ISSN 0026-2617, Microbiology, 2014, Vol. 83, No. 5, pp. 648–660. © Pleiades Publishing, Ltd., 2014.

EXPERIMENTAL ARTICLES

Microbiological and Biogeochemical Properties of the Caspian Sea Sediments and Water Column

A. Yu. Lein[a, 1], A. S. Savvichev[b], M. D. Kravchishina[a], N. V. Kozina[a], V. I. Peresypkin[a], E. E. Zakharova[b], E. F. Veslopolova[b], I. N. Mitskevich[b], N. A. Shul'ga[a], N. V. Lobus[a], N. V. Politova[a], and M. V. Ivanov[b]

[a] *Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia*
[b] *Winogradsky Institute of Microbiology, Russian Academy of Sciences, pr. 60-letiya Oktyabrya 7, k. 2, Moscow, 117312 Russia*

Received October 1, 2013

Abstract—The work presents the results of investigation of microbial and biogeochemical processes at the water–sediment interface in the samples of three Caspian Sea profiles obtained during the 39th cruise of RV "Rift" in May–June 2012. The decrease in suspended C_{org} content from the surface to the bottom resulted from the activity of aerobic heterotrophic microorganisms. Autotrophic methanogenesis occurred in anoxic water of deep-sea depressions, where methane concentrations were up to 2.2–3.75 μL CH_4 L^{-1}, which was an order of magnitude higher than in the aerobic water column (0.04–0.32 μL CH_4 L^{-1}). Methanogenesis was accompanied by a considerable decrease in $\delta^{13}C$ of suspended C_{org} (–26 to –30‰). The numbers of microbial cells in the water column varied from 40 to 3200 × 10^3 cells mL^{-1}. The results of microbiological and biogeochemical investigation demonstrated that, in spite of the absence of connection with the ocean and other specific features, the Caspian Sea has the characteristics of a typical marine basin.

Keywords: microbial abundance, microbial processes, isotope composition of suspended organic carbon, Caspian Sea, water–bottom sediments interface

DOI: 10.1134/S0026261714050178

The Caspian Sea is located at the border of two climatic zones: the humid zone in the west and the northwest and the arid zone in the east. In the humid area, the inflow of suspended matter into the sea occurs primarily with the discharge of large and small rivers, while in the arid zone, it comes mainly by the eolian pathway. Previous studies analyzed the quantities and the composition of suspended matter in the Northern Caspian [1], the Northern and the Central Caspian [2], as well as in the water column along the Trans-Caspian axial profile, which includes the two major Caspian deep-sea basins: the Derbent Basin and the South-Caspian Basin [3].

In late May and early June 2012, the water column of both of these basins exhibited a stable temperature and hydrochemical stratification. Both deep-sea depressions were found to contain hydrogen sulfide; its concentration increased from the upper detection layer to the near-bottom layers of the water column [3, 4].

The major purpose of our study was to identify the characteristics of the geochemically important microbial processes and the patterns of the transformation of suspended matter into bottom sediments under aerobic and anaerobic conditions at the water column bottom sediments interface along the Trans-Caspian axial profile.

Important features of the Caspian Sea are the presence of oil and gas deposits in the sediment mass, numerous tectonic dislocations, and mud volcanoes on the sea bottom. All of these factors may cause diffuse or focused hydrocarbon emission into the water column. The second purpose of our study was to detect migratory hydrocarbons in Caspian water and sediments along the Trans-Caspian profile.

MATERIALS AND METHODS

Materials were collected during the 39th cruise of RV "Rift" in May–June 2012 (Shirshov Institute of Oceanology; cruise supervisor, A.K. Ambrosimov). The water column was studied at nine stations of the Trans-Caspian axial profile in the Central and Southern Caspian, as well as at five stations of the latitudinal profile and five stations of the eastern meridional profile in the Central Caspian Sea (Fig. 1). Water samples for microbiological and hydrochemical analysis were collected using a Rosette system with Niskin water samplers. Samples of near-bottom water, warp (0.0–0.5 cm), and sediments of the water–bottom interface were col-

