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## Methane Content in the Bottom Sediments and Water Column of the Black Sea

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**Abstract**—The methane content in the bottom sediments and water column of the Black Sea was determined using various methods of desorption and analysis of gases and various methods of calculating their concentrations. The head-space method with the use of salting out and calculation by an internal standard proved to be the most accurate procedure for the analysis of methane concentration in bottom sediments. The methane content in bottom sediments increased downward along the sediment thickness. In the upper 50–70 cm of shelf sediments, two minimums of methane concentration were revealed; in deep-sea sediments, only one minimum was recorded (in the 20–50 cm horizons). In the water column, methane concentrations slowly grew from the surface to a depth of 150–200 m and abruptly increased to a depth of 700–1200 m, remaining virtually constant in underlying layers. In certain deep-sea regions, peaks of methane content in the 1000–1200 m horizons of the water column were revealed, which were most probably due to local influx of abyssal waters enriched with this gas.

*Key words:* methane, concentration profiles, water, bottom sediments, desorption of gases.

Although methane is de novo formed by methanogenic archaea in spatially limited and unique anaerobic ecological niches, the potential contribution of this greenhouse gas to the hydrosphere and atmosphere of the Earth may be considerable. However, uncertainty still exists as to the contribution of methane fluxes to the global carbon cycle, and this leaves room for numerous hypotheses and suggestions. Therefore, the Black Sea, which is a powerful anaerobic ecosystem constantly producing methane, has recently been attracting keen interest from microbiologists, biogeochemists, and climatologists. Experimentally substantiated estimates of methane fluxes in terrestrial and marine ecosystems remain scarce [1–4], whereas mathematical modeling of climatic changes and forecasts of the effect of greenhouse gases on climate require a large amount of data obtained by monitoring.

In the case of the use of the radioisotopic method for determining the rate of any biogeochemical process, the calculation formulas necessarily include the value of the concentration of the compound metabolized; therefore, the accuracy of measurement of the latter value is one of the bottlenecks of the calculation. Nevertheless, the available literature still lacks a profound analysis of the efficiency of methods of retrieval and determination of methane present in water, bottom sediments, and soils.

The recent discovery in the Sea of Okhotsk, the Black Sea [5, 6], and other seas of the so-called *cold methane seeps*, which are seafloor sources of light hydrocarbons and methane, occupy very large areas, and are characterized by high biological productivity, considerably increased the interest in the Black Sea ecosystem as a potential powerful source of atmospheric methane. Formerly (in 1980, 1984, and 1990), we undertook one submarine and two surface expeditions in the Black Sea, which were aimed at investigation of the biogeochemical processes of the methane cycle. However, the results of those expeditions were not published in sufficient detail (although a few papers are available [1, 7]); therefore, we consider it necessary to publish a greater amount of the data obtained. The data are quite voluminous and fail to fit into a single paper; therefore, they will be presented in this paper, the accompanying paper “Rates of Microbial Production and Oxidation of Methane in the Bottom Sediments and Water Column of the Black Sea,” and a forthcoming paper “On the Microbial Anaerobic Oxidation of Methane.”

The aim of the present paper is to present the results of numerous determinations of the methane content in the Black Sea made in 1980–1990 and to compare various methods of retrieval and determination of methane present in seawater and bottom sediments.

**Table 1.** Geographical coordinates of the stations investigated

Station	Sea depth, m	Lat. N	Long. E
I. Calamite polygon			
795-1	147	44°45'5	32°37'0
795-4	150	44°45'5	32°50'8
791	772	44°37'8	32°31'8
II. Danubian polygon			
843	52	44°39'5	29°48'0
848	118	44°02'5	30°18'0
601*	1050	44°02'1	29°28'2
852	1450	43°32'3	30°56'4
842	1458	43°25'6	30°41'7
III. Bulgarian polygon			
555*	22		
559*	26		
598*	55		
870	57	42°47'4	28°08'1
862	61	43°04'1	28°25'1
568*	86	41°40'3	29°25'0
580*	330		
620*	520		
546*	1240	42°29'4	28°38'5
804 (water)	1485	42°26'2	28°51'5
616*	1620		
805-1	1605	42°27'1	28°52'1
545*	1620	42°26'3	28°44'5
IV. Anatolian polygon			
812 (water)	2160	42°54'3	34°48'5
834 (water)	2172	42°52'9	34°25'7
807 (water)	2064	42°14'8	35°18'0
823	105	41°50'8	35°29'5
821	442	41°54'1	35°46'4
817	1420	42°00'4	35°36'5
814 (water)	2180	42°50'9	34°45'9
814	2180	42°14'8	35°18'1
V. Eastern gyristase			
838 (water)	2114	42°56'3	34°45'3
839	2154	43°30'6	36°31'1
839	2160	43°30'6	36°20'5
VI. Western gyristase			
840 (water)	2110	42°54'8	31°40'3
806-2 (water)	2108	42°50'2	31°39'0

\* Stations of the voyage of R/V *Professor Shtokman* (1980–1981).

