Original article

Studying Diurnal Dynamics of Vertical Methane Distribution in the Black Sea Aerobic Zone Combined with Acoustic Research of the Sound-Scattering Layers

T. V. Malakhova [1, ✉], Yu. G. Artemov [1], A. I. Khurchak [1], L. V. Reshetnik [1], A. V. Fedirko [2], V. N. Egorov [1]

[1] *A. O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences, Sevastopol, Russian Federation*
[2] *Marine Hydrophysical Institute of RAS, Sevastopol, Russian Federation*
✉ *t.malakhova@imbr-ras.ru*

Abstract
Purpose. The purpose of the study is to assess the diurnal dynamics of CH_4 vertical distribution in the aerobic zone of the Black Sea at the stations of different depths joint with surveying the sound scattering layers (SSL).
Methods and Results. The surveys were performed in the 113th cruise of the R/V *Professor Vodyanitsky* (June, 2020) in the upper 100-m layer at the deep-water station (1570 m) in the northeastern Black Sea, and at the shallow-water station (39 m) in the Yalta Bay. The differences in vertical distribution of the CH_4 concentration in the seawater in these areas were found. Diurnal range of the CH_4 concentrations in the surface water layer (0–1 m) was 0.8–16 nmol/l and 0.2–7 nmol/l for the shallow and deep-water areas, respectively. Shown was the fluxes' high variability at the water – atmosphere boundary in course of a day, namely, from the atmospheric CH_4 inflow to the seawater up to the CH_4 emission (up to 3 μmol/m^{2}day) to the atmosphere.
Conclusions. The maximum CH_4 fluxes to the atmosphere recorded at both stations were observed at night. It was shown that the atmospheric CH_4 emission to seawater was not a significant factor in the CH_4 redistribution in a water column since the calculated values of the atmosphere – seawater specific daily CH_4 flux constituted the fractions of a percent of its store in the water column. Diurnal dynamics of the vertical CH_4 distribution and SSL in the aerobic layer of the deep-water station was revealed to be of a similar pattern. Against high variability of the data for the individual time ranges, obtained were significant determination coefficients between the CH_4 concentration and the sound-scattering coefficient of layer *ml'* as a characteristic of the biomass amount.

Keywords: methane, "methane paradox", emission, aerobic layer, sound-scattering layers, Black Sea

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Introduction

Methane (CH_4) is one of the main climatically significant gases contained in the World Ocean waters [1]. In coastal and shelf areas, the bottom water layers, as a rule, are enriched with CH_4 and exceed the equilibrium concentration levels by several orders of magnitude. This is primarily due to the wide distribution of methane seeps and intense diffusion flows from bottom sediments in productive shelf regions of the World Ocean [2].

In addition to the near-bottom CH_4 maximum, the presence of its concentration peak in the subsurface layers in both brackish and freshwater basins (the so-called "methane paradox"), including in the aerobic Black Sea layer, was shown [3, 4]. The first detailed profiles of the vertical methane distribution in the aerobic waters of the Black Sea shelf were obtained in the mid-1990s [5, 6], as well as in 2002 in the northeastern part of the sea [7]. The presence of a concentration CH_4 maximum in the layer, which corresponded to the conditional density value of 14 kg/m^3, was shown. Below, there was a minimum of CH_4 content, separating the methane of the aerobic and anaerobic strata of the Black Sea. CH_4 concentrations in the maximum layer exceeded the surface concentrations by an average of 1.5 times [5].

Despite the fact that over the past decades the phenomenon of the "methane paradox" in various basins has been repeatedly described in the literature, there is still no unequivocal answer to the question of the process being responsible for the increased dissolved CH_4 concentrations in the upper water layers [8–12]. The established paradigm about the microbial CH_4 production by methanogenic archaea in anaerobic niches [1] [13–15] has recently been expanded by new data that CH_4 in oxygen-containing waters can be produced by cyanobacteria [4], algae [16, 17], and fungi [18], purple bacteria [19, 20], etc. The dominant mechanism of CH_4 formation in various water systems may depend on the season, trophic status, morphology and biocenosis of each individual water body [21, 22].