---

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

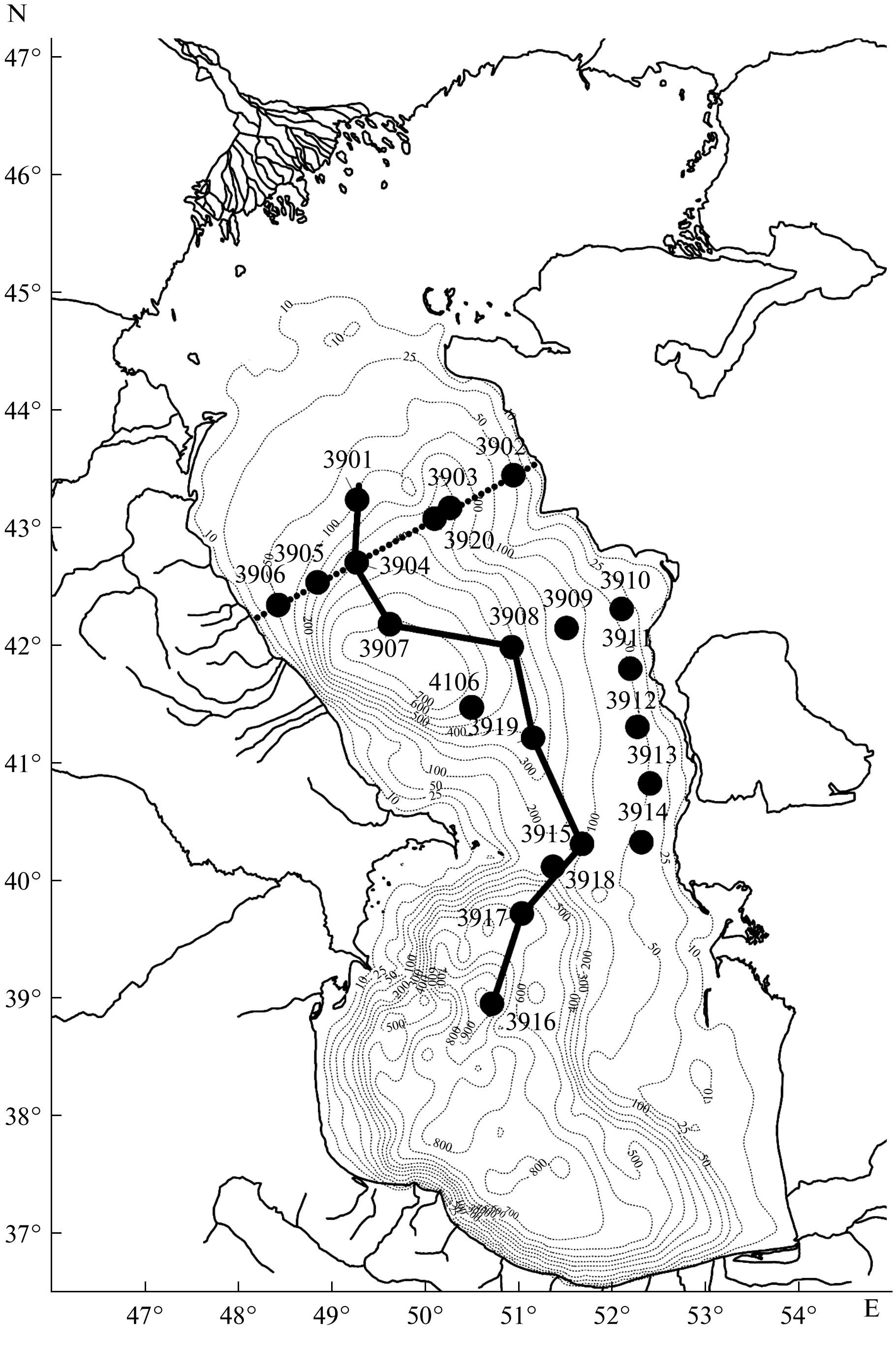

Fig. 1. Location of stations and reference profiles in the Caspian Sea: solid line, Trans-Caspian axial profile; dotted line, latitudinal profile in the Central Caspian; double line, eastern meridional profile (data from the 39th cruise of RV "Rift" (Institute of Oceanology, Russian Academy of Sciences), May–June 2012).

lected with a KUM. multicorer (Germany), which preserves the sample structure intact, in contrast to other bottom-grab samplers and geological tubes. The methods of chemical, biogeochemical, microbiological, radioisotope (^{14}C), and isotopic (δ^{13}C) analysis, as well as the biomarker assay, were used in this work as described in [5, 6].

RESULTS AND DISCUSSION

Characteristics of the water column. The Caspian Sea waters are diluted, with average salinity of 12.7–12.8 PSU [7]. In comparison to ocean water, it contains more sulfate ions (30.2–32 mM) and calcium and magnesium carbonates, and less chlorine. For example, in June 2010, salinity in the water column profile of the Derbent Basin ranged from 11.0 PSU in the surface layer to 11.43 PSU in the near-bottom layer, as was determined by a Shirshov Institute expedition.

Oxygen concentration decreased significantly with depth. In particular, along the vertical profile of the water column above the basins, it changed from 8–10 mg L^{-1} in the surface layer to 0.22 mg L^{-1} near the bottom, where oxygen concentrations were negligible, but free hydrogen sulfide, which had not been detected in the Caspian Sea for the previous 70 years [3, 4], appeared in the amounts of up to 0.4 mg H_2S L^{-1}.

In summer and autumn, vertical circulation in the Caspian Sea is restricted to the upper water layer 15–40 m deep, rarely up to 75 m deep. At the same time, a seasonal thermocline layer is formed at the lower border of the well-warmed (22–26°C) mixed water layer; it is characterized with a shift in temperature (7°C) and density and prevents the warming of deeper water layers, which have therefore the temperature not exceeding 5°C. In the oxic part of the water column, pH values ranged from 8.0 to 7.6, and in the near-bottom layer of deep-sea basins, from 6.75 to 7.0. The total alkalinity did not change much throughout the vertical profile and was in the range of 3.76–3.83 mg-eq L^{-1}.

In May and June 2012, methane concentrations in the water column ranged from 60 nL L^{-1} at the shelf and on basin slopes to 3500–3750 nL CH_4 L^{-1} in oxygen-depleted waters of the Derbent and Southern Basins (stations 3907 and 3916, Table 1), which was close to the values obtained in the fall of 2008 [2]. Methanogenesis occurred both in the water column and in bottom sediments.

The concentration of suspended matter in water samples collected along the Trans-Caspian profile was 0.8 mg L^{-1} in the surface water layer of the Southern Basin and decreased to 0.1 mg L^{-1} at the depths of 125–500 and 400–800 m in the Central and Southern Caspian, respectively (Fig. 2a). The lowest organic carbon content (C_{org}) in suspended matter was observed in the surface water layer of the Eastern meridional profile near the Mangyshlak Desert coast (0.2–5.9% C_{org} in suspended matter). In the Southern Caspian along the Trans-Caspian axial profile, C_{org} content in the suspended matter of the surface layer varied from 8.9% to 14.1% (Table 1).

Dissolved HCO_3^- is utilized by phytoplankton. In 12 water samples collected along the vertical profiles of the two major Caspian basins, $\delta^{13}C-HCO_3^-$ values ranged from –3.75 to +3.18‰, which suggests that bicarbonate ions were for the most part of marine origin (Table 2).

Isotope composition of suspended C_{org}. Isotope composition of suspended C_{org} provides information on the sources of organic matter (OM) entering the water body. According to our data, in the Northern Caspian, the most significant portion of suspended C_{org} is supplied by river discharge [2]. In the Southern Caspian, C_{org} isotope composition has never been studied before. Large and small rivers carrying terrigenous OM flow into the Caspian Sea from the north, the northeast, and the west. From the arid eastern coast, terrigenous OM is carried into the Caspian mainly as eolian material, which may contain the remnants not only of C_3 plants, as in polar seas, but also of C_4 plants and succulents with the isotope composition different from that of C_3 plants. In summer, the water body itself is inhabited mainly by diatoms and dinoflagellates, i.e., C_3 plants. The values of $\delta^{13}C-C_{org}$ for marine phytoplankton ranged from –17 to –22‰; for freshwater phytoplankton, from –20 to –30‰, for C_3 land plants, from –22 to –32‰, and for C_4 land plants, from –10 to –18‰. Carbon isotope composition of succulent plants is intermediate between the characteristics of C_3 and C_4 plants [8]. Thus, suspended C_{org} of the Caspian Sea probably originated from all the sources named above: both phytoplankton and terrigenous OM from river discharge or eolian material; the terrigenous OM may contain C_3 and C_4 plant remnants. To identify the contribution of each source, we determined the C_{org} isotope composition (Fig. 2b, Table 1). In our previous work, the isotope composition of suspended C_{org} in the Central Caspian was analyzed in autumn (November 2008) and summer (June 2010) [6].

In November 2008, the suspended C_{org} isotope composition in the surface layer of the eastern shelf shallow waters had $\delta^{13}C-C_{org}$ of –23.07‰, while in summer 2010, $\delta^{13}C-C_{org}$ values varied within a narrow range of –26.7 to –26.8‰ (with the average of –26.8‰), possibly indicating that in summer this region experienced a stronger inflow of terrigenous OM enriched with the light carbon isotope. In the surface layer of the Derbent Basin, C_{org} was richer in ^{13}C in November ($\delta^{13}C$ = –23.6‰) than in June ($\delta^{13}C$ from –25.0 to –25.7‰). In June, suspended C_{org} in the surface layer of the Southern basin had a $\delta^{13}C$ value by 2‰ higher (that is, it was richer in ^{13}C) than in the Derbent Basin (Fig. 2b). Apparently, the $\delta^{13}C-C_{org}$ values for the Derbent Basin were more strongly affected by the inflow of ^{12}C-enriched terrigenous material delivered by river discharge. On the eastern meridional profile of the Central Caspian shelf, the average $\delta^{13}C-C_{org}$ of suspended matter was –23.6‰ (Table 1); i.e., it contained more ^{13}C than suspended C_{org} of the central deep-sea regions of the Central Caspian ($\delta^{13}C$ = –25.6‰). Probably, this was due to admixture of eolian material containing the fragments of ^{13}C-enriched C_4 plants typical for steppes and deserts.

