane (*1*) and sulfate (*2*) in the sediments of the Vyborg Bay, Baltic Sea: station 1 (a), station 2 (b), and station 3 (c). The shaded regions on plates (b) and (c) indicate the methane sulfate transition zones.

exceeding 1 ×10^9 cells g^{-1} silt in the upper horizons. No filamentous forms were found.

Below 5 cm, TMN at stations 2 and 3 decreased two- to threefold and remained almost stable to 80-cm depth. At station 3, the TMN values were always 1.5–3 times higher than at station 2.

Similar to TMN, the highest SR rates of 70 μmol S dm^{-3} day^{-1} (determined by the radioisotope method) were found in the surface horizon of station 3 (Fig. 4). Deeper in the sediment, SR rate decreased rapidly, not exceeding 0.5 μmol S dm^{-3} day^{-1} below 50 cm. A smaller SR maximum of 15–17 μmol S dm^{-3} day^{-1}

was detected in subsurface sediments of station 3 within the 12–24-cm depth interval, where the highest rate of anaerobic oxidation of methane (AOM), 1.4 μmol CH_4 dm^{-3} day^{-1}, was also found (Fig. 5).

The profiles of AOM and methanogenesis (MG) in the Vyborg Bay sediments are presented on Fig. 5. At station 2, a pronounced AOM maximum was found at 15 cm. The MG peak was located immediately below the AOM maximum. Unlike station 2, no pronounced AOM maximum was found in gas-bearing sediments of station 3, where this process occurred from the surface to the 50-cm depth at the rates of 0.9–1.4 μmol dm^{-3} day^{-1}. The rate of methanogenesis varied significantly along the core. The highest MG rate of 4.9 μmol dm^{-3} day^{-1} was detected at 85–90 cm. Since acetoclastic MG was either not detected or occurred at significantly (by 2 orders of magnitude and more) lower rates than the hydrogenotrophic one, only the rates of the latter process were used for the calculations.

The sediments of station 1 exhibited extremely low rates of microbial processes, which occurred only in the upper 20 cm of the sediment, where a certain increase in methane and C_{org} contents was observed (Table 1). The highest rates of SR, MG, and AOM (0.11, 0.005, and 0.007 μmol dm^{-3} day^{-1}) were detected in the upper 17 cm. Radioisotope techniques revealed no evidence of modern microbial processes in the deeper, older deposits of the Acilic and Ice Lake sediments.

The isotopic composition of methane carbon ($\delta^{13}C$) for the horizons of gas-saturated sediments of stations 2 and 3 is shown in Table 1 and Fig. 6a. The $\delta^{13}C$–CH_4 values varied from –63 to –76.6‰, unequivocally indicating its biogenic formation via microbial methanogenesis.

In deeper sediment layers, the isotopic composition of the pore water soluble carbonates at stations 2 and 3 became enriched with the heavy ^{13}C, so that at station 3 its values below 25 cm varied from 3.1 to 5.1‰; at station 2, positive $\delta^{13}C$ values were observed only below 100 cm (Table 1, Fig. 6b).

