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MARINE GEOLOGY

Seasonal Dynamics of Biogeochemical Processes in the Water Column of the Northeastern Black Sea

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Abstract—Integrated studies on the hydrochemistry and water column rates of microbial processes in the eastern sector of the Black Sea along a standard 100-miles transect off Gelendzhik from the coast to the central part of the sea at water depths of 100–2170 m show that a series of warm winters and the absence of intense convective winter mixing resulted in a relatively low content of suspended particulate matter (SPM), particulate organic carbon (POC), and nutrients in the water column in March 2009. The relatively high SPM concentrations and the presence of isotopically light POC at the offshore station are indicative of the supply of terrigenous material from land and low contributions of phytoplanktonic organic matter to the composition of SPM. This may explain the low rates of biogeochemical processes in the water column near the coast. The surface layer at deep-water stations is dominated by isotopically heavy phytoplanktonic organic matter. This suggests that the supply of terrigenous material from land was insufficient in offshore deep-water areas. Therefore, warm winters and insufficient nutrient supply do not prevent photosynthesis in the photic layer of the deep-water zone, which generates organic substrates for heterotrophic aquatic communities. The results of isotopic analysis of POC, measurements of the rates biogeochemical processes, and the hydrochemical characteristics of the water column can be used to determine the nature and seasonal variability of the POC composition.

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INTRODUCTION

Warming in the northeastern Black Sea and weakened convective mixing in the winter could decrease the thickness of the aerobic zone due to an increase in the thickness of the anaerobic zone.

Biogeochemical processes in the water column of the northeastern Black Sea affect the environmental situation within the entire recreational area extending along the coast from Anapa to Sochi.

Long-term studies of the hydrochemical characteristics of the water column showed that the distribution and concentrations of nutrients in the water column are associated with the hydrological structure of waters [1]. The strong variability of dynamic processes in the upper layers of the water column causes seasonal variations in the concentrations and composition of biogenic components (HCO_3^{2-}, P, Si, nitrogen compounds, etc.) in the aerobic zone.

Analysis of the composition and distribution of SPM, i.e., particles of various origin varying in size from 0.1 μm to 1 mm that are passively suspended in seawater, has been included in the study of the water column from the end of the 20th century [10].

SPM is composed of a mixture of autochthonous (aquatic plankton) and allochthonous (terrigenous) organic matter (OM), which serves as a substrate for the activity of heterotrophic microorganisms involved in the transformation of particulate organic matter and including gas formation (CO_2, H_2S, CH_4, NH_4, etc.).

Primary production in the study area ranged from 128 to 298 mg/m^2/d [3].

Long-term observations show that a massive bloom of diatoms occurs mainly in March–May, and that of coccolithophores, in May–June [21]. For example, a coccolithophore bloom began in the second half of April in 1998 [13] or in June in 2011 [5].

The interdisciplinary oceanographic expedition of the Shirshov Institute of Oceanology, Russian Academy of Sciences, on board the R/V *Professor Shtokman* 100th (chief scientist M.V. Flint) was conducted during the spring phytoplankton bloom from March 5 to April 4, 2009. One of the objectives of this cruise was to study biogeochemical processes in the water column along a standard 100-miles transect off Gelendzhik from the shore to the central part of the sea, at water depths of 100–2170 m (Table 1, Fig. 1).

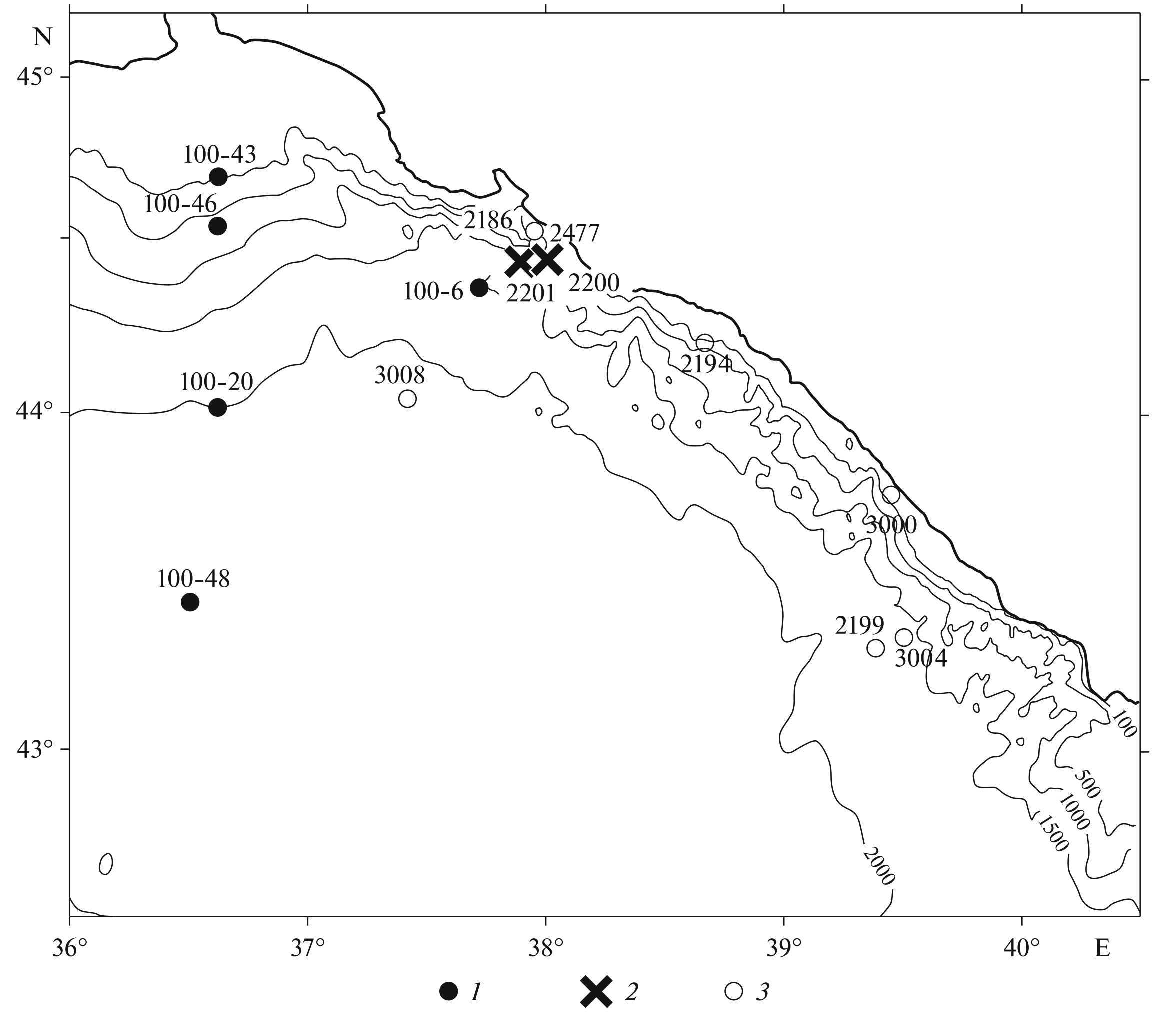

Fig. 1. Location of sampling stations: (*1*) March 2009 (cruise 100, R/V *Professor Shtokman*); (*2*) June 2005 (cruise 80, R/V *Akvanavt*); (*3*) June 2005 and 2007 (cruises 81, 99, and 123, R/V *Akvanavt*).

The study area covered the shelf with an aerobic water column, and the continental slope and pelagic zone, with a stratified water column. The effects of seasonal factors on the amount and composition of SPM were discussed in an earlier study [3] based on data from a 1999 Russian–Swiss expedition.