Thus, our data on the carbon isotope composition ($\delta^{13}C-C_{org}$) of suspended matter found in the mixed

Table 1. Biogeochemical characteristics of the water layer of the Caspian Sea (May–June 2012)

Station / Depth, m	Layer, m	C_{org}, % of suspended matter	$\delta^{13}C$–C_{org}, ‰	CH_4, nL L^{-1}	DCA, μg C L^{-1} day^{-1}	SR, μg S L^{-1} day^{-1}
Trans-Caspian axial profile						
3901	0	–	–	150	–	–
107	27	21.0	–24.88	60	0.35	–
	103	0.4	–24.17	130	1.55	–
3904	0	–	–	120	–	–
471	45	12.9	–24.35	140	0.13	–
	414	7.8	–22.75	160	0.07	–
	MC, nbw	6.2	–23.30	530	–	–
3907	0	–	–25.73	140	–	–
720	39	3.3	–25.17	110	0.60	–
	640	–	–29.93	830	0.10	0.31
	660	–	–29.24	2190	0.45	0.35
	680	–	–	2660	0.78	0.48
	700	–	–	3420	0.72	0.44
	710	–	–	3570	0.69	–
	715	3.5	–24.94	3750	0.74	1.01
	MC, nbw	2.3	–23.79	3490	–	2.76
3908	0	–	–	140	–	–
450	40	1.8	–24.93	170	0.16	–
	400	–	–23.84	250	0.20	0.00
	MC, nbw	5.1	–22.21	240	–	0.00
3919	0	–	–	310	–	–
420	43	–	–23.0	560	0.66	–
	418	–	–23.0	320	0.61	–
	MC, nbw	–	–	330	–	–
3915	0	–	–	140	–	–
99	40	4.3	–23.26	310	0.60	–
	98	1.1	–23.31	330	0.80	–
3916	0	–	–23.73	180	–	–
1003	37	14.1	–22.36	260	0.74	–
	600	–	–29.56	50	0.28	0.00
	700	–	–26.32	40	0.21	0.00
	800	–	–27.53	210	0.31	0.17
	820	–	–	750	0.16	–
	850	–	–	1030	–	–
	870	–	–	1400	–	–
	890	–	–	2440	0.63	1.16
	900	–	–26.99	2990	0.59	1.58
	1000	–	–26.67	3280	0.52	1.75
	MC, nbw	8.7	–	3360	–	1.67
3917	0	–	–23.16	220	–	–
665	43	8.9	–23.01	270	0.58	–
	661	–	–26.08	300	<0.08	0.0
	MC, nbw	8.0	–21.56	300	1.86	0.0

Table 1. (Contd.)

Station Depth, m	Layer, m	C_{org}, % of suspended matter	$\delta^{13}C–C_{org}$, ‰	CH_4, nL L^{-1}	DCA, μg C L^{-1} day^{-1}	SR, μg S L^{-1} day^{-1}
Latitudinal profile (Central Caspian)						
3902	28	14.2	–25.60	160	0.29	–
57	55	8.1	–27.77	170	0.39	–
3920	0	–	–	110	–	–
386	37	–	–	110	0.59	–
	377	–	–	240	0.31	–
	MC, nbw	–	–	220	–	–
3906	0	–	–	120	–	–
55	28	10.8	–25.41	150	0.21	–
	55	11.7	–24.37	130	0.74	–
Eastern meridional profile						
3910	0	–	–	220	–	–
42	25	3.9	–24.52	410	0.46	–
	38	2.5	–22.94	170	1.73	–
3911	0	–	–	120	–	–
67	39	1.4	–24.32	180	0.64	–
	64	0.2	–21.90	760	0.62	–
3913	0	–	–	180	–	–
49	37	2.7	–23.39	300	0.64	–
	47	2.4	–22.52	310	1.12	–
3914	0	–	–	120	–	–
46	30	5.9	23.24	210	0.21	–
	41	1.9	–24.67	220	1.90	–

DCA, dark CO_2 assimilation; SR, sulfate reduction; MC, multicorer; nbw, near-bottom water.

upper water layer of the Central and Southern Caspian indicate that freshwater discharge and terrigenous OM had a more significant impact in the Central Caspian than in the Southern Caspian, where $\delta^{13}C–C_{org}$ values of suspended matter were typical of marine basins with little river inflow. The species composition of phytoplankton inhabiting the Southern and the Central Caspian is very similar. Due to the land vicinity, samples collected at the near-shore stations of the latitudinal profile (stations 3906 and 3902) contained suspended matter depleted of ^{13}C.

Interesting results were obtained by isotopic analysis of suspended C_{org} in deep-sea basins: from the 600 m layer and deeper, $\delta^{13}C–C_{org}$ values ranged from –25.0 to –29.9‰ (station 3907) and from –26.3 to –28.5‰ (station 3916) (Fig. 2b, Table 1).

As was already mentioned, at depths below 600 m, anoxic water layers of deep sea basins were found to contain increased amounts of dissolved methane (Table 1), which was produced by autotrophic methanogenesis, as was shown for the deep-sea part of the Derbent Basin [2]. In the course of methanogenesis, methanogenic biomass is enriched with the light ^{12}C isotope, which may affect the general suspended C_{org} isotope composition in the anoxic water column of deep depressions of the Caspian Sea.

Direct microscopic investigation of water samples in June 2012. The total microbial abundance (TMA) in the maximal luminescence layer of the water column (25–45 m) was 180 to 750 × 10^3 cells mL^{-1} (Table 3). The lowest TMA of 180 × 10^3 cells mL^{-1} was observed at the westernmost station of the latitudinal profile in the Central Caspian (station 3906), while the highest TMA (750 × 10^3 cells mL^{-1}) was found in the water samples of the most shallow station, which was located on the eastern meridional profile on the border of the Central and Southern Caspian (station 3914).

