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EXPERIMENTAL ARTICLES

Microbial Processes of the Carbon and Sulfur Cycles in the White Sea

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Abstract—The present paper contains the results of our microbiological and biogeochemical investigations carried out during a series of expeditions to the White Sea in 2002–2006. The studies were conducted in the open part of the White Sea, as well as in the Onega, Dvina, and Kandalaksha bays. In August 2006, the photosynthetic productivity in the surface water layer was low (47–145 mg C m^{-2} day^{-1}). Quantitative characteristics of microbial numbers and activity of the the key microbial processes occurring in the water column of the White Sea were explored. Over the 5-year period of observations, the total number of bacterial cells in the surface layer of the water column varied from 50 to 600 thousand cells ml^{-1}. In August 2006, bacterioplankton production (BP) was estimated to be 0.26–3.3 μg C l^{-1} day^{-1}; the *P*/*B* coefficient varied from 0.22 to 0.93. The suspended organic matter had a lighter isotope composition (from –28.0 to –30.5‰) due to the predominance of terrigenous organic matter delivered by the Northern Dvina waters. The interseasonal and interannual variation coefficients for phytoplankton production and BP numbers are compared. The bacterioplankton community of the White Sea's deep water was found to be more stable than that of the surface layer. In the surface layer of bottom sediments, methane concentration was 0.2–5.2 μl dm^{-3}; the rate of bacterial sulfate reduction was 18–260 μg S dm^{-3} day^{-1}; and the rates of methane production and oxidation were 24–123 and 6–13 nl CH_4 dm^{-3} day^{-1}, respectively. We demonstrated that the rates of microbial processes of the carbon and sulfur cycles occurring in the sediments of the White Sea basin were low.

Key words: bacterioplankton, microbial processes, methane cycle, sulfate reduction, stable carbon isotopes ($\delta^{13}C$), Arctic Seas, White Sea.

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Among the Arctic seasof Russia, the White Sea has been studied in the most detail. A large amount of data on the White Sea ecosystem has been collected [1]. After the 1990s, when the scientific activity declined, a series of investigations were carried out under the White Sea System Project within the framework of the LOIRA project (Land-Ocean Interactions in the Russian Arctic) [2]. Investigation into the microbial processes of methane turnover occurring, both in the water column and bottom sediments, is the major issue concerning microbial biogeochemistry inof the Arctic seas [3].

The White Sea ecosystem is largely dependent on the fresh waterfrom the rivers, mixing with the waters of the shallow Dvina and Onega bays. Thus, all the biogeochemical processes occurring in the water column and bottom sediments of the White Sea depend on the composition of both the mineral and organic matter contained in the river water. Another important characteristic of the White Sea ecosystem, typical of all Arctic seas, is the pronounced seasonal variation of all biogenic processes. The vast expanse of the White Sea coastal zone, as well as the presence of the boundary tidal area, determine the rates of destruction for organic matter (both allochthonous and autochthonous) by sulfate-reducing and methanogenic microorganisms [4, 5]. The heterogeneity of the spatial and seasonal structure of the White Sea ecosystem explains the fact that there is no unified conception of the trophic state of the sea [6]. The phytoplankton activity in seasons other than summer was reported [7]. Construction of mathematical models describing the biogeochemical cycles is complicated by the abundance of empirical data varying within a wide range [8].

Therefore, the aim of the present work was to obtain reliable, quantitative characteristics of the key microbial processes of the carbon cycle, such as methanogenesis (MG), methane oxidation (MO), sulfate reduction (SR), and CO_2 dark assimilation (DA) by both

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autotrophic and heterotrophic microorganisms in the water column and bottom sediments of the White Sea, as well as to determine the carbon isotope composition of suspended organic matter.

MATERIALS AND METHODS

Materials for research were obtained during the 80th cruise of the *Professor Stockman* research vessel (August 2006). Some of the results presented (primary production values, total bacterial counts) were obtained by the authors in the course of the expeditions of the Shirshov Institute of Oceanology, Russian Academy of Sciences on the *Professor Stockman* (2002, 2004, 2005) and *Ivan Petrov* (2005) research vessels. Considerable parts of the White Sea, including the Basin, the Gorlo, as well as the Dvina, Kandalaksha, and Onega bays, have been studied.

The water was sampled with 5-l bathometers mounted on the Rozett system (Woods Hole, United States) and equipped with sensors for temperature, salinity, turbidity, fluorescence, and oxygen content. In order to avoid air bubbles, the water samples were removed from the bathometers into glass bottles with overflow; the bottles were then sealed with gastight stoppers.

The bottom sediments were sampled with a Niemisteö corer. At three stations, sediment samples were taken at a depth of up to 3 m with large-diameter geological tubes (LDT). Undamaged samples of bottom sediment were placed into truncated 5-cm^3 plastic syringes with rubber pistons and sealed with rubber stoppers. The redox potential and pH were determined at the moment of sampling with a pH 320/Set-1 potentiometer (Germany).

Primary production (PP) was determined by the radiocarbon method [9]. The experiments were carried out in transparent and darkened glass bottles supplemented with $NaH^{14}CO_3$ solution (20 μCi). At station 6042, the flasks were incubated for 24 h at a buoy station at the corresponding horizons. The samples collected at other stations were incubated in the continuous-flow deck basin for 12 h. An individual, perforated dark sheath of known light transmittance (100, 50, 10, or 5%) was used for each transparent bottle [10]. The resulting illumination was equal to the intensity measured at the relevant sampling horizon. The temperature in the continuous-flow deck basin (11–13°C) corresponded to that of the surface waterlayer; it was 2–3°C higher than the temperature measured in the lower horizons of the photic layer (8–11°C). It is well known that changes in the incubation temperature within this range are not a critical factor for determination of PP values [10]. After the exposure, the content of the bottles was filtered through 0.2 μm Nylon membrane filters. In order to remove residual carbonates, the filters were washed with filtered, slightly acidified seawater. When calculating PP values, we assessed both bacterial biomass production and incorporation of ^{14}C from carbon dioxide into the extracellular excretions, for which purpose the filtrate was combusted with sodium persulfate and the incorporated label was then determined [11].

The rates of microbial dark CO_2 assimilation (DA), MG, and MO were determined by the radioisotope method with $NaH^{14}CO_3$, $^{14}CH_4$, and $^{14}CH_3COONa$. The syringes with sediment samples and the glass bottles with water samples were injected with 0.1 ml of labeled compounds (4000 μCi per one dm^3 of sediments and 60 μCi per one liter of water). The samples of near-bottom water and bottom sediment were incubated in a refrigerator at 1–4°C for 12–48 h. After the incubation, the samples were fixed with 1 ml of 0.2 N KOH. The separation of the ^{14}C-containing products and measurement of their radioactivity (on a Rack Beta 1219 scintillation counter, LKB, Sweden) were carried out according to the previously described procedure [11]. For estimation of the methane oxidation rate, both the CO_2 formed via methane oxidation and the methane carbon incorporated in bacterial biomass and extracellular organic metabolites were taken into account. The rate of exometabolite formation was determined from the difference between the values obtained by potassium persulfate oxidation of the total organic matter and of the biomass precipitated on the filters [12]. For the estimation of bacterioplankton production, we used the values of dark CO_2 assimilation (not including the extracellular exometabolites), as well as the empirical coefficient (20, according to Yu.I. Sorokin), which represents the ratio between the bacterial production values and the rate of heterotrophic CO_2 assimilation [13].

To determine the carbon isotope composition of suspended organic matter ($\delta^{13}C_{org}$), water samples were filtered through calcined 47 mm GF/F glass fiber filters. The values of $\delta^{13}C_{org}$ were determined on a Delta Plus mass spectrometer (Germany). The accuracy of the measurements was ± 0.1‰.

