Microbiology, Vol. 73, No. 4, 2004, pp. 457–468. Translated from Mikrobiologiya, Vol. 73, No. 4, 2004, pp. 540–552.

EXPERIMENTAL ARTICLES

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

A. S. Savvichev*, I. I. Rusanov*, S. K. Yusupov*, N. V. Pimenov*, A. Yu. Lein, and M. V. Ivanov***

**Winogradsky Institute of Microbiology, Russian Academy of Sciences, pr. 60-letiya Oktyabrya 7, k. 2, Moscow, 117312 Russia*
***Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117851 Russia*

Received June 3, 2003; in final form, August 14, 2003

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_2 assimilation in the shallow and littoral sediments was 35–27800 μg C/(dm^3 day) in summer and 32.8–88.9 μg C/(dm^3 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^3 day)). The maximal level of MO was observed in the shallow estuarine sediments (up to 2450 μl/(dm^3 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^3 day), while the MO rate was 0.06–0.7 μl/(dm^3 day). The isotopic data obtained indicate that the C_{org} of the mats and of the upper sediment layers is enriched with the heavy ^{13}C isotope by 1–4‰ as compared to the C_{org} 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_4/(m^2 day); in stormy discharge stretch sediments, it was 1670 μl CH_4/(m^2 day); and under stones and in silted pits, 1370 μl CH_4/(m^2 day). The calculation, performed with consideration of the microlandscape areas with a high production, allowed the CH_4 production of 1 km^2 of the littoral to be estimated as 192–300 l CH_4/(km^2 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 pronounced 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^2, 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_2 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 $NaH^{14}CO_3$ 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^3 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 $NaH^{14}CO_3$, $^{14}CH_3COONa$, and $^{14}CH_4$. 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 ^{14}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 ($\delta^{14}C_{org}$) and of the bicarbonate ion carbon ($\delta^{14}C\text{-}HCO_3^-$) 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_2 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_2 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^-, g/l	Bacterial numbers, $\times 10^4$ cells/ml	Dark CO_2 assimilation, µg C/(dm^3 day)	Photosynthetic production		CH_4, µl/dm^3	CH_4 production, µl/(dm^3 day)	MO rate, µl/(dm^3 day)	Methane portion oxidized to CO_2, %
						µg C/(l day)	mg C/(m^2 day)				
Stations of the open part of the bay											
00-10	Krasnaya Bay,	0	16.4	20	3.12	5.1	77.4	0.08		0.001	
66°025′334 N	beyond Cape	18		22	1.84	3.5		0.09		0.001	
33°038′20 E	Kuzokotskii	0–10			35			3.5	0.22	0.02	50
99-11	Sea channel	0	5.3	60	5.5	12.9	180	0.98		0.005	
67°007′807 N	in line of Tely-	18		20	6.0	7.2		0.66		0.001	
032°019′952 E	achii Island	0–5			216			5.5	0	0.04	50
		5–17			170			5.8	0.68	0.06	67
		17–25			95			8.3	0.82	0.04	25
99-6	Oil base opposite	0	6.4	20	7.5	10.2	146	0.55		0.005	
67°004′965 N	the pier	13		40	8.8	10.8		0.28		0.002	
032°019′460 E		0–6			121			7.6	0.8	0.08	75
		10–15			95			4.5	1.6	0.07	71
99-4	Buoy opposite	0	11.7	15	12.8	14	271	0.38		0.003	
67°006′806 N	Ovechii Island	23		6	7.4	9.6		0.30		0.002	
032°026′740 E		0–5			110			19.1	0.94	0.3	53
		10–15			85			28.3	1.34	0.6	67
Stations in little bays or separated from the open bay by island chains											
99-10	Remote part	0	5.9	30	6.0	17.4	165	0.53		0.003	
67°008′145 N	of a small bay	13		10	8.0	8.0		0.32		0.001	
032°017′808 E		0–2			1205			11.2	0.38	0.14	71
		2–10			711			14.0	0.68	0.16	38
		10–17			448			16.5	0.50	0.13	80
99-9	Port of Kandalak-	0	15.3	20	7.7	19.6	269	0.91		0.003	
67°009′091 N	sha	19.5		4	12.0	8.0		0.32		0.002	
032°022′658 E		0–3			532			31.3	0.66	0.47	97
		3–13			341			46.0	3.42	0.41	73
99-2	Voron'ya Bay,	0	9.5	40	8.9	17.4	84.6	0.48		0.007	
66°056′654 N	central part	6		20	12.6	10.8		0.38		0.005	
032°025′677 E		0–7			515			130	0.8	0.87	55
		7–15			409			182	7.6	2.1	46
99-12	Sea channel	0	2.2	40	3.4	12.0	210	0.60		0.005	
67°008′214 N	at the port of	25		4	5.8	4.8		0.35		0.007	
032°023′944 E	Kandalaksha	0–10			241			260	2.64	3.1	68
		10–17			182			899	10.66	4.1	51