In the water column of deep-sea basins (stations 3907 and 3916), TMA values showed little change below the maximal luminescence layer: they ranged within 90–50 × 10^3 cells mL^{-1} in the Derbent Basin and 40–70 × 10^3 cells mL^{-1} in the Southern Basin, remaining constantly low from the depths of 600–800 m and to the hydrogen sulfide-containing layer at

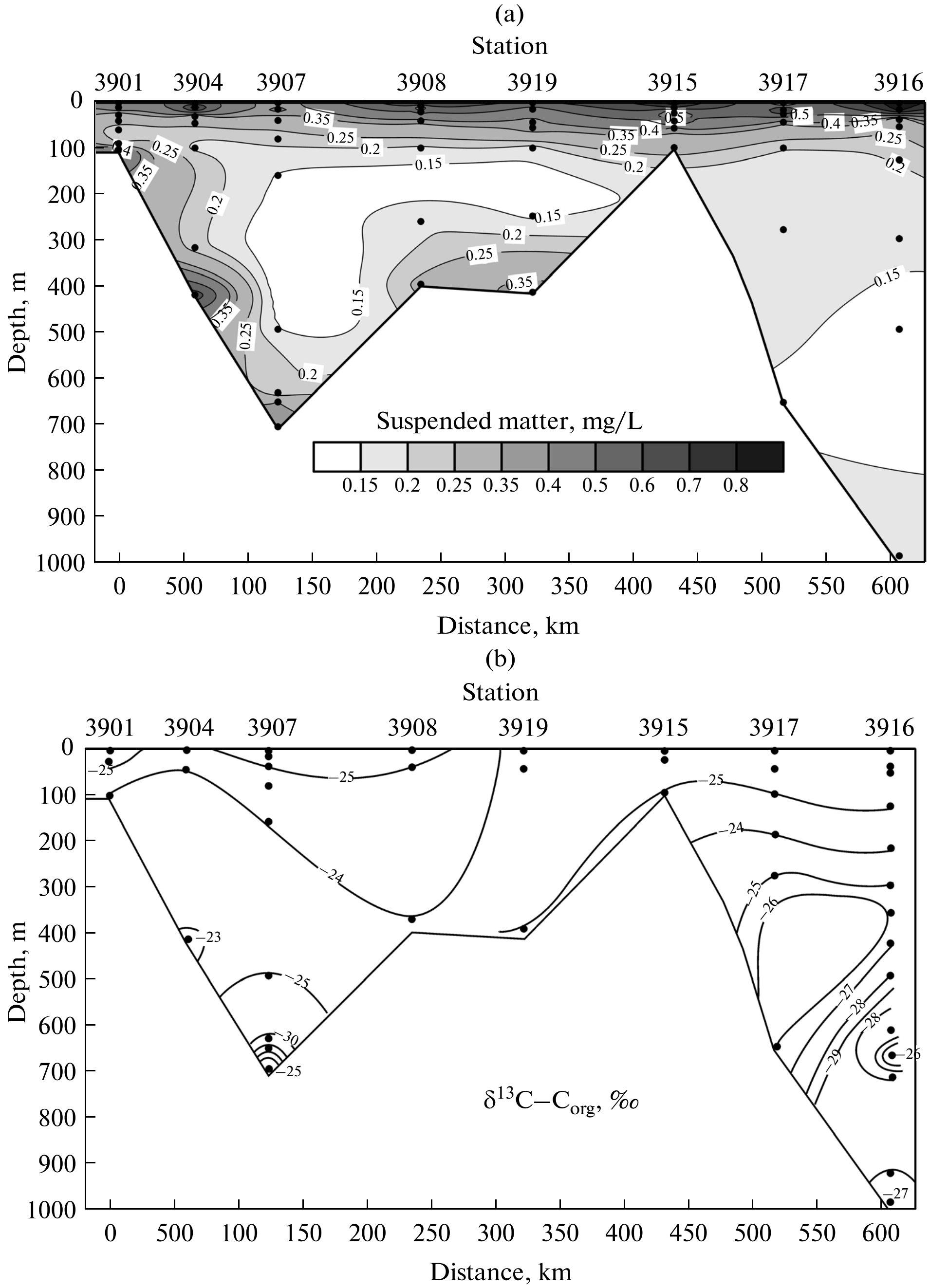

Fig. 2. Distribution of suspended matter concentrations (C_{org}/L, (a)) and $\delta^{13}C$–C_{org} values (b) along the Trans-Caspian axial profile. Dots represent the layers of sample collection.

the bottom. This fact was possibly related to the decreased C_{org} content in the suspended matter.

In both basins, we observed numerous thin filaments typical of the microflora developing at the interface of oxygen- and sulfide-containing waters; for instance, it was observed in the water column of the Black Sea [3]. In both basins, suspended matter of near-bottom waters was mostly composed of dense organic particles thickly populated by large microorganisms. Water samples from the depths below 200 m contained considerable amounts of pennate diatoms, which were later also found in the upper sediment layer in the Derbent Basin. The concentration of chlorophyll *a* was 0.2–1.7 μg L^{-1}, which was unusual for such depths; in most samples, the share of pheophytin *a* in the total amount of chlorophyll *a* and pheophytin *a* did not exceed 10%. At all deep-sea stations (3907, 3916, and 3917), microbial communities exhibited the traits typical for anoxic environments,

Table 2. Carbon isotope composition of bicarbonate ion in the Caspian Sea water, May–June 2012

Station / Depth , m	Layer, m	δ^{13}C–HCO$_3$, ‰
3916 / 1003	0	–1.54
	15	+0.47
	37	–1.53
	53	+1.96
	300	+3.18
	1000	–0.83
3907 / 720	500	–1.28
	710	+2.94
	715	–3.39
	660	+0.22
	680	+3.00
	700	–3.75
Average		–1.31

including the presence of numerous thin and thick filaments.

Rates of microbial processes in the water column. In most water samples taken along the Trans-Caspian profile, the rates of dark carbon dioxide assimilation (DCA) ranged from 0.10 to 0.66 μg C L^{-1} per day; only in the samples from deep-sea zones of the Derbent Basin, DCA rates reached 0.74–0.78 μg C L^{-1} per day (Table 1). The highest DCA rates were observed in the near-bottom layers at shallow-water stations of the latitudinal and the eastern meridional profiles (Table 1). Along the Trans-Caspian profile, DCA rates in the upper mixed water layer (25–43 m) varied from 0.16 to 0.66 μg C L^{-1} per day at the stations located on basin slopes to 0.74 μg C L^{-1} per day in the Southern Basin (Table 1). DCA variations along the vertical profiles of the water column were unsystematic. The highest DCA values of 0.74–0.78 μg C L^{-1} per day were observed in the anaerobic zones of deep-sea basins with the highest methane concentrations (Table 1). At shallow-water stations of the latitudinal and the eastern profiles, DCA rates were the highest in near-bottom water layers (Table 1).

Sulfate reduction was observed only in the water samples from deep-sea basins, beginning from the layers below 640 m (Derbent Basin) and 800 m (Southern Basin); its rates ranged from 0.17–0.31 μg S L^{-1} per day at the upper border of the anoxic zone to 0.75 μg S L^{-1} per day at the bottom.

Biogeochemical processes at the interface of water and bottom sediments. Lithological, mineralogical, and geochemical characterization of Caspian sediments was provided in several monographs and individual publications; the very first of them were the studies by Klenova [9] and Kholodov et al. [1]. However, these works did not include information on the sediments of the bottom–water column interface, since at the time there were no sampling devices which could preserve the structure of the interface zone. In June 2012, samples of near-bottom water, warp, and sediments were collected using a multicorer.

