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## The Biogeochemical Cycle of Methane in the Coastal Zone and Littoral of the Kandalaksha Bay of the White Sea

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**Abstract**—Microbiological and biogeochemical investigations of the processes of methane production (MP) and methane oxidation (MO) in the coastal waters and littoral of the Kandalaksha Bay of the White Sea were carried out. The studies were conducted in the coastal zones and in the water areas of the Kandalaksha Preserve, Moscow State University White Sea Biological Station, and the Zoological Institute (RAS) biological station in August 1999, 2000, and 2001 and in March 2001. The rate of CO<sub>2</sub> assimilation in the shallow and littoral sediments was 35–27800 μg C/(dm<sup>3</sup> day) in summer and 32.8–88.9 μg C/(dm<sup>3</sup> day) in winter. The maximal rates of MP were observed in the littoral sediments in the zone of macrophyte decomposition, in local depressions, and in the estuary of a freshwater creek (up to 113 μl/(dm<sup>3</sup> day)). The maximal level of MO was observed in the shallow estuarine sediments (up to 2450 μl/(dm<sup>3</sup> day)). During the winter season, at the temperature of –0.5 to 0.5°C, the MP rate in the littoral sediments was 0.02–0.3 μl/(dm<sup>3</sup> day), while the MO rate was 0.06–0.7 μl/(dm<sup>3</sup> day). The isotopic data obtained indicate that the C<sub>org</sub> of the mats and of the upper sediment layers is enriched with the heavy <sup>13</sup>C isotope by 1–4‰ as compared to the C<sub>org</sub> of the suspension. A striking difference was found between the levels of methane emission by the typical littoral microlandscapes. In fine sediments, the average emission was 675 μl CH<sub>4</sub>/(m<sup>2</sup> day); in stormy discharge stretch sediments, it was 1670 μl CH<sub>4</sub>/(m<sup>2</sup> day); and under stones and in silted pits, 1370 μl CH<sub>4</sub>/(m<sup>2</sup> day). The calculation, performed with consideration of the microlandscape areas with a high production, allowed the CH<sub>4</sub> production of 1 km<sup>2</sup> of the littoral to be estimated as 192–300 l CH<sub>4</sub>/(km<sup>2</sup> day).

*Key words:* microbial processes, microbial number, methanogenesis, methane oxidation, methane production, littoral, the White Sea.

Qualitative estimation of methane inflow to the atmosphere from different ecosystems is presently an important task of microbial biogeochemistry and a subject of many studies [1, 2]. The flux of newly formed methane is determined as the difference between the rates of its production (MP) and oxidation (MO). In a number of natural and artificial ecosystems, activities of microorganisms consuming and producing methane were found. Investigations and calculations demonstrate that such terrestrial water-soaked ecosystems as bogs and rice paddies are the main sources of atmospheric methane [3, 4]. Marine ecosystems are not usually considered to be substantial sources of atmospheric methane. The methane produced in the sediments is oxidized in the water column by methanotrophic bacteria [5].

The coastal zone of seas and oceans is a natural barrier on the border between marine and terrestrial ecosystems. All biogeochemical processes are most pro-

nounced in the coastal zone of seas with pronounced tidal phenomena. The coastal waters are closely connected with the *littoral*, which is defined as the area located in the zone influenced by the tides, the high and low tide levels being its lower and upper boundaries [6]. The littoral is subject to noticeable diurnal and seasonal fluctuations of temperature, salinity, humidity, aeration, etc. The littoral has a pronounced zonal structure determined by the level of tidal effects, as well as microzonality related to its microprofile [7]. The littoral is closely connected to the sublittoral, i.e., the border zone between the littoral and the shallow sea, and to the supralittoral, the territory connected with the sea during seasonal and storm events.

Due to its physical and geographic properties, the coastal zone of the Kandalaksha Bay of the White Sea is a convenient site for studies of MP and MO. A substantial portion of the White Sea coastline is covered with macrophytes; the area covered is 1000 km<sup>2</sup>, and

the total biomass is 1.5 million tons [8]. In the formation of the coastal ecosystem, the decomposition of organic matter of both marine and terrestrial origin is involved. The coastal sediments vary greatly in the content of organic matter, in the periodicity of their contact with seawater, and in the effects of freshwater effluent. These are the factors determining the dynamics of microbial processes of MP and MO.

The main objective of our work was to reveal the regularities in the distributions of microbial numbers and of MP and MO intensities in the sediments and water column of the coastal zone and in characteristic microlandscapes of the littoral of the Kandalaksha Bay of the White Sea.

## MATERIALS AND METHODS

**Brief characterization of the region of work.** The materials for our investigation were obtained in a series of expeditions organized by the Institute of Microbiology, Russian Academy of Sciences, in August 1999 and 2000 and March and August 2001. The study was conducted in the waters and coastal zone of the Kandalaksha preserve, the Moscow State University White Sea Biological Station (BBS), and the Kartesh Biological Station of the Zoological Institute of the Russian Academy of Sciences. For the sake of convenience, the numerical data referring to the stations studied are presented as two tables. In Table 1, the data on the water column and on the coastal shallow-water sediments are presented. The coastal stations are in turn subdivided into three groups: (1) the stations of the open part of the bay; (2) the stations of the minor bays; (3) the abandoned mussel plantations and the Bab'e More Bay. In Table 2, the littoral stations are included; these stations are also subdivided into groups according to the typical littoral microlandscapes. The numeric index of each station mentioned in the text and in the tables includes the year and the station number proper. The scheme of the location of the sampling stations and the description of samples are given in a previously published paper [9].