Table 1. Sampling stations of cruise 100 of the R/V *Professor Shtokman* (March 2009) and cruise 80 of the R/V *Akvanavt* (June 2005)

Station no.	Coordinates		Depth, m
	N	E	
R/V *Professor Shtokman* (March 5–April 4, 2009)			
100-6	44°22.27	37°43.37	2000.0
100-20	44°01.1	36°37.60	2000.0
100-43	44°42.41	36°37.91	100.0
100-46	44°33.68	36°37.90	712.0
100-48	43°26.20	36°30.92	2170.0
R/V *Akvanavt* (June 25–30, 2005)			
2200	44°27.48	38°01.02	1300.0
2201	44°29.10	37°52.80	1600.0

Strong seasonal variations in the rate of biogeochemical processes were reported by Yu.I. Sorokin [16], who presented the results of sulfate reduction measurements (including the eastern part of the sea) in February–April 1991 with a ^{35}S radioisotope.

In June 2005, the rates of biogeochemical processes involving microorganisms were measured at stations located at the foot of the continental slope in the eastern sector of the sea using ^{35}S and ^{14}C radioisotopes, during a joint expedition of the Southern Brunch of the Shirshov Institute of Oceanology, Russian Academy of Sciences, and the Winogradsky Institute of Microbiology, Russian Academy of Sciences (Fig. 1).

During cruise 100 of the R/V *Professor Shtokman*, studies on biogeochemical processes in the water column of the northeastern sector of the sea were continued in the absence of (or with weak) winter convective mixing, which was unusual for this region. The warm winter of 2008–2009 did not intensify convective mixing of biogenic component fluxes into the water column, which might have affected the primary production rates, the concentrations of SPM, the organic carbon (C_{org}) content in SPM and, ultimately, the rate of biogeochemical processes.

The goal of this study was to determine the hydrochemical structure of waters and the rates of biogeochemical processes in the water column after a series of warm winters with possibly weak convective mixing of water masses.

MATERIALS AND METHODS

Water samples were taken during cruise 100 of the R/V *Professor Shtokman* in spring 2009 at five stations along a transect of the shelf (station 43), continental slope (station 46), and pelagic zone (stations 6, 20, and 48). During the cruise of the R/V *Akvanavt* in 2005, water samples were collected in 5–10 m intervals in the redox zone (boundary layer between aerobic and anaerobic zones) at two stations (2200 and 2201) located at the foot of the continental slope at water depths of 1300 and 1600 m (Table 1, Fig. 1).

The study was performed using hydrochemical, microbiological, radioisotopic, and isotopic geochemical methods [8].

Water samples for the analysis of aqueous suspensions were also collected during the June coccolithophore bloom from 2005 to 2007 as part of experimental ground-truth observations on cruises 81, 99, and 123 of the R/V *Akvanavt*.

All water samples were retrieved with Niskin plastic bottles attached to a Rosette sampler after completion of sound velocity profiles. SPM was vacuum-filtered through 0.45 μm preweighed membrane filters and glass-fiber filters (GF/F). GF/F filters were used to determine the content and isotopic composition ($\delta^{13}C-C_{org}$) of POC.

Sampling of SPM was performed simultaneously with short-term (12–48 h) experiments to determine the rate of microbial processes. e.g., dark CO_2 assimilation, sulfate reduction, methanogenesis, and methane oxidation, using radiolabeled substrates ($NaH^{14}CO_3$, $^{14}CH_4$, $Na_2{}^{35}SO_4$) under in situ conditions, following the procedure described elsewhere [2]. Chemical analyzes (O_2, Alk, etc.) were carried out on board the ship using standard hydrochemical analysis [15].

RESULTS

The northeastern part of the Black Sea includes the narrow shelf, steep continental slope, and pelagic zones.

Hydrochemical characteristics of the water column. Based on earlier data, the following layers were identified in the vertical temperature and salinity profiles at stations located at the foot of the continental slope: the upper quasi-homogeneous layer (0–10 m), seasonal pycnocline layer (10–15 m), cold intermediate layer (70–90 m), and main pycnocline layer (90–140 m, Fig. 2), which generally agrees with the average hydrological characteristics of the northeastern part of the sea [14].

The maximum oxygen concentrations were observed in the 15–50 m layer. The minimum oxygen concentrations (0.03–0.6 μM/L) were observed above a hydrogen sulfide zone.

In spring 2009, the concentrations of nutrients (especially phosphate phosphorus and nitrate nitrogen) were unusually low, decreasing to analytical zero in the upper 30–50 m layer (Fig. 3). This definitely had a limiting effect on the growth of phytoplankton. Our observations (March 2009) revealed the absence of the spring diatom and coccolithophore blooms, which typically start at this time of year. The absence of blooms can be explained by low biological activity throughout the water column. As a result of extreme warm winters in recent years, winter convection did not reach the cold intermediate layer (CIL), where the basic nutrients are formed. The rise of nutrients in the cold season can account for two-thirds of the annual photosynthetic production. The remaining organic matter in the open sea is formed by recycling of nutrients. The effect of continental runoff on water column primary production in open sea areas can be ignored. For example, earlier data [11] show that only about 2–6% of the nutrient flux supplied by rivers to the coastal zone in the northwestern part of the sea is almost completely consumed.

Another explanation may be the assumption that the spring phytoplankton bloom has already passed or has not yet occurred and that low nutrient levels reduce phytoplankton growth. The second assumption can be confirmed or rejected based on an analysis of the concentration and composition of SPM. Assuming the end of the phytoplankton bloom, the concentration of the biogenic component in SPM should be quite high. This can also be recorded by the isotopic composition of POC.

Concentrations of SPM. SPM concentrations in the water column depend on primary production, solid river runoff, aerosol input, marine abrasion, and erosion. The first two factors play a dominant role in the formation of suspended matter. In the study area, the maximum flux of biogenic components to SMP is associated with the annual bloom of diatomaceous and carbonaceous microalgae.

In March and April, in addition to high plankton concentrations, a high content of terrigenous (lithogenic) material in SPM is caused by river runoff.

Analysis of SPM concentrations in water samples collected during the cruise of the R/V *Akvanavt* in June 2005–2007 at shallow-water stations located at