Table 1. (Contd.)

Station no., coordinates	Station location	Sea depth, m; sediment horizon, cm	Cl^-, g/l	Bacterial numbers, $\times 10^4$ cells/ml	Dark CO_2 assimilation, µg C/(dm^3 day)	Photosynthetic production		CH_4, µl/dm^3	CH_4 production, µl/(dm^3 day)	MO rate, µl/(dm^3 day)	Methane portion oxidized to CO_2, %
						µg C/(l day)	mg C/(m^2 day)				
99-8	Remote part near	0	5.6	10	8.5	18.0	119	1.0		0.01	
67°009′446 N	the Virna River	7		20	9.8	16.0		1.2		0.006	
032°020′482 E		0–10			303			1195	9.6	49.6	61
		10–20			122			16830	58.8	96.3	72
00-2	Chernorechen-	0	11.2	8	6.14	17.0	68	0.14		0.0022	
66°031′20 N	skaya Bay,	4.5		25	5.22	13.3		0.14		0.0009	
033°001′07 E	remote part	0–2			492			2.4	0.56	0.136	59
		2–5			914			3.6	0.71	0.166	72
		5–10			680			8.8	0.90	0.40	73
		10–20			416			21.3	1.15	0.96	77
00winter-01	Small bay near	0	12.1	2	0.44	1.8	49	0.38		0.0005	
66°020′01 N	Kartesh station	5		2	0.73	1.0		0.28		0.0004	
033°010′10 E		10		2	1.4			0.41		0.0009	
		20		3	1.38			0.28		0.0004	
		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	Bab’e More	0	9.1	6	3.7	10.4	364	0.28		0.0014	
66°037′100 N	(central part)	5		4	4.5	11		0.28		0.0011	
033°010′100 E		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	Mussel	0	13.9	20	5.0	17.2	218	0.25		0.0026	
66°028'554 N	plantations	14		30	7.2	14.0		0.28		0.0029	
033°025'585 E	(Island Lushov)	0–1			625			85	1.1	3.55	87
		1–5						133	2.84	4.75	84
		5–12			427			143	4.24	2.84	80
00-4	Mussel	0	13.5	35	4.7	18.6	233	0.11		0.0086	
66°028'554 N	plantations	5		22	3.1	14.8		0.09		0.0014	
033°025'585 E	(Island Lushov)	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^-, g/l	Eh, mV	Dark CO_2 assimilation, µg C/(dm^3 day)	Photosynthetic production		CH_4, µl/dm^3	Process rates, µl/(dm^3 day)		Methane portion oxidized to CO_2, %
						µg C/(dm^3 day)	mg C/(m^2 day)		CH_4 production	CH_4 oxidation	
Bacterial mats and sediments in the shallow reservoirs on the littoral											
99-14-1	Lake Polusolenoe, the	Pink mat, 0–1	770	–70	16200	55500	555*	3825	5.7	198	85
66°032′90 N	mouth of a freshwater	Sediment, 1–7	820	–125	9400			1371	69.6	98.2	60
033°008′05 E	stream	5–7	790	–80	1100			1012	75.9	11.5	92
99-14-2	Lake Polusolenoe, mats	White mat, 0–1	3180	–30	4100	6040	60.4*	120	23.2	2.64	55