## MATERIALS AND METHODS

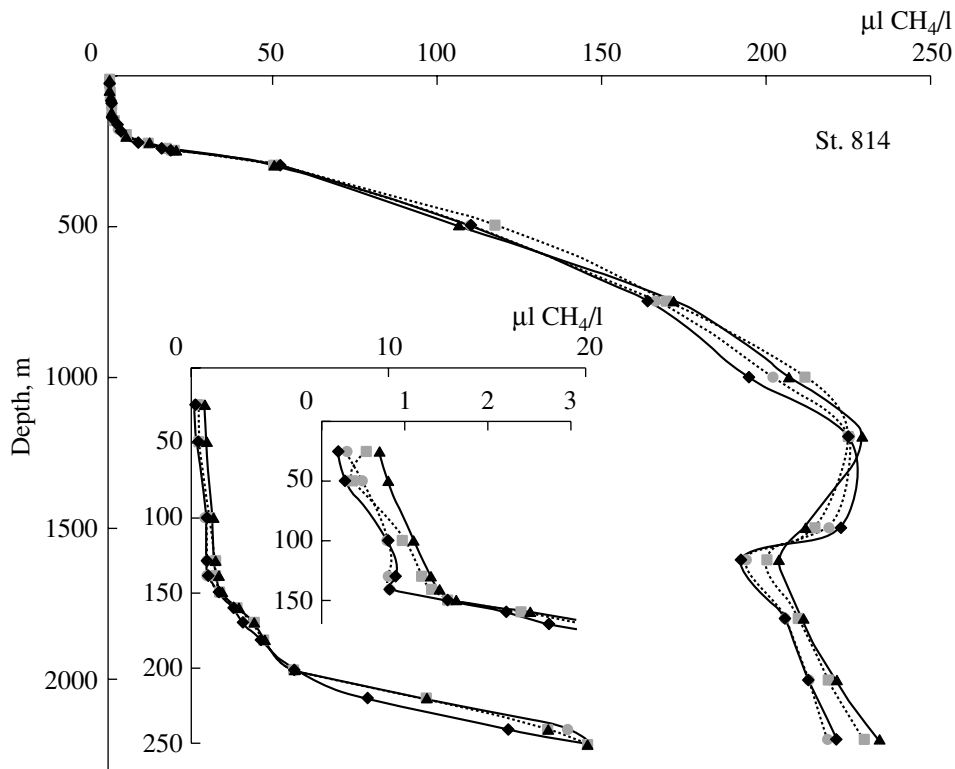
Materials for investigation were collected during the fifth voyage of the R/V *Professor Shtokman* in December 1980 at the Bulgarian and northwestern shelves of the Black Sea; during the eighth voyage of the R/V *Vityaz'* in October–December 1984 at polygons located in various regions of the Black Sea (Table 1): (I) Calamite, (II) Danubian, (III) Bulgarian, (IV) Anatolian, (V) eastern gyristase, and (VI) western gyristase; and during an expedition on board the *Bentos* submersible laboratory in December 1990 near two submarine stations at the northwestern shelf near the Calamite polygon.

Experiments were conducted onboard ship and in laboratories at the Institute of Biochemistry and Physiology of Microorganisms, Russian Academy of Sciences, and the Institute of Microbiology, Russian Academy of Sciences. Samples of bottom sediments were taken with an Okean dredger and straight-flow geological tubes with an inner diameter of 12 and 18 cm; water samples were taken with General Oceanics bathometers (United States) and through the Kingston valves of the Receptor system of the *Bentos* submersible.

Retrieval and determination of methane were conducted by several methods.

**Method A** (the head-space method with salting out) was developed by us in 1979–1980 and was used in all of the expeditions that followed [8]. Immediately after sampling a sediment core or block, 10 cm<sup>3</sup> of the sample was transferred, using a syringe without a needle holder, to Hungate tubes (17 cm<sup>3</sup>, Bellco Glass, United States) containing 3 g of NaCl and 1 g of KOH (and/or 1 mg merthiolate, C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>SNaHg, Loba Chemie, Germany); then, distilled water was added to a sign marking a 3-cm<sup>3</sup> volume of the tube's head space, and the tubes were hermetically closed with gas-tight stoppers made of butyl rubber with natural caoutchouc and screwed with plastic caps. Water samples were introduced into Balch tubes (27 cm<sup>3</sup>, Bellco Glass) containing 5 g of NaCl and 1 g of KOH (and/or 1 mg merthiolate); the sample volume was such as to reach a sign marking a 2-cm<sup>3</sup> volume of the tube's head space. The tubes were hermetically closed with stoppers made of the above-mentioned gas-tight rubber.

On the day of sampling, the tubes with samples were kept in a boiling water bath for 2 h for gas desorption and cooled to room temperature, and the content of methane in the gas phase was determined. The analysis was performed on a Carlo Erba Strumentazione chromatograph (Italy) equipped with a flame-ionization detector. Helium was used as the carrier gas; the detector and injector temperature was 225°C; the column length and inner diameter were 3 m and 2 mm, respectively; Latek activated aluminum (60–80 mesh, Germany) was used as the sorbent. The CH<sub>4</sub> concentration was calculated proceeding from the results of chromatographic analyses and the ratio of the volumes of



**Fig. 1.** Profiles of methane concentration in the water column at station 814, plotted based on the concentration values obtained by the A (●), B (■), C (▲), and E (◆) methods of gas desorption, analysis, and calculation. The insets show with greater resolution methane profiles in the upper water layers.

the sample (sediment or water) and of the gas phase in the tube according to the formula

$$C = \frac{V_{inj} S_p V_{hsp}}{V_s S_{st}}$$

where  $C$  is the sought in situ concentration of methane in the sample ( $\mu\text{l}/\text{dm}^3$  water or wet sediment);  $V_{inj}$  is the volume of the gas sample introduced into the injector of the chromatograph from the gas phase of the tube ( $\mu\text{l}$ ; usually 100  $\mu\text{l}$ );  $V_{hsp}$  is the volume of the gas phase in the tube (head space, ml);  $V_s$  is the volume of the sample introduced into a Balch tube (water, 27  $\text{cm}^3$ ) or a Hungate tube (sediment, 7  $\text{cm}^3$ );  $S_p$  is the area of the peak of methane present in the 100- $\mu\text{l}$  analyzed sample in relative units of the integrator; and  $S_{st}$  is the area of the peak of methane present in 100  $\mu\text{l}$  of a standard methane mixture.