Sulfate reduction rates were determined by the formation of labeled H_2S and total pyrite, elemental, and organic sulfur from $Na_2{}^{35}SO_4$ (0.2 ml, 35 μCi per 5 cm^3 of the sediment); the samples were treated as described previously [11]. The potential activity of ^{14}C acetate destruction (heterotrophic potential) was determined after 24-h incubation of the samples supplemented with 0.2 μl (10 μCi) of the labeled substrate at close to in situ temperatures. The methane concentration was determined by the head-space method. The methane concentration was measured on a Chrom-5 gas chromatograph (Czech Republic) equipped with a flame ionization detector. The concentrations of sulfate, chloride, and acetate were determined on a Biotronik ion chromatograph (Germany).

To determine the total numbers of bacterioplankton (BP) and bacterial biomass, water samples (30 ml) were fixed with a paraformaldehyde solution, at a final con-

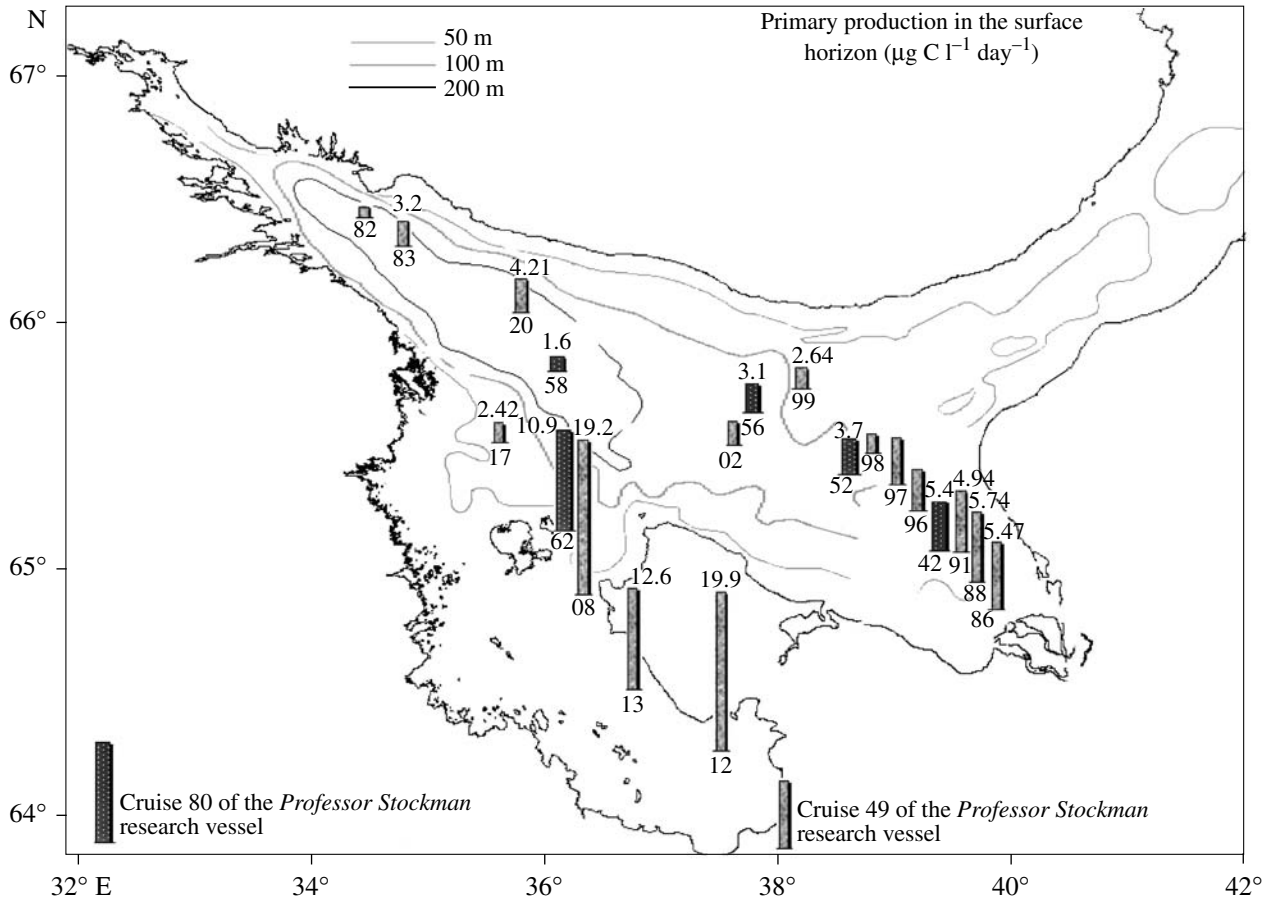

Fig. 1. Photosynthetic production rates (primary production) in the surface water layer of the White Sea (mg C m^{-3} day^{-1}).

centration of 2%. The fixed samples were filtered through 0.2-μm black polycarbonate Millipore filters.

Each filter was divided into several parts which were stained with acridine orange [14], DAPI (2 μg/ml) [15], and fluorescamine (4 μg/ml) [16]. The stained and dried filters were examined under a Lumam I-2 microscope (LOMO, Russia) at ×1100 magnification. The cells were counted in 20 microscope fields. The cells associated with detritus particles were counted separately.

The cell volumes were determined by measuring the cell length and width on the microphotographs obtained with a JSM-U3 scanning electron microscope (Japan). The volumes of the cocci and rods were calculated using the formulas for the volume of a sphere and a cylinder, respectively. About 200 cells were measured. When calculating the amount of the biomass, we used a correction coefficient of 1.6 [17]. When calculating the *P*/*B* coefficient (the ratio between the net production and the amount of biomass), the carbon content was assumed equal to 10% of wet biomass [13] in order to standardize the results obtained.

RESULTS

Primary production, total bacterial numbers, and the content and isotope composition of suspended carbon. In August, 2006, the rates of photosynthetic production (primary production, PP) in the surface layer of the water varied from 1.6 to 19.9 μg C l^{-1} day^{-1} (Fig. 1). In the open part of the Dvina Bay, PP values per square meter ranged from 46.8 to 51.2 mg C m^{-2} day^{-1} of the bay surface; in the Basin, PP values ranged from 61.5 to 67.4 mg C m^{-2} day^{-1} (Table 1). The highest PP (145 mg C m^{-2} day^{-1}) was recorded in a possible upwelling zone immediately near the Solovetsky Islands (station 6062). The highest PP rate was recorded at the surface (station 6042) and subsurface (station 6058) water layers; it was detected down to the depth of light penetration. The proportion of soluble exometabolites in the total photosynthetic production was 27 to 66%. A tendency towards a decrease in the ratio of the extracellular fraction in the horizons with high levels of primary production was observed. The PP rates generally correlated with both the values of fluorescence intensity and the suspension content (Fig. 2).

This study has shown that, in different parts of the White Sea, the total bacterioplankton (BP) numbers

Table 1. Primary production rates and the ratio of extracellular organic matter in the water column of the White Sea

Station	Depth, m	Primary production, μg C l^{-1} day^{-1}			Ratio of extracellular OM, %
		In biomass	In extracellular OM	Total	
6042	0	2.7	2.69	5.4	41
	5	1.2	2.08	3.3	43
	15	0.29	0.77	1.06	63
	20	0.16	0.17	0.33	51
	25	0.037	0.083	0.12	61
	61	0.028	0.038	0.066	66
				51.2 mg C m^{-2} day^{-1}	
6052	0	1.95	1.75	3.7	47
	10	0.68	0.89	1.57	56
	20	0.067	0.53	0.22	61
	120	0.007	0.003	0.01	
				46.8 mg C m^{-2} day^{-1}	
6056	0	1.51	1.62	3.13	52
	10	1.09	1.59	2.69	59
	20	0.042	0.27	0.31	65
	129	0	0.005	0.005	50
				61.5 mg C $m^{-2}$$day^{-1}$	
6058	0	0.95	0.68	1.63	42
	10	1.96	1.16	3.12	37
	20	0.67	0.73	1.4	52
	40	0.021	0.029	0.05	58
	300	0	0		
				67.4 mg C m^{-2} day^{-1}	
6062	0	8.5	2.45	10.95	27
	20	0.75	0.65	1.4	45
	40		0.31	0.31	
	68		0.01	0.01	
				145 mg C m^{-2} day^{-1}	

varied within a broad range (Fig. 3). In the surface water of the Basin and the Gorlo, the BP numbers ranged from 50 to 200 thousand cells ml^{-1} during the last 5 years of observations. Low bacterioplankton numbers (50–100 thousand cells ml^{-1}) were detected in June, 2003 and August, 2005 in the western and central parts of the Basin. Stable high bacterioplankton numbers (300–600 thousand cells ml^{-1}) are typical of the estuarial zone of the Dvina Bay (five years of observations), as well as for the shallow waters of the Onega Bay (2002). The greatest interannual variations in the BP numbers (from 100 to 470 thousand cells ml^{-1}) were detected in the surface waters near the Tersky Shore, as well as in the coastal zone of the Solovetsly Islands (from 50–100 thousand cells ml^{-1} to 200–300 thousand cells ml^{-1} in June, 2003 and August, 2006, respectively). A con-