**Research methods.** The coastal water samples were taken with a 1-l glass bathometer. To characterize the trophic state of the microlandscapes studied, primary production and dark CO<sub>2</sub> assimilation were determined using a radiocarbon modification of the bottle method [10]. For each sampling horizon, two transparent and one dark bottle were inoculated with NaH<sup>14</sup>CO<sub>3</sub> and incubated for 2–8 h in situ on a buoy station at the corresponding horizons. After the incubation, the contents of the bottles were filtered through 0.2-μm nylon membrane filters. To remove residual carbonates, the filters were washed with large volumes of slightly acidified filtered seawater.

The sediment sampling was carried out using a limnological stratimeter. The littoral mats and sediments were sampled with a plastic tube with a sharpened edge. The samples were transferred to 5-cm<sup>3</sup> plastic

syringes with rubber pistons and cut-off edges and closed without air access with gas-tight rubber stoppers. The rates of microbial dark and light carbon dioxide assimilation, MP, and MO were determined using the radioisotope method with NaH<sup>14</sup>CO<sub>3</sub>, <sup>14</sup>CH<sub>3</sub>COONa, and <sup>14</sup>CH<sub>4</sub>. For this purpose, the syringes with sediment samples and the glass bottles with water samples were inoculated with 0.1–0.2 ml of the respective labeled compound and incubated in situ. The samples were incubated at native temperature for 3–8 h in summer and for a day in winter. The littoral samples were incubated directly at the sampling site. After the incubation, the water and sediment samples were fixed with 2 ml of 1 N KOH. The separation of <sup>14</sup>C products and radioactivity measurement on a RackBeta 1219 scintillation counter (LKB, Sweden) were performed as described previously [11].

Direct determination of the methane flux in the ecosystems studied was performed by the chamber method using plastic chambers 170 mm in diameter and 160 mm in height. The exposure started when the tidal waters left the site. Gas sampling from the chambers was performed every 30 min. During the sampling time, the pH and the redox potential were determined using a pH 320/Set-1 potentiometer (Germany). Acetate was determined in distilled and concentrated samples using a Biotronic ion chromatograph (Germany). Methane concentration in the sediments and water column was determined by the desorption method on a Khrom-5 gas chromatograph equipped with a flame ionization detector. Total bacterial numbers were determined by the fluorescence method on DAPI-stained 0.2-μm polycarbonate membrane filters. The isotopic compositions of the organic matter carbon (δ<sup>14</sup>C<sub>org</sub>) and of the bicarbonate ion carbon (δ<sup>14</sup>C-HCO<sub>3</sub><sup>-</sup>) were determined on an MI-1201B mass spectrometer (Ukraine) equipped with an SNG-3 three-channel system of gas admission. The accuracy of determination was ±0.2‰. The methods used were described in detail in [12].

## RESULTS

**Total microbial number and light and dark CO<sub>2</sub> assimilation.** Total bacterial numbers varied from 20000 to 600000 cells per milliliter (Table 1). For some stations, a decrease in the bacterial numbers from the surface downwards was observed, although this tendency was not universal. The intensity of dark CO<sub>2</sub> assimilation in the water column of subcoastal stations varied slightly, in the range 1.84–12.8 μg C/(l day) in summer and between 0.44 and 1.38 μg C/(l day) in winter. Compared to the water column, the intensities of this process in the sediments of shallow waters (Table 1) and of the littoral (Table 2) varied widely: from 35 to 27800 μg C/(l day) in summer and from 32.8 to 88.9 μg C/(l day) in winter.

**Table 1.** General characterization of the stations of the coastal zone of the Kandalaksha Bay of the White Sea

Station no., coordinates	Station location	Sea depth, m; sediment horizon, cm	Cl <sup>-</sup> , g/l	Bacterial numbers, ×10 <sup>4</sup> cells/ml	Dark CO <sub>2</sub> assimilation, µg C/(dm <sup>3</sup> day)	Photosynthetic production		CH <sub>4</sub> , µl/dm <sup>3</sup>	CH <sub>4</sub> production, µl/(dm <sup>3</sup> day)	MO rate, µl/(dm <sup>3</sup> day)	Methane portion oxidized to CO <sub>2</sub> , %
						µg C/(l day)	mg C/(m <sup>2</sup> day)				
Stations of the open part of the bay											
00-10	Krasnaya Bay, beyond Cape Kuzokotskii	0 18	16.4	20 22	3.12 1.84	5.1 3.5	77.4	0.08 0.09		0.001 0.001	
99-11	Sea channel in line of Telyachii Island	0 18	5.3	60 20	5.5 6.0	12.9 7.2	180	0.98 0.66	3.5	0.005 0.001	50
99-6	Oil base opposite the pier	0 13	6.4	20 40	7.5 8.8	10.2 10.8	146	0.55 0.28	5.5 5.8 8.3	0.005 0.002	50 67 25
99-4	Buoy opposite Ovechii Island	0 23	11.7	15 6	12.8 7.4	14 9.6	271	0.38 0.30	7.6 4.5	0.003 0.002	75 71
99-10	Remote part of a small bay	0 13	5.9	30 10	6.0 8.0	17.4 8.0	165	0.53 0.32	19.1 28.3	0.003 0.001	53 67
99-9	Port of Kandalaksha	0 19.5	15.3	20 4	7.7 12.0	19.6 8.0	269	0.91 0.32		0.003 0.002	97
99-2	Voron'ya Bay, central part	0 6	9.5	40 20	8.9 12.6	17.4 10.8	84.6	0.48 0.38		0.007 0.005	73
99-12	Sea channel at the port of Kandalaksha	0 25	2.2	40 4	3.4 5.8	12.0 4.8	210	0.60 0.35		0.005 0.007	46
											68 51
Stations in little bays or separated from the open bay by island chains											
67°008'145 N 032°017'808 E		0-2 2-10 10-17									71 38 80
67°009'091 N 032°022'658 E		0-3 3-13									97
66°056'654 N 032°025'677 E		0-7 7-15									55 46
67°008'214 N 032°023'944 E		0-10 10-17									68 51

Table 1. (Contd.)