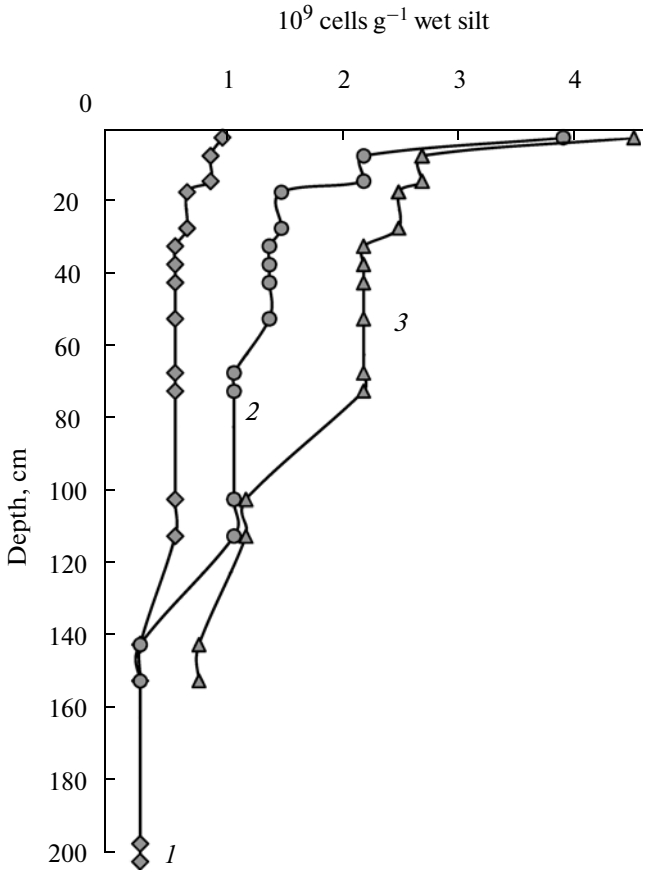

Fig. 3. Total number of microorganisms in the bottom sediments of the Vyborg Bay, Baltic Sea, collected at stations 1 (*1*), 2 (*2*), and 3 (*3*).

DISCUSSION

Microbiological and biogeochemical investigation revealed heterogeneity of the Vygorg Bay sediments. The highest rates of microbial processes were detected in the sediments of station 3, where C_{org} content in the upper 35–40 cm exceeded 4%. The profile of SR rates at this station, with a maximum in the upper 5-cm layer of the sediment, is typical of organic-enriched coastal silts [15], where the oxidized layer, if present, is only several mm thick due to high rates of destruction processes. For station 2, a similar profile was obtained, albeit with lower SR rates (Fig. 4). Due to the high SR rate leading to rapid sulfate consumption in pore water, the sulfate–methane transition zone (SMTZ) at stations 2 and 3 was close to the sediment surface, at 10–15 and 15–20 cm, respectively (Fig. 2). This pattern, which differs from the situation in the shallow eutrophic Danish fjords with similar C_{org} values and SR rates [16], where the SMTZ was located at 0.8–1.2-m depth, may result from water desalination in the Vyborg Bay, with almost 4 times lower sulfate content.

The combination of high OM content and rapid sulfate consumption is known to promote methanogenesis in the sediments [17]. In the sediments of stations 2 and 3, elevated methane content and increased MG rates were observed from the lower SMTZ border (Fig. 5), in agreement with the modern concepts of SR and MG in coastal silts [18] of highly productive marine environments.

High rates of methanogenesis in the sediments of stations 2 and 3 were confirmed by the data on carbon isotopic composition ($\delta^{13}C$) of pore water carbonates. We found that the pore water carbonates at station 3 became ^{13}C-enriched with depth (Fig. 6). The $\delta^{13}C$ value varied from –20.86‰ in the upper 5–15 cm of the sediment to 3.06–4.96‰ at 24–35 cm. At station 2, MG rate was significantly lower, and while pore water carbonates also became heavier with depth, positive $\delta^{13}C$

