## EXPERIMENTAL ARTICLES

# Microbial Processes of the Carbon and Sulfur Cycles in the Chukchi Sea

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**Abstract**—The research performed in August 2004 within the framework of the Russian-American Long-term Census of the Arctic (RUSALCA) resulted in the first data concerning the rates of the key microbial processes in the water column and bottom sediments of the Bering strait and the Chukchi Sea. The total bacterial counts in the water column varied from $30 \times 10^3$ cells $ml^{-1}$ in the northern and eastern parts to $245 \times 10^3$ cells $ml^{-1}$ in the southern part. The methane content in the water column of the Chukchi sea varied from 8 nmol $CH_4$ $l^{-1}$ in the eastern part of the sea to 31 nmol $CH_4$ $l^{-1}$ in the northern part of the Herald Canyon. Microbial activity occurred in the upper 0–3 cm of the bottom sediments; the methane formation rate varied from 0.25 to 16 nmol $CH_4$ $dm^{-3}$ $day^{-1}$. The rates of methane oxidation varied from 1.61 to 14.7 nmol $CH_4$ $dm^{-3}$ $day^{-1}$. The rates of sulfate reduction varied from 1.35 to 16.2 μmol $SO_4^{2-}$ $dm^{-3}$ $day^{-1}$. The rate of methane formation in the sediments increased with depth, while sulfate reduction rates decreased (less than 1 μmol $SO_4^{2-}$ $dm^{-3}$ $day^{-1}$). These high concentrations of biogenic elements and high rates of microbial processes in the upper sediment layers suggest a specific type of trophic chain in the Chukchi Sea. The approximate calculated balance of methane emission from the water column into the atmosphere is from 5.4 to 57.3 μmol $CH_4$ $m^{-2}$ $day^{-1}$.

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

Due to their high-latitude location, the Arctic seas are covered with ice for most of the year; their annual average temperatures are low, and the period of biological productivity is short. The Chukchi Sea differs in some respects from other Arctic seas. A considerable part of its area is influenced by the Alaskan stream, which continuously supplies great volumes of Pacific water. In the water intake of the Chukchi Sea, river flow plays a less important role than in other Arctic seas. The bottom of the Chukchi Sea is relatively level; the average depth of the continental shoal is 50–60 m, of the shallow banks, 20–30 m.

Russian and international research on the seas of the Arctic basin has become more active since 1990. The medium-term changes of the hydrological, hydrochemical, and biogeochemical parameters which determine the climatic regime of the region attract special atten-

tion [1–4]. The Chukchi Sea is still insufficiently studied; microbiological data are limited to the results of several expeditions [5–7]. The contribution of the Chukchi Sea ecosystem to the global methane turnover is still unknown.

For the long-term integrated study of the Chukchi Sea, the RUSALCA (*Russian-American Long-term Census of the Arctic*) program was established by the Russian Academy of Sciences, Roshydromet (Russian Federal Service for Hydrometeorolgy and Environmental Monitoring), and NOOA (National Oceanic and Atmospheric Administration, United States). The study of the biological processes of carbon turnover, primarily of production and oxidation of methane, the second most important greenhouse gas, is one of its tasks. The main goal of the present work was to obtain quantitative characteristics of the key microbial processes of carbon turnover: methane production (MG), methane oxidation (MO), anaerobic decomposition of organic matter

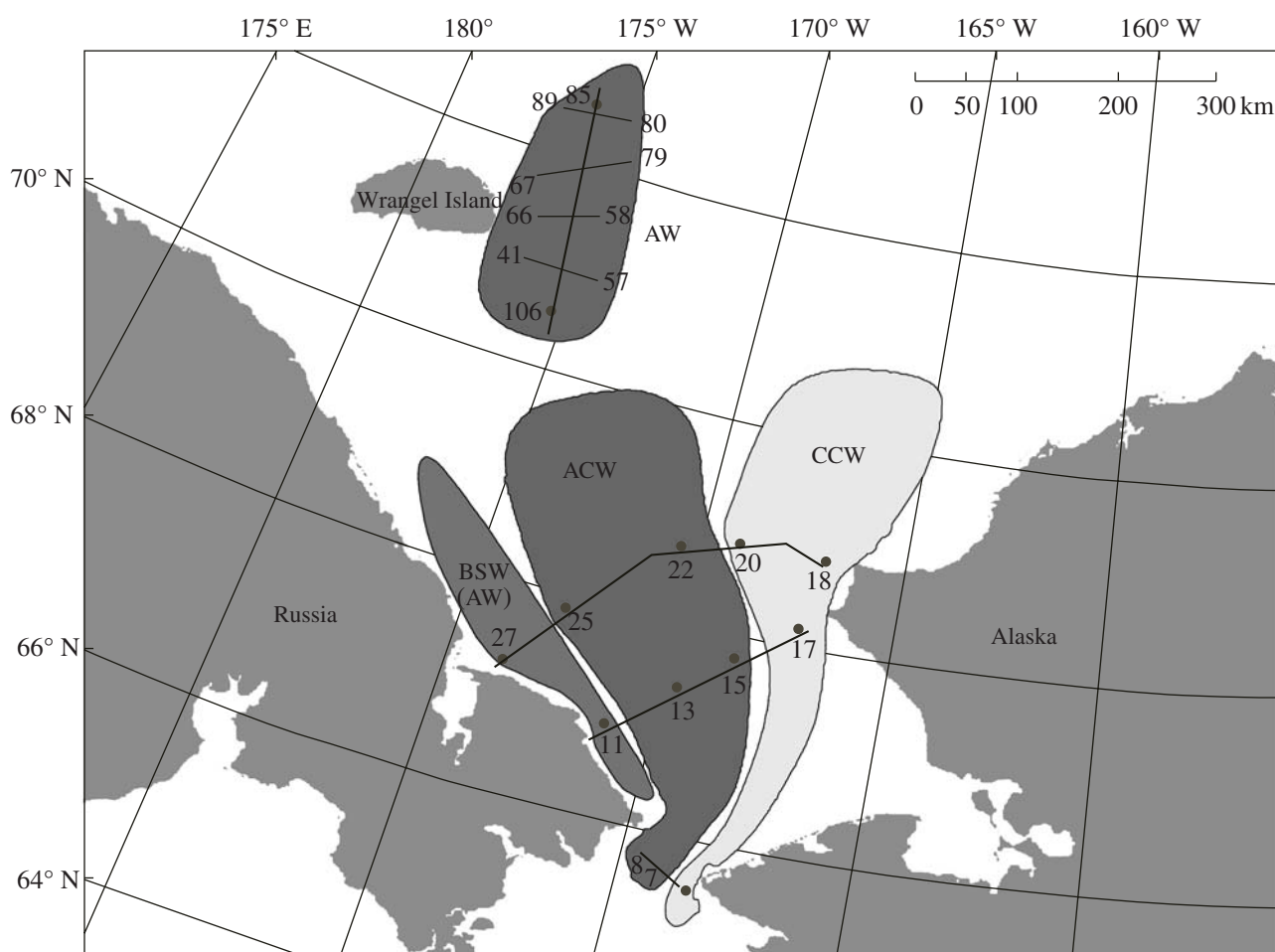[1] Corresponding author; e-mail: savvichev@mail.ru