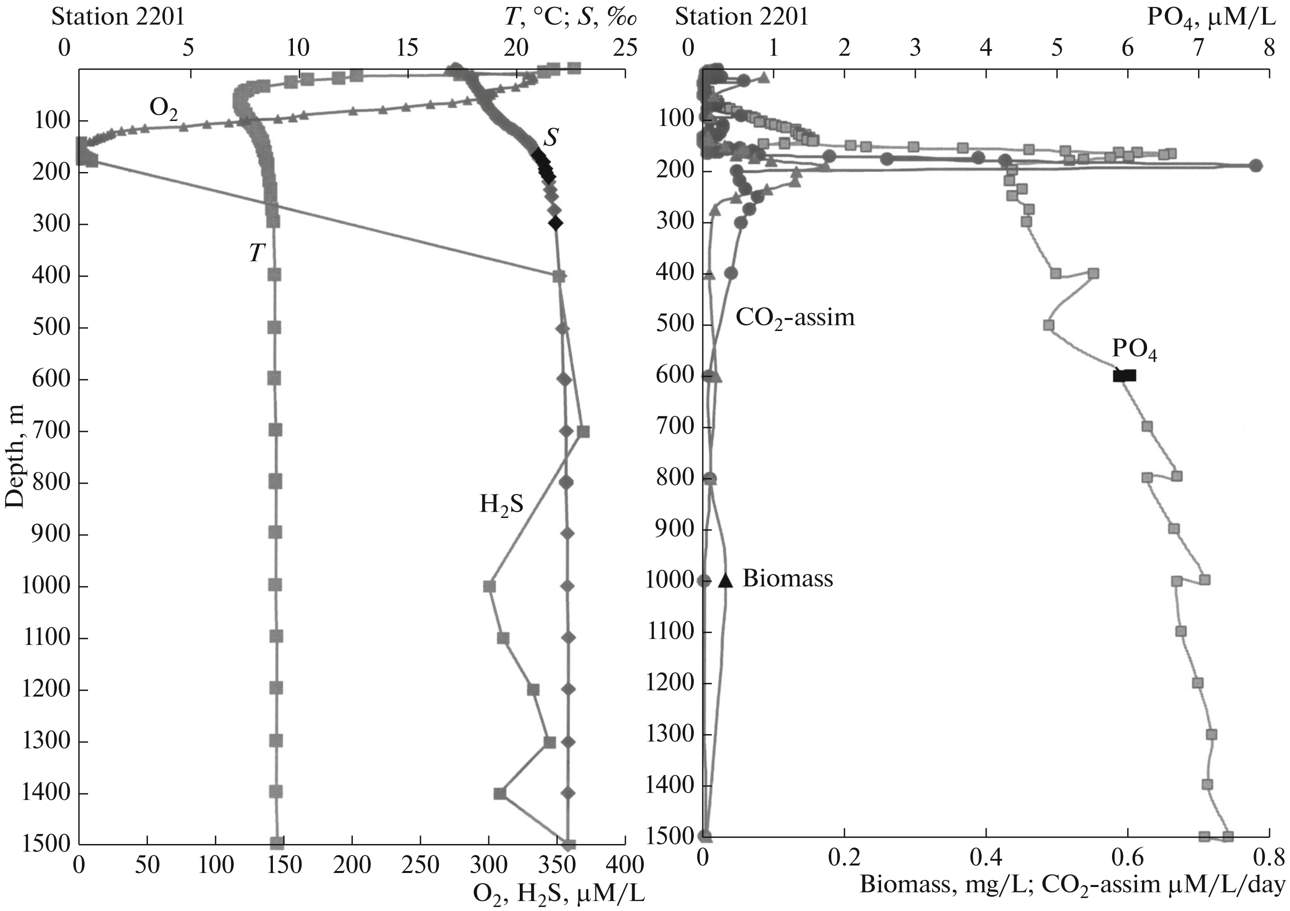

Fig. 2. Physicochemical and microbiological parameters of water column (station 2201) in June 2005: temperature (*T*), salinity (*S*), oxygen (O_2) and hydrogen sulfide (H_2S) concentrations, microbial biomass (biomass), CO_2 assimilation rate (CO_2-assim) and PO_4 concentration.

water depths of 25–200 m revealed a 40-fold variation in the allochthonous component of SPM (from 0.035 to 1.409 mg/L) in the surface layer of the water column (Fig. 4) and a sevenfold variation in C_{org} content in the same layer (from 0.026 to 0.168 mg/L). At shallow-water stations, SPM concentrations naturally decrease from the surface to the bottom. Maximum SPM concentrations were recorded in a subsurface (10–15 m) layer in June 2007, and a similar trend was observed in the vertical C_{org} profile. The heterogeneous SPM distribution in the surface layer was generally consistent (except for coastal stations) with the spatial pattern of the chlorophyll distribution from MODIS-Aqua satellite data.

In March 2009, the maximum SPM concentrations were measured in the surface layer on the shelf at station 43 (0.60 mg/L), which is caused by the proximity to the coast. The SPM concentrations in the surface layer decrease to 0.36 mg/L with distance from the coast (station 46) and remain constant (0.28–0.40 mg/L) at deep-water stations (6, 20, 48, and 50) (Fig. 5).

In a stratified water column, the SPM concentrations generally increase at the boundary layer between aerobic and anaerobic zones. For example, maximum SPM concentrations were measured in the 60 m layer (0.48 mg/L) at station 46, in the 140 m layer (0.70 mg/L) at station 6, in the 120–140 m layer (0.70 mg/L) at station 20, and in the 90 m layer (0.30 mg/L) at station 48 (Fig. 5).

A similar increase in SPM concentrations at the boundary layer between aerobic and anaerobic zones was reported earlier in the pelagic zone of the eastern halistatic area, e.g., up to 2.45 mg/L in May 1988 [3, 12]. This can be explained by the death of phytoplankton during oxygen depletion and H_2S and CH_4 enrichment. An increase in SPM concentrations in this zone can also be caused by the transfer of manganese from the dissolved phase to the particulate phase, as indicated by an earlier study on the same region of the sea [4]. SPM concentrations were two times lower below the redox zone and varied within a narrow range from this zone to the bottom.

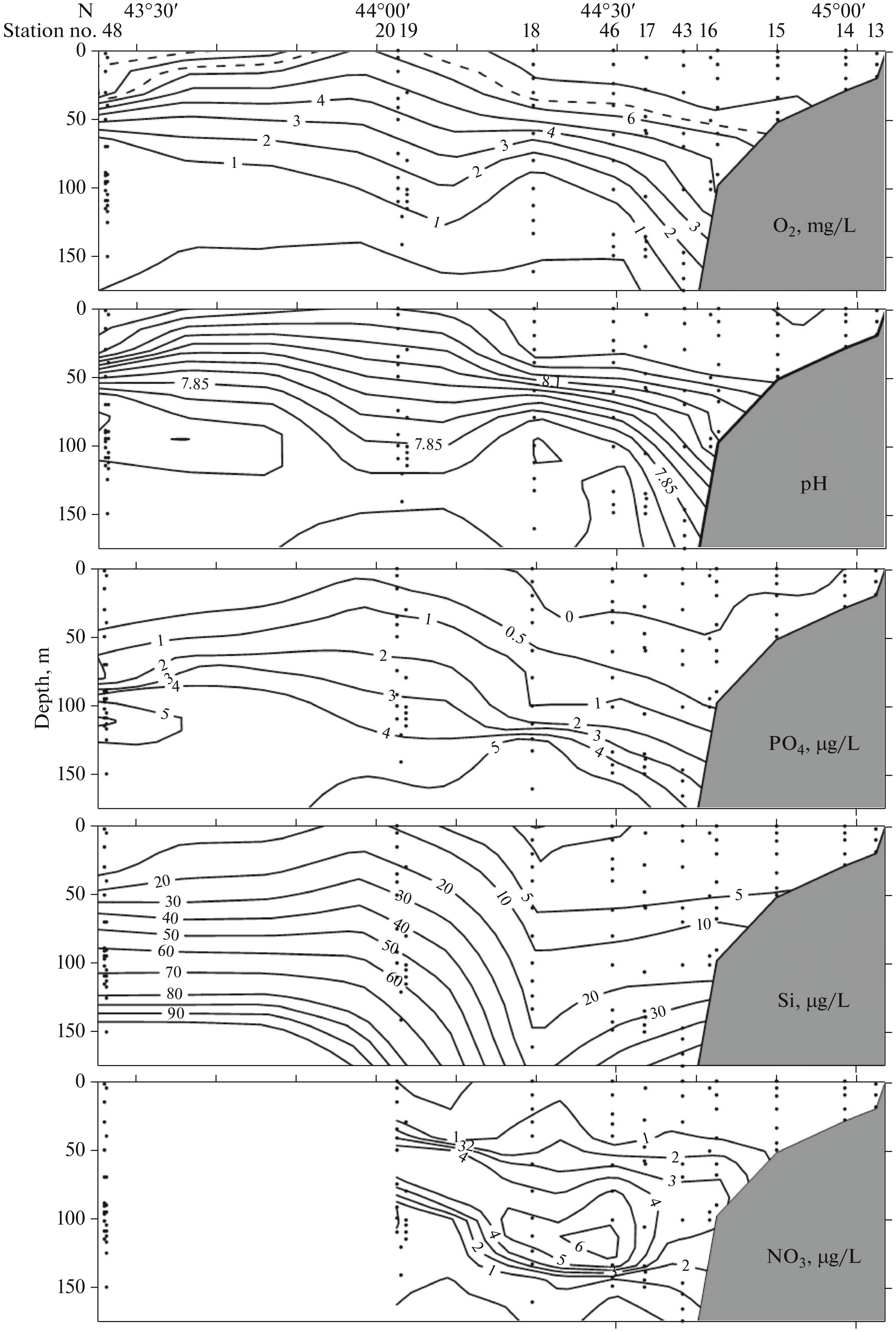

Fig. 3. Hydrochemical characteristics of upper 150 m of water column in March 2009: oxygen concentration (O_2), pH, concentrations of PO_4, Si, and NO_3.