Table 4 provides a description of the sediments of the interface zone; Fig. 3 shows the δ^{13}C–C$_{org}$ values along the vertical sediment profiles. The warp (0.0–0.5 cm) was a layer of heavily watered flocculated sediments found at the bottom—water interface: aleuropelitic and pelitic material of dark green, olive-green, dark gray, black, or beige colors. The water content of the warp was over 90%; its color depended on the carbonate content, the amounts of plant debris, and redox conditions. In most warp samples, C$_{org}$ content was considerably higher than in the underlying sediments, ranging from 3.56% (station 3919) to 8.70% (station 3916). The lowest C$_{org}$ content (2.31%) was observed in the surface warp layer at station 3904; apparently, there were no recent sediments at this location.

Carbon isotope composition of suspended OM indicated its mixed origin: phytoplanktonic and terrigenous. The δ^{13}C–C$_{org}$ values in the warp could be different from or similar to δ^{13}C of suspended C$_{org}$ in the near-bottom water layer (Fig. 2b). The differences in δ^{13}C–C$_{org}$ values were observed at the stations located in both deep-sea basins with sulfide-containing waters. In warp samples collected at deep-sea stations, δ^{13}C–C$_{org}$ values were up to 4.5‰ higher than those of suspended C$_{org}$ of anoxic water layers (Fig. 2b). Below the warp layer (layer 0.5–10 cm), C$_{org}$ content varied from 3.8 to 5.0% of dry matter. Deeper in the mud, C$_{org}$ content decreased to 2–3% (Table 4).

Previous studies reported high C$_{org}$ levels in the surface sediment layer of the Derbent Basin [6–8]. In this work, high C$_{org}$ abundance was also observed in the Southern Basin (Table 4). The abundance of OM in deep-sea sediments was due to their finely dispersed structure (over 60–70% of the pelitic fraction), the presence of methane and hydrogen sulfide, and to other factors that prevent degradation of OM that has reached the bottom. This suggestion is supported by high concentrations of chlorophyll *a* found in the thin (20 cm) lowermost layer of water (over 26 μg L^{-1}), in the warp, and in the upper sediment layer (3–5 μg cm^{-3} of wet sediment). Pheophytin *a* content in the total amount of chlorophyll *a* and pheophytin *a* increased from 1% in the near-bottom water layer to 70% in the sediment. The isotope composition of sediment C$_{org}$ was characterized with δ^{13}C values lying within the narrow range of –21.0‰ to –23.5‰ (Fig. 3), with the mean value (for 20 samples) of –22.72‰, which was most probably due to bottom currents transferring suspended matter from basin slopes. Characteristic

Table 3. Total abundance, cell volume, and biomass of microorganisms in the water column, May–June 2012

Station/Depth, m	Layer, m	TMA, 10^3 cells/mL	Cell volume, μm^3	Biomass, mm^3/m^3	Sea region
Latitudinal profile, Central Caspian					
3902/57	28	440	0.10	44	Central Caspian
	55	620	0.10	62	
3920/386	39	500	0.12	60	
	377	230	0.15	35	
3904/417	45	310	0.08	25	Intersection of the latitudinal and the Trans-Caspian profiles
	424	240	0.18	43	
	nbw	760	0.20	152	
3095/270	MC, 37	290	0.15	44	Central Caspian
	265	260	0.18	47	
3906/55	26	180	0.14	26	
	55	380	0.12	46	
Trans-Caspian axial profile					
3901/107	27	290	0.13	38	Central Caspian, the northern end of the profile
	103	230	0.14	32	
3907/720	39	250	0.10	25	Derbent Basin
	640	90	0.24	22	
	660	??	0.25	28	
	680	110	0.24	26	
	700	150	0.25	38	
	710	150	0.25	38	
	715	150	0.25	38	
	nbw	3200	0.23	745	
3908/450	40	270	0.10	27	Central Caspian, Derbent Basin, eastern edge
	400	120	0.18	22	
	nbw	700	0.22	154	
3919/420	43	340	0.11	37	Central Caspian, Derbent Basin, eastern edge
	418	190	0.10	19	
	nbw	520	0.18	94	
3915/99	40	450	0.12	54	
	99	210	0.13	27	
3917/665	43	360	0.14	50	Southern Caspian, Southern Basin, northern edge of the Southern Basin
	661	160	0.24	38	
	nbw	1100	0.23	253	

Table 3. (Contd.)

Station/Depth, m	Layer, m	TMA, 10^3 cells/mL	Cell volume, μm^3	Biomass, mm^3/m^3	Sea region
3916/1003	37	650	0.14	91	Southern Basin
	600	40	0.24	10	
	700	40	0.24	10	
	800	50	0.25	13	
	900	60	0.24	14	
	1000	70	0.25	18	
	nbw	940	0.22	207	
Eastern meridional profile					
3910/42	25	420	0.10	42	Central Caspian
	38	330	0.11	36	
3911/67	39	460	0.12	55	
	64	400	0.14	56	
3919/49	37	550	0.13	72	Central Caspian, southern border
	49	400	0.13	52	
3914/46	30	750	0.12	90	
	41	450	0.12	54	

features of the basin bottom were the presence of a nepheloid layer approximately 20 m thick, as well as specific averaging of C_{org} content and $\delta^{13}C$–C_{org} values at the water–bottom interface.

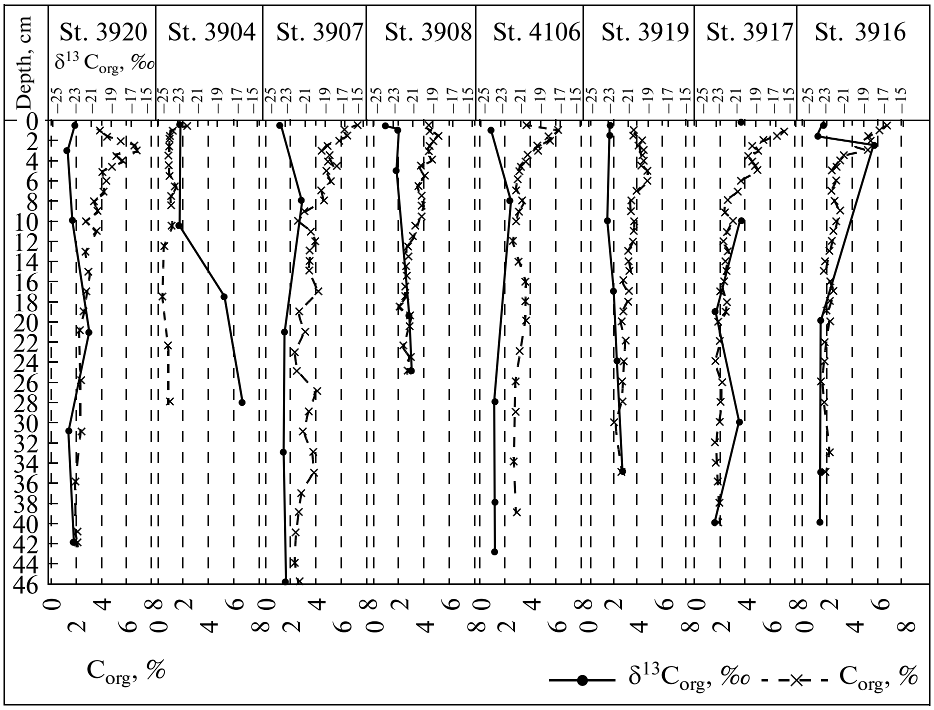

Fig. 3. Distribution of $\delta^{13}C$–C_{org} values, ‰ in the sediments along the Trans-Caspian axial profile.