66°032′90 N	near the mainland shore	Pink mat, 0–1	3100	–90	12700	19700	197*	120	14.6	5.04	50
033°008′05 E		Green mat, 0–1	3200	110	5300	8500	85*	120	11.6	4.81	42
99-14-3	Lake Polusolenoe, mats	Pink mat, 0–1	3530	–60	27800	46800	468*	120	78.7	3.55	62
66°032′90 N	near the island shore	Sediment, 1–2	3600	–150	3900			326	36.1	3.22	90
033°008′05 E		2–20	3600	–290	1050			720	35.4	21.2	34
00-14-1	Lake Polusolenoe, the	Pink mat, 0–2	5420	–50	4980	11300	226**	438	6.33	7.5	57
66°032′90 N	mouth of a freshwater	Sediment, 2–5	5400	–90	3430			1480	48.6	32.4	49
033°008′05 E	stream	5–10	5460	30	1210			1810	77.8	54.0	41
		10–15	5420	50	980			1415	64.6	13.6	72
00-14-2	Lake Polusolenoe, mats	Olive mat, 0–1	5520	–70	3760	7940	79.4*	25.9	16.9	8.3	85
66°032′90 N	near the mainland shore	Pink mat, 0–1	5500	–90	2050	8810	88.1*	16.7	12.7	6.1	82
033°008′05 E											
00-14-3	Lake Polusolenoe, mats	Pink mat, 0–1	5860	40	18460	26500	265*	269.2	13.4	12.7	61
66°032′90 N	near the island shore	Sediment, 1–3	5880	–150	6600			68.5	14.7	11.4	59
033°008′05 E		3–7	5900	–160	3900			73.8	26.5	11.5	59
01-14-1	Lake Polusolenoe, the	Pink mat, 0–5	6500	–230	25110	29200	584**	909	15.55	11.7	79
66°032′90 N	mouth of a freshwater	Sediment, 5–15	6400	–160	3947			1127	25.7	16.8	77
033°008′05 E	stream										
Sediments of the open area of the littoral											
99-21	BBS, sediment along	0–10	1520	80	510	ND		4.8	0.88	0.16	87
66°032′80 N	the upper waterline		1470					8.6	1.44	0.23	82
033°004′5 E	of the sandy littoral										
Finely dispersed sediments containing organic matter (soil humus) at different littoral levels											
99-1	Voron'ya Bay, soil hu-	0–0.2	10180	100	13400	ND		1577	17.2	966	95
66°056′654 N	mus sites at the lower	0.2–1	9950	–80	10800			7331	41.0	2448	92
032°025′677 E	part of the littoral	1–5	10050	–10	5900			15627	112.6	180	76
00-8	BBS, soil humus sites on	0–3	9880	–20	4430	ND		2.7	0.3	2.1	64
66°032′99 N	the littoral	3–10	9860	–115	1425			12.2	1.65	0.402	52
033°007′14 E		10–20	9940	–30	225			12.4	2.90	0.20	45
99-22	Luven'ga, Ilistaya Bay,	0–3	6600	–60	940	ND		446.3	12.9	24.59	86
67°005′6 N	soil humus sites	3–10	6950	–150	310			427.5	32.7	10.53	87
032°043′2 E											

Table 2. (Contd.)