Station no., coordinates	Station location	Sea depth, m; sediment horizon, cm	Cl <sup>-</sup> , g/l	Bacterial numbers, ×10 <sup>4</sup> cells/ml	Dark CO <sub>2</sub> assimilation, µg C/(dm <sup>3</sup> day)	Photosynthetic production		CH <sub>4</sub> , µl/dm <sup>3</sup>	CH <sub>4</sub> production, µl/(dm <sup>3</sup> day)	MO rate, µl/(dm <sup>3</sup> day)	Methane portion oxidized to CO <sub>2</sub> , %
						µg C/( day)	mg C/(m <sup>2</sup> day)				
99-8 67°009'446 N 032°020'482 E	Remote part near the Virna River	0	5.6	10	8.5	18.0	119	1.0		0.01	
		7		20	9.8	16.0		1.2	9.6	0.006	61
00-2 66°031'20 N 033°001'07 E	Chernorechen- skaya Bay, remote part	0	11.2	8	6.14	17.0	68	0.14	58.8	0.0022	72
		4.5		25	5.22	13.3		0.14		0.0009	
00winter-01 66°020'01 N 033°010'10 E	Small bay near Kartesh station	0	12.1	2	0.44	1.8	49	0.38	0.56	0.0005	59
		5		2	0.73	1.0		0.28	0.71	0.0004	72
		10		2	1.4			0.41	0.90	0.0009	73
		20		3	1.38			0.28	1.15	0.0004	77
		40		4	1.14			0.33		0.0004	
		0-7			88.9			0.9	0.67	0.0033	64
		7-15			57.7			1.0	0.87	0.008	88
Shallow Bab'e More Bay and abandoned mussel plantations											
99-19 66°037'100 N 033°010'100 E	Bab'e More (central part)	0	9.1	6	3.7	10.4	364	0.28		0.0014	
		5		4	4.5	11		0.28		0.0011	
		12.5		10	6.8	24.8		0.34		0.0051	
		25		5	8.0	12.0		0.60		0.0026	
		0-5			2908			7.1	1.0	0.16	81
		5-15			182			6.0	7.2	0.39	79
		15-23			790			6.0	3.8	0.10	70
		23-30			54			6.5	12.0	0.09	89
99-17 66°028'554 N 033°025'585 E	Mussel plantations (Island Lushov)	0	13.9	20	5.0	17.2	218	0.25		0.0026	
		14		30	7.2	14.0		0.28		0.0029	
		0-1			625			85	1.1	3.55	87
		1-5			427			133	2.84	4.75	84
		5-12						143	4.24	2.84	80
00-4 66°028'554 N 033°025'585 E	Mussel plantations (Island Lushov)	0	13.5	35	4.7	18.6	233	0.11		0.0086	
		5		22	3.1	14.8		0.09		0.0014	
		10		15	2.76	16.8		0.10		0.0009	
		15		24	2.88	12.0		0.11		0.0008	
		0-2			1013			1.9	0.36	0.097	93
		2-10			765			2.7	0.61	0.14	93