Table 4. Content and isotope composition ($\delta^{13}C$) of C_{org} and C_{carb}, CH_4 content, sulfate reduction (SR) rate, and the total microbial abundance (TMA) at the geochemical water–sediment interface (0–10 cm) along the Trans-Caspian axial profile

$\frac{\text{Station}}{\text{Depth, m}}$	Brief sediment description	Layer, cm	C_{org}, %	$\delta^{13}C$–C_{org}, ‰	$CaCO_3$, %	$\delta^{13}C$–C_{carb}, ‰	CH_4, µL dm^{-3}	SR, µg S L^{-1} day^{-1}	TMA*, 10^6 cells cm^{-3}
$\frac{3904}{424}$	Flocculent dark-green aleuropelitic mud with shells	Warp 0.0–0.5	2.31	–22.90	21.7	–0.34	3.5	–	1200/ 3300
	Heavily watered red aleuro-pelitic mud	0.5–2.0	1.20	–21.55	23.3	–	13.3	–	–
	Thin layers of pelitic mud with black hydrotroilite intercalations*	2.0–10	1.10	–23.09	30.1	–	–	21.75	–
$\frac{3907}{720}$	Flaky gray pelitic mud, terrigenous, with a smell of H_2S	Warp 0.0–0.5	7.22	–23.54	0.6	–4.82	24.1	7.38	165/ 520
	Intermittent black and red pelitic layers, smell of H_2S	0.5–8.0	5.02	–21.41	4.6	–1.44	26.4	5.21	–
$\frac{3908}{450}$	Flaky black pelitic mud, terrigenous, with a smell of H_2S	Warp 0.0–0.5	4.37	–23.11	21.3	+1.615	3.5	2.78	110/ 780
	Dark-gray fine pelitic mud with red (oxidized) patches	3.0–5.0	–	–22.69	14.9	–5.89	14.1	–	900/ 4200
	Intermittent fine layers of black or gray pelitic mud and hydrotroilite	5.0–10.5	4.19	–	16.7	–	–	15.0	–
$\frac{3916}{1000}$	Black and green floccules, smell of H_2S	Warp 0.0–0.5	8.70 (6.59)	–22.70 (–22.99)	5.1	–0.96	3.3	1.67	150/ 180
	Greenish red (oxidized) pelitic mud with numerous black inclusions, carbonate–terrigenous	0.5–1.5 1.5–2.5	3.82	–23.49	23.9 8.9	–6.46	29.8 35.7	78.4 49.8	1500/8400 1400/ 7600
	Intermittent thin black and light layers of pelitic mud. At 10 cm, large hydrotroilite patches	2.5–10.5 20–22	–	–23.16	24.7	–	40.6	–	–
$\frac{3917}{670}$	Flaky carbonate-terrigenous mud; green terrigenous pelitic mud with a smell of H_2S	Warp 0.0–0.5	7.13	–26.08 –21.56	3.0	–	4.0	6.1	140/ 350
	Black jelly-like pelitic mud with a smell of H_2S	0.5–2.0	–	–	8.0	–	22.3	23.1	1600/ 5200
	Intermittent thin black, greenish black, and gray layers. Heavily watered pelitic mud with a smell of H_2S	2.0–10.0	4.46	–20.47	12.7	–2.94	39.4	16.3	1300/ 7200
$\frac{3919}{420}$	Oxidized film with light beige clots; below, flaky black pelitic mud with a smell of rotting plants, but no smell of H_2S	Warp 0.0–0.5	3.559	–22.66	5.3	–1.10	2.5	20.4	260/ 320
	Thin (2 mm) layers of black hydrotroilite, with gray-green-red sheets, with diatoms	0.5–1.5	–	–22.83	10.8	–3.22	17.2	99.9	2400/ 7200
	Watered fine black pelitic mud, jelly-like with hydrotroilite intercalations	1.5–10	4.04	–23.05	13.0	–4.95	21.8	49.5	7100/ 8200
$\frac{3920}{380}$	Flaky (black flakes) with debris, oxidized	0.0–0.5	3.832	–22.66 (–22.90)	2.9	–0.03	2.7	0.61	220/ 280
	Black pelitic mud with admixture of green mud; much debris*	0.5–3.0	–	–23.38	10.9	–0.32	–	–	–
	Thin gray pelitic mud with large hydrotroilite adhesions	3.0–5.0	–	–	13.1	–	81.9	–	1300/ 7000
	Below 8 cm, darker sediments, jelly-like, watered	5.0–10.0	–	–22.89	15.7	–0.84	–	9.15	–

* TMA: numbers before and after the slash represent the data obtained without ultrasound treatment and after such treatment.

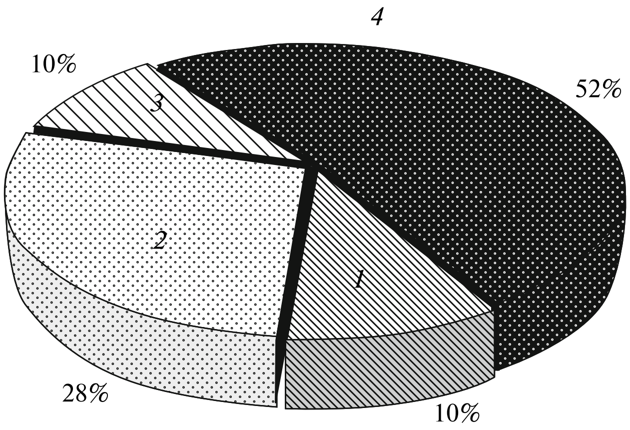

Fig. 4. Average abundance of *n*-alkanes in organic matter (relative percentage): (*1*) $\Sigma(C_{10}-C_{14})$, migratory; (*2*) $\Sigma(C_{15}-C_{20})$, planktonic; (*3*) $\Sigma(C_{20}-C_{24})$, microbial; (*4*) $\Sigma(C_{23}-C_{40})$, terrigenous.

In the near-bottom water, TMA was significantly higher than in the low layers of the water column (Table 3). In the warp, TMA values were hundreds of millions cells per 1 cm^3, and in the upper sediment layer (0.5–20 cm), TMA values were higher still, reaching billions of cells per 1 cm^3 of wet mud (Table 4).

Sulfate reduction rates in the warp were considerably higher than in the water column (Table 1) but lower than in the underlying sediments, where they reached 100 μg S dm^{-3} per day (station 3919, Table 4).

Distribution of normal alkanes (*n*-alkanes) in surface sediments along the Trans-Caspian axial profile. The presence of oil and gas deposits in Caspian submarine sediments is a well-known fact. The Caspian bottom also features numerous tectonic dislocations, which discharge hydrocarbon-containing fluids; in particular, in the Azerbaijan sector alone, there are at least 300 mud volcanoes on the Caspian Sea bottom [10].