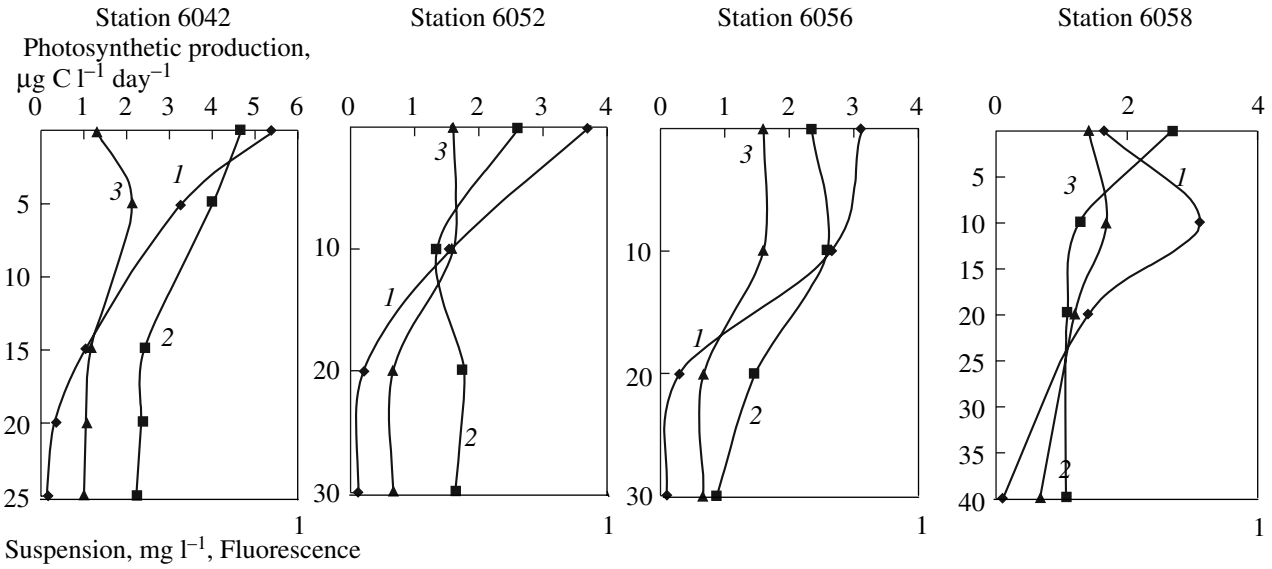

Fig. 2. Distribution of the photosynthetic production (*1*), suspended matter (*2*), and fluorescence intensity (*3*) in the White Sea water column, Cruise 80 of the *Professor Stockman* research vessel. The ordinate shows the depth of the water layer, m.

stant decrease in bacterioplankton numbers from the surface downwards was observed (Fig. 4). In June, 2003 and August, 2004, the total numbers of bacterioplankton in deeper horizons were lower than 50 thousand cells ml^{-1}; in other years, the total BP numbers were 50–100 thousand cells ml^{-1}.

In August, 2006, bacteria were represented mostly by small thin or ovoid rods, as well as by small cocci. The average volumes of bacterial cells in different horizons and at different sampling stations varied insignificantly and comprised 0.28 μm^3 (taking into account the coefficient 1.6). When counting bacterioplankton cells on the filters, we counted single cells and cells associated with suspended particles separately (Table 2). In the surface water layer, bacterial cells attached to suspended particles constituted 20–30% of the total bacterial counts. The number of single (unattached) BP cells decreased downward in the water column. By contrast, the number of bacterial cells attached to suspended particles remained unchanged or increased slightly from the surface to the bottom and, in the close-to-bottom horizons, comprised up to 80% of the total bacterial counts. On the whole, the distributional pattern of bacterial biomass corresponded to the distributions of bacterial numbers. The amount of biomass decreased from 6–7 μg C/l (in the surface horizons) to 1–2 μg C/l (in the close-to-bottom horizons).

In order to assess the bacterioplankton production, experiments were carried out to determine dark CO_2 assimilation (DA). Low DA values (0.2–0.48 μg C l^{-1} day^{-1}) were detected in the surface water horizons of the sampling stations. The rate of dark CO_2 assimilation decreased downward along the water column; it was quite low close to the bottom (to 0.05 μg C l^{-1} day^{-1}; station 6058, 100 m). The proportion of ^{14}C detected in the cell biomass in the total DA value was 20–48% (Table 2). When calculating the net BP production and the *P*/*B* coefficient, we used the data on DA rates obtained from labeled carbon incorporation into the cell biomass. The values of the *P*/*B* coefficient ranged from 0.22 to 0.93. No significant dependence of *P*/*B* values on the sampling depth has been demonstrated.

In the Dvina Bay and the Basin, the data on the isotope composition of suspended organic matter have been obtained for the first time; the results indicated that in August, 2006, isotopically lighter organic matter (from –28.0 to –30.5‰) delivered by the water of the Northern Dvina composed the bulk of suspended organic matter (Table 3). The isotope composition of suspended OM of the close-to-bottom water layers (from –27.3 to –28.4‰) and surface sediment (from –25.4 to –26.6‰) was heavier due to the presence of the suspension of planktonogenic origin formed during spring blooming.

Methane content and rates of microbial methane oxidation in the water column. This study revealed that the methane content in the surface layer of the White Sea water column was low, from 0.04 to 0.16 μl CH_4 l^{-1} (in the Gorlo and the central part of the Basin, respectively) (Fig. 5). The highest methane concentrations were detected in the Dvina Bay (up to 0.42 μl CH_4 l^{-1}; station 6045). We did not detect any evident distributional patterns dependent on the water depth (Table 4). At station 6056, methane concentration virtually did not change with depth. At station 6052, methane content gradually increased from the surface horizon to the near-bottom, ranging from 0.05 to 0.25 μl CH_4 l^{-1}. The rates of methane oxidation were also low and correlated well with the methane concentrations. The rates of methane oxidation in the open part of the