**Fig. 1.** Distribution of the water masses in the Chukchi Sea. ACW, Alaskan coastal waters (warm, desalinated); CCW, Chukotka coastal waters (cold, saline); BSW, Bering Sea waters (cooled, slightly desalinated); AW, arctic waters (very cold, saline).

(OM) in the course of sulfate reduction (SR), and $CO_2$ dark assimilation (DA) by both autotrophic and heterotrophic microorganisms in the water and sediments of the Chukchi Sea, as well as to determine the carbon isotopic composition in suspended organic matter.

## MATERIALS AND METHODS

Materials for research were obtained in the course of the RUSALCA Russian–American expedition on the *Professor Khromov* research vessel (August 2004). The location of the sampling stations is presented on Fig. 1. The research was carried out in the Bering Strait, in two parallel trends in the northern part of the Chukchi Sea from Alaska to Chukotka shores, and on four short trends of the Herald Canyon in the northwestern part of the Chukchi Sea.

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 in glass bottles with overflow; the bottles were then sealed with gas-tight stoppers.

The bottom sediments were sampled with a van Veen dredge equipped with a gravity core. Undamaged samples of the bottom sediments were placed into truncated 5-ml plastic syringes with rubber pistons and sealed with rubber stoppers. The redox potential and pH were determined at the time of sampling with a pH 320/Set-1 potentiometer (Germany). All experiments with water and sediments were carried out during the first hours after sampling at close to in situ temperatures within the range from –1.0 to +6°C.

To characterize the trophic state of the water basin, primary production was determined by the radiocarbon modification of the bottle method [8]. The experiments were carried out in transparent and darkened glass bottles; after the introduction of $NaH^{14}CO_3$ (20 µCi), the bottles were incubated in the deck basin for 8–24 h. An individual perforated dark sheath of known light transmittance was used for each bottle. After the exposure, the content of the bottles was filtered through 0.2 µm

Nylon membrane filters. For removal of residual carbonates, the filters were washed with large amounts of slightly acidified seawater.

The rates of microbial dark $CO_2$ assimilation (DA), MG, and MO were determined by the radioisotope methods with $NaH^{14}CO_3$, $^{14}CH_4$, and $^{14}CH_3COONa$. For this purpose, 0.1 ml of a labeled compound was added to the bottles with water samples (60 µCi/l) and to the syringes with sediment samples (4000 µCi/dm$^3$). The samples were incubated for 12–48 h at native temperature. 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-Betta 1219 scintillation counter, LKB, Sweden) were carried out according to the previously described procedure [9]. In the estimates of 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 on the filters [10].

To determine the total concentration of suspended matter (SM), water samples were filtered through calcined and weighted 47 mm GF/F glass fiber filters. The filters were then dried at 60°C to constant weight and weighed.

The sulfate reduction rate was determined by the formation of $^{35}S$-labeled $H_2S$ and total pyrite and 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 according to the procedures described previously [9]. The potential activity of $^{14}C$ glucose and $^{14}C$ acetate destruction (AG and AA, respectively), i.e., heterotrophic potential, were determined after 24-h incubation 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 equipped with a flame ionization detector. The concentrations of sulfate, chloride, and acetate were determined on a Biotronik ion chromatograph (Germany). The carbon isotopic composition of OM ($\delta^{13}C$) was determined with a Delta Plus mass spectrometer (Germany). The accuracy of the measurements was ±0.1%.

The quantitative determination of microorganisms in the water samples was carried out by direct count in an epifluorescence microscope. Water samples (30 ml) were filtered through 0.19 µm polyester filters (Dubna, Russia) pretreated with Sudan black. The filters were fixed with 96% and stained with DAPI. The stained and dried filters were embedded in a nonfluorescent immersion oil and examined under a Lumam-3 microscope (LOMO, Russia) at ×900 magnification. The cells were counted in 20 microscope fields.

## RESULTS

The temperature and salinity measurements suggested the subdivision of the water area of the Chukchi Sea into four zones (Fig. 1). According to the Rozett sensors, the in situ temperature of Alaskan coastal water (ACW) was as high as 11°C; salinity was 31.3‰ (station 7). The average temperature of Chukotka coastal water (CCW) varied within the range from –1.5 to +2.5°C; salinity varied from 32 to 33‰ (station 11). The temperature of the southern and central part of the Chukchi Sea (Bering Sea water, BSW), influenced by the Bering Strait current, was positive. The water column of the Herald Canyon (arctic water, AW) had mostly negative temperatures; the surface layer, which was formed by ice thawing, had decreased density and salinity.