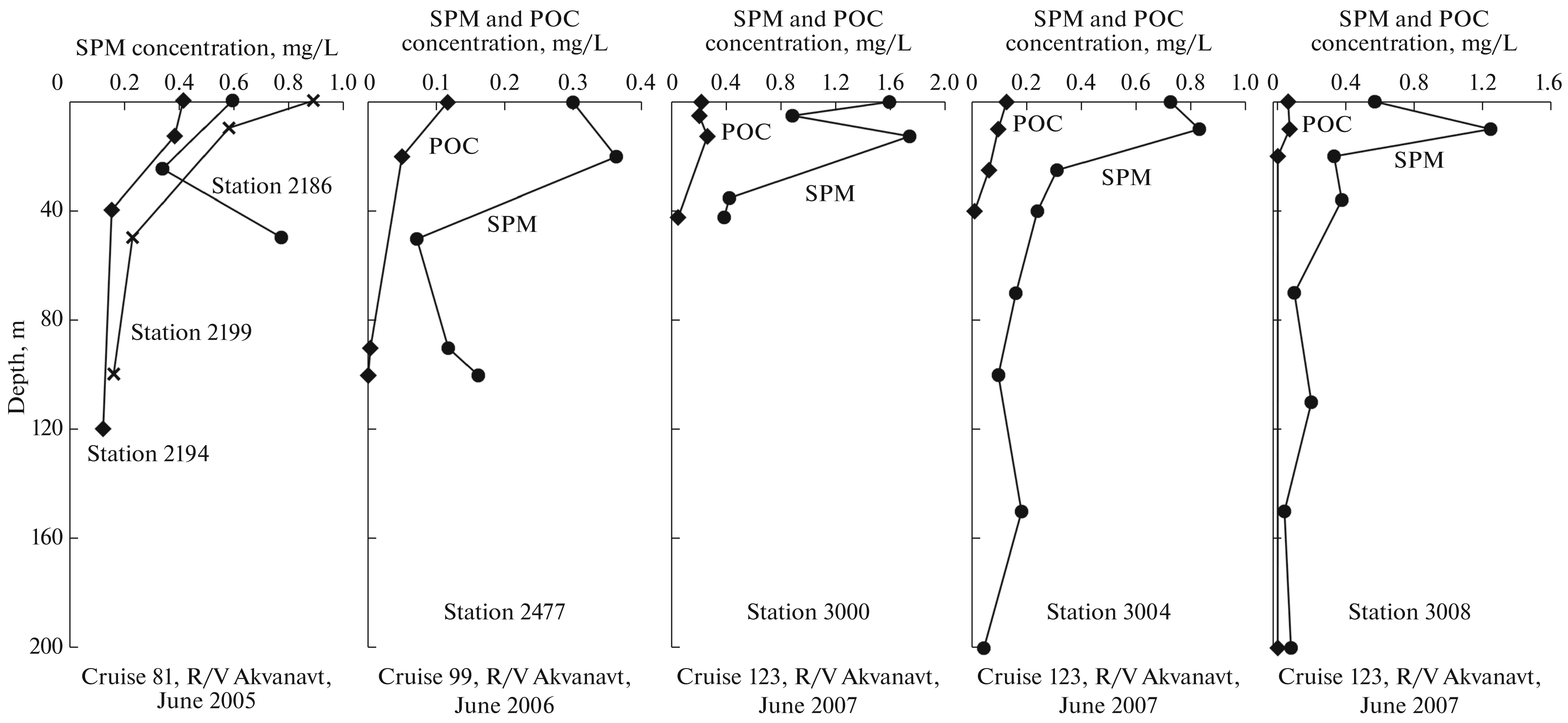

Fig. 4. SPM and POC concentrations in water column in shelf zone in June 2005–2007.

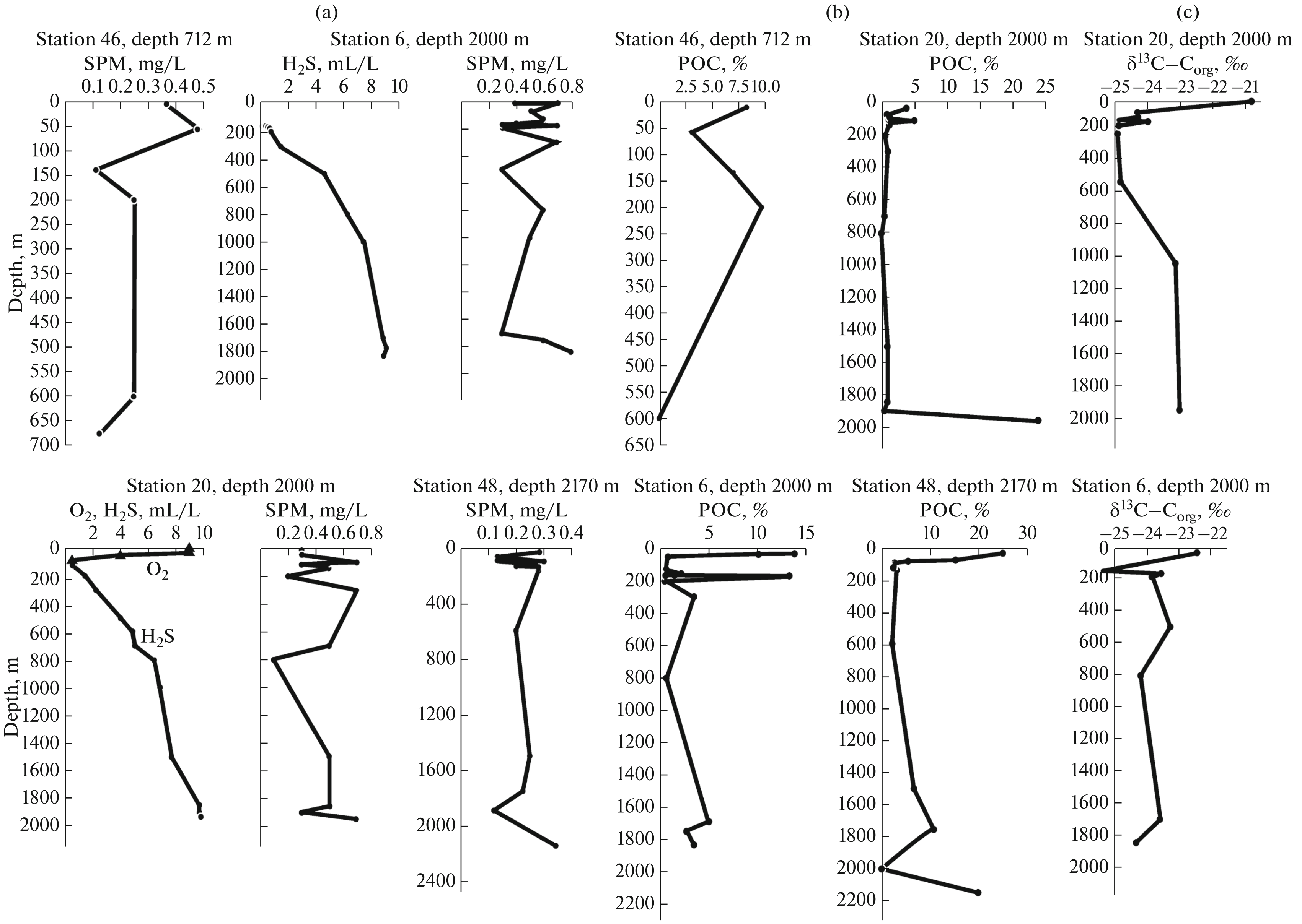

Fig. 5. (a) Water-column O_2, H_2S, and SPM concentration profile on continental slope and in pelagic zone in March 2009; (b) distribution of C_{org} in % of total SPM on continental slope (station 46) and in pelagic zone (stations 6, 20, and 48); (c) $\delta^{13}C-C_{org}$ values of SPM from deep-water (stations 6 and 20).