**Table 2.** General characterization of the stations of the littoral

Station no., coordinates	Station location	Sediment horizon, cm	Cl <sup>-</sup> , g/l	Eh, mV	Dark CO <sub>2</sub> assimilation, µg C/(dm <sup>3</sup> day)	Photosynthetic production		CH <sub>4</sub> , µl/dm <sup>3</sup>	Process rates, µl/(dm <sup>3</sup> day)		Methane portion oxidized to CO <sub>2</sub> , %
						µg C/(dm <sup>3</sup> day)	mg C/(m <sup>2</sup> day)		CH <sub>4</sub> production	CH <sub>4</sub> oxidation	
Bacterial mats and sediments in the shallow reservoirs on the littoral											
99-14-1 66°032'90 N 033°008'05 E	Lake Polusolence, the mouth of a freshwater stream	Pink mat, 0-1 Sediment, 1-7 5-7	770 820 790	-70 -125 -80	16200 9400 1100	55500	555*	3825 1371 1012	5.7 69.6 75.9	198 98.2 11.5	85 60 92
99-14-2 66°032'90 N 033°008'05 E	Lake Polusolence, mats near the mainland shore	White mat, 0-1 Pink mat, 0-1	3180 3100	-80 -90	4100 12700	6040 19700	60.4* 197*	120 120	23.2 14.6	2.64 5.04	55 50
99-14-3 66°032'90 N 033°008'05 E	Lake Polusolence, mats near the island shore	Green mat, 0-1 Pink mat, 0-1 Sediment, 1-2 2-20	3200 3530 3600 3600	110 -60 -150 -290	5300 27800 3900 1050	8500 46800	85* 468*	120 120	11.6 78.7	4.81 3.55	42 62
00-14-1 66°032'90 N 033°008'05 E	Lake Polusolence, the mouth of a freshwater stream	Pink mat, 0-2 Sediment, 2-5 5-10 10-15	5420 5400 5460 5420	-50 -90 30 50	4980 3430 1210 980	11300	226**	438 1480 1810 1415	6.33 48.6 77.8 64.6	7.5 32.4 54.0 13.6	57 49 41 72
00-14-2 66°032'90 N 033°008'05 E	Lake Polusolence, mats near the mainland shore	Olive mat, 0-1 Pink mat, 0-1	5520 5500	-70 -90	3760 2050	7940 8810	79.4* 88.1*	25.9 16.7	16.9 12.7	8.3 6.1	85 82
00-14-3 66°032'90 N 033°008'05 E	Lake Polusolence, mats near the island shore	Pink mat, 0-1 Sediment, 1-3 3-7	5860 5880 5900	40 -150 -160	18460 6600 3900	26500	265*	269.2 68.5 73.8	13.4 14.7 26.5	12.7 11.4 11.5	61 59 59
01-14-1 66°032'90 N 033°008'05 E	Lake Polusolence, the mouth of a freshwater stream	Pink mat, 0-5 Sediment, 5-15	6500 6400	-230 -160	25110 3947	29200	584**	909 1127	15.55 25.7	11.7 16.8	79 77
Sediments of the open area of the littoral											
99-21 66°032'80 N 033°004'5 E	BBS, sediment along the upper waterline of the sandy littoral	0-10	1520 1470	80	510	ND	ND	4.8 8.6	0.88 1.44	0.16 0.23	87 82
Finely dispersed sediments containing organic matter (soil humus) at different littoral levels											
99-1 66°056'654 N 032°025'677 E	Voron'ya Bay, soil humus sites at the lower part of the littoral	0-0.2 0.2-1 1-5	10180 9950 10050	100 -80 -10	13400 10800 5900	ND	ND	1577 7331 15627	17.2 41.0 112.6	966 2448 180	95 92 76
00-8 66°032'99 N 033°007'14 E	BBS, soil humus sites on the littoral	0-3 3-10 10-20	9880 9860 9940	-20 -115 -30	4430 1425 225	ND	ND	2.7 12.2 12.4	0.3 1.65 2.90	2.1 0.402 0.20	64 52 45
99-22 67°005'6 N 032°043'2 E	Luven'ga, Ilistaya Bay, soil humus sites	0-3 3-10	6600 6950	-60 -150	940 310	ND	ND	446.3 427.5	12.9 32.7	24.59 10.53	86 87

Table 2. (Contd.)

Station no., coordinates	Station location	Sediment horizon, cm	Cl <sup>-</sup> , g/l	Eh, mV	Dark CO <sub>2</sub> assimilation, µg C/(dm <sup>3</sup> day)	Photosynthetic production		CH <sub>4</sub> , µl/dm <sup>3</sup>	Process rates, µl/(dm <sup>3</sup> day)		Methane portion oxidized to CO <sub>2</sub> , %
						µg C/(dm <sup>3</sup> day)	mg C/(m <sup>2</sup> day)		CH <sub>4</sub> pro- duction	CH <sub>4</sub> oxi- dation	
01-06 66°032'95 N 033°004'01 E	BBS, soil humus sites on the littoral	0-15	9860	-220	2980			82	3.38	1.72	82
99-20 66°032'80 N 033°004'5 E	BBS, stormy discharge stretch	0-5	9450 9500	-150	5820	ND	ND	5.6 48.5	1.75 12.8	2.20 6.93	80 73
01-03 66°032'78 N 033°010'05 E	BBS, stormy discharge stretch in the mouth of a fresh- water stream on the littoral	0-5 5-20	5690 5900	-330 -280	19760 3570			493 247	25.6 26.4	11.5 11.4	91 93
00-9 66°032'99 N 033°007'14 E	BBS, a silted "bath" on the littoral	0-1 1-5	9800 9860	120 -15	9757 2604	ND	ND	1.6 1.5	1.19 2.1	1.7 1.06	85 61
99-23 67°005'4 N 032°043'1 E	Luven'ga, a silted pit near Gorelyi Isle	5-10 0-4 4-10	9940 5860 5860	10 20 -220	816 2430 1310	ND	ND	2.2 3825 25322	2.79 2.07 105	0.59 219 145	61 89 89
01-05 66°032'99 N 033°007'14 E	BBS, a pit under a stone at the lower part of the littoral	0-10	9940	-350	12740	18700	374**	16.3	10.7	4.8	71
00-5/2 66°032'99 N 033°007'14 E	BBS, a pit near a stone at the lower waterline of the littoral, during low tide	Mat, 0-1 Sediment, 1-8 8-11	9940 9850 9880 9840	-65 -95 -75 -340	17680 9740 6086 8160	ND	ND	29.6 60.9 84 64	2.28 7.41 10.9 11.85	6.60 6.53 1.49 4.5	71 81 58
01-04 66°032'78 N 033°010'05 E	BBS, a pink mat in the mouth of the freshwater stream on the littoral	0-7	9840	-340	8160	19800	396**	64	11.85	4.5	58
01 winter-6 66°020'01 N 033°041'1 E	Kartesh, the upper water- line of the littoral	0-10	12540	-50	33.9	ND	ND	31.9	0.336	0.70	30
01 winter-7 66°020'01 N 033°041'1 E	Kartesh, central part of the littoral	0-5 5-10	12600 12580	-20 -60	32.8 39.1	ND	ND	5.8 18.4	0.022 0.016	0.33 0.22	45 38
01 winter-8 66°020'01 N 033°041'1 E	Kartesh, central part of the littoral	0-15	12460	10	86.1	ND	ND	3.8	0.30	0.062	36
01 winter-9 66°020'01 N 033°041'1 E	Kartesh, the lower waterline with a <i>Fucus</i> community	0-15	12540	-50	46.8	ND	ND	11.6	0.21	0.322	43

\* Photosynthetic production was calculated for the 0-1 cm layer. \*\* Photosynthetic production was calculated for the 0-2 cm layer.