**Method B.** As distinct from the previous method, sample analysis was performed at the laboratory 3 months after the return from an expedition. Tubes with samples were heated on a water bath for 1 h. The gas phase was analyzed on a M-3700 chromatograph (Varian-licensed, AO Khromatograf, Russia) equipped with a flame-ionization detector. The carrier gas was helium; the injector and detector temperature was 100°C; the column length and inner diameter were 3 m and 3 mm, respectively; the column temperature was

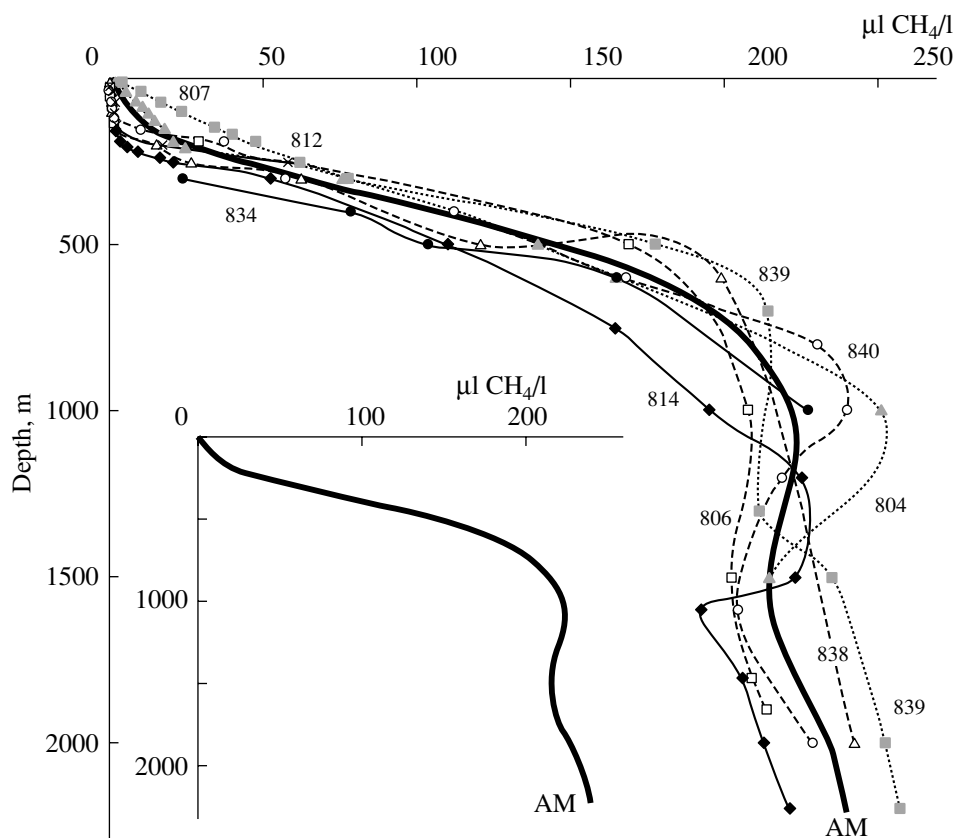
40°C; Porapak Q 80/100 mesh (Serva) was used as the sorbent. The calculations of methane concentration were performed as in method A.

**Method C** is analogous to method B, but the calculation of  $\text{CH}_4$  concentration is performed by the internal standard method using high-purity methane (99.99%). Methane (50  $\mu\text{l}$ ) was introduced into the head space of the tube with a sediment/water sample in which analysis of native methane had already been performed; the total of native and introduced methane was determined chromatographically. The calculations were performed according to the formula

$$C = \frac{KC_1}{C_2 - C_1},$$

where  $C$  is the sought native methane concentration ( $\mu\text{l}/\text{dm}^3$  water or wet sediment);  $C_1$  is the concentration of native methane (vol %) in the head space of the tube before the introduction of standard methane;  $C_2$  is the concentration of the total of native and introduced methane (vol %) in the head space after the introduction of standard methane; and  $K$  is the calculation coefficient, equal to 7143 for bottom sediment samples (7  $\text{cm}^3$ ) in Hungate tubes and to 3572 for water samples (27  $\text{cm}^3$ ) in Balch tubes [8].

**Method D**, or the vacuum degassing method. These analyses were performed by A. Bol'shakov and



**Fig. 2.** Profiles of methane concentration in the water column of various Black Sea regions. Numerals in the figure are station numbers. The inset shows averaged profile of  $\text{CH}_4$  concentrations. AM, arithmetical mean.

A. Egorov on the day of sampling. Sediment ( $0.5 \text{ dm}^3$ ) was placed in a special device for degassing and trapping the gas components of the sample, followed by analysis on a chromatograph with a flame-ionization detector.

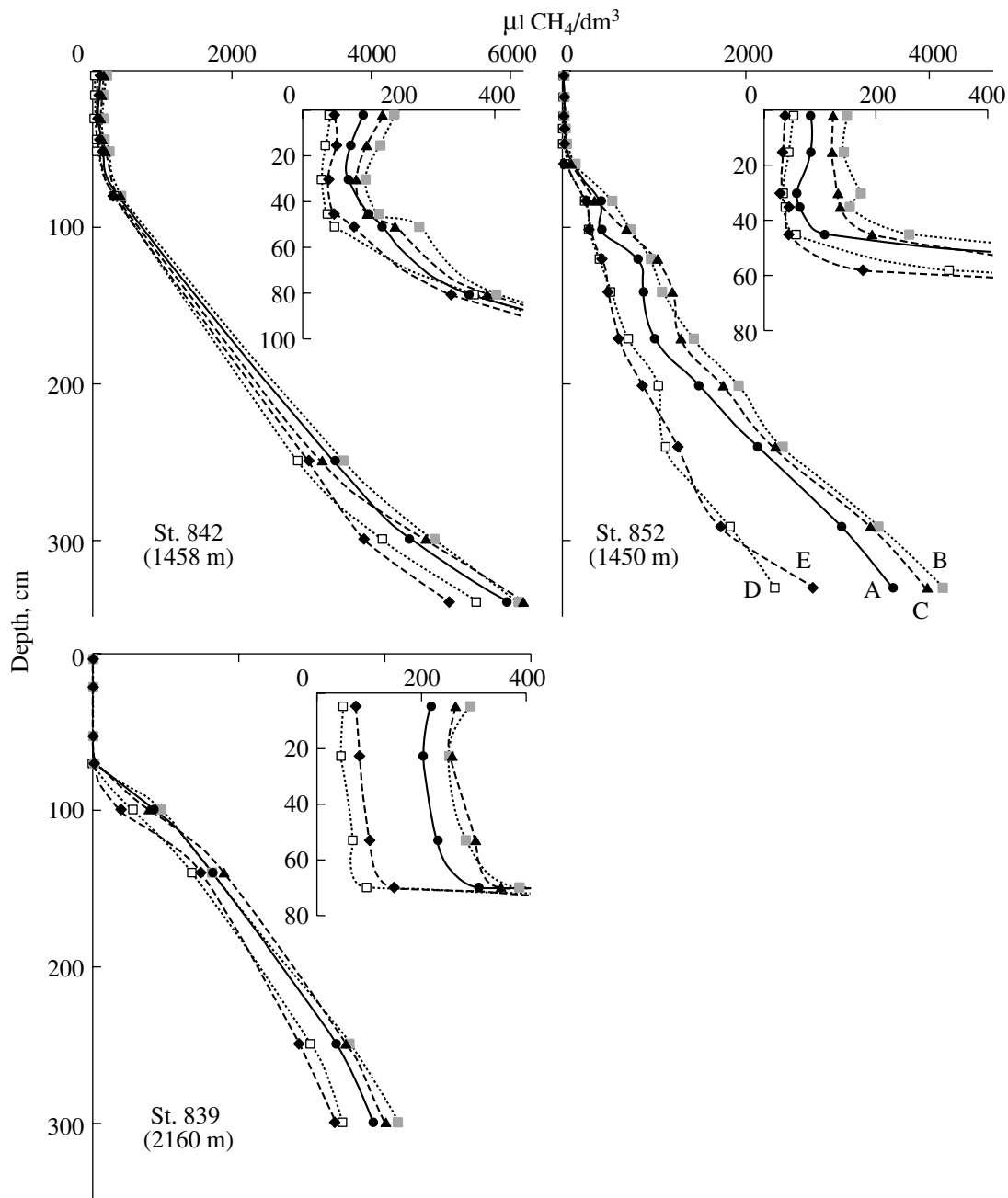
**Method E**, or phase-equilibrium degassing [9], is actually identical to the earlier described head-space method [10]. Method E is analogous to method A, but differs from it by omission of salting out (desorbing) compounds (NaCl) and bactericidal compounds (NaOH and/or merthiolate). The analysis of the gas phase was performed on the day of sampling on a Carlo Erba Strumentazione chromatograph (see method A) after 1 h of heating in a boiling water bath. The calculations of methane concentrations were performed analogously to method A.