Content and isotopic composition of POC. *Shelf.* The content of C_{org} in the water column at shelf station 43 varied from 8.2% in the surface layer to 10.2% in the bottom layer.

The $\delta^{13}C$–C_{org} values of the surface layer (–26.0 ‰) indicate the presence of terrigenous C_{org} in SPM, which was supplied from coastal zones, and, to a lesser extent, planktonic OM. In the near-bottom water layer, POC generally became depleted in ^{13}C (–28.2‰), suggesting its predominantly allochthonous origin, which can be explained by the accumulation of a considerably "older" terrigenous SPM in the 95 m layer. The SPM was supplied in the autumn–winter period and is almost completely devoid of the phytoplanktonic POC.

Continental slope and pelagic zone. On the continental slope (station 46), two peaks of C_{org} contents were observed in the water column. They were confined to the photic layer (8% C_{org}) and redox zone (9.47% C_{org}), respectively. Between these two peaks, the average C_{org} content of SPM was less than 3% (Fig. 5). The content of C_{org} in SPM from the surface layer of deep-water stations (6, 20, 48, and 50) varied from 25.8% (station 48) to 4.32% (station 20) (Fig. 5). The C_{org} content can decrease to trace levels below the photic zone down the water column. In the redox zone, the C_{org} content of SPM was higher than that of the boundary layers.

The C_{org} isotopic composition of SPM from the photic layer at deep-water stations varied from –20.71‰ (station 20) to –22.55‰ (station 6, Fig. 5). This indicates a predominantly autochthonous origin of the bulk C_{org} in the surface layer with low terrigenous inputs from the coast. Below the photic layer, the $\delta^{13}C$–C_{org} values varied from –25.26‰ (station 48, 150 m layer) to –22.97‰ (station 20, 1900 m layer), with an average of –24.14‰ (16 samples), suggesting a mixed composition of C_{org} in SPM below the photic layer.

From March 9 to April 4, 2009, the composition of SPM from deep-water stations showed a slight enrichment in terrigenous C_{org} as compared to stations 43 and 46 located closer to the coast. In the redox zone, the isotopic composition of C_{org} was almost independent of the C_{org} content of SPM.

Methane distribution in the water column. In the shelf zone (station 43), the concentration of methane in the water column varied from 0.08 μL/L in the surface layer and in the 95 m layer to 0.37 μL/L at the water–bottom interface. Such an increase in methane concentrations can be explained by the input of methane from sediments.

On the continental slope (station 46), the methane concentrations in the water column to the 160 m layer varied from 0.34 to 0.57 μL/L (average 0.485 μL/L, Fig. 6). At a depth of 160–200 m and at the redox zone boundary, the methane concentrations increased by an order of magnitude and two orders of magnitude, respectively. In the anaerobic zone (at 600 and 675 m), the methane concentrations were almost 500 times higher than in the 0–140 m layer (Fig. 6).

In the pelagic zone (station 48) of the aerobic layer, the water column was characterized by a heterogeneous methane distribution of methane, with a gradual increase from 0.16 to 16.2 μL/L down to the 125 m layer. In the redox zone (175–300 m), the methane concentrations increased to 115.7 μL/L and varied within a narrow range from 213.2 to 244.0 μL/L in the 600 m layer and down to the bottom. A similar pattern was observed at stations 6 and 20 (Fig. 6).

Hydrogen sulfide distribution in water-column of the pelagic zone. At station 6, hydrogen sulfide first appeared in the 150 m layer and its concentration increased gradually from 0.01 to 0.65 mL/L down the water column to the 200 m layer. From a depth of 300 m down the bottom, the concentration of dissolved H_2S increased from 1.66 to 9.14 mL/L (Fig. 7).

At the boundary of the shallowest appearance of hydrogen sulfide, the C_{org} content of SPM, the rates of methane generation, and CO_2 assimilation sharply increased, peaking at 155 m. In other words, when dead plankton sinks to the bottom, it is then decomposed by anaerobic processes shortly after its accumulation. The response to these processes was ^{13}C depletion of C_{org} (–25.6‰) within the 150 m layer (Fig. 5).

At station 20, the first appearance of hydrogen sulfide (0.26 mL/L) was recorded in the 120 m layer (Fig. 7). The distribution of H_2S throughout the water column is similar to that detected at station 6, with a gradual increase from 1.40 mL/L in the 200 m layer to 8.85 mL/L in the 1940 m layer (Fig. 7). The C_{org} content at this station increased to 5% at 110 m. The peak of CO_2 assimilation (up to 6.88 μgC/L/d) was detected in the 120 m layer, but in the two neighboring layers (115 and 140 m), the assimilation rate was also higher than in other layers of the water column.

At the deepest station 48, the first appearance of hydrogen sulfide was detected at 109 m and the peak of CO_2 assimilation (6.88 μg C/L/d) was observed down to 125 m (Fig. 7).

Below the 300 m depth and down to the bottom at stations 6 and 20, the concentrations of hydrogen sulfide and methane increased to 9 mL/L and 250 μL/L, respectively (Fig. 6).

The rates of biogeochemical processes in water-column. *Methanogenesis. On the shelf* (station 43), the rate of methane production reached its maximum (40 nL/L/d) in the surface layer of the water column and decreased to 6.8 nL/L/d down to the bottom. This methane production rate profile suggests that methane generation took place in situ, mainly in the water layers with the highest SPM concentrations.