The works of the late 20th century describe the "zooplankton" theory of CH_4 formation by methanogenic archaea associated with copepod intestinal flora and their fecal pellets [23, 24]. The methanogenic archaea produce CH_4 by degrading methylated products such as methylamine, dimethyl sulfide and methanol, which are produced directly or indirectly from the phytoplankton metabolism, food of zooplankton. In radioisotope experiments with zooplankton, it was shown that the methanogenesis intensity was proportional to the number of copepods [15]. Later, in special incubation experiments, the specific rates of daily CH_4 production were calculated for individual species of zoo- and phytoplankton [2] [24, 25].

Under natural conditions, many species of living organisms actively migrate in the water column during the day, which should complicate the formation of stable CH_4 concentration maxima. Also, the CH_4 maximum depth can be associated with periodic changes in the depth of density-gradient layers, which are related to the concentration of terrigenous suspensions and detritus [26]. It is possible to track the migration of living organisms and gradient fields in the water column using hydroacoustic studies of the sound-scattering layer (SSL), due to the presence of

[1] Rusanov, I.I., 2007. [*Microbial Biogeochemistry of the Methane Cycle in the Black Sea Deep Zone*]. Extended Abstract of Cand. Diss. Moscow, 24 p. (in Russian).

[2] Kovalev, A.V., Shmeleva, A.A. and Petran, A., 1982. [*Zooplankton of the Western Part of the Sea from the Bosporus to the Danube Mouth in May, 1982*]. Moscow: Ministry of Coal Industry Publishing, pp. 356-367 (in Russian).

mineral suspension, detritus, phyto-, zoo-, ichthyoplankton and adult fish. The main trend in the diurnal SSL variation is associated with its rise and thickening in the subsurface sea layers at night and deepening to 120 m during the day with a more uniform distribution of sound backscatterers in the water column [27].

The studies of temporal trends in CH_4 concentration changes in marine areas are more often devoted to long-term and seasonal dynamics [8, 28], and monitoring is carried out much less frequently on a synoptic or daily time scale. Our own data of seasonal studies of CH_4 vertical distribution in the upper photic water layer of the Black Sea, carried out on 102nd, 103rd, 105th, 106th and 110th cruises onboard the R/V *Professor Vodyanitsky*, did not reveal a clear seasonal and spatial dependence in the CH_4 subsurface maxima distribution. This distribution is probably associated with the processes of smaller time and space scales [29]. In this regard, the present paper is aimed at studying daily dynamics of the vertical CH_4 distribution in the oxygen zone of the Black Sea combined with with the acoustic studies of SSL.

Research methods

Research areas and sampling. The studies were carried out at two stations in the northern Black Sea during 113th cruise of the R/V *Professor Vodyanitsky*. At coastal station 123 (44°28.970′N; 34°10.940′E) the work was carried out in June 8–9, 2020, from 07:00 to 07:00, at deep-water station 220 (44°17.260′N; 36°08.963′E) – June 13–14, 2020 from 11:00 to 14:00.

The water to determine a dissolved CH_4 concentration from the corresponding horizons was sampled using 10-liter Niskin bottles of a Rosette-type probing complex. At shallow station 123 (39 m) the water samples were taken at the anchor station from the surface to the bottom layer with 5 m step every 2 hours. At deep-water station 220 (1,570 m) the water samples were taken drifting from the surface to the 100 m depth with 10 m step every 4 hours. At the beginning of each sampling series, the vessel was positioned at the initial coordinates. At all horizons, the samples were taken in duplicate.

The hydrophysical parameters were measured during the immersion of the Rosette probing complex equipped with a *Seabird-Electronics, Inc.* probe (USA) with temperature, salinity and pressure, oxygen and chlorophyll a sensors.