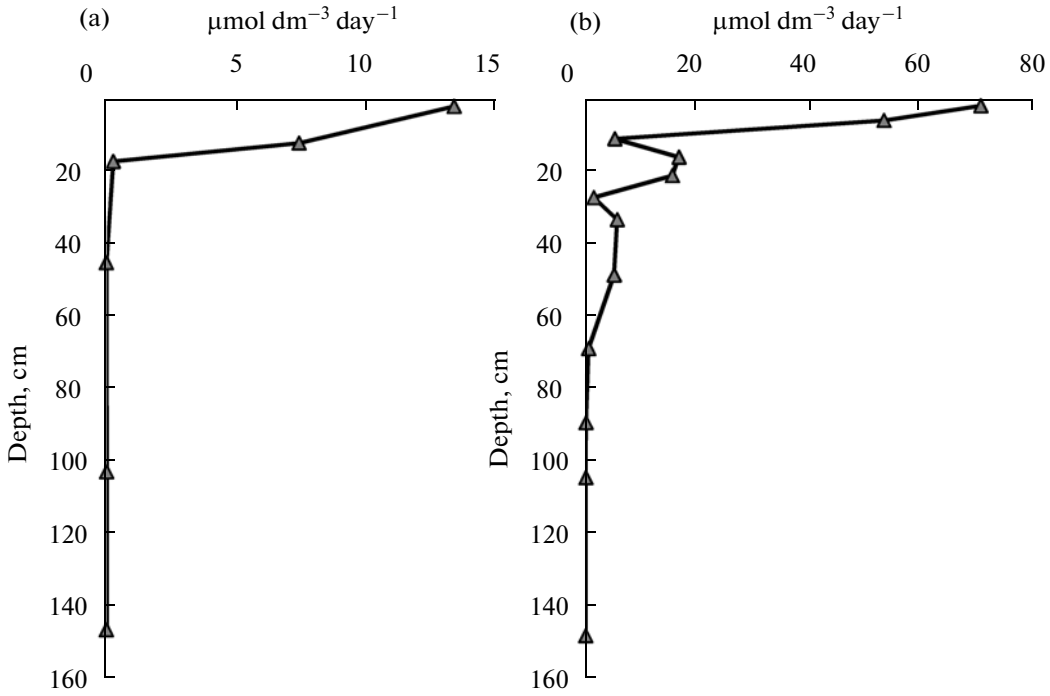

Fig. 4. Sulfate reduction rates in the gas-bearing sediments of the Vyborg Bay, Baltic Sea: station 2 (a) and station 3 (b).

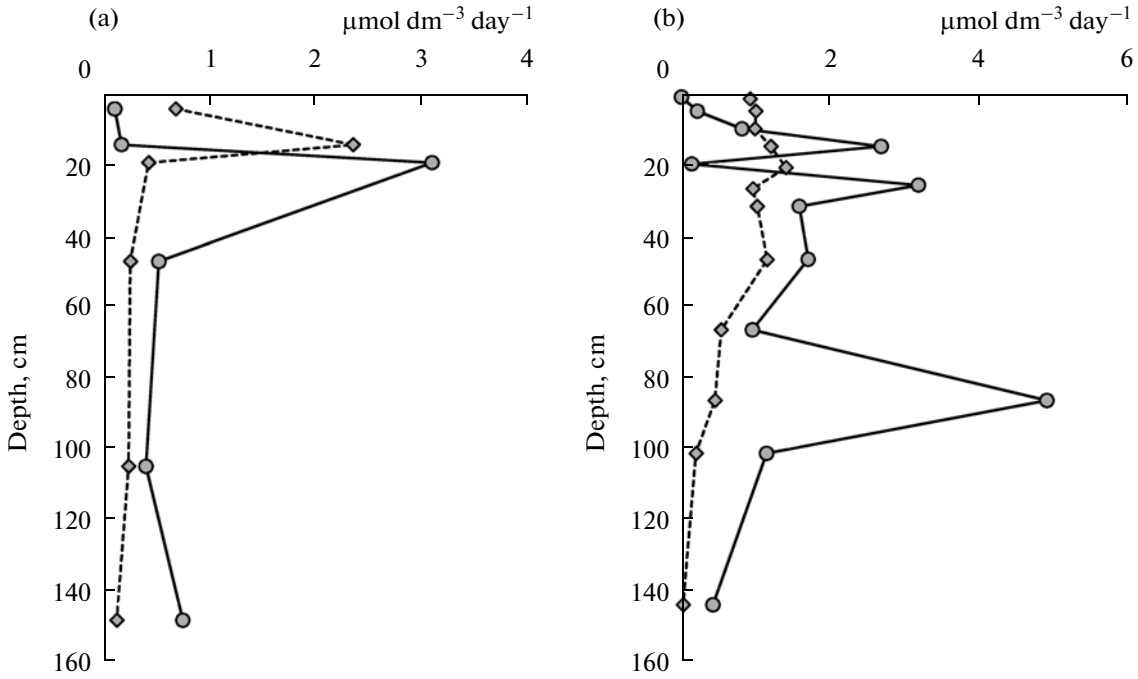

Fig. 5. Rates of methane oxidation (dotted line) and methanogenesis (solid line) in the gas-bearing sediments of the Vyborg Bay, Baltic Sea: station 2 (a) and station 3 (b).