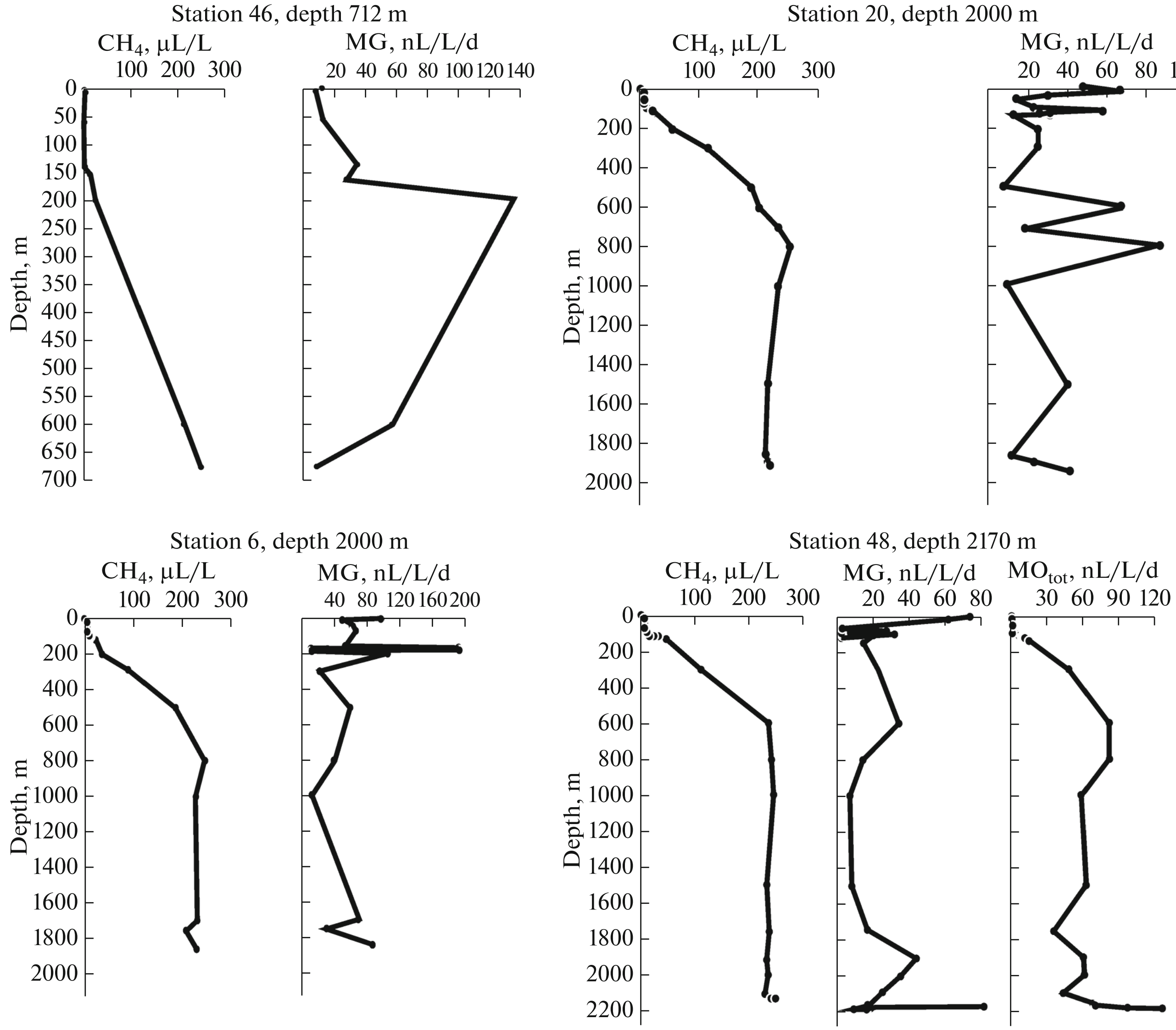

Fig. 6. Profiles of methane concentrations (μL CH_4/L), methanogenesis rates (MG, nL CH_4/L/d) and methane oxidation rates (MO, nL CH_4/L/d) in water column on continental slope (station 46) and in pelagic zone (stations 6, 20, and 48).

On the continental slope (station 46), the rates of methane production were characterized by an uneven distribution pattern throughout the water column. In the aerobic zone, they varied from 0.7 to 34.1 nL/L/d, increasing dramatically (by an order of magnitude) to 132.5 nL CH_4/L/d in the C_{org}-rich redox zone. Below 200 m, the rate of methane production decreased to 8.0–57.0 nL CH_4/L/d (Fig. 6).

The profile of methane production rates on the continental slope is indicative of in situ methane production, at least in the aerobic and redox zones.

In the pelagic zone, within the aerobic layer, the rate of methane production decreased from the surface layer to the upper limit of the redox zone (station 48). The peak (61–75 nL CH_4/L/d) of methanogenesis in the presence of oxygen occurred in the surface layer with the highest C_{org} content of SPM (Fig. 6).

The rate of methane production decreased to 1.4–2.7 nL/L/d down to 105 m and increased again to 34.4 nL/L/d in the redox zone (at 109–117 m) (Fig. 6). From a depth of 120 m, the rate of methane production varied irregularly from 9.0 to 45 nL CH_4/L/d increasing to 80.9 nL CH_4/L/d at the bottom (at 2169 m) (Fig. 6).

A similar pattern in the distribution of methane production rates was observed at stations 6 and 20 (Fig. 6). In the aerobic zone, the highest rates of methane production were confined to the photic layer with a high C_{org} content of SPM. The upper (150 m layer) and lower (170 m layer) boundaries of the redox zone at station 6 were characterized by the highest rates of

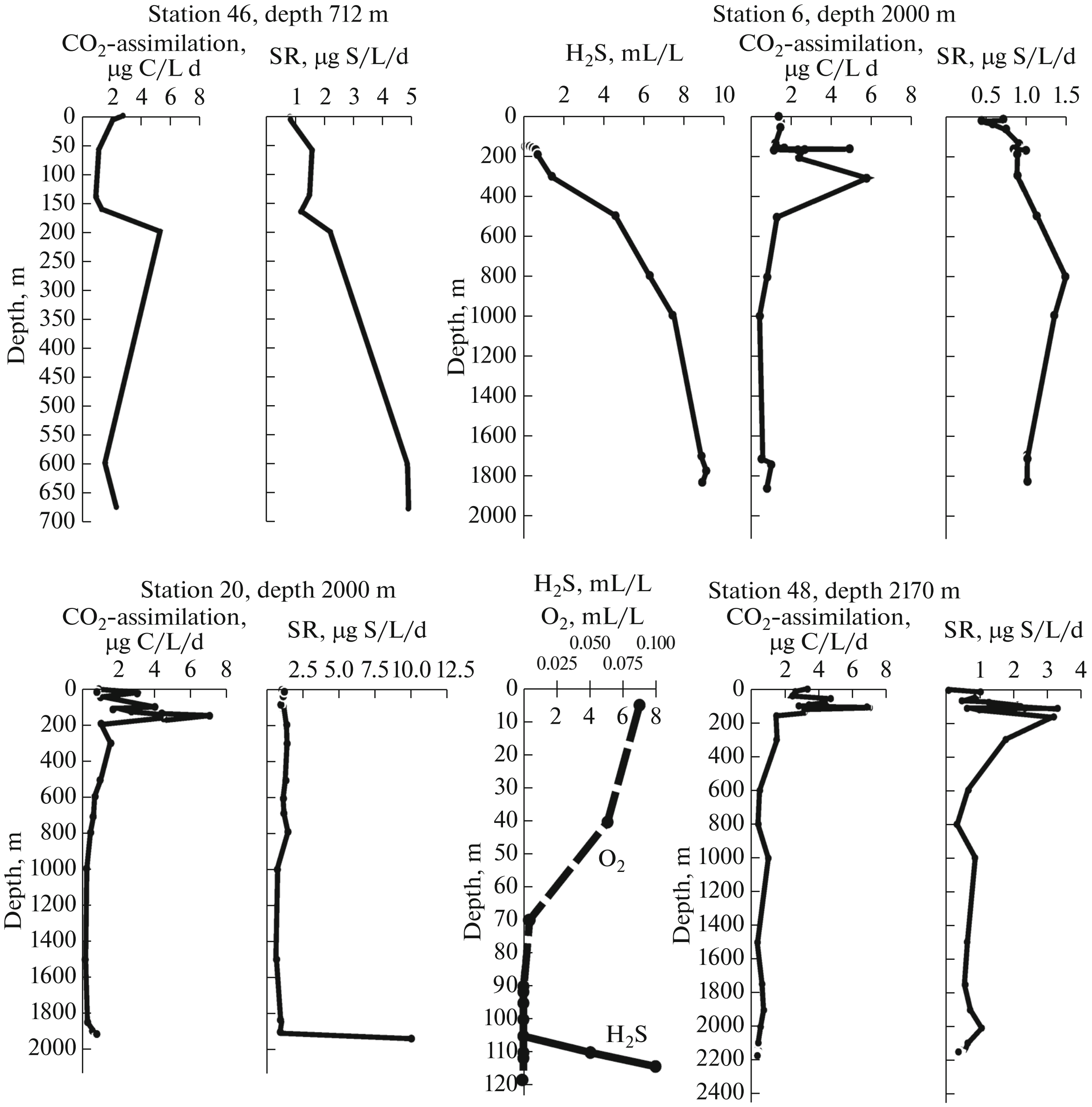

Fig. 7. Profiles of hydrogen sulfide concentrations (H_2S), sulfate reduction rates (SR, µg S/L/d), and CO_2 assimilation rates (µg C/L/d) in the water column on the continental slope (station 46) and in the pelagic zone (station 6, 20, and 48).

methane production (190.5 and 192.5 nL CH_4/L/d). Below 300 m, the rate of methane production varied from 13.9 to 70.7 nL/L/d, increasing, as is the case with station 48, to 86.1 nL CH_4/L/d at the bottom (Fig. 6). At station 20, the highest rate of methanogenesis occurred near the upper boundary of the redox zone (55.9 nL CH_4/L/d at 105 m, Fig. 6).