## RESULTS AND DISCUSSION

So far, for methane retrieval from samples of water and bottom sediments, researchers have used vacuum degassing [9] or the head-space method [10–15]. To increase the fullness of methane retrieval, high-velocity shaking (from 10 min to 10–12 h) [11–13], sample sparging with helium or nitrogen [10], and boiling [12] have been used. Whelan [16] and Reeburgh [17]

employed degassing of interstitial water squeezed from bottom sediments with a press. In all of these works, the authors actually determined only the methane contained in interstitial water and not total methane, which includes dissolved methane and methane sorbed in the mineral and aqueous components of sediments [10, 11, 16]. To suppress biological methane production/oxidation, which interferes with the determination, samples were often supplemented with mercuric chloride [13], sodium azide [11], or NaOH [14, 15].

For mass-scale gas analyses in samples of seawater and bottom sediments, Bol'shakov and Egorov suggested, instead of the vacuum degassing earlier used by them, the phase-equilibrium method [9]. Undoubtedly, this method can be successfully used for the determination of gases in water samples. However, the equilibrium between gases in the aqueous and gaseous (head space) phases is adequately described by Henry's law only in the case of fresh water. Salinity of natural waters imposes significant restrictions on the applicability of Henry's formula in the calculations. It is evident that, without taking into account the ionic strength of an aqueous solution, it is impossible to accurately calculate the actual content of a gas proceeding from



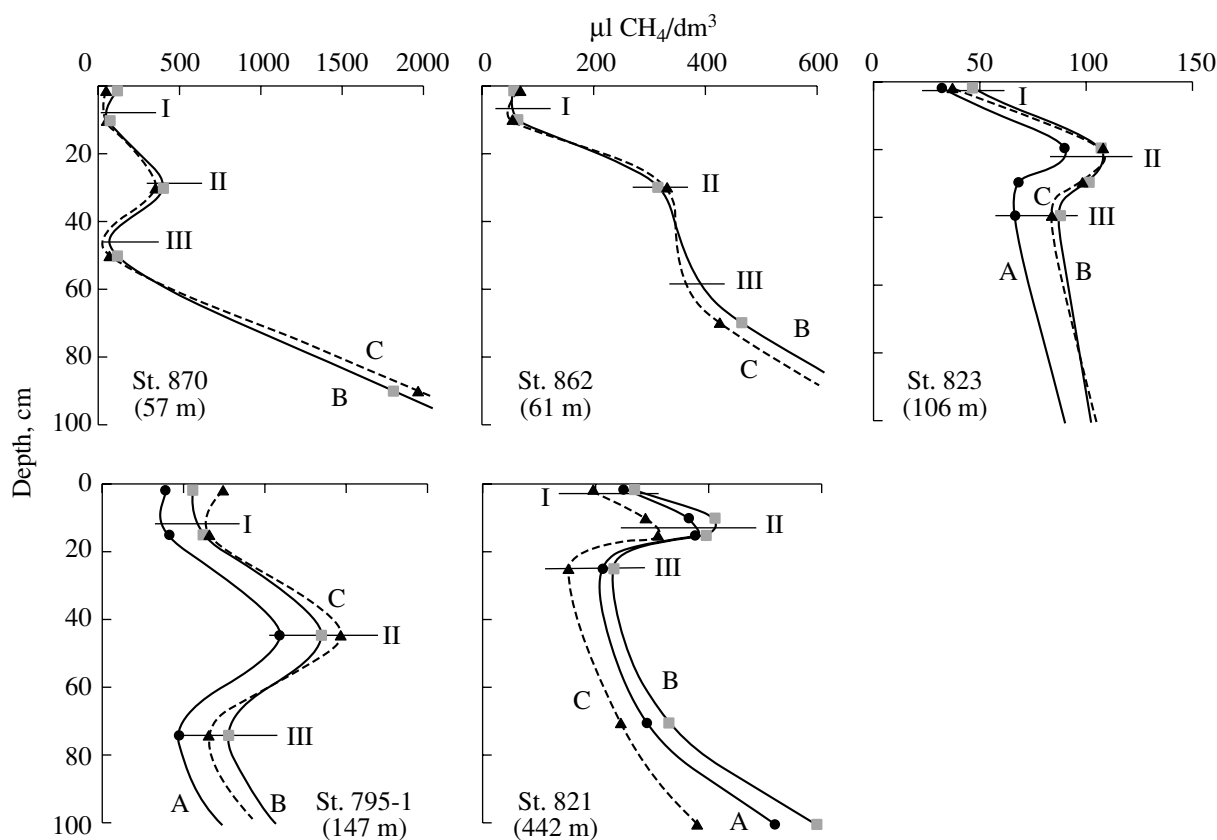
**Fig. 3.** Profiles of methane concentration in abyssal bottom sediments, plotted based on the concentration values obtained by the A (●), B (■), C (▲), D (□), and E (◆) methods.