**Primary production, total microbial numbers, and the content and isotopic composition of suspended carbon.** During the period of the expedition, the measured values of the primary production (PP) in the Chukchi Sea were different for the different parts of its area (Table 1). The lowest PP (110 mg C m$^{-2}$ day$^{-1}$) was recorded for the cold northern water (station. 85); Alaskan coastal waters also had low productivity of 180 mg C m$^{-2}$ day$^{-1}$ (station 20). In the southern and southwestern parts of the sea, PP values were high, up to 1400 mg C m$^{-2}$ day$^{-1}$ (station 11).

The total numbers of bacterioplankton (BP) in different parts of the Chukchi Sea were also different. Low levels of BP ($30–190 \times 10^3$ cells ml$^{-1}$) were detected near the Alaskan shores (station 20). In the Herald Canyon, BP numbers were even lower, from 10 to $102 \times 10^3$ cells ml$^{-1}$ (stations 85 and 106). In that zone, where active thawing of sea ice occurs, the highest BP numbers were detected in the surface water layer with decreased salinity. The highest BP were revealed in the southern part of the sea (up to $200–245 \times 10^3$ cells ml$^{-1}$, stations 8 and 22). Microscopy revealed that large rods associated with detritus particles predominated near the Alaskan coast and in the Bering Strait. In the Chukotka coastal waters, loosely aggregated cells embedded in a common matrix predominated; they often contained diatoms and large bacterial cells. At most of the stations, a significant portion of the cells were contained within aggregates; their enumeration was therefore difficult. The results of bacterial counts therefore reflect the minimal reliable estimate.

In order to assess the total bacterial activity, experiments were carried out to determine dark $CO_2$ assimilation (DA). Relatively high DA values (up to 112 nmol C l$^{-1}$ day$^{-1}$) were revealed in productive regions of the southwestern part of the Chukchi Sea (station 11). In the northern part of the sea (station 85), the process was less pronounced (on average 35 nmol C l$^{-1}$ day$^{-1}$); however, DA values in the desalinated surface layer reached 158 nmol C l$^{-1}$ day$^{-1}$.
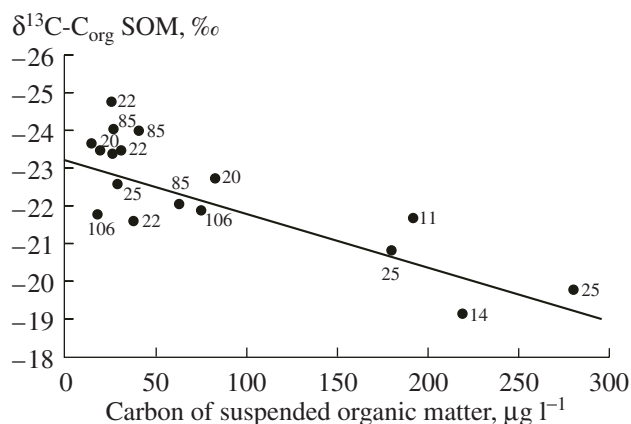
The carbon content of suspended organic matter (SOM) and dissolved organic matter (DOM) were determined at some stations (Table 2). High SOM con-

**Table 1.** Primary production (PP), total bacterioplankton numbers (BP), methane concentration, and rates of methane oxidation (MO) and dark $CO_2$ assimilation (DA) in the water column of the Chukchi Sea in August 2004

| Station; depth, m | PP, mg C m$^{-2}$ day$^{-1}$ | BP, $\times 10^3$ cells ml$^{-1}$ | Aggregated cells, % | CH$_4$, nM | MO, nmol l$^{-1}$ day$^{-1}$ | DA, nmol l$^{-1}$ day$^{-1}$ |
|---|---|---|---|---|---|---|
| ACW | | | | | | |
| 20 (50) | 180 | 30–190 (53) | 5–80 (35) | 10–13 (12) | 0.03–0.05 (0.04) | 11–43 (33) |
| CCW | | | | | | |
| 11 (40) | 1400 | | | 12–13 (13) | 0.05–0.09 (0.07) | 72–112 (85) |
| BSW | | | | | | |
| 7 (50) | | 11–85 (53) | 5–60 (35) | 8–10 (9) | | 8–76 (53) |
| 8 (40) | 270 | 208–244 (227) | 52–72 (61) | 8–9 (9) | | |
| 14 (48) | | | | 9–12 (10) | 0.06–0.09 (0.08) | |
| 22 (57) | | 67–200 (108) | 72–90 (77) | 8–14 (11) | 0.04–0.08 (0.06) | |
| 25 (53) | | | | 9–19 (14) | 0.06–0.16 (0.12) | |
| AW | | | | | | |
| 85 (103) | 110 | 10–77 (35) | 10–95 (32) | 12–21 (18) | 0.09–0.23 (0.19) | 6–158 (35) |
| 106 (72) | | 14–102 (38) | 70–90 (80) | 18–21 (19) | 0.08–0.19 (0.17) | |

Note: First line, value ranges; average values are given in parentheses.

tent was detected for the waters with high levels of primary production (191 µg C l$^{-1}$, station 11 and 29.1–280 µg C l$^{-1}$, station 25). The water arriving from the Bering Sea varied in the SOM content (219 µg C l$^{-1}$, station 14 and 26–38 µg C l$^{-1}$, station 22). SM near the Alaskan coast (41.7 µg C l$^{-1}$, station 20) and in the northern part of the Chukchi Sea (18–75 µg C l$^{-1}$, stations 85 and 106) contained less SOM. The content of DOM in the water area investigated varied from 1.86 to 5.19 mg C l$^{-1}$, i.e., 94.7 to 99% of the total organic matter. The major part of organic matter was therefore represented by the soluble excreta of living plankton.



**Fig. 2.** Relation between the carbon isotope composition of suspended organic matter ($\delta^{13}$C-C$_{org}$ (‰)) and the carbon content of suspended organic matter (SOM, µg l$^{-1}$).