Methane oxidation. In the aerobic zone of deep-water stations (station 48), the rate of methane oxidation varied from 0.09 to 3.60 nL/L/d from the surface layer down to a depth of 109 m (Fig. 6), which was lower than the rate of methane production. From a depth of 109 m and below (the upper boundary of the redox zone), methane oxidation rates increased gradually, outpacing that of methane production starting from the 175 m layer down to the bottom.

Obviously, in this case, in addition to in situ methane production, methane was supplied by diffuse leakage and/or seepage.

In 2005, a similar trend was observed below the redox zone, where methane oxidation rates were higher than methane production rates at stations 2200 and 2201. This phenomenon may have the same explanation.

Sulfate reduction. Microbial sulfate reduction was a major anaerobic process operating in the water column at all stations. Water-column rates of sulfate reduction varied within a narrow range from 0.94 µg S/L/d at shelf station 43 to 1.35 μg S/L/d in the aerobic zone of slope and deep-water stations, slightly increasing in the redox zone of station 48 (109–175 m), where sulfate reduction rates exhibited variations, increasing to 3.25 and 3.12 μg S/L/d, respectively, at the upper and lower boundaries of the redox zone (Fig. 7).

In the redox zone at stations 6 and 20, the rate of sulfate reduction rates varied slightly, increasing (up to 1.55 μg S/L/d) in the 105 m layer, i.e. at the upper boundary of the redox zone (Fig. 7). Below this depth, the water-column sulfate reduction rates remained constantly low at all stations.

It should be noted that the sulfate reduction rates at the boundary of the redox zone reached 25.6 μg S/L/d (0.8 μM/L/d, Fig. 8) in June 2005. In March 2009, high rates were not observed, which appear to indirectly indicate a lower rate of photosynthetic primary production.

$\underline{CO_2 \text{ assimilation.}}$ In the offshore area (station 43), the integrated rate of microbial processes, expressed in terms of CO_2 assimilation rates calculated from experimental measurements of ^{14}C-labeled carbon dioxide, increased insignificantly from the surface layer of the water column to the bottom (from 2.50 to 3.02 μg C/L/d (Fig. 7).

On the continental slope (station 46) in the aerobic zone, the highest rate of CO_2 assimilation (2.08–2.65 μg C/L/d) occurred in the upper 5 m layer. Toward the redox zone, the rate of CO_2 assimilation decreased, increasing sharply (to 5.33 μg C/L/d) in the 200 m layer, i.e., in the redox zone, and then decreased again (Fig. 7).

In the pelagic zone (stations 6, 20, 48, and 50), from the aerobic layer to a depth of 109 m, the CO_2 assimilation rate varied from 2.32 to 4.63 μg C/L/d (station 48, Fig. 7), averaging 3.37 μg C/L/d throughout eight layers. The rate was highest in the aerobic zone as compared to other pelagic stations, where it varied at station 6 from 1.41 to 1.93 μg C/L/d (average 1.57 μg C/L/d) at the boundary with the anaerobic zone in the 150 m layer, and from 0.77 to 3.99 μg C/L/d (average 2.03 μg C/L/d) at station 20.

In the redox zone, the CO_2 assimilation rate increased sharply: up to 6.88 μg C/L/d at stations 48 and 20 and to 4.77 μg C/L/d at station 6 (Fig. 7). Below the redox zone, the CO_2 assimilation rate decreased to 1.51 μg C/L/d at stations 48 and 20 down to the 300 m layer. Below this depth they decreased again by an order of magnitude and varied only slightly throughout the water column.

In the redox zone, the peak of CO_2 assimilation rates (1.21–4.13 μg C/L/d) was found to be driven by anaerobic processes and the input of "fresh" biomass of autotrophic microorganisms. The higher rates of CO_2 assimilation in the redox zone may coincide with the maximum rate of sulfate reduction (station 48): sulfate-reducing and other anaerobic heterotrophs growing in this zone begin to decompose the autotrophic biomass.

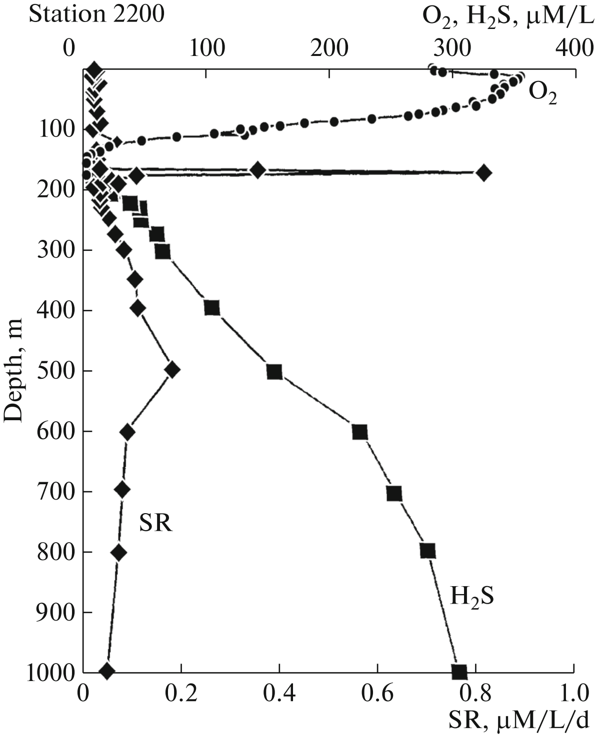

Fig. 8. Profiles of oxygen concentrations (O_2), hydrogen sulfide concentrations (H_2S), and sulfate reduction rates (SR) in water column on continental slope (station 2200) in June 2005.

The additional production of OM as a result of the activity of autotrophic microorganisms is confirmed by the appearance of maxima of $P{-}PO_4$ and NH_4 peaks (Figs. 2 and 3).

DISCUSSION

Earlier studies show that the rates of biogeochemical processes primarily depend on primary production rates, which vary significantly with season (Fig. 9). In the Black Sea, the main peak of the plankton bloom occurs in the spring and lasts until early summer. The autumn bloom tends to be less intense than spring blooms (Fig. 9).

The 2009 expedition found no evidence of an increased rate of photosynthetic primary production in March using hydrophysical and biological methods.

The integrated hydrochemical and biogeochemical study confirmed the absence of peak plankton bloom activity and revealed the predominance of phytoplankton-derived organic matter over terrigenous matter at deep-water stations in the photic layer, based on the isotopic composition of POC ($\delta^{13}C{-}C_{org}$ between –20.0 and –22.0‰ (Fig. 5).