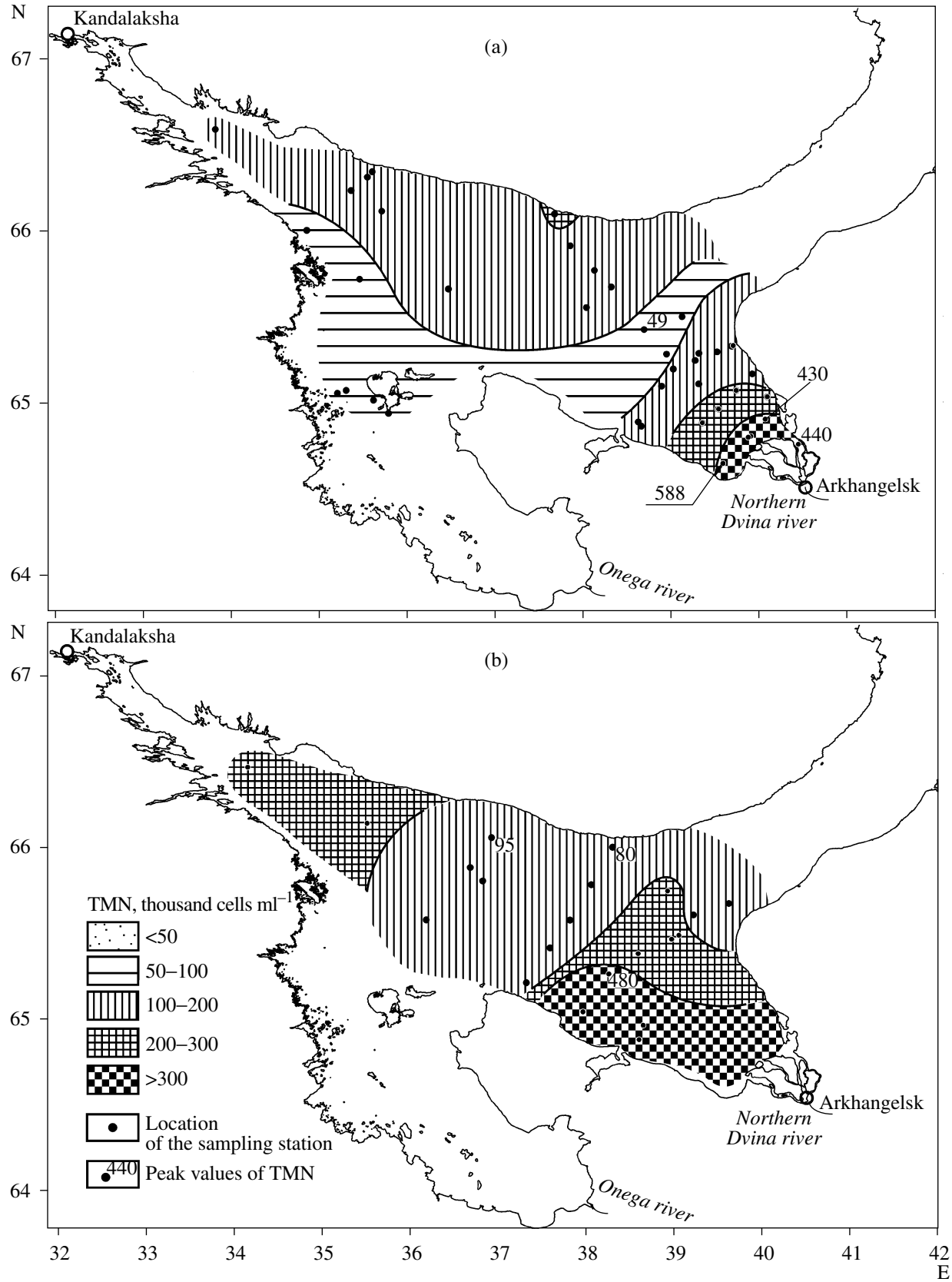

Fig. 3. Total microbial number (TMN) in the surface horizon of the water column of the White Sea: (a) June, 2003, cruise 57 of the *Ivan Petrov* research vessel; (b) August, 2004, cruise 64 of the *Professor Stockman* research vessel; (c) August, 2005, cruise 71 of the *Professor Stockman* research vessel; (d) August, 2002 and 2006, cruise 52 of the *Ivan Petrov* research vessel and cruise 80 of the *Professor Stockman* research vessel, respectively. TMN, total microbial number.

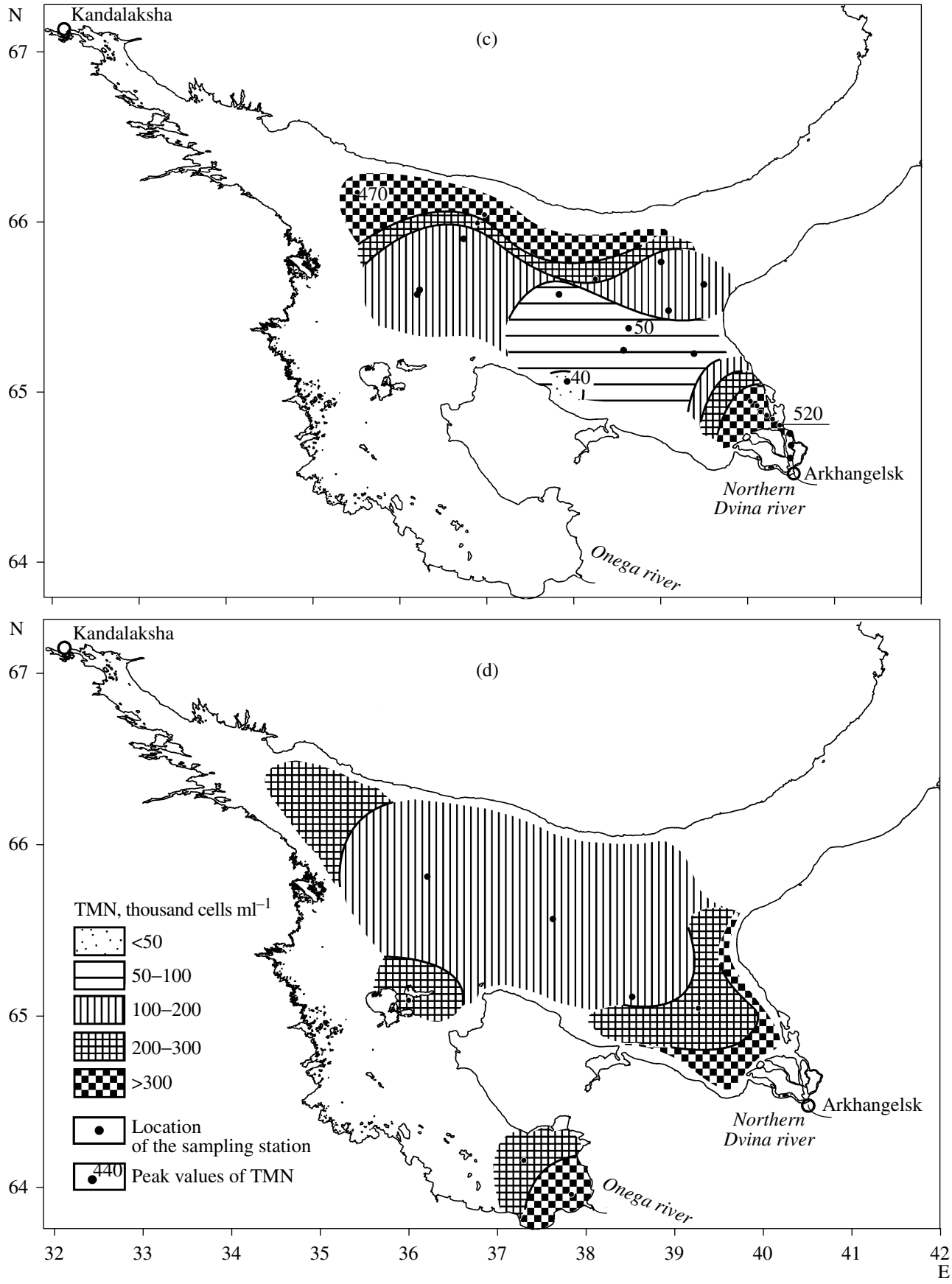
N
Kandalaksha
(c)
67
66
65
64
470
50
40
520
Arkhangelsk
Northern
Dvina river
Onega river
N
Kandalaksha
(d)
67
66
65
64
TMN, thousand cells ml^{-1}
<50
50–100
100–200
200–300
>300
Location
of the sampling station
440
Peak values of TMN
Arkhangelsk
Northern
Dvina river
Onega river
32
33
34
35
36
37
38
39
40
41
42
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Fig. 3. Contd.