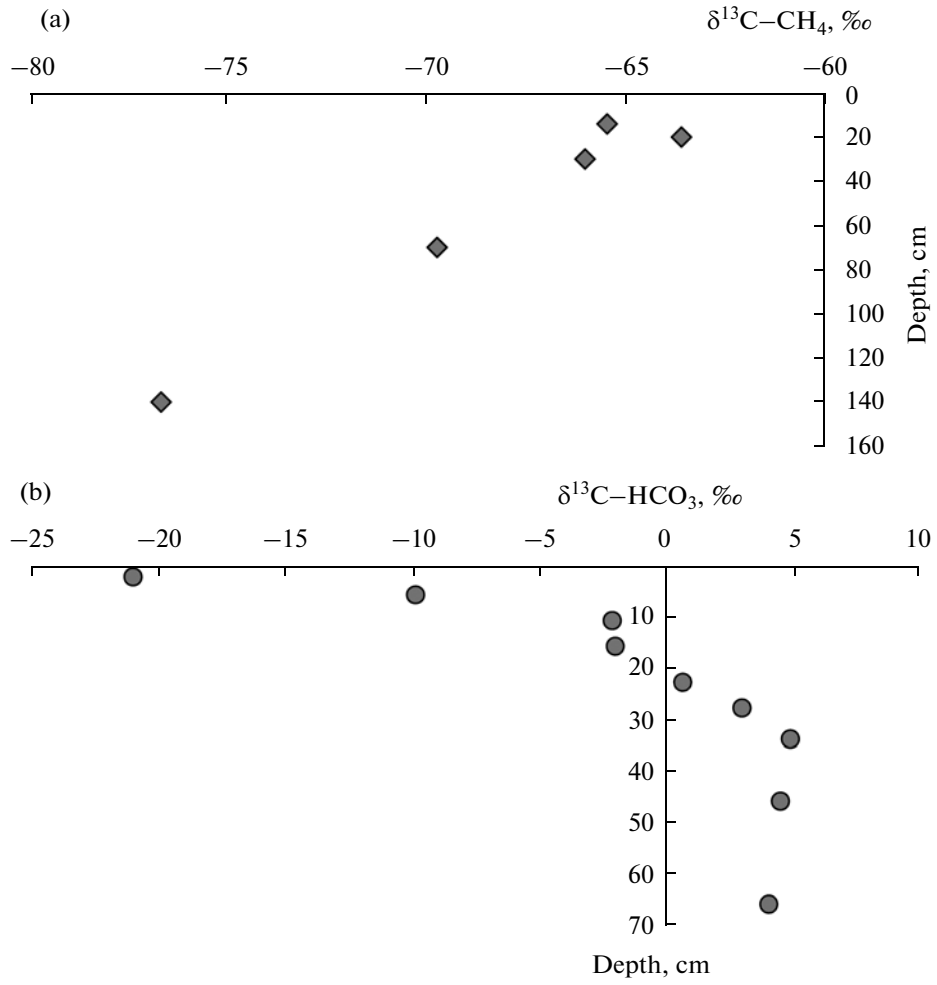

Fig. 6. Isotopic composition ($\delta^{13}C$) of methane (a) and silt water carbonates (b) in the gas-bearing sediments of station 3, Vyborg Bay, Baltic Sea.

values were found only below 50 cm (Table 1). A similar increase in the $\delta^{13}C$ content of pore water carbonates with depth was found in the silts of Eckernförde Bay [19].