The photosynthetic production in the water column (Table 1) varied in August in the range 3.5–24.8  $\mu\text{g C}/(\text{l day})$  (since the experiments were conducted during polar summer, we consider it necessary to specify that the unit “day” in this paper has its most common scientific meaning, i.e., 24 h). The maximal production was usually found in the uppermost horizon of the water column, although at some stations (99-6, 99-8, 99-17, and 00-4) the production values near the bottom were close to the surface values. In the Bab'e More (station (st.) 99-19), the maximal production was found in the 6.8-m layer; this finding is in accordance with data on the tidal mixing of the surface layer only of this partially isolated water body. The production estimates for the water column showed that the values varied from 68 to 364  $\text{mg C}/(\text{m}^2 \text{ day})$  (Table 1). The primary production measured in winter under the ice layer was 49  $\text{mg C}/(\text{m}^2 \text{ day})$ .

In the 1–2 cm layer, the photosynthetic production was 6040–55500  $\mu\text{g C}/(\text{dm}^3 \text{ mat day})$  (Table 2). The production in the Lake Polusolenoe mats calculated for the 1–2 cm layer varied between 60 and 584  $\text{mg C}/(\text{m}^2 \text{ day})$ . Similar values of photosynthetic production (374 and 396  $\text{mg C}/(\text{m}^2 \text{ day})$ ) were obtained for the littoral mats (sts. 01-04, 01-05).

**Methane production process.** Methane production in the water column in all of the horizons studied varied from 0.08 to 1.2  $\mu\text{l}/\text{l}$ . At most of the stations, the methane concentration in sediments was several to tens of microliters per  $\text{dm}^3$ . Hundreds of microliters per  $\text{dm}^3$  were found in the sediments of stations 99-12, 99-2, and 99-17. A high methane content was demonstrated for the sediments of station 99-8 (1.2–16.8  $\text{ml}/\text{dm}^3$ ). The methane content in the littoral sediments was found to vary greatly. At some stations, the methane concentration reached 15–25  $\text{ml}/\text{dm}^3$  (sts. 99-1, 99-23).

At most of the shallow coastal stations, MP intensities were very low (as a rule, below 1  $\mu\text{l CH}_4/\text{dm}^3$  wet sludge per day). Higher values of MP intensity were found in the lower horizons of the columns at some stations (99-9, 99-12, and 99-19: up to 58.8  $\mu\text{l CH}_4/(\text{dm}^3 \text{ day})$ ) in the part of the bay near the Virna River. This high  $\text{CH}_4$  concentration, together with the relatively low rate of methane production in the 0–20 cm horizons of columns 99-12 and 99-8, indicate that active MP possibly occurs deeper in the sediment. During the winter season, when the temperature was from  $-0.5$  to  $0.5^\circ\text{C}$ , MP rates were 0.67–0.87  $\mu\text{l}/(\text{dm}^3 \text{ day})$ .

As a rule, the MP rate increased with the sediment depth. The MP rate profiles obtained at stations 99-1, 99-8, and 99-23 indicate that the maximal rates possibly occur in the deeper horizons, not studied in this experiment. The calculated methane production rates per square meter of the sediments are therefore accepted as the minimally possible. Active MP processes were detected not only in the reduced horizons of the sediments but also in the layers with a positive redox potential (sts. 99-1, 00-2, etc.). This observation

is rather unusual, although similar data have been reported by other researchers (for semidecomposed bacterial mats in White Smokes Lake [11]). The high MP activity is most probably due to the presence in the sediment of local anoxic microenvironments, where the MP processes actually occur.

The research on Lake Polusolenoe was performed at permanent stations during three summer seasons. The differences in the water level in the lake and its mineralization were caused by the annual variations of the weather and storm conditions (Table 2). At point 14-1, which was located in the mouth of a freshwater creek, the lowest MP rate (up to 25.7  $\mu\text{l}/(\text{dm}^3 \text{ day})$  in the sediment under the mat) was observed in 2001. The studies of 1999 and 2000 revealed that MP rates in the sediment below the mat were respectively 3.5 and 3.1 times higher than the 2001 data.

In the sediment columns collected on the littoral, MP rates varied widely (Table 2). The lowest values (0.88–1.44  $\mu\text{l}/(\text{dm}^3 \text{ day})$ ) were found in the column of reduced sediment from the silt-sandy littoral (st. 99-21). The highest values were shown to occur in the fine sediments, in the sediments under decomposing macrophytes, in local depressions, and in the mouth of a freshwater creek (up to 112  $\mu\text{l}/(\text{dm}^3 \text{ day})$ ). The research performed on the littoral during the winter season revealed that MP in ice-and-snow-covered sediments (st. 01winter-6-9) is very low and does not exceed 0.336  $\mu\text{l}/(\text{dm}^3 \text{ day})$ .

In the sediments of the coastal stations, aceticlastic methanogenesis constitutes not more than 10% of the net value. Practically all the methane is produced via the hydrogenotrophic process. The aceticlastic process was noticeable (up to 45%) at stations 01-14-1, 99-23, and 01-03. The low rates of the aceticlastic process are possibly due to the active acetate consumption by sulfate-reducing bacteria, which have a higher affinity to this substrate [12].