Gas chromatographic determination of CH_4 concentration. The CH_4 concentration in water samples was determined by the "headspace" method of phase-equilibrium degassing [30]. High-purity helium (Argon LLC, 5.0 grade) was used to create the "headspace" volume [31]. Tableted potassium hydroxide was used as an inhibitor of microbial processes. Gas chromatographic dissolved CH_4 measurement was carried out on a Hewlett Packard 5890 gas chromatograph with FID under the following conditions: carrier gas – nitrogen, flow rate – 30 ml/min, detector temperature – 225 °C, injector temperature – 120 °C, packed steel column, column length – 1 m, inner diameter – 2 mm, sorbent – Porapack Q 80/100 mesh (Serva). The instrument was calibrated daily using gas calibration mixtures of 0.01 and 99.9% CH_4 in nitrogen (Monitoring LLC). The measurement error did not exceed 10%, the CH_4 detection limit in gas samples was 0.1 ppm.

Calculation of CH_4 emission at the water-atmosphere interface. Calculation of $F(CH_4)$ emission (μmol/m^2·day) at the water–atmosphere interface was carried out applying the described method [32] according to the equation

$$F = k\left(C_{CH_4} - C_{eq}\right), \quad (1)$$

where k is the exchange rate (m/day); C_{CH4} is the dissolved methane concentration in surface water; C_{eq} is the equilibrium CH_4 concentration in the surface layer of sea water with atmospheric air (nmol/l).

To calculate the equilibrium CH_4 concentration in water, the equation from [33] was used

$$\ln C_{eq} = \ln CH_4 + A_1 + A_2(100/T) + A_3\ln(T/100) + A_4(T/100) + \\ + S[B_1 + B_2(T/100) + B_3(T/100)^2], \quad (2)$$

where CH_4 is the atmospheric concentration of methane (ppm); T is the absolute temperature (K); S is the salinity (‰); A_n and B_n are constants (nmol/l). Hydrological data (T, S) were obtained using the SBE 911plus CTD probe. For each station, the equilibrium concentration value was calculated using temperature and salinity data measured *in situ*. The CH_4 concentration in the atmosphere for all stations was assumed to be 2 ppm.

The CH_4 supply per square meter V (CH_4, μmol/m^2) was calculated as the sum of the volumes for each individual layer, assuming that the CH_4 concentration between the layers was equal to the value measured for the upper boundary of the layer. The diurnal turnover was estimated as the ratio of the specific CH_4 flow at the water–atmosphere interface to the CH_4 reserve in the studied layer.

Hydroacoustic research of SSL. The spatial SSL characteristics were studied using a Lowrance Hook Reveal 5 mobile echo sounder with 50 and 200 kHz operating frequencies, equipped with a built-in GPS receiver. The presence in the echo sounder of the device for recording profiles of backscattered sound signal made it possible to detect the echo responses of marine organisms that form SSL in the water column, as was shown in [34–38].

Acoustic observations of SSL were carried out at drift stations or at anchor at calm sea conditions. The echo sounder antenna was installed in its normal position, and the backscattering profile was recorded for 15–20 min every hour at the 200 kHz frequency in the active sea layer. A preliminary artifact absence analysis in acoustic data was carried out using the Wavelens program [39].

For data processing and analysis, a program was created that works in the MATLAB environment. Recorded on a micro-SD card, echo envelope readings were converted from 8-bit integers into logarithmic format and corrected for wavefront expansion loss and losses due to sound attenuation in the aquatic environment according to the equation

$$SV' = D_{log} + 20\log(R) + \alpha R/1000, \quad (3)$$

where SV' (dB) is the analogue of volume backscattering strength; D_{log} is the logarithmic format of the echo signal; R (m) is the distance to the echo sounder antenna; α is the sound attenuation coefficient (dB/m).

The *SV'* values, linearly related to the true volume backscattering strength, were used to graphically display and digitally process the acoustic data in the postprocessing mode.

To compare the intensity of sound scattering in different water column layers, an analogue of the layer sound scattering coefficient *ml'* was used:

$$ml' = \int_{h_1}^{h_2} 10^{SV'/10} dh, \tag{4}$$

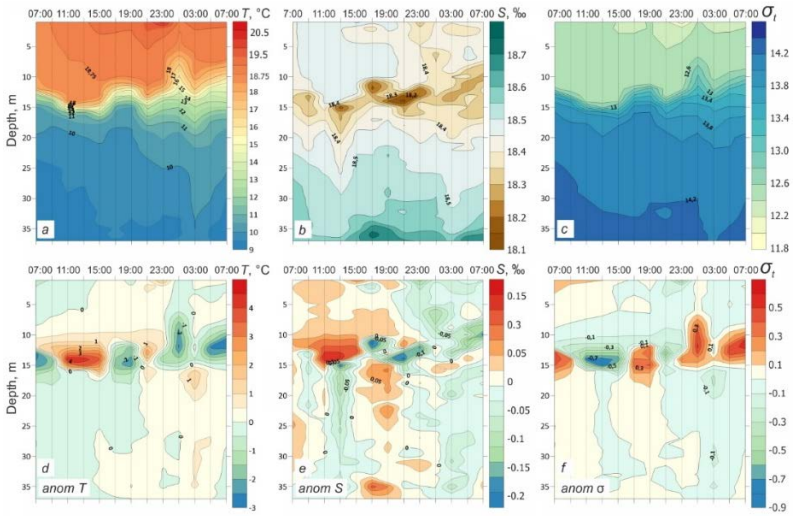
where h_1 and h_2 are the depths of the lower and upper SSL bounds. In the context of this paper, the *ML'* (dB) layer strength analogue was considered as a measure of the abundance of organisms and sound-reflecting particles:

$$ML' = 10\log\left(ml'\right), \tag{5}$$

since for SSL in the marine environment, this parameter is easier to compare with the bio productivity of water masses [39].