Station no., coordinates	Station location	Sediment horizon, cm	Cl^-, g/l	Eh, mV	Dark CO_2 assimilation, μg C/(dm^3 day)	Photosynthetic production		CH_4, μl/dm^3	Process rates, μl/(dm^3 day)		Methane portion oxidized to CO_2, %
						μg C/(dm^3 day)	mg C/(m^2 day)		CH_4 production	CH_4 oxidation	
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
Deposits of the stormy discharge stretch											
99-20 66°032′80 N 033°004′5 E	BBS, stormy discharge stretch	0–5	9450	–150	5820	ND		5.6	1.75	2.20	80
			9500					48.5	12.8	6.93	73
01-03 66°032′78 N 033°010′05 E	BBS, stormy discharge stretch in the mouth of a freshwater stream on the littoral	0–5	5690	–330	19760			493	25.6	11.5	91
		5–20	5900	–280	3570			247	26.4	11.4	93
Depressions under stones, silted pits retaining water during low tide, sediments in the mouth of a freshwater stream											
00-9 66°032′99 N 033°007′14 E	BBS, a silted "bath" on the littoral	0–1	9800	120	9757	ND		1.6	1.19	1.7	85
		1–5	9860	–15	2604			1.5	2.1	1.06	61
		5–10	9940	10	816			2.2	2.79	0.59	61
99-23 67°005′4 N 032°043′1 E	Luven'ga, a silted pit near Gorelyi Isle	0–4	5860	20	2430	ND		3825	2.07	219	89
		4–10	5860	–220	1310			25322	105	145	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	9940	–65	17680	ND		29.6	2.28	6.60	71
		Sediment, 1–8	9850	–95	9740			60.9	7.41	6.53	81
		8–11	9880	–75	6086			84	10.9	1.49	
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
Littoral sediments studied in the winter period											
01winter-6 66°020′01 N 033°041′1 E	Kartesh, the upper waterline of the littoral	0–10	12540	–50	33.9	ND		31.9	0.336	0.70	30
01winter-7 66°020′01 N 033°041′1 E	Kartesh, central part of the littoral	0–5	12600	–20	32.8	ND		5.8	0.022	0.33	45
		5–10	12580	–60	39.1			18.4	0.016	0.22	38
01winter-8 66°020′01 N 033°041′1 E	Kartesh, central part of the littoral	0–15	12460	10	86.1	ND		3.8	0.30	0.062	36
01winter-9 66°020′01 N 033°041′1 E	Kartesh, the lower waterline with a *Fucus* community	0–15	12540	–50	46.8	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 μg C/(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 mg C/(m^2 day) (Table 1). The primary production measured in winter under the ice layer was 49 mg C/(m^2 day).

In the 1–2 cm layer, the photosynthetic production was 6040–55500 μg C/(dm^3 mat day) (Table 2). The production in the Lake Polusolenoe mats calculated for the 1–2 cm layer varied between 60 and 584 mg C/(m^2 day). Similar values of photosynthetic production (374 and 396 mg C/(m^2 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 μl/l. At most of the stations, the methane concentration in sediments was several to tens of microliters per dm^3. Hundreds of microliters per 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 ml/dm^3). The methane content in the littoral sediments was found to vary greatly. At some stations, the methane concentration reached 15–25 ml/dm^3 (sts. 99-1, 99-23).

At most of the shallow coastal stations, MP intensities were very low (as a rule, below 1 μl CH_4/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 μl CH_4/(dm^3 day)) in the part of the bay near the Virna River. This high 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°C, MP rates were 0.67–0.87 μl/(dm^3 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 μl/(dm^3 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 μl/(dm^3 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 μl/(dm^3 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 μl/(dm^3 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 nl CH_4/(dm^3 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 nl CH_4/(dm^3 day), and the Yenisei Bay, 2.0–12 nl CH_4/(dm^3 day).

In the shallow water sediments, MO rates varied within the range 0.02–4.8 μl CH_4/(dm^3 day) except for station 99-8 (50–96 μl CH_4/(dm^3 day)). MO rates in mats and sediments of most of the littoral stations varied from 1.7 to 200 μl CH_4/(dm^3 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 μl CH_4/(dm^3 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_{org}, %	$\delta^{13}C–C_{org}$, ‰	$\delta^{13}C–HCO_3^-$, ‰
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_4/(dm^3 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_3^- in the surface deposits (Table 3).