**Methane oxidation process.** The MO rates were determined for the water column and the mats and sediments of the littoral and of the coastal shallow waters. The MO rate in the water column was not high, with the maximum values (not exceeding 10  $\text{nl CH}_4/(\text{dm}^3 \text{ day})$ ) in the most shallow bays. These data fall into the range known for the outer seas and bays of the Arctic basin: the Kara Sea, 0.4–26.1  $\text{nl CH}_4/(\text{dm}^3 \text{ day})$ , and the Yenisei Bay, 2.0–12  $\text{nl CH}_4/(\text{dm}^3 \text{ day})$ .

In the shallow water sediments, MO rates varied within the range 0.02–4.8  $\mu\text{l CH}_4/(\text{dm}^3 \text{ day})$  except for station 99-8 (50–96  $\mu\text{l CH}_4/(\text{dm}^3 \text{ day})$ ). MO rates in mats and sediments of most of the littoral stations varied from 1.7 to 200  $\mu\text{l CH}_4/(\text{dm}^3 \text{ day})$ . A low MO rate was demonstrated for the sandy sediments of the upper part of the littoral (st. 99-21). The highest activity was observed in the fine sediments (st. 99-1, up to 2248  $\mu\text{l CH}_4/(\text{dm}^3 \text{ day})$ ).

The highest MO rate in the shallow water sediments is usually localized in the lower horizons of the sedi-

**Table 3.** Content and isotopic composition of the organic matter and bicarbonate carbon in water, mats, and sediments

Station no.	Horizon, cm	C <sub>org</sub> , %	δ <sup>13</sup> C-C <sub>org</sub> , ‰	δ <sup>13</sup> C-HCO <sub>3</sub> <sup>-</sup> , ‰
00-4	Surface water	33.5*	-21.1	ND
	Bottom water	34.3*	-21.3	ND
	Surface sediment, 0-2	2.1	-20.8	ND
00-14-1	Pink mat, 0-2	66.3	-19.8	-7.6
	Sediment below the mat, 2-5	30.9	-18.1	
00-14-3	Pink mat, 0-1	68.9	-20.8	-14.8
	Sediment below the mat, 1-3	30.4	-17.3	
	3-7	22.8	-18.2	
00-8	Surface sediment, 0-3	6.0	-20.3	ND
00-5/1 (99-20)	Surface sediment, 0-1			
	1-5	22.8	-18.7	-7.2
		8.9	-20.4	
00-9	Surface sediment, 0-1	8.5	-20.8	
00-5/2	Mat, 0-1	42	-20.2	-7.2
	Sediment below the mat, 1-8		-18.8	
	8-11		-19.0	

\* The suspension obtained by filtering water samples through GF-F filters was analyzed.

ment and correlates well with the methane concentration. In the littoral mats and sediments, MO reaches its peak at the boundary between the aerobic and anaerobic zones and this peak does not necessarily coincide with the peak of methane concentration (sts. 99-2, 99-3, 00-5/2). Very low rates of the process were found during the winter research (up to 0.0004 in the water column and up to 0.70 μl CH<sub>4</sub>/(dm<sup>3</sup> day) in sediments. Carbon dioxide was shown to be the main product of MO. As much as 10–30% of the methane carbon was incorporated in the cell biomass and in soluble extracellular metabolites.

**Isotopic composition of carbon compounds.** The knowledge of the isotopic composition of various carbon compounds is essential for the understanding of both the methane biogeochemical cycle and of the carbon cycle in a water body as a whole. Unfortunately, it proved impossible to collect methane samples of the volume required for isotopic analysis. However, we performed several determinations of the isotopic composition of organic carbon in suspended particles, in the biomass of microbial mats, and in the sediments, as well as of C-HCO<sub>3</sub><sup>-</sup> in the surface deposits (Table 3).

The isotope data shown indicate that the C<sub>org</sub> of the mats and of the surface deposits is 1–4‰ enriched with the heavy isotope <sup>13</sup>C compared to C<sub>org</sub> of the suspended particles. The values of δ<sup>13</sup>C-HCO<sub>3</sub><sup>-</sup> are characteristic for sediments where the processes of active C<sub>org</sub>

destruction shift the isotopic composition of ΣHCO<sub>3</sub><sup>-</sup> to negative values (Table 3).

## DISCUSSION

Photosynthetic production in the shallow water column determines the rates of anaerobic destruction, including MP, and was comparable to the primary production in the Barents and Kara seas at the end of the summer season [14]. Photosynthetic rates in Lake Polusolenoe (st. 99-14) and in other temporarily or permanently submerged littoral sediments, in 1 and 2 cm water layers, are comparable to or exceed production in the water column of the marine stations (Table 2). Photosynthetic production rates at the end of the winter season under ice cover (49 mg C/(m<sup>2</sup> day)) were close to the values obtained for permanently ice-covered Antarctic water bodies (4.1–49.9 mg C/(m<sup>2</sup> day)) [15]. The isotopic composition of C<sub>org</sub>, including the carbon of the phytoplankton biomass in suspension (Table 3), indicates insignificant carbon input from dry land, even at station 99-14-1 in the mouth of a freshwater creek. The C<sub>org</sub> of the sediments being enriched with the heavy isotope as compared to the phytoplankton biomass is not typical for most marine water bodies. On the contrary, the sediments usually are poorer in the heavy isotope as the result of more rapid decomposition of the protein-carbohydrate part of the phytoplanktonic biomass and therefore of accumulation of the lighter, more resistant lipid fraction of organic matter.