the gas content determined in the gas space after the establishment of the equilibrium.

In the case of determination of methane content in bottom sediments, another factor that should not be neglected is gas adsorption by the mineral component. Unfortunately, Bol'shakov and Egorov did not present in their paper [9] the experimental data obtained; thus, it does not seem possible to verify the competence of their calculations, which did not take into account gas

sorption in molecular pores of sediment particles. Many finely divided minerals and sedimentary rocks, e.g., clays, are known to possess a considerable sorbing capacity. By the example of tundra soils, we showed [4] that the content of methane in the soil atmosphere is tenfold inferior to the content of methane adsorbed by soil particles.

It is evident that the methane adsorbed on the surfaces of pycnometric pores and methane dissolved in



**Fig. 4.** Profiles of methane concentration in the upper meter of bottom sediments of the continental slope (st. 821) and shelf. Profiles were plotted based on the concentration values obtained by the A (●), B (■), and C (▲) methods. Horizontal lines show concentration extrema: I, 0–10 cm (5 cm for st. 821); II, 25–45 cm (15 cm for st. 821); III, 40–75 cm (25 cm for st. 821).

interstitial water can be quite easily retrieved by vacuum degassing. The smaller the pores, the stronger the attraction of gas molecules to the surface of the sorbing agent (adsorption). Therefore, if methane is concentrated in molecular pores of the sorbent, the sorption of gas molecules is strongest and their retrieval is most difficult. The presence in bottom sediments of other gases complicates the pattern of methane sorption/desorption, primarily due to differences in the extent of sorption of the gases. For example, in activated carbon, CH<sub>4</sub> sorption is twofold superior to the sorption of oxygen or nitrogen, but threefold inferior to the sorption of CO<sub>2</sub>, not to mention hydrogen sulfide, whose adsorbability is six times greater. Most complete retrieval of gas from bottom sediments can be achieved by decreasing the solubility of gases in the liquid phase of the sorbing carrier by increasing the ionic strength of the aquatic solution. This approach makes it possible to concentrate in the small volume of the gaseous head space almost all gas, both dissolved in interstitial water and sorbed in the molecular pores of the carrier.

During the expeditions in 1980–1984, we tested several methods of methane desorption from samples of water and bottom sediments. The analyses of methane content in water samples from the deep-sea station

814 performed by different methods of desorption and analysis yielded virtually the same results (Table 2; Fig. 1). On the whole, the methane concentrations in water measured at nine stations of four polygons characterized by different height of the water column were comparable (Table 2) and can be presented in a graphical form as an averaged concentration profile (Fig. 2). The methane concentrations slightly grew from the surface to a depth of 150–200 m, increased abruptly (20- to 100-fold) between the depths of 200 and 700–1200 m, and showed little change in the underlying layers. A phenomenon attracting attention is occurrence of peak values of CH<sub>4</sub> concentrations in the 1000–2000 m horizons at some of the deep-sea stations. In bottom sediments and the water column of such stations, an active methanogenesis process was found.

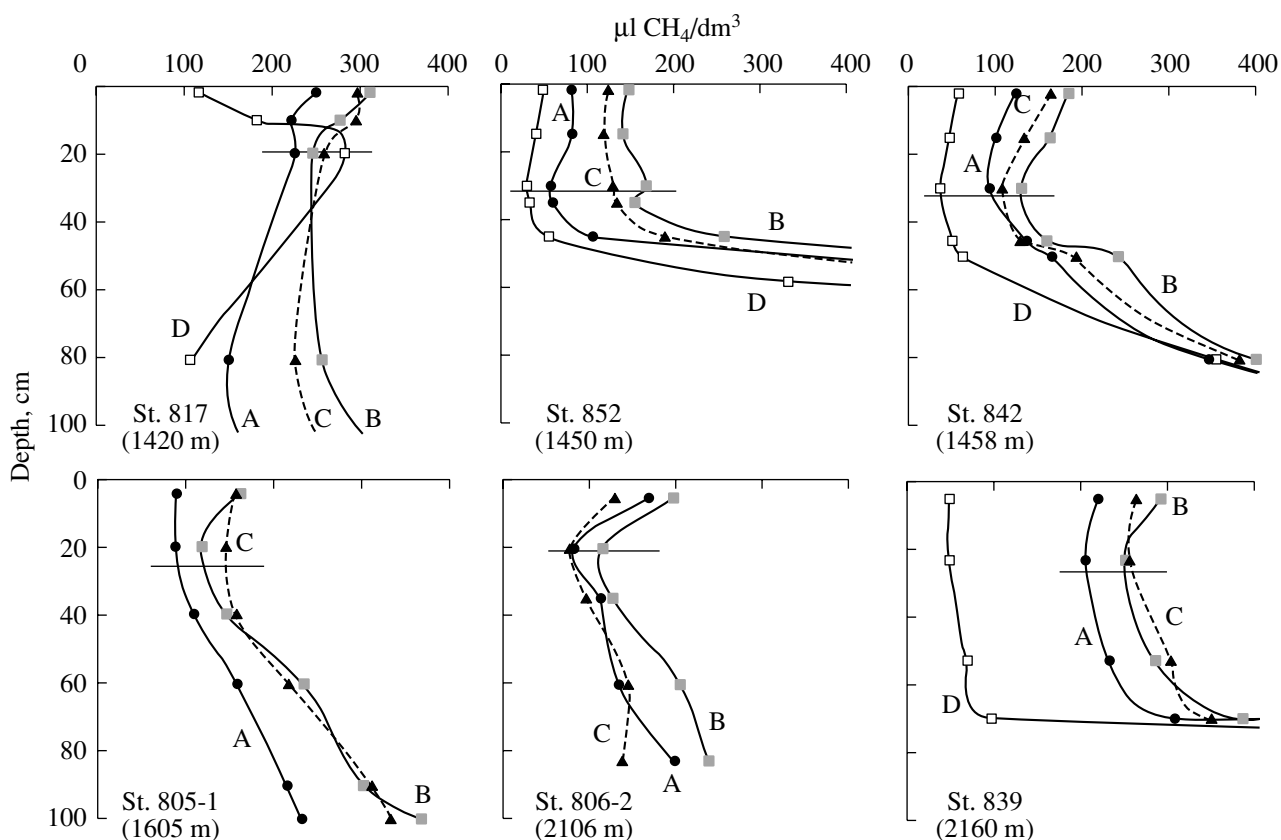
Nevertheless, the source of the increased methane content in the 1000–1200 m layer of the Black Sea water remains an open question. In the Black Sea, both of the methanogenesis processes—the heterotrophic (acetoclastic) and autotrophic ((CO<sub>2</sub> + H<sub>2</sub>)-utilizing) ones—depend, the first one directly and the second one indirectly, on the organic compounds arriving from the photic layer or brought from the continent by rivers. Neither of these sources of organic matter can be