The range of $\delta^{13}C$ values for methane at stations 2 and 3 (from –76.6 to –63.5‰) is typical of biogenic methane of microbial origin. The tendency towards enrichment of methane with ^{13}C observed in the upper 40–60 cm of station 3 sediments (Fig. 6) may result from more active ^{12}C consumption in the course of anaerobic oxidation of methane in subsurface silts, resulting in ^{13}C-enriched residual methane [20].

A consortium of methanotrophic archaea and sulfate-reducing bacteria is presently considered responsible for anaerobic oxidation of methane: $CH_4 + SO_4^{2-} \longrightarrow HCO_3^- + HS^- + H_2O$ [21, 22]. Taking into account the stoichiometry of the AOM reaction, the calculated integral rates for SR and AOM in the upper 1.5-m sediment layer show (Table 2) that reduced sulfur produced in the course of AOM (1.21 mmol m^{-2} day^{-1}) was about 16% of the HS^- production coupled to OM oxidation (7.37 mmol m^{-2} day^{-1}).

Comparison of the integral rates of methane production and oxidation at station 3 sediments showed that daily methane production was more than 3 times higher than oxidation (Table 2). While integral rates of sulfate reduction, methanogenesis, and methane oxidation at station 2 were significantly (2 to 8 times) lower, methanogenesis also prevailed over methane oxidation. Since the rates of methanogenesis at stations 2 and 3 exceeded the rates of methane oxidation, accumulation of significant amounts of biogenic methane in the surface sediments occurred.

The physicochemical, gas–geochemical, and microbiological characteristics of the sediments collected at station 1 in the zone of the crater-shaped geomorphological structure differed from those of the sediments at stations 2 and 3. The modern postlittorina sediments were limited to the upper 15–20 cm. In the uppermost horizons of station 1 sediments, increased methane content and elevated numbers of

Table 2. Integral rates of microbial processes in the upper 1.5 m of the sediments of the Gulf of Finland, Baltic Sea

Station no./depth	Rates of microbial processes, mmol m^{-2} day^{-1}		
	Sulfate reduction	Methanogenesis	Methane oxidation
1/26.1	0.17	<0.01	<0.01
2/25.8	1.06	0.87	0.63
3/29.5	8.58	3.80	1.21

microorganisms were observed, along with the low rates of microbial processes. In the deeper layers of nearly homogeneous silt with low content of both methane and organic matter, radioisotope measurement of microbial activity revealed its absence or extremely low rates. In these horizons, the calculated integral rates for MG and AMO, although comparable, were several orders of magnitude lower than at stations 2 and 3 (< 0.01 mmol m^{-2} day^{-1}). Thus, formation of the craterlike structure in the Vyborg Bay was certainly not related to modern gas seepage. Such structures may be formed as a result of groundwater discharge. A similar phenomenon was observed previously in the Eckernförde Bay [7]. However, no indication of desalination, which is typical of the zones of groundwater seepage, was found in the pore water of station 1 surface sediments. Since anthropogenic origin of the craters can not be ruled out, further research is required to elucidate this issue, including direct sampling by divers.

In conclusion, it should be noticed that preliminary estimates by the workers of the Russian Geological Research Institute indicate the presence of modern gas-saturated silts on at least one third of the shallow Vyborg Bay area (shaded area on Fig. 1a). Our research demonstrated that formation of gas-bearing sediments in the Gulf of Finland depends on the activity of modern microbial OM transformation, resulting in production of significant amounts of reduced gases (CH_4 and H_2S). Rapid consumption of sulfate in the course of sulfate reduction coupled to OM decomposition both inhibits AOM and promotes microbial methanogenesis. The combination of high MG rates and low rates of methane oxidation may result in the formation of an ascending methane flow. Since the near-bottom water of the studied stations contains more CH_4 than the surface waters, gas-bearing sediments of the Vyborg Bay are a source of methane, which seeps into the water column.

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