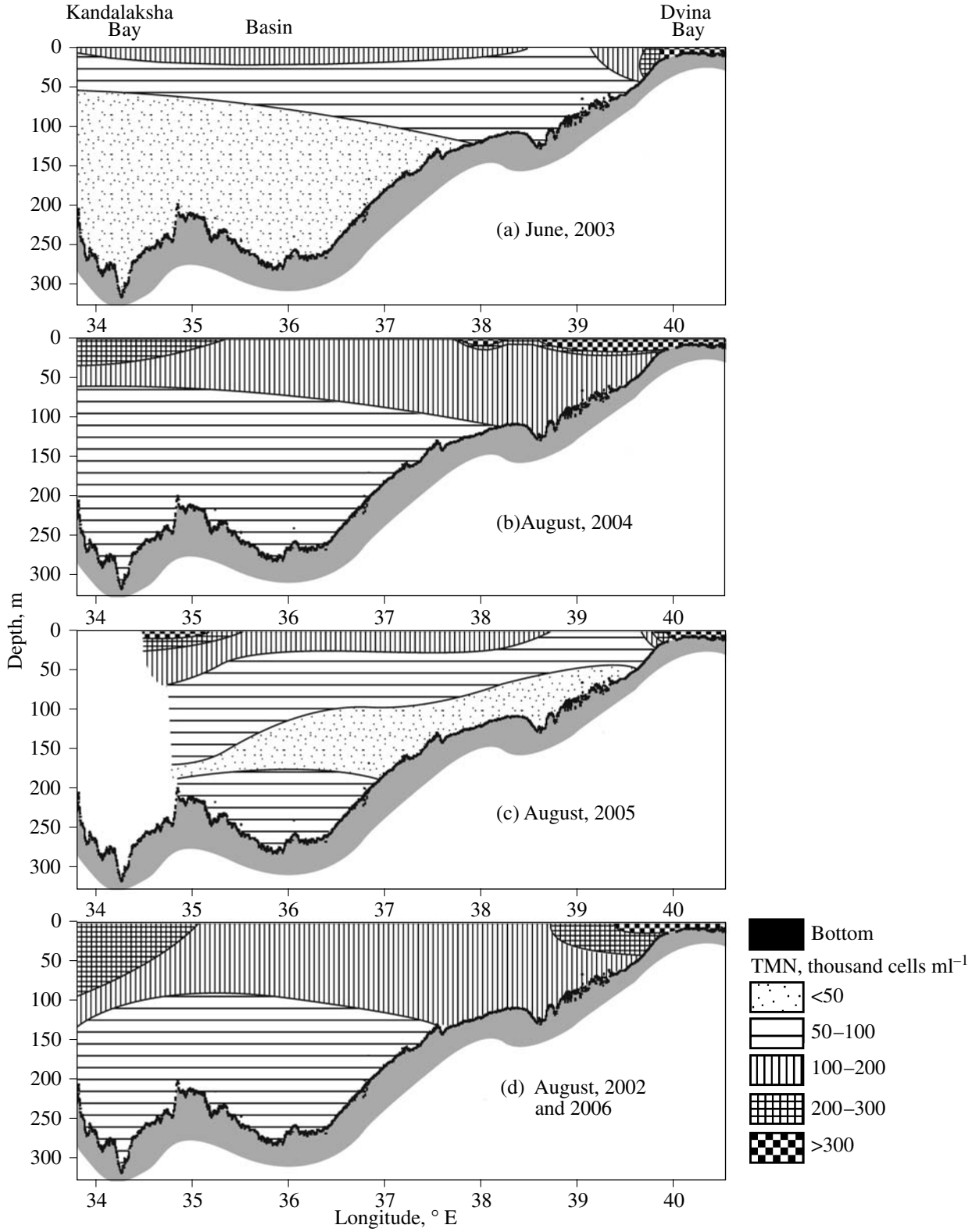

Fig. 4. Total numbers of microorganism in the water column of the White Sea at the Kandalaksha Bay–Basin–Dvina Bay transect stations.

Table 2. Total microbial numbers, biomass, and production of bacterioplankton in the water column of the White Sea (August, 2006)

Station no.; depth, m		BP total numbers, thousand cells ml^{-1}			BP Biomass*, μg C l^{-1}	Dark CO_2 assimilation, μg C l^{-1} day^{-1}		BP production*, μg C l^{-1} day^{-1}	*P/B*
		Free	On particles	Total		In cells	Total		
6042	0	180	60	240	7	0.165	0.48	3.3	0.47
	5	100	90	190	5.5	0.135	0.43	2.7	0.49
	15	40	40	80	2.0	0.085	0.30	1.7	0.85
	20	40	50	90	2.5	0.061	0.16	1.2	0.48
	25	20	40	60	1.5	0.072	0.18	1.4	0.93
	55	20	40	60	1.5	0.058	0.18	1.2	0.8
6052	0	180	40	220	6.0	0.191	0.40	3.8	0.63
	10	120	80	200	5.0	0.162	0.42	3.2	0.64
	20	80	110	190	4.5	0.13	0.36	2.6	0.58
	120	20	70	90	2.5	0.079	0.13	1.6	0.64
6056	0	160	40	200	5.5	0.058	0.20	1.2	0.22
	10	140	60	200	4.0	0.112	0.35	2.3	0.58
	20	90	20	110	3.0	0.04	0.14	0.8	0.27
	130	20	50	70	2.0	0.038	0.12	0.8	0.4
6058	0	170	70	240	7.0	0.182	0.42	3.6	0.51
	20	100	20	120	3.5	0.115	0.35	2.3	0.66
	50	20	30	50	1.5	0.0175	0.06	0.35	0.23
	100	20	30	50	1.5	0.013	0.05	0.26	0.17

* The values of net production and bacterial biomass are expressed in μg C l^{-1} (μg C l^{-1} day^{-1}); the carbon content was assumed equal to 10% of wet biomass.

Table 3. Distribution of C_{org} content and $\delta^{13}C$–C_{org} in the water suspension, close-to-bottom water, and the upper sediment layer (0–3 cm) of the White Sea

Station no.	Depth, m	Surface water layer (bathometer)		Near-bottom water layer (bathometer)*		Close-to–bottom water layer (Niemistö corer)**		Surface sediment layer (Niemistö corer)	
		C_{org}, %	$\delta^{13}C$–C_{org}, ‰	C_{org}, %	$\delta^{13}C$–C_{org}, ‰	C_{org}, %	$\delta^{13}C$–C_{org}, ‰	C_{org}, %	$\delta^{13}C$–C_{org}, ‰
6042	61		–29.3	0.37	–29.0	1.27	–27.7	1.65	–26.6
6048	80	0.49	–29.2	0.44	–28.0	1.90	–27.7	1.78	–25.8
6056	133	0.65	–28.6	0.19	–29.0	–	–27.4	1.60	–25.4
6058	300		–28.6	–	–30.5	1.08	–28.4	1.73	–25.8
6066	264	–	–	–	–	2.84	–27.3	1.69	–25.8

Notes: * Near-bottom water was sampled from the bathometer; the bathometers were submerged to 1–2 m from the bottom.
** Close-to-bottom water was sampled with a Niemistöcorer; the samples were collected 2–10 cm above the bottom sediments.