The isotope data shown indicate that the C_{org} of the mats and of the surface deposits is 1–4‰ enriched with the heavy isotope ^{13}C compared to C_{org} of the suspended particles. The values of $\delta^{13}C$-HCO_3^- are characteristic for sediments where the processes of active C_{org} destruction shift the isotopic composition of ΣHCO_3^- 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^2 day)) were close to the values obtained for permanently ice-covered Antarctic water bodies (4.1–49.9 mg C/(m^2 day)) [15]. The isotopic composition of C_{org}, 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_{org} 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, µl CH_4/(dm^3 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 (150–2500 µl CH_4/(m^2 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 l CH_4/km^2 per day and in the smaller bays, 69 l CH_4/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_{org} consumption via MP and sulfate reduction in the coastal waters and littoral of the White Sea

Station no.	MP*, μl/(m^2 day)	MO rate, μl/(m^2 day)*			MP – MO, μl/(m^2 day)	C_{org} consumption via MP, mg/(m^2 day)	C_{org} consumption via sulfate reduction, mg/(m^2 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, μl/(m^2 day)			Methane emission*, μl/(m^2 day)
	CH_4 production	CH_4 oxidation	$CH_{4\,prod} - CH_{4\,oxid}$	
Stations of the open part of the bay	22–208 / 142	38–133 / 74	0–150 / 72	ND
Stations in little bays and shallows in river mouths	62–6840 / 1295	52–14646 / 2860	47–399 / 169	ND
Small basins on the littoral stretch	1635–8704 / 3900	811–6253 / 3337	730–4202 / 1367	1600
Sandy and sandy–silty sediments of the littoral	116	20	96	150
Finely dispersed sediments	507–6062 / 2653	111–28700	249–1254 / 675	1200
Deposits of the stormy discharge stretch	728–5255 / 2992	357–2285 / 1321	371–2970 / 1670	2500
Bogs [3]	0–53 / 2.9	0–94.8 / 11.4	0–19.6 / 3.7	151
Dry bogs [3]	0–3.4 / 0.39	0–53 / 2.9		84.1
Lakes [3]	0–6.0 / 1.6	0–12.3 / 2.9	0–2.7	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, l/(km^2 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 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 km^2 of the littoral (August) was estimated as 192–300 l CH_4/(km^2 day) (Table 7).

ACKNOWLEDGMENTS

We thank A.N. Plishkin, V.I. Peresypkin, S.N. Korsun, N.V. Belyaev, and V.P. Shevchenko from the Institute of Oceanology, Russian Academy of Sciences, and V.V. Bianki and A.S. Koryakin from the Kandalaksha State Preserve for their assistance in field investigations.

This work was supported by the Russian Foundation for Basic Research, project no. 02-04-49296; the Federal Program "Integration," project nos. C0073 and

C0085; and the President of the Russian Federation, grant no. NSh-2068.2003.4.