The isotopic composition of suspended organic matter ($\delta^{13}$C$_{opr}$) is an indicator of its origin. Our results for the surface water layers demonstrate that the productive water masses of the western and southern parts of the Chukchi Sea had a heavy isotopic composition of $\delta^{13}$C$_{org}$ in ($\delta^{13}$C$_{org}$ = –19.2 and –21.7‰) (Table 2). This isotopic composition is common for marine phytoplankton. In the Bering Strait and near Alaskan coasts, the carbon of suspended organic matter was significantly lighter; this is the result of the presence of terrigenous organic matter (stations 20, 22; $\delta^{13}$C$_{org}$ = –23.4 and –24.8‰). In the Herald Canyon, the $\delta^{13}$C values of SOM varied from –21.8‰ in the surface water layer (station 106) to –24.0‰ (station 85). The lighter isotope composition of C$_{org}$ in the surface layer near the edge of ice (station 85) was caused by the presence of arctic phytoplankton rich with lipids.

A correlation between $\delta^{13}$C$_{org}$ and the carbon content in suspended organic matter can be discerned (Fig. 2). The heavy carbon isotope composition in organic matter was revealed in the samples with high OM content in the suspension of phytoplanktonic origin. In the water masses of primarily terrigenous origin, a lighter isotope composition of SOM was detected.

**Methane content and rates of microbial methane oxidation in the water column.** The methane content in the water column of the Chukchi Sea was very low, from 8–13 nmol CH$_4$ l$^{-1}$ in the eastern part to 15 nmol CH$_4$ l$^{-1}$ in the western part (Table 3, Fig. 3). The highest methane concentration in the Chukchi Sea was detected in the northern part of the Herald Canyon (up to

31 nmol $CH_4$ $l^{-1}$, station 89). In the whole area of the Chukchi Sea, methane oxidation rates were low (Fig. 4). On station 20, the rates of methane oxidation virtually did not change with depth (from 0.03 to 0.05 nmol $CH_4$ $l^{-1}$ $day^{-1}$). On station 15, methane oxidation rates increased steadily from 0.05 nmol $CH_4$ $l^{-1}$ $day^{-1}$ at the surface to 0.1 nmol $CH_4$ $l^{-1}$ $day^{-1}$ in the near-bottom horizon. In the near-bottom horizons of the Herald Canyon (station 106), elevated rates of MO were detected, up to 0.23 nmol $CH_4$ $l^{-1}$ $day^{-1}$. These values are similar to the minimal rates known for the marginal seas and gulfs of the Arctic basin (Kara Sea, 0.08–0.54 nmol $CH_4$ $l^{-1}$ $day^{-1}$) [11].

**Chemical composition of silt waters and rates of microbial processes in the upper layers of bottom sediments.** The physicochemical state of the Chukchi Sea bottom sediments is known to be determined by the inflow of autochthonous sediment material, products of shore abrasion, and ice transfer [12]. Sandy and silt–sandy sediments predominate in the Bering Strait. Finely dispersed pelitic sediments are concentrated in the upper layer of the sediments of the continental terrace.

The samples of the upper layer of bottom sediments were collected in the investigated area of the Chukchi Sea. Semiliquid pelitic–aleuric silt was present in the upper layer of most samples. In the upper silt layer (0–5 cm), Eh values were positive and varied from +188 mV (station 11) to +15 mV (station 15) (Table 4). The content of organic matter in the upper sediment layer varied from 0.39 (station 17) to 1.9–2.0% (stations 15, 25, and 24). On the sludgy sediments of the southwestern part of the sea (stations 11 and 13), bivalves *Macoma calcarea* were abundant; their biomass reached 2000 g $m^{-2}$ of wet sediment. Basket stars (*Ophiuroidea*) and other echinoderms were also present [13].

At the stations with high density of bottom dwellers, the silt waters of the upper sediment layers contained extremely high concentrations of biogenic elements: ammonium nitrogen (up to 17900 μmol $NH_4^+$ $dm^{-3}$, station 11) and phosphorus (up to 400 μmol P $dm^{-3}$, station 13). This is an indication of intense destruction of organic matter. Assimilation of $C^{14}$-labeled glucose and acetate was determined experimentally in order to estimate the potential activity of heterotrophic processes. In the upper sediment layers of stations 11 and 15, a maximum of acetate consumption was evident (22.5 and 13.2 μmol $dm^{-3}$ $day^{-1}$, respectively). At stations 20 and 106, acetate assimilation was less pronounced (3.08 and 5.25 μmol $dm^{-3}$ $day^{-1}$). Dark $CO_2$ fixation is another criterion of integral (autotrophic and heterotrophic) microbial activity. The values of dark $CO_2$ assimilation in the upper sediment layers varied from 1.2–1.6 (stations 106 and 85) to 2.9–3.9 μmol $dm^{-3}$ $day^{-1}$ (stations 11 and 15).