There have been several attempts to identify the signs of potential “hydrocarbon breathing” of Caspian deposits lying close to the bottom surface based on the distribution of alkane hydrocarbons (C_{12}–C_{40}) which can be treated as a sort of biomarkers [11, 12]. The authors of these works proposed to differentiate between immature sedimentary OM as such and migratory hydrocarbons as OM fractions of modern sediments. The *n*-alkanes are particularly important geochemical molecular markers: due to their poor solubility in seawater, they accumulate in the sediments, while their resistance to microbial activity helps them persist for the periods of time considered long even on the geological scale.

The *n*-alkane composition depends first of all on the type of source OM and on the extent of its transformation in the course of sedimentation and at initial stages of diagenesis. The immature OM analyzed contained predominantly even-numbered low-molecular *n*-alkanes. However, at the early stage of diagenesis, hydrocarbon distribution was already characterized by a pronounced predominance of odd-numbered hydrocarbons of the $C_{23,\,25,\,27,\,29}$ series. The distribution where the peaks corresponding to odd- and even-numbered *n*-alkanes are smoothed and the concentrations of both fractions are equally high may indicate increasing OM maturity.

The concentration of *n*-alkanes in sediment samples was rather low and ranged from 0.5 to 3.38 μg g^{-1} of air-dry sediment (Table 5). The major sediment fraction (51% on the average) was constituted by terrigenous matter, that is, *n*-alkanes C_{23}–C_{40}. Low-molecular hydrocarbons C_{15}–C_{20} (hydrocarbons of hydrobionts and zooplankton) constituted 29% of the total *n*-alkane amount. The portion of microbial OM (C_{20}–C_{24}) did not exceed 11% of total *n*-alkanes on the average (Table 5, Fig. 4).

All samples of recent sediments contained C_{10}–C_{14} *n*-alkanes representing light oil fractions, i.e., migratory hydrocarbons (Table 5). Their content decreased from the lowest layer sampled to the surface, which supported the notion that they originated from the underlying sediment mass. The highest content of C_{10}–C_{14} hydrocarbons was observed in presumably ancient (not recent) sediments at station 3904 (Table 5). Sokolova and Ablya described the presence of migratory hydrocarbons in recent sediments of the Northern and Central Caspian [12]. It should be noted that OM of recent sediments was characterized with a bimodal *n*-alkane distribution, with a $\Sigma(C_{10}-C_{22})/\Sigma(C_{23}-C_{40})$ ratio of 0.94; i.e., this OM was of planktonic and terrigenous origin and very weakly transformed.

Thus, the C_{org} isotope composition in the surface layer of the water column varied considerably across the Northern, Central, and Southern Caspian. The lowest $\delta^{13}C$–C_{org} values (–25.5‰) were observed in the Northern Caspian. In the Southern Caspian, suspended OM of the surface layer contained the highest portion of the heavier carbon isotope ($\delta^{13}C$–C_{org}, –22 to –23‰, Fig. 2b), whereas the Central Caspian was characterized by intermediate $\delta^{13}C$–C_{org} values (–24‰, Fig. 2b). The observed distribution of $\delta^{13}C$–C_{org} values resulted from a significant inflow of isotopically light OM with river discharge in the Northern Caspian and from the decreasing effect of this discharge from the north to the south.

The values of $\delta^{13}C$–C_{org} obtained at the westernmost (station 3906) and easternmost (station 3902) points of the latitudinal profile in the Central Caspian (–25.4 and –25.6‰, respectively; Table 1) further confirmed the influence of terrigenous OM inflow on the isotope composition of suspended C_{org}. In shallow waters near the Mangyshlak Peninsula (the eastern meridional profile), eolian inflow of terrigenous mate-

Table 5. C_{org} content and distribution of *n*-alkanes in the sediments along the Trans-Caspian axial profile

Station, layer	C_{org}, %	$\Sigma(C_{10} + C_2)/\Sigma(C_{23} + C_4)$	*n*-alkanes, μg/L	$\Sigma(C_{10} - C_{14})$	$\Sigma(C_{15} - C_{20})$	$\Sigma(C_{10} - C_{24})$	$\Sigma(C_{23} - C_{40})$
3920 (0–10 cm)	4.69	0.54	1.38	5.3	24.4	14.0	64.8
3920 (10–21 cm)	2.85	0.48	1.20	6.7	21.2	12.4	67.4
3920 (31–42 cm)	2.13	1.00	1.80	13.7	32.8	10.1	50.0
3904 (0–10.5 cm)	1.10	1.49	0.79	19.3	36.3	11.0	40.2
3904 (0–10 cm)	0.52	3.69	1.41	36.2	40.6	5.2	21.3
3907 (0–10 cm)	5.02	0.38	2.44	4.1	19.5	10.4	72.7
3907 (10–21 cm)	3.46	0.70	2.28	8.0	30.5	8.6	58.9
3907 (33–46 cm)	2.87	0.74	1.74	10.3	29.4	9.0	57.4
3908 (0–10.5 cm)	4.19	0.72	0.88	6.	31.8	11.4	58.1
3908 (10.5–19.5 cm)	2.67	1.09	0.76	10.0	37.1	13.1	47.8
3919 (0–10 cm)	4.04	0.48	2.12	4.6	23.3	12.2	67.5
3919 (24–35 cm)	2.46	0.69	1.47	9.8	27.2	11.3	59.1
3917 (0–10 cm)	4.46	0.66	0.51	6.2	25.6	14.7	60.1
3917 (10–19 cm)	2.42	0.83	1.66	8.6	31.6	12.4	54.6
3917 (30–40 cm)	1.78	0.91	1.17	12.1	30.7	12.4	52.3
3916 (0–9 cm)	3.82	0.59	1.91	6.0	26.7	13.5	62.8
1916 (9–22 cm)	2.14	1.04	3.38	11.8	35.4	10.0	48.9

rial increased the portion of the heavier carbon isotope in suspended C_{org}, probably due to the ^{13}C-enriched OM derived from succulent plants of the desert. Below the mixed water layer, the isotope composition of suspended C_{org} showed little variation throughout the water column, with δC^{13} values ranging from –22 to –24‰ (Fig. 2). The only exception was suspended C_{org} in anoxic water layers of deep-sea basins: below 600 m, $\delta^{13}C–C_{org}$ ranged from –26.0 to –29.9‰ (Fig. 2). In addition to sulfide, these layers of the water column also contained increased amounts of methane (up to 3.5 μg L^{-1}).

Methanogens present in the water column preferably utilized the isotopically light carbon dioxide, and the resulting microbial biomass was characterized with a lighter isotope composition. The contribution of this novel C_{org} to the total suspended matter may explain the extremely low $\delta^{13}C–C_{org}$ values observed at deep-sea stations.