**Table 2.** Methane content ( $\mu\text{l/l}$ ) in samples from the Black Sea water column

Sampling depth (m)	812 (1208)		834 (2052)		807 (2064)		806-2 (2108)		838 (2184)		804 (1485)			840 (2139)			839-1 (2154)			St. 814 (2180)		
	E*	E	E	E	E	E	E	E	E	A	C	E	A	C	E	A	C	E	A	B	C	E
25	0.5	0.7		0.7	1	5.3	5.6	5.5		7	5.5	4	7	5.5	4	7	5.5	4	0.3	0.5	0.7	0.2
50	0.5	0.4		0.4	1	8.2	7.8	8.6		10	11	10	10	11	10	10	11	10	0.5	0.4	0.8	0.3
75		0.8		0.8		9.9	10	9.6		15	17	16	15	17	16	15	17	16				
100	0.7	1.4		1.4	1.3	13	13	12		23	21	23	23	21	23	23	21	23	0.8	1	1.1	0.8
125						16	15	14														
130																			0.8	1.2	1.3	0.9
140																			0.8	1.3	1.4	0.8
150	2.4	1.3		1.3	0.6	18	19	18		37	34	35	37	34	35	37	34	35	1.5	1.5	1.6	1.5
160																			2.4	2.4	2.5	2.2
170																			3.1	3.2	3.3	2.7
175						21	22	21		41	40	39	41	40	39	41	40	39	3.6	3.7	3.7	3.6
180																			5.2	5.3	5.2	5.2
200	17	16		16	15	26	29	24		47	49	47	47	49	47	47	49	47	12	12	12	9
220																			19	18	19	16
240																			21	21	20	21
250	58	57		57	26	62	67	76		65	60	57	65	60	57	65	60	57	50	50	51	52
300																			113	105	112	9
400																			173	181	168	16
500																			210	220	214	110
600																			167	170	172	164
700																			202	212	207	195
750																			225	225	229	225
800																			218	221	212	223
1000																			242	238	235	223
1200																			243	231	240	193
1300																			230	225	219	206
1500																			213	221	211	206
1600																			232	235	229	213
1800																			248	242	242	213
1900																			261	250	234	222
2000																			219	219	230	213
2200																			219	230	234	222

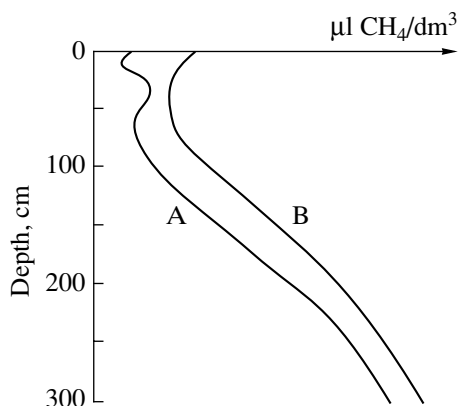
Note: The numerals in the upper row are sampling station numbers; in parentheses, station depth is indicated. The letters A, B, C, D, and E in the second row designate the methods of methane desorption and determination (see Materials and Methods).

\* Data obtained by method E (E columns) were kindly provided by Hans Richnov (University of Hamburg).



**Fig. 5.** Profiles of methane concentration in the upper meter of abyssal bottom sediments, plotted based on the concentration values obtained by the A (●), B (■), C (▲), and D (□) methods. Horizontal lines show concentration minima (at 15–30 cm).

responsible for the local increase in the methane concentrations that we revealed in the depth interval of 1000–1200 m. Moreover, despite the significantly different inflows of organic compounds at deep-sea stations and stations less remote from the coast, the methane concentration profiles there turned out to be quite similar.



**Fig. 6.** Averaged profiles of methane concentration in bottom sediments of the (A) shelf and (B) abyssal zone.

It can be supposed that abyssal methane, intensely formed in bottom sediments or geologically buried (we discovered methane gas hydrates during the expeditions in 1980 and 1984) is released as bubbles, which, most probably after partial dissolution, are trapped in the 1200–1000 m water layers due to anomalies of water density. Other possibilities that cannot be excluded are local (lenticular) transfers of abyssal waters, which contain much more methane, and arrival of  $\text{CH}_4$  with powerful gas flows from the vast fields of methane seeps, discovered in the late 1980s [6, 7].