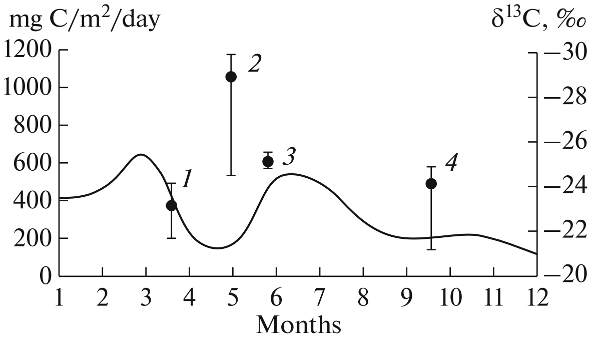

Fig. 9. Seasonal variations in rate of primary production (P, mg C/m^2/d) in western deep-water part of the Black Sea [17] and variations in isotopic composition of POC from photosynthetic zone. (*1*) March–April 1969 [18]; (*2*) early May 1998 [3]; (*3*) late May 1988 [19]; (*4*) late September–early October 1992 [6].

At the shelf station, the POC composition was dominated by terrigenous organic carbon with $\delta^{13}C-C_{org}$ between −25.0 and −28.0‰. Consequently, a massive algal bloom was not reported on the shelf, despite the presence of terrigenous runoff from land.

In March 2009, the rates of microbial processes in the aerobic layer were much lower in the eastern sector of the sea than those in the western sector [9, 20, 22]. An analysis of SPM concentrations and their comparison with the data obtained during cruises 81, 99, and 123 of the R/V *Akvanavt* (June 2005–2007, Fig. 4) can be used to study the water column structure in March 2009.

At all stations, SPM concentrations in the photic layer varied in June from 0.46 to 0.69 mg/L at depths of 25–200 m and from 0.26 to 0.60 mg/L in March 2009 at offshore station 43 (100 m depth), peaking within the upper 0–5 m (Fig. 4). On the continental slope (station 46) and deep-water areas (station 6, 20, and 48), SPM concentrations were lower in the photic layer (0.28–0.40 mg/L) than on the shelf. They were also much lower than the water-column SPM concentrations in the eastern halistatic area in May 1998 after a normally cold winter (0.56–2.45 mg/L) [3, 12]. The above data may indicate much lower SPM concentrations observed in the eastern sector of the sea in March 2009 as compared to other years and sea areas.

In March 2009, the first appearance of hydrogen sulfide in the 109 m layer (station 48) caused a marked increase in the rate of all microbial anaerobic processes with increasing $N-NH_4$ and $P-PO_4$ and decreasing $N-NO_3$. The first appearance of hydrogen sulfide was also recorded at station 20 in the 110 m layer. Concentrations of $N-NH_4$ and $P-PO_4$ tend to increase while $N-NO_3$ concentrations and CO_2-assimilation rates tend to decrease below this depth.

At station 6, the presence of oxygen was noted even at 155 m, and hydrogen sulfide was found to appear at a depth of 150 m. The content of nutrients and CO_2 assimilation rates increase from the 154 m layer.

A detailed analysis of the content of nutrients and rates of biogeochemical processes in the redox zone, using the data from the March 2009 and 2005 summer expeditions, allowed us to conclude that the increased rates of anaerobic microbial processes at deep-water stations were driven by the appearance of hydrogen sulfide, an increase in NH_4 and PO_4, and a decrease in NO_3.

The first isotopic data on the composition of C_{org} in the Black Sea were collected in March–April 1969 during a major phytoplankton bloom [18]. These data show that the composition of SPM in the photic layer (and at two stations in the eastern sector of the sea) was dominated by phytoplanktonic organic matter with $\delta^{13}C-C_{org}$ between −22.0 and −24.0‰ (average −23.0‰).

In late May 1989, the C_{org} content was measured in the entire water column (21 samples) at one station in the western halistatic area [19]. The spread in $\delta^{13}C-C_{org}$ values was approximately 1‰, with an average value of −25.0‰. It is clear that the plankton bloom had already ended by the end of May 1989, while the supply of terrigenous material was still ongoing.

In late September and early October 1992, the $\delta^{13}C-C_{org}$ values of particulate matter varied from −21.0 to −25.0‰, with an average value of −24.0‰ for 34 samples [6].

Finally, our data obtained in early May 1998, mainly in the deep-water zone of the western sector of the sea (56 samples), show a marked ^{13}C depletion of C_{org} ($\delta^{13}C$ between −24.2 and −30.2‰) [3].

The above data indicate a strong seasonal variation in the C_{org} isotopic composition, i.e., its dependence on the rate of photosynthetic primary production (Fig. 9). A strong ^{13}C enrichment of C_{org} ($\delta^{13}C$ between −21.0 and −23.0‰) occurs during the peak blooms of microalgae (coccoliths and diatoms). The distribution of C_{org} and its isotopic composition show that planktonic and terrigenous C_{org} with $\delta^{13}C-C_{org}$ of −26.0‰ is present in POC from the photic layer at the shelf station and planktonic organic matter with $\delta^{13}C-C_{org}$ between −20.71 and −22.55‰ is detected in the surface layer at deep-water stations.

Therefore, the absence of the massive plankton bloom in May 2009 was caused by low concentrations of nutrients and terrigenous supply from land did not reach any of the deep-water stations.

Analysis of the distribution of water-column methane concentrations on the shelf, continental slope, and in the pelagic zone in March 2009 shows that methane in the aerobic zone is generated by microbial methanogenesis in the anaerobic share of SPM. This methane is emitted to the atmosphere from shallow-water areas with depths less than 100 m [20, 23].

In the anaerobic zone of the water column, below the redox zone, the methane concentration increased irregularly to a depth of 600 m and remained constantly high below this depth. The increase in methane concentrations is associated with the acceleration of methane production and supply of methane from the bottom by diffuse leakage and/or seepage [7, 8].

Active aerobic and anaerobic processes of microbial methane oxidation were recognized in the water column. The slow rate of methane production relative to methane oxidation is indicative of additional input of methane from the outside. The presence of hydrogen sulfide in the water column at deep-water stations was identified at 109 m (station 48), 120 m (station 20), and 150 m (station 6). The appearance of hydrogen sulfide caused a sharp increase in C_{org} content, methane concentrations, and rates of methane production, CO_2 assimilation, and sulfate reduction, as was noted earlier in other areas of the sea [16, 22].

In the aerobic zone, the rate of methane production was highest in the surface layer of the water column with a high C_{org} content. In the anaerobic zone, the highest rates of methane production are confined to the upper boundary of the redox zone, where the largest amount of dead phytoplanktonic organic matter precipitates out of the photic layer.

CONCLUSIONS

The integrated studies on hydrochemistry and water-column rates of microbial processes in the eastern sector of the Black Sea along a standard 100-miles transect off Gelendzhik from the shore to the central part of the sea at water depths of 100–2170 m show that a series of warm winters and the absence of intense convective winter mixing resulted in a relatively low content of SPM, POC, and nutrients in the water column in March 2009.

The relatively high SPM concentrations and the presence of isotopically light POC at the offshore station are indicative of the supply of terrigenous material from land and low contributions of phytoplanktonic organic matter to the composition of SPM. This can explain the low rates of biogeochemical processes in the water column near the coast.

The surface layer at deep-water stations is dominated by isotopically heavy phytoplanktonic organic matter. This suggests that the supply of terrigenous material from land was insufficient in the offshore deep-water areas.

Therefore, warm winters and insufficient nutrient supply do not prevent photosynthesis in the photic layer of the deep-water zone, which generates organic substrates for heterotrophic aquatic communities.

The concentration of nutrients and the rate of microbial processes in the redox zone and below differ slightly from those measured in June 2005 in the same region.

The results of POC isotopic analysis, the measurements of the rates biogeochemical processes, and the hydrochemical characteristics of the water column, can be used to determine the nature and seasonal variability of the POC composition.

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