**Table 2.** Main characteristics of suspended and dissolved organic matter of the Chukchi Sea water column

| Station no. | Horizons, m | SM, mg $l^{-1}$ | SOM, mg $^{-1}$ | $\delta^{13}C_{org}$ SOM, % | DOM, mg $l^{-1}$ |
|---|---|---|---|---|---|
| ACW | | | | | |
| 20 | 1 | 5.39 | 0.027 | –23.38 | 1.92 |
| | 22 | 5.68 | 0.015 | –23.66 | 4.75 |
| | 50 | 14.63 | 0.083 | –22.73 | 3.30 |
| CCW | | | | | |
| 11 | 1 | 7.45 | 0.019 | –21.67 | 2.34 |
| BSW | | | | | |
| 7 | 1 | 4.62 | | –22.01 | 2.35 |
| | 20 | 6.02 | | –22.68 | 5.19 |
| | 50 | 5.90 | | –23.46 | 2.56 |
| 8 | 1 | 5.39 | | –23.79 | 3.54 |
| | 20 | 8.00 | | –24.18 | 1.86 |
| 14 | 1 | 11.00 | | –19.15 | |
| | 10 | 9.27 | 0.022 | –19.13 | |
| | 15 | 7.14 | | –19.83 | |
| | 40 | 7.13 | | –23.14 | |
| 22 | 1 | 4.90 | 0.026 | –24.75 | |
| | 25 | 5.55 | 0.031 | –23.49 | |
| | 50 | 7.36 | 0.038 | –21.61 | |
| 25 | 1 | 5.28 | 0.029 | –22.57 | |
| | 20 | 8.76 | 0.028 | –19.76 | |
| | 50 | 13.70 | 0.018 | –20.81 | 3.74 |
| AW | | | | | |
| 106 | 1 | 3.88 | 0.018 | –21.78 | |
| | 25 | 8.30 | 0.075 | –21.88 | |
| | 66 | 6.30 | 0.020 | –23.49 | 3.95 |
| 85B | 1 | 5.28 | 0.041 | –24.00 | |
| | 30 | 7.21 | 0.063 | –22.04 | |
| | 101 | 8.91 | 0.027 | –24.03 | |

Our research revealed that the methane concentration in the upper sediment layers was low and varied from 0.24 (station 11) to 1.1 μmol $CH_4$ $dm^{-3}$ (stations 20 and 106). Methane formation occurred in all the samples of surface silts, although redox electrode measurements demonstrated their oxidized condition. The rate of this process varied from 0.25 (station 22) to 12–16 nmol $CH_4$ $dm^{-3}$ $day^{-1}$ (stations 20 and 15). Methane oxidation concomitant with methane formation was quantitatively determined. The values of methane oxidation rate varied from 1.61 (station 11) to 14.7 nmol $CH_4$ $dm^{-3}$ $day^{-1}$ (station 106). It should be noticed that a considerable portion of the methane carbon (35–85%) was revealed in the fraction of dissolved organic matter;

**Table 3.** Methane concentration in the upper (1 m) water horizon and the average concentration in the water column

| Station no.; depth, m | $CH_4$ (1 m), nmol $l^{-1}$ | $CH_4$ (average), nmol $l^{-1}$ |
|---|---|---|
| ACW | | |
| 20 (50) | 10 | 12.5 |
| CCW | | |
| 11 (40) | 12.6 | 13 |
| BSW | | |
| 7 (50) | 8 | 9 |
| 8 (40) | 9 | 9 |
| 14 (48) | 6 | 11.6 |
| 15 (45) | 12 | 10.6 |
| 21 (50) | 8 | 10.2 |
| 22 (57) | 8 | 10.8 |
| 24 (50) | 9 | 13.1 |
| 25 (50) | 9 | 15.1 |
| AW | | |
| 106 (67) | 12 | 18.1 |
| 44 (50) | 12 | 15.5 |
| 56 (50) | 8 | 11.2 |
| 58 (50) | 9 | 12.1 |
| 60 (90) | 8 | 16.3 |
| 61 (80) | 9 | 16.2 |
| 62 (62) | 9 | 14.0 |
| 64 (50) | 11 | 14.6 |
| 67 (36) | 10 | 17.4 |
| 70 (54) | 9 | 17.6 |
| 71 (57) | 14 | 18.7 |
| 74 (69) | 11 | 18.2 |
| 75 (73) | 13 | 16.6 |
| 80 (49) | 12 | 17.0 |
| 81 (58) | 12 | 15.5 |
| 82 (78) | 15 | 16.1 |
| 83 (80) | 12 | 18.8 |
| 85B (103) | 18 | 19.5 |
| 86 (82) | 18 | 19.9 |
| 88 (72) | 16 | 24.0 |
| 89 (73) | 18 | 31.2 |

only 3–6% of the methane carbon was detected in the cell biomass.

Sulfate reduction was detected in all the samples of bottom sediments. Sulfate reduction rates varied from 1.35 (station 20) to 16.2 $\mu$mol $SO_4^{2-}$ $dm^{-3}$ $day^{-1}$ (station 85) (Table 4). Comparison of the two major anaerobic processes (sulfate reduction and methanogenesis) revealed a much greater role of the former in consumption of organic matter.

Thus, high rates of microbial processes were found in all the samples of the upper sediment layers. In the sediments of productive areas of the southwestern and central parts of the sea (stations 11, 13, and 15), both the rates of microbial processes and the concentration/numbers of the benthos fauna were higher [13]. Microbial activity in the Herald Canyon, which is high for a polar oligotrophic aquatic environment, is probably the result of slipping down of fresh surface sediments along the canyon walls and formation of complex multilayer precipitates.

**Microbial processes within the bottom sediments.** Four cores of Chukchi Sea bottom sediments were collected. The cores were taken along the trend line connecting the southwestern and northeastern parts of the Chukchi Sea (stations 15, 22, 106, and 85). The sediment thickness was from 70 to 210 cm. (Fig. 5). Throughout the thickness of the sediments from the central part of the Chukchi Sea, redox potential was weakly positive; negative values as low as Eh = –60 mV were recorded only for some horizons. In the sediments from the Herald Canyon (stations 106 and 85), dense sediments with negative Eh values reaching –170 mV were located directly below the upper sediment layer.

Chemical analysis of the silt water revealed an increase in the total alkalinity with depth (from 7.0 to 33.5 mmol $l^{-1}$, station 106). For example, the content of ammonium nitrogen measured at station 15 was very high in the upper horizon and decreased sharply at 10 cm depth (from 14.9 to 3.20 mmol $l^{-1}$ in the 0–3 and 3–20 cm layers, respectively); the subsequent decrease with depth was insignificant. Phosphorus concentration changed with depth in a similar way. The processes of $^{14}C$ acetate assimilation occurred at high rates only in the thin upper layer of the sediment. In the sediment of station 15, the decreasing gradient of acetate accumulation rate was most pronounced (from 13.2 to 2.9 $\mu$mol $dm^{-3}$ $day^{-1}$ in the 0–3 and 3–20 cm layers, respectively).