The maximal sulfate reduction rate, the highest methane concentration, and the highest TMA were observed in the sediment layer 0.5–1.5 cm (up to 3.5 cm), rather than in the warp. The fact that the most intensive biogeochemical activity was associated not with the warp, but with the underlying sediments made the processes of suspended matter transformation at the bottom—water sediment interface in the Caspian Sea different from those described for the Russian Arctic seas, where the highest rates of suspended matter transformation were observed mainly in the warp [2, 6]. Apparently, this difference may be explained by the effects of bottom currents that transport suspended matter to deeper regions of the Caspian, as well as by the fact that considerable transformation of suspended matter and particularly of its planktonic fraction occurs in the water column itself, in contrast to the shallow Arctic seas.

The microbial population of the sea bottom has the most important effect on sediment formation in the Caspian. Microbial communities actively participate in all biogeochemical processes that take place in the near-bottom water and sediments [2, 6, 13, 14]. Following the pioneering study by Waksman (1937), most researchers have noted the increased microbial abundance in the upper sediment layers, which are at the early stages of diagenesis [13]. Sediment samples collected in the Central and Southern Caspian were no exception to this pattern. The water-sediment interface was characterized by a systematic increase in TMA values from the near-bottom water to the upper sediment layer. An increase in TMA was associated with de novo formation of OM, including microbial biomass and metabolic products, and affects the rate of diagenesis in the sediments. A study by Salmanov [15] provided a detailed microbiological investigation of Caspian sediments, which not only registered total microbial numbers but also analyzed the species composition by different physiological groups. It was shown that TMA values in the Caspian muds varied considerably with bottom location and the observation season: from tens of millions to billions of cells per 1 g mud (up to 13 × 10^9 cells g^{-1}). Our data on the TMA in mud samples collected along the Trans-Caspian axial profile were of the same order of magnitude: 1.1 × 10^8 to 8.4 × 10^9 cells per 1 cm^3. On the whole, sediment OM may be characterized as immature OM of mixed autochthonous and allochthonous origin, diagenetically little transformed, with active anaerobic sulfate reduction and methanogenesis, and with the minimal contribution of migratory hydrocarbons.

To sum up, we can agree with the conclusion proposed by Academician A.P. Lisitsyn: "The principal mechanisms governing the present-day processes of sediment accumulation are biogeochemical, and not physicochemical ones. The dominance of physicochemical processes was over with the appearance of life in the ocean!" [16, p. 311].

ACKNOWLEDGMENTS

The authors are grateful to A.K. Abrosimov and A.A. Klyuvitkin, cruise supervisors, and to the cruise participants who helped to collect the water and sediment samples.

This work was supported by the Presidium of the Russian Academy of Sciences (basic research programs nos. 23 and 28) and by the Russian Foundation for Basic Research (project no. 14-04-00682).

REFERENCES

1. Kholodov, V.N., Khrustalev, Yu.P., Lubchenko, I.Yu., Kovalev, V.V., and Turovskii, D.S., *Kaspiiskoe more: problemy sedimentogeneza* (Caspian Sea: Problems of Sedimentogenesis), Moscow: Nauka, 1989.
2. Lein, A.Yu., Rusanov, I.I., Klyuvitkin, A.A., Kravchishina, M.D., Zakharova, E.E., Veslopolova, E.F., Makkaveev, P.N., and Ivanov, M.V., Biogeochemical processes in the water column of the Caspian Sea in November 2008, *Doklady Earth Sci.*, 2010, vol. 434, no. 2, pp. 1381–1385.
3. Ambrosimov, A.K., Klyuvitkin, A.A., Goldin, Yu.A., Zakharova, E.E., Korzh, A.O., Kravchishina, M.D., Mutovkin, A.D., Novigatskii, A.N., Politova, N.V., Savvichev, A.S., and Chul'tsova, A.L., Integral investigation of the Caspian Sea system during the RV *Rift#* 39th cruise, *Okeanologiya*, 2014, vol. 54, no. 3, pp. 428–432.
4. Ivanov, M.V., Savvichev, A.S., Klyuvitkin, A.A., Chul'tsova, A.L., Zakharova, E.E., Rusanov, I.I., Lein, A.Yu., and Lisitsyn, A.P., Resumption of hydrogen sulfide contamination of the water column of deep basins in the Caspian Sea, *Doklady Earth Sci.*, 2013, vol. 453, pt. 1, pp. 1094–1099.
5. Lein, A.Yu. and Ivanov, M.V., *Biogeokhimicheskii tsikl metana v okeane* (Methane Biogeochemical Cycle in the Oceans), Moscow: Nauka, 2009.
6. Lein, A. Yu., Rusanov, I.I., Kravchishina, M.D., and Ivanov, M.V., Genesis of organic and carbonate carbon in sediments of the North and Middle Caspian basins inferred from the isotope data, *Lithol. Mineral Res.*, 2012, vol. 47, no. 4, pp. 281–294.
7. Deev, M.G., Caspian Sea, in *Great Russian Encyclopedia*, vol. 13, pp. 275–279.
8. Galimov, E.M., *Geokhimiya stabil'nykh izotopov ugleroda* (Geochemistry of Stable Carbon Isotopes), Moscow: Nedra, 1969.
9. Klenova, M.V., *Geologiya morya* (Geology of the Sea), Uchpedgiz, 1948.
10. Aliev, Ad.A., Guliev, N.S., and Guseinov, D.A., Mud volcanism of the Southern Caspian oil basin, *Geol. Azerbaidzhana*, vol. 7 (oil and gas), Nafta-Press, 2008, pp. 444–512.
11. Verkhovskaya, Z.I., Marina, M.M., Berlin, Yu.M., Gazenko, A.O., and Parfenova, L.M., Geochemical investigation of the Northern Caspian bottom sediments,, *Caspian Sea Bull.*, 2007, no. 4, pp. 62–69.
12. Sokolova, M.N. and Ablya, E.A., Biomarker investigation in organic matter of Central and Northern Caspian bottom sediments, *Mos. Univ. Geol. Bull.*, vol. 4, no. 2, pp. 49–57.
13. Ivanov, M.V., Belyaev, S.S., Laurinavichus, K.S., and Obraztsova, A.Ya., Microbiological formation of H_2S and CH_4 in modern and Quaternary sediments of the Caspian Sea, *Geokhimiya*, 1980, no. 3, pp. 416–422.
14. Ivanov, M.V., Vainshtein, M.B., Gal'chenko, V.F., Gorlatov, S.N., and Lein, A.Yu., Distribution and geochemical activity of bacteria in the Western Black Sea sediments, in *Neftegazogeneticheskie issledovaniya Bolgarskogo sektora Chernogo morya* (Research on Oil and Gas Genesis in the Black Sea Bulgarian Sector), Sofia, 1984, pp. 150–180.
15. Salmanov, M.A., *Rol' mikroorganizmov i fitoplanktona v produktsionnykh protsessakh Kaspiiskogo morya* (Role of Microorganisms and Phytoplankton in Productive Processes of the Caspian Sea), Moscow: Nauka, 1987.
16. Lisitsyn, A.P., *Protsessy okeanskoi sedimentatsii. Litologiya i geokhimiya* (Processes of Oceanic Sedimentation. Lithology and Geochemistry), Moscow: Nauka, 1978.

Translated by D. Timchenko