As shown above, different methods of desorption proved to be equally efficient for studies of water samples; however, for the analysis of sediment samples, the conclusion has to be different. By the example of six sediment cores lifted from the deep part of the sea (1450–2160 m), we tested all four methods of methane desorption and analysis. The methane concentration profiles obtained as a result were sometimes significantly different for different methods of gas retrieval and determination (Table 3; Fig. 3). Notably lower values of methane concentrations were obtained by methods D (vacuum degassing) and E (phase-equilibrium degassing); higher values were yielded when the salting-out procedure was employed (A, B, and C). When internal standard was used (method C), the values



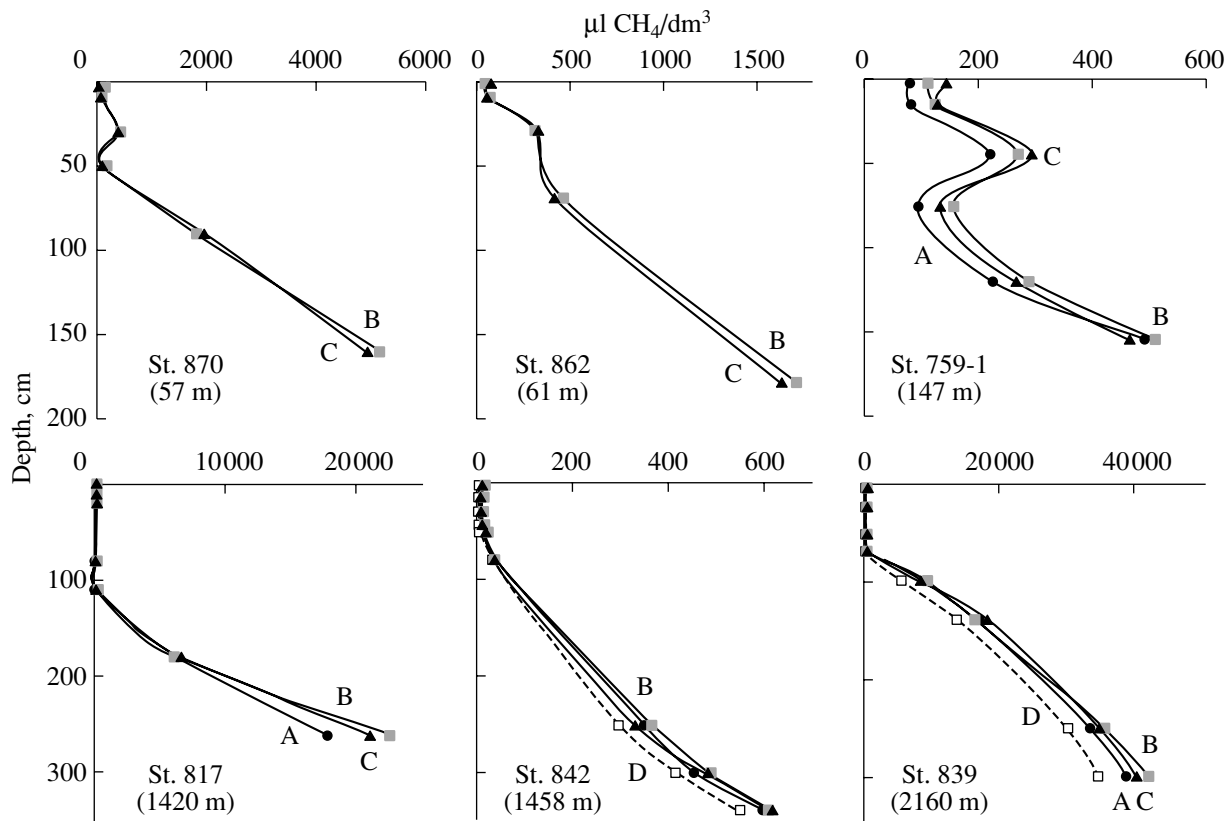


Fig. 7. Profiles of methane concentration in the upper 2–3 meters of bottom sediments of the shelf and abyssal zone. The profiles were plotted based on the concentration values obtained by the A (●), B (■), C (▲), and D (□) methods.

determined were somewhat lower than those obtained with methods A and B. Although method C is more laborious, we consider it to be the most accurate.

The methane content in bottom sediments increased with the depth of sampling. In upper horizons (to 40–60 cm), however, a certain decrease in the methane concentration occurred downward along the sediment thickness (Table 2). The patterns of this decline were, however, different in shelf and deep-sea sediments. In shelf sediments, two concentration minima were observed: 0–10 and 40–70 cm from the sediment surface (Figs. 4, 6); in deep-sea sediments, there was only one minimum, at a sampling depth of 20–50 cm (Figs. 5, 6). The methane concentration profile in the upper sediment horizons of the continental slope was of an intermediate type (Fig. 4; st. 821, 442 m). Analogous declines in methane concentration were reported by other researchers for marine shelf sediments [15], as well as for marine marshes, where the minima, recorded in the 10–12 and 70–75 cm horizons, were, however, less pronounced [16]. Since the experimentally recorded concentration profiles differ from those predictable in terms of diffusion laws, it does not seem impossible that the cause of the above-described minima is anaerobic methane oxidation.

On the whole, the content of  $\text{CH}_4$  in shelf and abyssal bottom sediments considerably increased (often by

one to two orders of magnitude), beginning with the 40–70 cm horizons, to the 100–300 cm horizons (Fig. 7). Earlier, similar profiles of methane concentrations were found in other marine sediments [18–20]. However, the methane concentration profiles recorded in Atlantic bottom sediments along the Texas coast [11] differed from the profiles characteristic for the Black Sea sediments, where the content of methane increased with depth: near the Texas coast, the content of methane was maximum in the 20–50 cm layer of sediments and decreased abruptly in the 50–70 cm layer. In this connection, it is necessary to stress that the ecological conditions in the Atlantic sediments differed significantly from those in the Black Sea sediments, where both the rate of modern bacterial methanogenesis and the methane content were several orders of magnitude higher than in the Atlantic sediments.