These data on the rates of microbial processes can be compared with those for both marine and terrestrial

**Table 4.** Rates of the processes of methane production and oxidation in marine and freshwater basins, damp soils, and bogs

Object	Process rate, $\mu\text{l CH}_4/(\text{dm}^3 \text{ day})$		Reference
	MP	MO	
Lake Dolgoe	ND	540–2720	[16]
Lake Kuznechikha	4870–7700	ND	[17]
Damp soils and bogs of Western Siberia	up to 0.102	up to 0.122	[3]
The Banger Hills Oasis water bodies (Antarctica)	0.93–74.8	0.094–56	[11]
Lake Mogil'noe (Kil'din Island, Barents Sea)	0.028–0.43	0.14–0.43	[12]
Vostok Bay, Troitsa Bay (Sea of Japan)	0.17–3.9	0.008–0.11	[18]
Batabano Bay (Cuba)	0.1–4.9	0.04–0.77	[19]
Coastal sediments of the Black Sea	0.02–84.7	0.35–4000	[20]
Kandalaksha Bay (shallow sediments)	0.22–58.8	0.02–96.3	The present work
Kandalaksha Bay (littoral sediments)	0.3–113	0.2–2448	The present work

ecosystems (Table 4). Methane production rates obtained in this study exceed the ones known for most marine sediments, where the processes of sulfate reduction (SR) are known to dominate. The methane production rate is much less than in anaerobic lake sediments, where SR is less pronounced than MP. The methane production rate was comparable with the rate of this process in lake sediments but was less than the high values known for the coastal sediments of the Black Sea northwestern shelf.

The study of microbial processes occurring on the littoral revealed several typical zones sharing common landscape characteristics [9]. The typical zones are defined primarily according to the vertical zonality. Thus, microlandscapes differing in the composition of the floral and faunal community can be defined. The littoral biotopes include the phytal zone, which mostly occupies the lowermost part of the littoral; the *nyashi*, the zones where dead macroalgae are deposited by storms; and the local silted pits where moisture is preserved during low tide. Our investigations revealed sharp differences between these microlandscapes in their level of hydrogen sulfide production [9]. The processes of SR and MP are known to be mutually related to a certain degree since they both compete for reduced substrates and both require anaerobic conditions. High hydrogen sulfide production, however, does not always coincide with high methane production, and vice versa. Our calculations demonstrate that high methane production is characteristic for sediments that are enriched with organic matter and are in contact with fresh water (sts. 99-14-1, 01-03, 99-8, Table 5). Such an effect of fresh water influx on high methane production, however, is not obligatory (99-1, 99-22, 99-23).

At some stations, MO rates were especially high (99-8, 99-1, 99-23). At negative balance in the net methane production was shown there (Table 5). We

believe that the calculated negative balance is not caused by methodological or experimental errors but rather was caused by the underestimation of MP below the sampling depth.

It is reasonable to compare the rates of MO and SR considering the ratio of organic matter consumed by each process. In marine and oceanic sediments, the contribution of sulfate reducers to anaerobic destruction is known to exceed the contribution of MP by several orders of magnitude. For bodies of fresh water and bogs, the opposite situation was demonstrated to occur. Our calculations demonstrate that, in the analyzed littoral sediments as a whole, the sulfur cycle processes dominated (Table 5). At some stations, however, up to 13% of organic matter was consumed via MP processes; this is unusual for marine sediments.

At a number of littoral stations, representing varied types of microlandscapes, the chamber method revealed methane emission into the lower atmosphere ( $150\text{--}2500 \mu\text{l CH}_4/(\text{m}^2 \text{ day})$ , Table 6). The lowest values of emission were found on the upper edge of the littoral; the highest, in the zone of stormy discharge. The results obtained by the chamber method confirmed our calculations based on the radioactive isotope experiments (Table 6). These methods show the best accord for the microlandscapes of silted pits, pools, and stormy discharge stretches. These are the places where microbial processes occur mostly in the upper horizons; the effect of unaccounted-for MP was therefore inconsiderable. In terrestrial landscapes, the difference between methane flows determined by these two methods is known to be especially high [3]. Methane flow into the atmosphere for aquatic stations was estimated by calculation. This calculation demonstrated that methane emission in the open part of the bay constituted an average of  $24.0 \text{ l CH}_4/\text{km}^2$  per day and in the smaller bays,  $69 \text{ l CH}_4/\text{km}^2$  per day (Table 7).

**Table 5.** Daily balances of MP and MO in the sediments (0–25 cm) and water column and C<sub>org</sub> consumption via MP and sulfate reduction in the coastal waters and littoral of the White Sea