The methane concentration in the upper sediment layers was usually very low and increased with depth; this increase was smooth at stations 22 and 106 and sharp at station 85. The methane formation rate in the sediments increased with depth; in the deepest core, however (station 106), local decreases in MG rate were revealed at 50 and 110 cm (Fig. 5). Active methanogenesis was detected not only in reduced horizons of the sediment, but also in those with positive Eh values (stations 15 and 22). The high rates of methanogenesis in
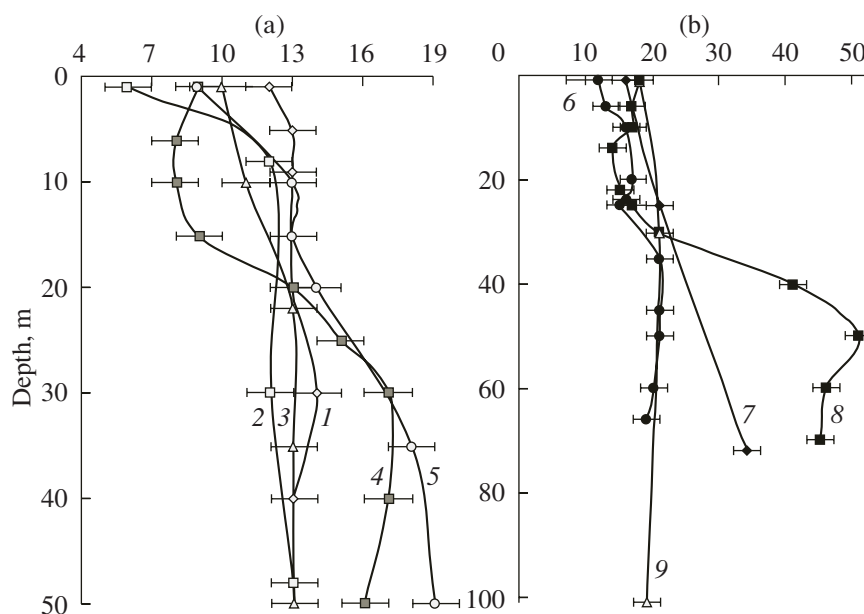
**Fig. 3.** Methane concentration in the water column of the Chukchi Sea, nmol l$^{-1}$: ((a), southern part of the area; (b), Herald Canyon); *1*, station 11; *2*, station 14; *3*, station 20; *4*, station 23; *5*, station 25; *6*, station 106; *7*, station 88; *8*, station 89; *9*, station 85.

the sediments with positive Eh are probably the result of the presence of local anaerobic microniches where anaerobic microbial processes occur.

No visible tendencies were revealed for methane oxidation rates. At stations 106 and 85, the rate evidently decreased with depth, while an opposite picture was recorded at station 22. The methodological approach used in this work did not enable us to determine the relative contribution of aerobic and anaerobic methane oxidation; these processes are carried out by different groups of organisms and require different conditions. Activity of aerobic methanotrophs can be expected only in the oxidized sediment (surface horizon; stations 85 and 106); in the local microzones of these sediments, however, anaerobic methane oxidation cannot be excluded. In the reduced body of the cores (stations 15 and 22), anaerobic methane oxidation most probably occurs.

Active sulfate reduction was detected only in the surface (station 85, Table 4, Fig. 5) and subsurface (station 15) sediment layers. In deeper horizons, the rate of sulfate reduction did not exceed 2 µmol S dm$^{-3}$ day$^{-1}$.

## DISCUSSION

The photosynthetic productivity of the Chukchi Sea determined during the expedition varied within a broad range; the southern and southwestern parts of the sea can be described as mesotrophic–eutrophic, while the eastern and northwestern parts, as oligotrophic. Our measurements of the primary production yielded results close to those obtained in the works with bicarbonate labeled with the $^{13}$C stable carbon isotope

($^{13}$HCO$_3^-$) [14]. Thus, the productivity of the southwestern part of the Chukchi Sea is within the range typical for the most productive Arctic waters, southwestern Barents Sea (over 1000 mg N m$^{-2}$ day$^{-1}$) [15].

The carbon concentration in suspended organic matter is known to correlate well with the phytoplankton content and (indirectly) with the primary production [16]. Our results on SOM content enable us to compare the southern and southwestern parts of the Chukchi Sea with the Barents Sea productive coastal waters (150–266 µg N l$^{-1}$), while Alaskan coastal waters and the northwestern Chukchi Sea can be compared with



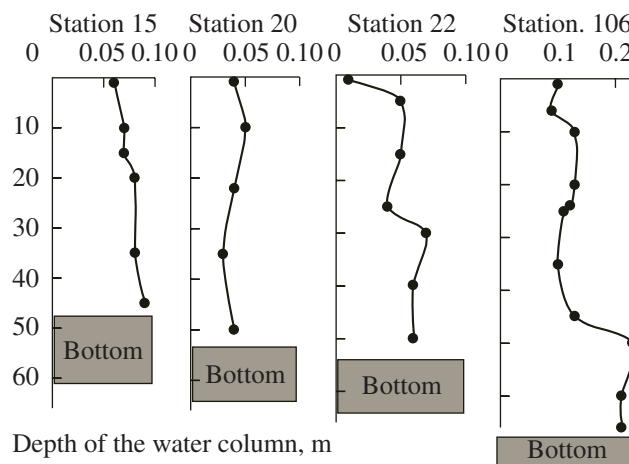**Fig. 4.** Representative profiles of methane oxidation rate in the water column of the Chukchi Sea, nmol CH$_4$ l$^{-1}$ day$^{-1}$.