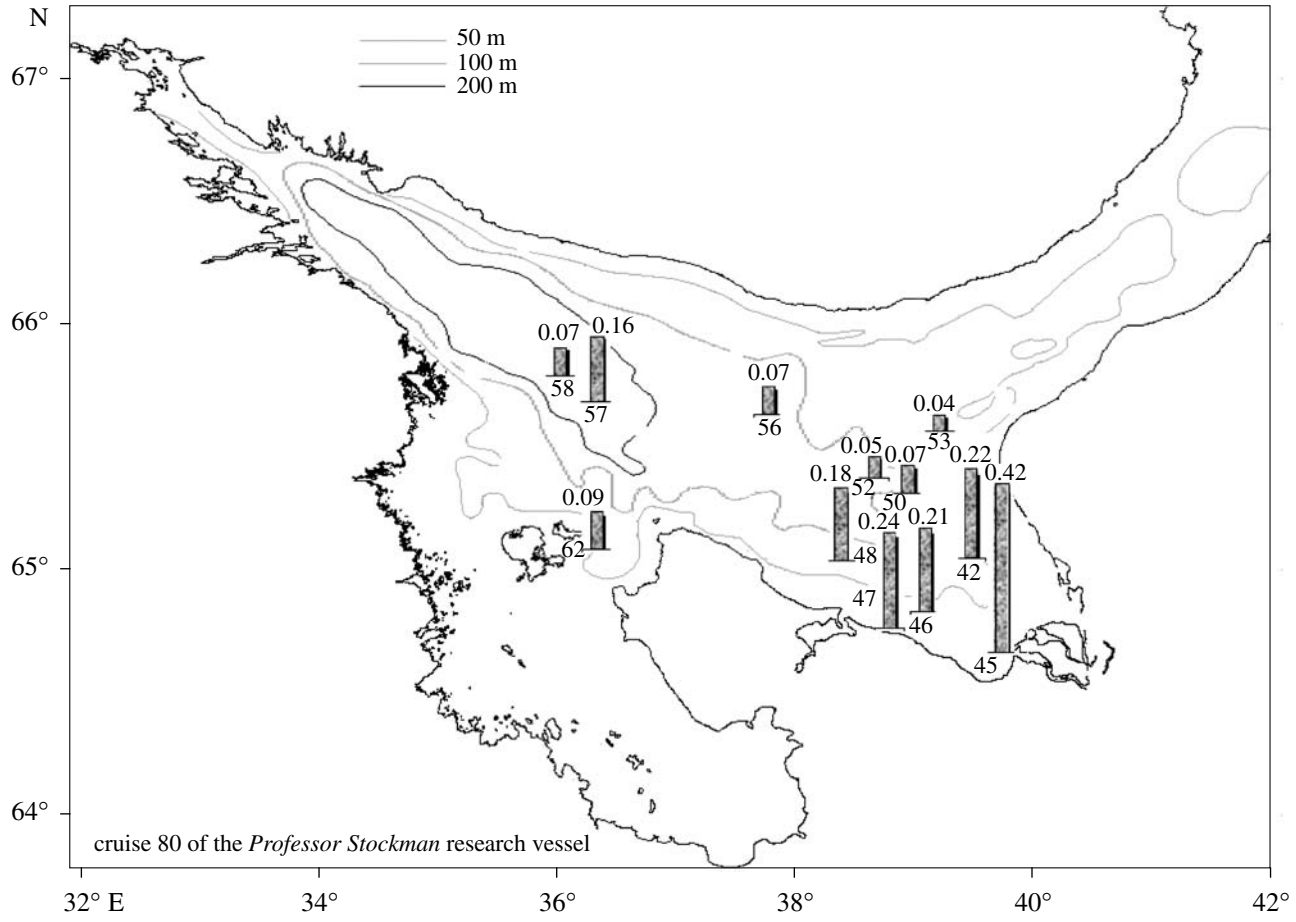

Fig. 5. Methane content in the surface horizon of the White Sea water column in August, 2006 (μl CH_4 l^{-1}).

Basin corresponded to the lowest values detected in the marginal seas of the Arctic basin, such as the Kara Sea (0.08–0.3 nl CH_4 l^{-1} day^{-1}) [18].

Rates of other microbial processes in the White Sea water column. The rate of acetate oxidation (AO) may serve as an indicator of the potential activity of heterotrophic processes (Table 4). The acetate oxidation rate was 2–4 times lower in the near-bottom horizon than in the surface layer, correlating with the rates of dark CO_2 assimilation (Table 2). Oxygen deficiency was not detected throughout the whole water column of the White Sea. However, the results of our experiments indicate that the processes of methanogenesis and sulfate reduction occur in some horizons, although their rates are extremely low (for methanogenesis, up to 18 nl CH_4 l^{-1} day^{-1} in the 20-m horizon at station 6042 and up to 29 nl CH_4 l^{-1} day^{-1} in the surface layer at station 6058; for sulfate reduction, up to 2.0–2.3 μg S l^{-1} day^{-1} in the surface layer and the 10-m horizon at station 6058; Table 4).

We have previously demonstrated that in the aerobic part of the Black Sea, the processes carried out by anaerobic bacteria occurred [19]; however, these processes have not been detected in the Arctic seas. Anaerobic processes are known to occur in the digestive tracts of zooplankton, as well as in pellets. The fact that anaerobic processes were not detected in many water samples can be attributed to the fragmentary character of ingress of relatively large particles (picoplankton and pellets) in the test flasks.

Characterization of bottom sediments: organic matter and chemical composition of silt waters. In the White Sea, the process of sedimentation is predominantly terrigenous and is characterized by differentiation of the sedimentary material. The bottom sediment of the continental slope and basins are composed of graded pelitic-aleuritic, aleuritic-pelitic, and pelitic sediments that, according to Nevesskii [20], contain 5–15% of finely dispersed material delivered by the river waters. Four cores of the White Sea's bottom sediment were collected. The cores were taken along the trend line connecting the southeastern and northwestern parts of the sea (stations 6042, 6056, and 6058), as well as near the Solovetsky Islands (station 6062). The sediment thickness was between 180 and 450 cm. The upper 0.2–5 cm layer of the sediment was brown or brownish-colored; it was followed by dark or light, greenish-grey layers with hydrotroilite inclusions. The

Table 4. Methane concentration and rates of microbial processes: methane oxidation (MO), methanogenesis (MG), acetate oxidation (AO), and sulfate reduction (SR) in the water column of the White Sea in August, 2006

Station, horizon, m	$[CH_4]$	MO	MG	AO	SR
	$\mu l\ l^{-1}$	nl $CH_4\ l^{-1}\ day^{-1}$	nl $CH_4\ l^{-1}\ day^{-1}$	$\mu g\ C\ l^{-1}\ day^{-1}$	$\mu g\ S\ l^{-1}\ day^{-1}$
6042					
0	0.22	0.25	0	24	0
5	0.22	0.22	0	13	0
15	0.23	0.15	6	14	0.58
20	0.26	0.17	18	27	0
25	0.16	0.07	0	8	0
55	0.21	0.05	9	6	0.21
C/B water*	1.16		11	42	0.34
6056					
0	0.06	0.04	0	10	1.89
10	0.06	0.01	25	12	0
20	0.05	0.01	0	4	0
130	0.06	0.02	9	5	3.68
C/B water	0.14	0.02	2	19	0.53
6058					
0	0.07	0.04	29	15	1.98
10	0.12	0.03	3	4	2.27
20	0.14	0.03	2	11	0
30	0.19	0.02	0	5	1.26
50	0.19	0.02	0	7	1.14
100	0.25	0.02	0	8	0
295	0.15	0.03	2	6	0
C/B water	0.32				0.38

Note: *C/B water stands for the close-to-bottom water samples from the Niemistö corer.

average content of carbonate minerals ranged from 1% in the Dvina Bay sediments to 0.5% in the sediment of the central and western basins (Table 5). The production of authigenic minerals is limited to iron oxides (goethite), as well as manganous and sulfide minerals, including primarily hydrotroilite and pyrite. The simultaneous presence of iron oxides and iron sulfides in the upper sediment layers indicates the thermodynamic nonequilibrium of these sediment.

The upper sediment layer of the open part of the Dvina Bay contained 1.65% of C_{org}; the sediments of the western basin contained 1.59% of C_{org}; the sediment samples collected near the Solovetsky Islands contained 0.65% of C_{org} (Table 5). As the sediment depth increased, the content of C_{org} decreased. This indicates that the amount of OM utilized for diagenetic processes is small. The $\delta^{13}C$–C_{org} values in the surface layer of bottom sediments varied from –25.8‰ near the Kandalaksha Bay outlet to –26.6‰ in the sediment of the open part of the Dvina Bay. This demonstrates the major contribution of isotopically light terrigenous C_{org} in the OM composition near the Northern Dvina estu-

ary, where high concentrations of lignin (a product of pinewood and herb decay) were detected. A slight decrease in the *Eh* and pH values of the sediment suggests low rates of sulfate reduction, although an increase in the total alkalinity (up to 8.0–10.5 mg equiv in the 45–58 cm horizon and up to 13.5 mg equiv at a depth of 160–250 cm; Table 6) and $N–NH_4^+$ concentration (up to 5.62 mg/l in the 46–58 cm horizon, station 6058) with sediment depth, as well as a decrease in the sulfate ion concentration, are due to anaerobic processes, especially sulfate reduction.