REFERENCES

1. Ivanov, M.V., Lein, A.Yu., and Gal'chenko, V.F., The Global Cycle of Methane in the Ocean, *Geokhimiya*, 1992, no. 7, pp. 1035–1045.
2. Zavarzin, G.A., Methane Emission from the Territory of Russia, *Mikrobiologiya*, 1997, vol. 66, no. 5, pp. 669–673.
3. Gal'chenko, V.F., Dulov, L.E., Cramer, B., Konova, N.I., and Barysheva, S.V., Biogeochemical Processes of Methane Cycle in the Soils, Bogs, and Lakes of Western Siberia, *Mikrobiologiya*, 2001, vol. 70, no. 2, pp. 215–225.
4. Yavitt, J. and Lang, G., Methane Production in Contrasting Wetland Sites: Response to Organic-Chemical Components of Peat and to Sulfate Reduction, *Geomicrobiol. J.*, 1990, vol. 8, pp. 27–46.
5. Galchenko, V.F., Lein, A.Yu., and Ivanov, M.V., Biological Sinks of Methane, *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, Andreae, M.O. and Schimel, D.S., Eds., Chichester: Wiley, 1989, pp. 59–71.
6. Stephenson, B. and Stephenson, A., The Universal Features of Zonation between Tidemarks on Rocky Coast, *J. Ecol.*, 1944, vol. 37, no. 2, pp. 34–49.
7. Kalyakina, N.M., Biotopes of the White Sea Littoral, *Problemy izucheniya, ratsional'nogo ispol'zovaniya i okhrany prirodnykh resursov Belogo morya: Tez. Dokl. III region. Konf. Kandalaksha* (Various Aspects of Investigation, Rational Use, and Preservation of Natural Resources: Abstracts of the III Regional Conf., Kandalaksha), 1987, pp. 168–170.
8. Bek, T.A., The Coastal Zone in the Ecosystem of the White Sea, *Zh. Obshch. Biol.*, 1990, vol. 51, no. 1, pp. 117–124.
9. Savvichev, A.S., Rusanov, I.I., Yusupov, S.K., Bairamov, I.T., Pimenov, N.V., Lein, A.Yu., and Ivanov, M.V., The Process of Microbial Sulfate Reduction in the Coastal Zone and Littoral Sediments of the Kandalaksha Bay of the White Sea, *Mikrobiologiya*, 2003, vol. 72, no. 3.
10. Kuznetsov, S.I. and Dubinina, G.A., *Metody izucheniya vodnykh mikroorganizmov* (Methods for Studying Aquatic Microorganisms), Moscow: Nauka, 1989.
11. Gal'chenko, V.F., Sulfate Reduction, Methanogenesis, and Methane Oxidation in Different Water Bodies of Banger Hills Oasis, Antarctica, *Mikrobiologiya*, 1994, vol. 63, no. 4, pp. 683–698.
12. Ivanov, M.V., Rusanov, I.I., Pimenov, N.V., Bairamov, I.T., Yusupov, S.K., Savvichev, A.S., Lein, A.Yu., and Sapozhnikov, V.V., Microbial Processes of the Carbon and Sulfur Cycles in Lake Mogil'noe, *Mikrobiologiya*, 2001, vol. 70, no. 5, pp. 675–686.
13. Namsaraev, B.B., Rusanov, I.I., Mitskevich, I.N., Veslopolova, E.F., Bol'shakov, A.M., and Egorov, A.V., Bacterial Oxidation of Methane in the Yenisei River Estuary, *Okeanologiya*, 1995, vol. 35, no. 1, pp. 88–93.
14. Vedernikov, V.I. and Gagarin, V.I., Primary Production and Chlorophyll in the Barents Sea in September–October 1997, *Okeanologiya*, 1998, vol. 38, no. 5, pp. 710–718.
15. Gal'chenko, V.F., Bol'shiyanov, D.Yu., Chernykh, N.A., and Andersen, D., Bacterial Processes of Photosynthesis and Dark Carbon Dioxide Assimilation in the Lakes of Banger Hills Oasis, Eastern Antarctica, *Mikrobiologiya*, 1995, vol. 64, no. 6, pp. 833–844.
16. Gal'chenko, V.F., *Metanotrofnye bakterii* (Methanotrophic Bacteria), Moscow: GEOS, 2001.
17. Belyaev, S.S. and Ivanov, M.V., A Radioisotopic Method of Determination of the Intensity of Bacterial Methanogenesis, *Mikrobiologiya*, 1975, vol. 44, no. 1, pp. 166–168.
18. Ivanov, M.V., Namsaraev, B.B., Nesterov, A.I., Karnachuk, O.V., Borzenkov, I.A., and Bol'shakov, A.M., Involvement of Microorganisms in the Degradation of Organic Matter in Coastal Bottom Sediments of the Sea of Japan, *Mikrobiologiya*, 1990, vol. 59, no. 2, pp. 321–329.
19. Namsaraev, B.B., Lukhioio, M., Beiota, M., Miravet, M.E., Mitskevich, I.N., Karnachuk, O.V., and Ivanov, M.V., Involvement of Microorganisms in the Degradation of Organic Matter in Bottom Sediments of the Batabano Bay (Cuba), *Mikrobiologiya*, 1990, vol. 59, no. 5, pp. 903–911.
20. Rusanov, I.I., Lein, A.Yu., Pimenov, N.V., Yusupov, S.K., and Ivanov, M.V., The Biogeochemical Cycle of Methane at the Northwestern Shelf of the Black Sea, *Mikrobiologiya*, vol. 71, no. 4, pp. 558–566.