**Table 4.** Physicochemical characteristics of the surface (0–3 m) layer and rates of microbial processes in the Chukchi Sea bottom sediments

| Chukchi Sea area (station) | CCW (station 11) | ACW (Station 20) | BSW (station 15) | BSW (station 22) | AW (station 106) | AW (station 85B) |
|---|---|---|---|---|---|---|
| $Eh$, mV | +188 | +90 | +15 | +66 | +65 | +120 |
| $C_{org}$, % | 0.739 | 1.084 | 1.930 | 1.560 | 1.771 | 1.186 |
| $NH_4^+$ ($\mu$mol l$^{-1}$) | 17860 | 3810 | 15000 | 14280 | n.d. | 9070 |
| P ($\mu$mol l$^{-1}$) | 125 | 24.8 | 400 | 230 | n.d. | 115 |
| Methane, nmol dm$^{-3}$ | 246 | 1049 | 741 | 576 | 1049 | 665 |
| Glucose assimilation, $\mu$mol dm$^{-3}$ day$^{-1}$ | 13.2 | 4.33 | 8.5 | 9.83 | 7.9 | n.d. |
| Acetate assimilation, $\mu$mol dm$^{-3}$ day$^{-1}$ | 22.5 | 3.08 | 13.2 | 6.42 | 5.25 | n.d. |
| $CO_2$ assimilation, $\mu$mol dm$^{-3}$ day$^{-1}$ | 2.94 | 1.72 | 3.85 | 0.80 | 1.15 | 1.60 |
| MG, nmol $CH_4$ dm$^{-3}$ day$^{-1}$ | 18.2 | 12.0 | 16.0 | 0.25 | 3.57 | 1.34 |
| MO, nmol $CH_4$ dm$^{-3}$ day$^{-1}$ | 1.61 | 5.76 | 4.64 | 2.72 | 14.73 | 11.3 |
| SR, $\mu$mol S dm$^{-3}$ day$^{-1}$ | 14.9 | 1.35 | 10.53 | 4.41 | 1.51 | 16.18 |

the oligotrophic waters of the Franz Victoria Trough (41–72 $\mu$g N l$^{-1}$) [2].

The carbon isotopic composition of suspended organic matter ($\delta^{13}C_{org}$), which reflects its origin, is the fundamentally important biogeochemical characteristic revealed in our research. Predominance of organic matter of marine phytoplankton was demonstrated for the southern part of the Chukchi Sea, while a suspension of terrigenous origin was revealed in the Bering Strait and at the Alaskan shore.

The total bacterioplankton numbers determined by us were significantly lower than the values obtained by Tsyban' et al. in summer 1988 ($913 \times 10^3$ cells ml$^{-1}$ in the northern part of the Chukchi Sea and $967 \times 10^3$ cells ml$^{-1}$ near the Chukotka coast [7]). In contrast to these data, which clearly indicate uniform distribution of bacterioplankton in the Chukchi Sea, our research revealed that bacterioplankton numbers in contrast areas differed severalfold (Table 1). A high degree of cell aggregation was demonstrated for the Chukchi Sea BP. 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 [17].

In the classical concept of the trophic network of the Arctic seas, which is based mainly on studies of the productive regions of the Barents Sea and the Sea of Norway, a pronounced pasturable component prevails [18]. The biomass of producers, represented mainly by diatoms, is sequentially consumed by producers of different levels; only 10% of the energy accumulated at a level is utilized at the following one. Apart from the pasturable component, processes related to the detritus part of the trophic chain also occur in the water column. These include bacterial destruction of organic matter excreted by the organisms of every level and of dead biomass. Only poorly degradable organic matter reaches the bottom sediments.

In productive waters of the southern and southwestern parts of the Chukchi Sea, the picture is different from this classical one. The pasturable trophic chain of consumers feeding on primary producers was short and inefficient [19]. The low efficiency of bacterial destruction of organic matter in the water column is due to the low depth of the Chukchi Sea and to the aggregation of bacterioplankton on suspended particles; fresh organic matter rapidly precipitates to the bottom sediments. The biomass of the phytoplankton consists primarily of diatoms; the low degree of its transformation is caused by low zooplankton concentrations in the water. All significant transformations of organic matter are therefore transferred to the thin ecotone zone (the oxidized surface layer of the sediments). In this thin layer, the biomass of bottom dwellers, which transform organic matter, is extremely high [13]. The activity of the animals causes constant mixing and aeration of the semiliquid sediment. Our research revealed active processes of microbial destruction in the upper layer of the sediments; they influence the chemical composition of silt water. In spite of the generally oxidized condition of the upper sediment layer, the rates of sulfate reduction are high; the process occurs in anaerobic microniches.