Methane concentrations and rates of methanogenesis (MG) and methane oxidation (MO) in the bottom sediment. In the Basin, the methane content in the oxidized layer of the sediment (0–1 cm) ranged from 0.2 μl CH_4 dm^{-3} to 3.5 μl CH_4 dm^{-3} at the depths of 133 m and 300 m, respectively (Fig. 6). In the possible upwelling zone near the Solovetsky Islands, methane concentration in the upper sediment horizon reached 3.8 μl CH_4 dm^{-3}. The highest CH_4 concentration (5.2 μl CH_4 dm^{-3}) was detected in the Dvina Bay (station 6042) in the 0–1 cm layer. The concentration of methane in the upper layers of all sampled sediment was one order of magnitude higher than that in the near-bottom water horizon. This fact indicates an intense methane diffusion along the concentration gradient across the sediment–water interface. Hence, the non-uniform distribution of methane content in the upper layers of bottom sediments is characteristic of the White Sea, due to the differences in the supply of suspended organic matter determining the process of organic matter transformation. Throughout the thickness of the sediments, the CH_4 concentration increased in the upper 5-cm layer in all cores and continued to increase gradually. The highest CH_4 concentrations (29.8, 56.7, and 22.5 μl CH_4 dm^{-3}) were detected in the 160–180 cm (station 6058), 245–246 cm (station 6062), and 280–290 cm (station 6042) layers, respectively. In deeper layers, methane concentration in the sediment decreased steadily.

Methanogenesis was detected in all the sampled sediment, starting from the oxidized upper layer (Table 7). As a rule, the process intensity was minimal (24–71 nl CH_4 dm^{-3} day^{-1}) in the surface layer and increased at a depth of 10–15 cm and then hardly changed with depth. The relatively high MG rates (up to 160–180 nl CH_4 dm^{-3} day^{-1}) were detected in the bottom sediments of the Dvina Bay, whereas the rates of methanogenesis in the sediments of the Basin did not exceed 88 nl CH_4 dm^{-3} day^{-1}.

The processes of methane production and oxidation were observed simultaneously. The average values of methane oxidation rates were one order of magnitude lower than those of methanogenesis. At station 6058, the highest MO rate (13.5 nl CH_4 dm^{-3} day^{-1}) was detected in the oxidized, upper horizon of the sediment; in the underlying horizons, MO rate decreased sharply and reached 0.7–2.8 nl CH_4 dm^{-3} day^{-1}. At stations 6042 and 6056, high MO rates (up to 15–18 nl CH_4 dm^{-3} day^{-1}) were detected at a depth of 45–70 cm. The methods used were insufficient to analyze the contribution of aerobic and anaerobic methane oxidation by different groups of microorganisms developing under different conditions. It can be suggested that aerobic methanotrophs are active only in oxidized sediments; however, it is possible that anaerobic methane oxidation occurs in the local microzones of these sediment. In the slightly reduced body of the cores, anaerobic methane oxidation probably occurs.

Table 5. Content of C_{org} and the values of $\delta^{13}C–C_{org}$ in the White Sea bottom sediment

Station no.	Sediment horizon, cm	C_{org}, %	$\delta^{13}C–C_{org}$, ‰
6042	0–5	1.65	–26.54
	5–10	1.29	–26.53
	10–15	1.18	–26.51
	15–27	1.21	–26.53
	40–48	1.22	–26.40
	48–55	1.16	–26.39
6058	7–16	1.59	–25.82
	16–21	1.57	–25.73
	24–46	1.39	–25.70
	46–58	1.55	–24.67
6062	2–5	0.65	–25.15
	10–21	0.35	–24.93
	20–30	0.52	–25.20
	50–60	0.40	–25.61
	90–100	0.58	–26.52
	185–195	0.49	–29.23
	200–210	0.42	–30.66
	220–230	0.32	–30.91
	240–250	0.24	–30.79
	330–340	0.49	–29.41

Table 6. Chemical composition of the silt waters of the bottom sediment of the White Sea

Station no.	Sediment horizon, cm	Alkalinity, mg equiv/l	SO_4^{2-}, g/l;	$N–NH_4^+$, mg/l	Humidity, %
6042	0–1	3.0	2.07	0.73	84.7
	2–5	3.0	2.07	0.96	66.86
	5–10	2.0	2.45	1.0	62.60
	10–15	2.1	2.43	1.6	61.45
	15–27	2.7	2.26	2.12	
	40–48	3.3	2.13	3.16	
	48–55	3.6	2.10	2.81	65.37
6056	0–6	4.0	2.2	2.0	82.43
	13–30	6.3	2.2	3.25	
	30–31	7.5	2.1	3.08	67.78
	50–55 LDT	9.0	2.0	4.17	71.87
	100–110	12	2.23	8.66	64.02
	140–150	12.5	1.78	9.45	60.69
	170–180	13	1.89	10.39	60.36
6058	0–6	4	2.14	0.41	80.67
	7–16	7	2.05	4.30	
	26–46	6	2.00	4.80	70.60
	46–58	8	1.79	5.62	72.93
	45–55 LDT	10.5	2.01	11.90	70.93
	110–120	12.9	2.00	9.74	67.03
	160–180	13.5	1.89	10.71	61.81
	230–250	13.5	1.78	9.04	59.46

Note: The 0–50 cm sediment layers were sampled with Niemistö corer (NC); the sediment layers with thickness of above 50 cm were sampled with large-diameter geological tubes (LDT).

Active assimilation of ^{14}C acetate (potential activity) was detected mostly in the surface layer of oxidized sediment. In the sediment of station 6042, the decreasing gradient of acetate accumulation rate was most pronounced (from 170 to 43 μg C dm^{-3} day^{-1} in the 0–5 cm and 10–30 cm layers, respectively).

Relatively high rates of sulfate reduction (up to 260 μg S dm^{-3} day^{-1}) were detected in the surface (station 6058) and subsurface (stations 6042 and 6056) sediment layers. In deeper horizons, the rate of sulfate reduction decreased and varied from 7.5 μg S dm^{-3} day^{-1} (in the 230-cm layer of station 6058) to 92 μg S dm^{-3} day^{-1} (50 cm, station 6042). The results of comparative analysis of the two main anaerobic processes indicate that the rate of C_{org} consumption during sulfate reduction was 200–1000 times higher than that during methanogenesis.

DISCUSSION

Large seasonal variations in the primary production values are the subject of debate about the White Sea's trophicity. The White Sea is historically considered a water bodywith low productivity [21]. According to other authors [6], the White Sea is one of the most productive seas of the Russian sector of the Arctic Ocean in the context of the level of plankton primary production. Indeed, the daily phytoplankton production in the Kandalaksha Bay in August, 1972 did not exceed 50 mg C m^{-2} day^{-1} (radiocarbon method), according to the data obtained by Korsak [21]; however, at the beginning of the summer season of 1991, PP values in the same bay reached 1300 mg C m^{-2} day^{-1} (oxygen method), according to [22]. The results of our measurements of primary production corresponded to the minimal values typical of oligotrophic water bodies (49–67 mg C m^{-2} day^{-1}). The results of the comparison of these data indicate that the rate of primary production in the White Sea during the short period of phytoplankton bloom may be tens of times higher than that recorded at the end of summer. High content of dissolved organic compounds (37–66%) in the total primary production (which is probably a specific feature of the Arctic seas in general) is noteworthy. The proportion of exometabolites in the total organic matter in oligotrophic tropical water bodies is known to range from 30 to 40%, according to the data obtained by Sorokin [23].

Our measurements of the total numbers of bacterioplankton, performed during the 5 year period indicate that the interannual coefficient of variation in the number of bacterioplankton in the surface water layer during the summer season (50–200 thousand cell ml^{-1}, Fig. 3) is 2–4. As compared to the values of phytoplankton production and, consequently, to the rate of autochthonous OM influx, this is a very stable indicator. In the deep water of the Kandalaksha Bay and the Basin, stable low BP numbers were detected (Fig. 4). The interannual coefficient of variation in the number of bacterioplankton in the deep water horizons is only 1.5–2.0. Thus, one can assume that the bacterioplankton community of the deep water horizons of the White Sea is more stable than that of the surface water horizons.