Thus, our data allow us to draw the following conclusions:

- (1) Any of the gas desorption methods that we tested can be successfully used for the analysis of methane content in seawater; the head-space method is preferable due to its simplicity.
- (2) During methane analysis in bottom sediments, the most accurate results were obtained by the use of

**Table 3.** Methane content in samples from the Black Sea bottom sediments

Station (polygon; depth)	Sampling horizon (cm)	CH <sub>4</sub> content, µl/dm <sup>3</sup>				
		A	B	C	D**	E
795-1 (I; 147 m)	0-5	77	112	149		
	10-20	82	127	132		
	40-50	219	271	294		
	70-80	93	156	132		
	115-125	223	285	265		
	150-157	493	512	466		
795-4* (I; 150 m)	0-2	120	484	170		
	2-6	108	475	332		
	6-11	103	574	439		
	11-25	59	879	339		
791* (I; 772 m)	0-4	64	94			
	6-10	125	97			
	11-13	100	214			
	17-21	108	354			
	23-26	194	250			
843* (II; 52 m)	0-2	48	98	72		
	3-5	106	195	125		
	20-25	70	171	87		
848* (II; 118 m)	0-5	7	44	30		
	20-25	8	24	16		
	41	5	22	14		
852 (II; 1450 m)	0-3*	232	377	218		
	18-22*	269	760	504		
	0-5	82	147	124	50	35
	12-20	82	140	120	41	32
	22-30	58	169	130	31	27
	32-38	62	153	133	35	43
	40-45	107	257	190	55	43
	55-58	861	1179	679	330	173
	80-82	4086	5503	3661	2420	2590
	100-105	4102	7300	6900	2750	2860
	118-120	8261	9800	10300	3960	4170
	140-142	8763	10900	12000	5225	5040
	168-170	10018	14200	12700	7150	6100
	195-200	14930	19100	17300	10450	8700
	235-240	21160	24000	23200	11220	12500
	290-295	30200	34400	33300	18150	17130
328-330	36000	41300	39500	23100	27200	
842 (II; 1458 m)	0-5	124	187	167	59	65
	12-15	100	161	134	48	70
	25-32	93	129	108	37	51
	40-50	134	158	129	51	65
	50-60	165	242	190	62	106
	80-85	345	400	383	354	307
	245-250	3477	3600	3280	2950	3080
	295-300	4540	4880	4800	4150	3890
	335-345	5960	6090	6170	5500	5100

**Table 3.** (Contd.)

Station (polygon; depth)	Sampling horizon (cm)	CH <sub>4</sub> content, µl/dm <sup>3</sup>				
		A	B	C	D**	E
870 (III; 57 m)	0-2		113	45		
	8-10		62	48		
	30		394	350		
	45-55		105	66		
	80-90		1800	1943		
	150-160		5120	4947		
862 (III; 61 m)	0-2*		123	98		
	12-14*		171	132		
	0-3		60	73		
	8-10		70	54		
	28-30		317	333		
	68-70		463	423		
805-4* (III; 1583 m)	178-180		1723	1633		
	0-3	200	251	172		
805-1 (III; 1605 m)	5-8	195	436	82		
	15-18	193	475	328		
823 (IV; 106 m)	0-13	91	160	157		
	15-25	90	117	147		
	35-45	108	148	157		
	54-64	159	233	216		
	86-92	214	304	311		
	92-105	230	365	332		
833 (IV; 108 m)	0-5	32	47	36.2	3	
	15-20	90	106	107	5	
	20-30	68	101	98		
	30-40	66	87	83		
	100-110	93	104	107		
821 (IV; 442 m)	0-2	52	91	74	5	
	3-6	30	61	53		
	7-10	52	70	45		
	12-15	65	110	109		
817 (IV; 1420 m)	20-25	49	84	49	4	
	0-4	250	266	195		
	8-12	366	411	284		
	14-18	374	394	312		
	20-30	211	231	154		
	55-70	288	326	242		
817 (IV; 1420 m)	90-100	514	590	374		
	420-430	10044	4443			
	0-5	248	310	295	118	
	7-14	220	276	295	184	
	15-25	225	244	258	282	
	70-80	150	256	225	105	
	100-110	172	322	263		
170-180	6290	6030	6650			
255-265	17900	22600	21000			

**Table 3.** (Contd.)

Station (polygon; depth)	Sampling horizon (cm)	CH <sub>4</sub> content, µl/dm <sup>3</sup>				
		A	B	C	D**	E
814* (IV; 2180 m)	0–5	141	229	154		
	10–15	160	252	168		
	20–25	188	237	117		
839-1 (V; 2154 m)	5–10	217	291	263	49	75
	20–25	204	249	254	49	80
	40–55	230	284	303	69	102
	60–70	307	384	349	95	148
	95–100	8440	9400	8000	5400	4000
	140–145	16511	16200	17900	13600	14760
	245–250	33100	34900	34400	29800	28300
290–310	38300	41500	39700	34000	33070	
838 (V; 2164 m)	17–25	98	164	126	14	
	70–76	134	205	128	13	
806-2 (VI; 2108 m)	0–7	171	198	130		
	15–20	81	115	78		
	32–36	112	126	95		
	50–60	133	204	144		
	80–83	196	137	138		
806-3* (VI; 2141 m)	0–5	124	158	114	34	
	20–25	108	146	97	32	

Note: The letters A, B, C, D, and E in the second row designate the methods of methane desorption and determination (see Materials and Methods).

\* Sampling was performed with an Okean dredger (at other stations, samples were taken with geological tubes).

\*\* Data obtained by method D (D columns) were kindly provided by A. Egorov (Institute of Oceanology, Russian Academy of Sciences).

the head-space method with salting out and calculation by an internal standard (method C).

(3) Methane concentrations in the Black Sea water column slightly grew from the surface to a depth of 150–200 m, increased 20- to 100-fold from 200 m to the 1000–1200 m horizon, and remained virtually unchanged in underlying layers. At some deep-sea stations, peaks of methane content in the 1000–1200 m horizons of the water column were revealed, which were most probably due to a local influx of methane-enriched abyssal waters.

(4) The content of methane in the Black Sea bottom sediments increased downward along the sediment thickness. In the upper 70 cm of shelf sediments, two methane concentration minima were revealed, whereas only one minimum was found in deep-sea sediments.

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