Station no.	MP*, μl/(m <sup>2</sup> day)	MO rate, μl/(m <sup>2</sup> day)*			MP – MO, μl/(m <sup>2</sup> day)	C <sub>org</sub> consump- tion via MP, mg/(m <sup>2</sup> day)	C <sub>org</sub> consump- tion via sulfate reduction, mg/(m <sup>2</sup> day)**
		In the water column	In the sediments	Total			
Stations of the open part of the bay							
00-10	22	18	20	38	–16	0.024	2.03
99-11	157	54	12.4	66.2	91	0.169	3.53
99-6	208	45.5	12	57.5	150	0.22	6.0
99-4	181	57.5	75	132.5	48	0.195	30.3
Stations in little bays and shallows in river mouths							
01winter-1	116	17.2	0.87	18	108	0.13	1.28
99-10	98	26	25	51	47	0.11	2.63
99-9	62	29	55	84	–22	0.065	7.8
99-2	664	36	229	265	399	0.69	29.6
99-12	108	150	597	747	–639	0.114	32.2
99-8	6840	56	14590	14646	–7806	6.9	52.9
00-2	193	6.8	124	131	62	0.21	182
Shallow Bab'e More Bay and abandoned mussel plantations							
99-19	1266	63	61	124	1143	1.35	98.3
99-17	450	38	471	509	–59	0.49	72.3
00-4	56	44	13	57	–1	0.062	153
Bacterial mats and sediments in the shallow reservoirs on the littoral							
99-14-1	2277	1980	4273	6253	–3976	2.46	133
99-14-3	3540	36	2754	2810	730	3.82	113
00-14-1	8704	150	4352	4502	4202	9.40	1229
00-14-3	1635	127	684	811	824	1.77	276
01-14-1	3348	590	1678	2268	1080	3.62	2816
Sediments of the open area of the littoral							
99-21	116	–	19.5	19.5	96	0.131	1.27
Finely dispersed sediments containing organic matter (soil humus)							
99-1	6062	–	28700	28700	–22638	6.6	56.7
00-8	1365	–	111	111	1254	1.42	75.1
99-22	2676	–	1475	1475	1201	2.9	82.5
01-06	507	–	258	258	249	0.56	159
Deposits of the stormy discharge stretch							
99-20	728	–	357	357	371	0.79	130
01-03	5255	–	2285	2285	2970	5.82	970
Depressions under stones and silted pits retaining water during low tide							
00-9	257	–	97	97	160	0.28	371
99-23	6383	–	17460	17460	–10777	6.89	464
01-05	1070	–	480	480	590	1.16	7980
00-5/2	646	–	372	372	274	0.71	4216
Littoral sediments studied in the winter period							
01winter-6	33.6	–*	70	70	–36	0.037	2.34
01winter-7	2.7	–*	38.5	38.5	–36	0.0029	33.4
01winter-8	45	–*	9.3	9.3	36	0.049	4.16
01winter-9	31	–*	48	48	–17	0.0034	40.7

\* Calculation performed for 10–15 cm of the surface sediment.

\*\* Data originally published in [9].

**Table 6.** Methane emission into the atmosphere in the main ecotopes of the coastal shallow waters and silty–sandy stripe of the littoral of the Kandalaksha Bay of the White Sea and bogs and lakes of Eastern Siberia

Ecotopes studied	Process rates, $\mu\text{l}/(\text{m}^2 \text{ day})$			Methane emission*, $\mu\text{l}/(\text{m}^2 \text{ day})$
	$\text{CH}_4$ production	$\text{CH}_4$ oxidation	$\text{CH}_4_{\text{prod}} - \text{CH}_4_{\text{oxid}}$	
Stations of the open part of the bay	$\frac{22-208}{142}$	$\frac{38-133}{74}$	$\frac{0-150}{72}$	ND
Stations in little bays and shallows in river mouths	$\frac{62-6840}{1295}$	$\frac{52-14646}{2860}$	$\frac{47-399}{169}$	ND
Small basins on the littoral stretch	$\frac{1635-8704}{3900}$	$\frac{811-6253}{3337}$	$\frac{730-4202}{1367}$	1600
Sandy and sandy–silty sediments of the littoral	116	20	96	150
Finely dispersed sediments	$\frac{507-6062}{2653}$	$\frac{111-28700}{3337}$	$\frac{249-1254}{675}$	1200
Deposits of the stormy discharge stretch	$\frac{728-5255}{2992}$	$\frac{357-2285}{1321}$	$\frac{371-2970}{1670}$	2500
Bogs [3]	$\frac{0-53}{2.9}$	$\frac{0-94.8}{11.4}$	$\frac{0-19.6}{3.7}$	151
Dry bogs [3]	$\frac{0-3.4}{0.39}$	$\frac{0-53}{2.9}$		84.1
Lakes [3]	$\frac{0-6.0}{1.6}$	$\frac{0-12.3}{2.9}$	$\frac{0-2.7}{2.9}$	6.5

Note: The ranges of values recorded and the mean values are presented.

\* The results were obtained by the chamber method.

**Table 7.** Calculated methane emission from the stretch of boulder–stone littoral of the Kandalaksha Bay of the White Sea with the relative areas of various types of microlandscapes taken into consideration

The main zones of the littoral	Area, %	Methane emission, $\text{l}/(\text{km}^2 \text{ day})$	
		By radioisotopic method	By chamber method
1. Sandy and sandy–silty sediments	84–94	85	134
2. Thin silts (soil humus)	5–10	51	90
3. Stormy discharge stretches	0.5–3	29	44
4. Small basins, silted pits, and depressions	1–3	27	32
Total on the littoral	100	192	300

The estimate of the portion of the microlandscapes with enhanced production performed on a strip of sandy–stony and sandy–silty littoral (length, 1 km; width, 30–80 m; total area,  $0.065 \text{ km}^2$ ) revealed that fine sediments constitute 5–10%, stormy discharge stretches, 0.5–3.0%; and silted pits retaining water at low tide, 1.0–3.0% of the littoral area (Table 7). The pools in depressions on the surfaces of stones and plates were not taken into account. Thus, the remaining part of the littoral area was estimated as 84–94%, with at least 20% under rock outcroppings and separate plates and boulders. The calculated daily methane production

from  $1 \text{ km}^2$  of the littoral (August) was estimated as  $192\text{--}300 \text{ l CH}_4/(\text{km}^2 \text{ day})$  (Table 7).

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