Detailed studies of the total numbers, biomass content, average volume of microbial cells, and productivity of bacterioplankton in the Barents Sea were carried out in 1983–1992 by the scientists from the Murmansk

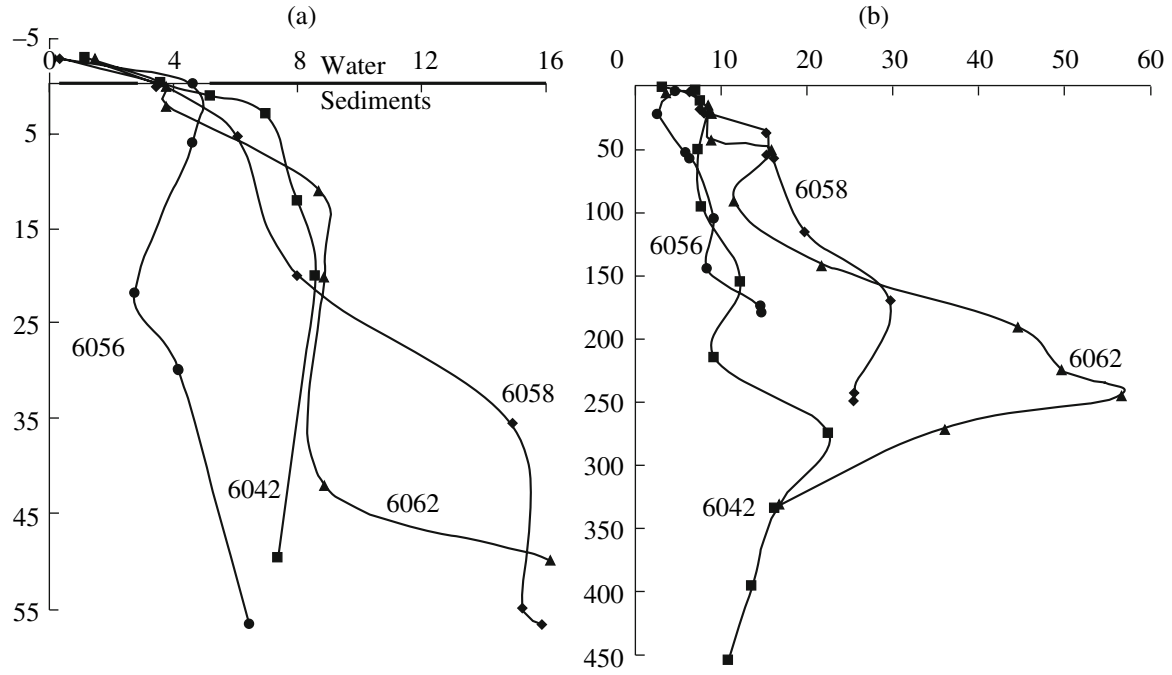

Fig. 6. Methane concentrations in the close-to-bottom water and bottom sediment of the White Sea (μl CH_4 dm^{-3}): (a) in pre-bottom water and up to the 55-cm layer (Niemistö corer); (b) to the total sampling depth (Niemistö corer and LDT). The ordinate shows the depth of the sediment layer, m.

Marine Biological Institute, Kola Science Centre, Russian Academy of Sciences [24]. In July–August, BP numbers in the surface water layer of the Barents Sea (227–420 thousand cells/ml) were 1.2–1.8 times higher than those in the White Sea Basin. In the Barents Sea, the average volume of BP cells (0.24 μm^3) was 1.16 times less than in the White Sea. The daily bacterial production in the Barents Sea varied within a wide range, from 17.7 to 150 μg/l; its average value was 61 μg/l (wet biomass), which was two times higher than in the White Sea. As a result, *P*/*B* coefficients calculated for the surface water horizons, varied within a close range, 0.22–0.63 and 0.22–0.75 (in the White Sea and Barents Sea, respectively). Significant differences in the *P*/*B* coefficients calculated for bacterioplankton inhabiting different horizons of one water column indicate that bacterial populations are at different development stages. It was shown that the White Sea bacterioplankton is distinguished by the high variability of the ratio of aggregated cells (17–78%) in the total cell counts. The degree of BP aggregation is known to have a significant effect on the species composition of the organisms consuming bacterioplankton as a food source [25].

The suspended organic matter had a lighter isotope composition (from –28.0 to –30.5‰) due to the predominance of organic matter delivered by the Northern Dvina waters. Comparison of these results with the $\delta^{13}C$–C_{org} values of the Kandalaksha Bay suspension, sampled near the Lushov Island during the blooming season of bacterioplankton (from –21.1 to –21.3‰) [4] suggests that in August, 2006, the content of planktonogenic isotopically heavier C_{org} did not exceed 5% of the total C_{org}.

One of the aims of this study was to determine the balance between microbial methanogenesis and methane oxidation, both in the water column and in the bottom sediment. The rates of methanogenesis and methane oxidation in some water horizons were low.

The rate of methanogenesis in the sediment varied from 19.3 to 54 μl CH_4 m^{-2} day^{-1} in the White Sea Basin (station 6056) and the Dvina Bay, respectively; the calculations were made for the average thickness (55 cm) of the late Holocene sediment of the White Sea. The produced methane was partially oxidized in the sediment (3.71–6.14 μl CH_4 m^{-2} day^{-1}), both anaerobically deeper in the sediment and aerobically in the oxidized upper layer. Our calculations demonstrated that the methane flow from the sediment into the water column was 14.1–48 μl CH_4 m^{-2} day^{-1} (the highest value was detected in the Dvina Bay). Comparison of the rates of methane production in the sediment of the White Sea bottom and that in the sediments of the Kara [26] and Chukchi [27] seas demonstrate that the values of methane production in the White Sea are comparable

Table 7. Rates of microbial processes: methane oxidation (MO), methanogenesis (MG), dark CO_2 assimilation (DA), acetate oxidation (AO), and sulfate reduction (SR) in the bottom sediment of theWhite Sea

Sediments, cm	MG	MO	SR	DA	AO ⟶ CO_2
	nl CH_4 dm^{-3} day^{-1}		μg S dm^{-3} day^{-1}	μg C dm^{-3} day^{-1}	
St. 6042					
0–1 TSE	71	6.30	140.4	170.0	115
2–5	48	5.02	261.3	88.7	173
10–15	144	4.85	55.7	27.4	28
15–27	126	2.29	65.8	68.1	43
48–55	61	14.83	91.8	83.6	15
90–100 LDT	123	4.33	27.5	37.0	23
150–160	133	8.01	31.7	94.5	84
210–220	160	4.8	28.1	87.3	29
270–280	167	1.53	41.6	43.9	49
330–340	188	1.32	31.0	73.8	31
390–400	85	11.49	19.5	23.2	48
450–460	135	1.08	27.1	19.1	36
St. 6056					
0–6 TSE	32	6.39	18.1	22.5	99
13–30	33	9.02	39.4	30.4	97
45–70	41	18.38	19.3	19.8	23
50–55 LDT	78	17.41	17.1	26.7	22
100–110	88	1.42	12.2	18.3	46
140–150	74	3.38	15.1	14.8	75
170–180	86	8.87	12.1	12.6	19
St. 6058					
0–6 TSE	24	13.51	97.4	69.5	68
7–16	42	0.95	61.3	139.8	58
26–46	47	2.48	30.0	42.5	8
46–58	41	2.78	14.0	84.2	4
45–55 LDT	51	5.68	19.5	81.3	6
110–120	62	0.69	19.4	60.4	21
160–180	77	2.66	27.0	42.3	13
230–250	89	2.16	7.5	64.1	22

to those in the less productive sediment of the Kara and Chukchi seas near the Alaskan coast.

Production of reduced sulfur compounds in the sampled sediment of the White Sea was low and varied from 3,9 mg S m^{-2} day^{-1} in the central basin to 21,9 mg S m^{-2} day^{-1} in the Dvina Bay; the calculations were made for the surface horizon (15 cm). Hence, the sediment of the main basin of the White Sea are characterized by low intensities of the processes of the carbon and sulfur cycles, whereas, in the sediment of the Kandalaksha Bay littoral, the production rates for methane and reduced sulfur compounds in the summer season reach 2–6 ml CH_4 m^{-2} day^{-1} and 1–5 g S m^{-2} day^{-1}, respectively [5].

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