Below this thin "bioreactor" layer, sulfate reduction rates decrease drastically; this phenomenon is not typical for marine sediments. Only the methane formation rate increases with depth. Thus, a specific type of
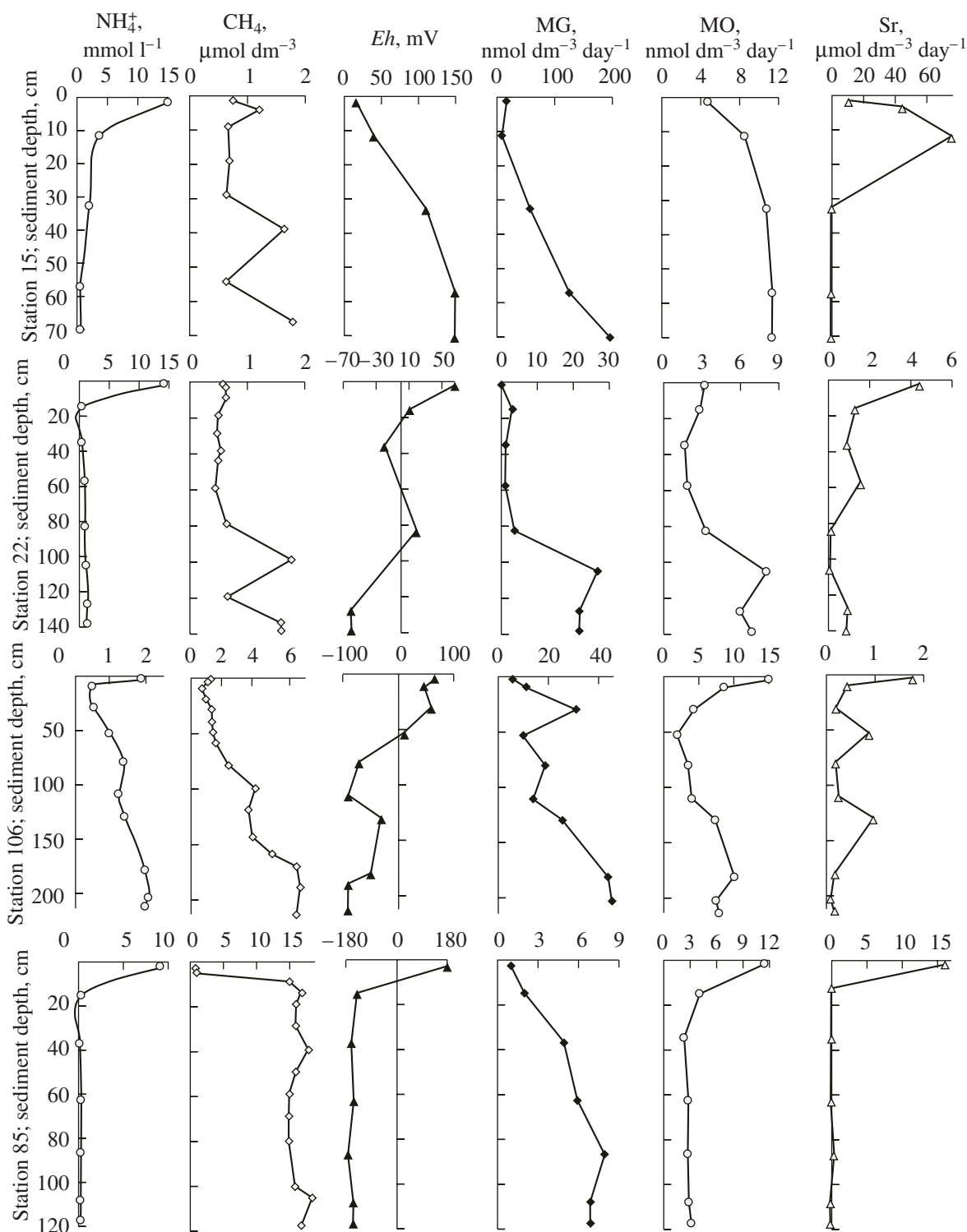
**Fig. 5.** Profiles of $NH_4^+$, $CH_4$, $Eh$, and the rates of microbial processes in the Chukchi Sea bottom sediments.

trophic chain was encountered, where bacterial decomposers and detritus-eating animals play the key role.

One of the tasks of this investigation was to determine the balance between microbial methane oxidation and methanogenesis, both in the water column and in the bottom sediments. No reliable quantitative evidence of methanogenesis in the water column was obtained; we have previously demonstrated such a phenomenon for the Black Sea [20]. The rate of methanogenesis in

**Table 5.** Calculated rates of methanogenesis in the sediments and of methane oxidation in the water and sediments ($\mu$mol CH$_4$ m$^{-2}$ day$^{-1}$) of the Chukchi Sea in August 2004

| Sea area | MG$_{sed}$ | MO$_{sed}$ | MG$_{sed}-$MO$_{sed}$ | MO$_{water}$ | MG$_{sed}-$$\Sigma$MO |
|----------|------------|------------|------------------------|--------------|------------------------|
| BSW | | | | | |
| station 15 | 66.9 | 6.3 | 60.6 | 3.3 | 57.3 |
| station 22 | 12.9 | 5.1 | 7.8 | 2.4 | 5.4 |
| AW | | | | | |
| station 106 | 31.5 | 12.2 | 19.3 | 9.8 | 9.5 |
| station 85 | 6.4 | 3.8 | 2.6 | 17.7 | −15.1 |

the sediments varied from 0.6 to 67 $\mu$mol CH$_4$ m$^{-2}$ day$^{-1}$ near the Alaskan coast and in the most productive southern part of the sea, respectively (Table 5). Methane was partially oxidized in the sediments, both aerobically in the oxidized upper layer and anaerobically deeper in the sediment. Our calculations revealed that the methane flow from the sediment into the water column was 0.3–61 $\mu$mol CH$_4$ m$^{-2}$ day$^{-1}$; the highest value was observed at the highly productive station 15. Methane is oxidized in the water column; the overall range of this process is significantly affected by the thickness of the water layer. Low rates of MO (1.9–3.3 $\mu$mol CH$_4$ m$^{-2}$ day$^{-1}$) were revealed in the shallow waters of the southern part of the Chukchi Sea; the highest MO values (17.7 $\mu$mol CH$_4$ m$^{-2}$ day$^{-1}$) were found at the deepest station of the Herald Canyon. From the overall balance, calculated as the difference between the quantities of methane production per day over 1 m$^2$ of sediment and oxidized in the sediment and water column during the same period, an approximate estimate of methane emission from water into the surface layer of the atmosphere was made (from 5.4 to –57.3 $\mu$mol CH$_4$ m$^{-2}$ day$^{-1}$). The negative balance of methane production in the northern part of the Herald Canyon (station 85) cannot be explained by methane drain from the atmosphere, since for a number of northern stations (71, 82, 85, 86, and 89) methane concentration in the upper water layer was higher than its average concentration in the surface layer of the atmosphere of polar seas (14 nmol l$^{-1}$) [21]. Horizontal transfer of the water masses which deliver methane from some still unknown sources can be suggested, but only as a preliminary hypothesis. Our calculations are not definitive since they are based on data obtained over a short period.

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