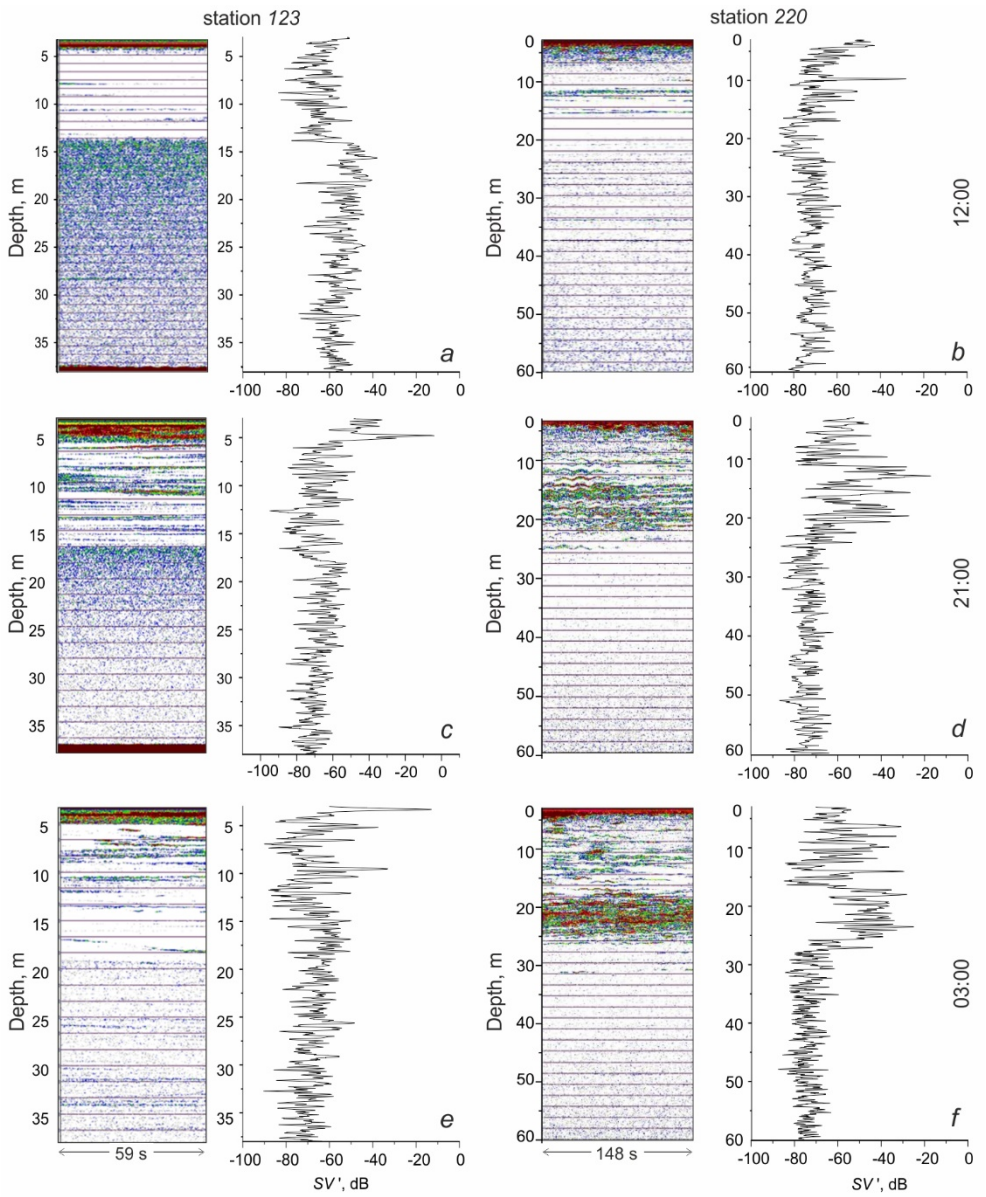
Research results

Hydrological parameters at stations 123 and 220. Comparison of the obtained vertical distribution profiles of the main hydrological parameters with the results of previous studies showed that their average daily values did not go beyond the natural variability limits. Deep-water station 220 was located in the northeastern Black Sea, where, according to climatic data of geostrophic calculations, the core of the Black Sea Rim Current passes. The upper quasi-homogeneous layer (UQL) thickness in this area during the study period was relatively small (up to 5 m), the vertical thickness of seasonal thermocline, halocline and pycnocline was 25–30 m. In the temperature field, the CIL core was observed at the 59 m depth, the temperature in it was 8.56 °C.



F i g. 1. Diurnal dynamics of vertical distribution of the hydrological parameters and their anomalies – temperature (*a*, *d*) salinity (*b*, *e*) and conditional density (*c*, *f*) at station *123* (sounding step is 2 hours, time is indicated on the horizontal scale)

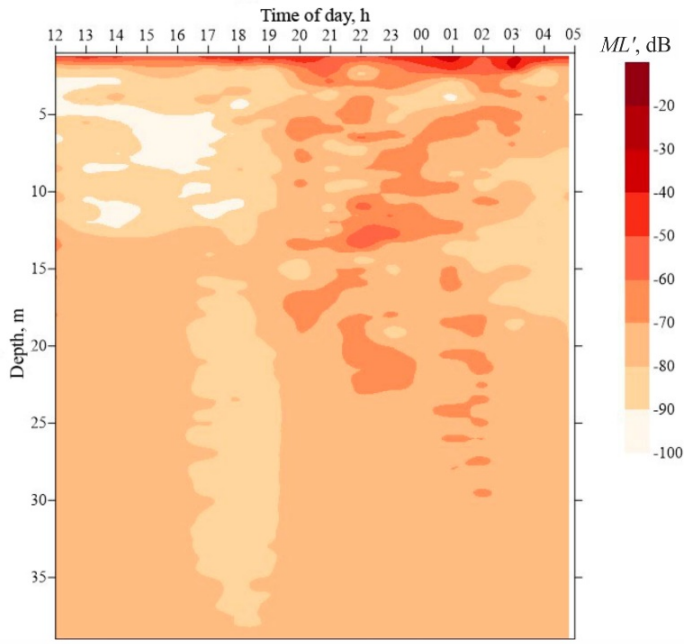
Shallow station *123* is located in the Yalta Bay. In the period from 07:00 to 19:00, a pronounced UQL 10–14 m thick was observed on the profiles of thermohaline parameters. A shock layer (thermocline, halocline and pycnocline) 5–7 m thick was located under the UQL (Fig. 1, *a*). Later, in the period from 21:00 to 07:00 the next day, the UQL was less uniform, the temperature on the surface increased, and the water salinity and density somewhat decreased (Fig. 1, *a* – *c*). The shock layer thickness increased to 10–15 m. The main diurnal variability was observed at shock layer depths for all thermohaline characteristics (Fig. 1, *d* – *f*).



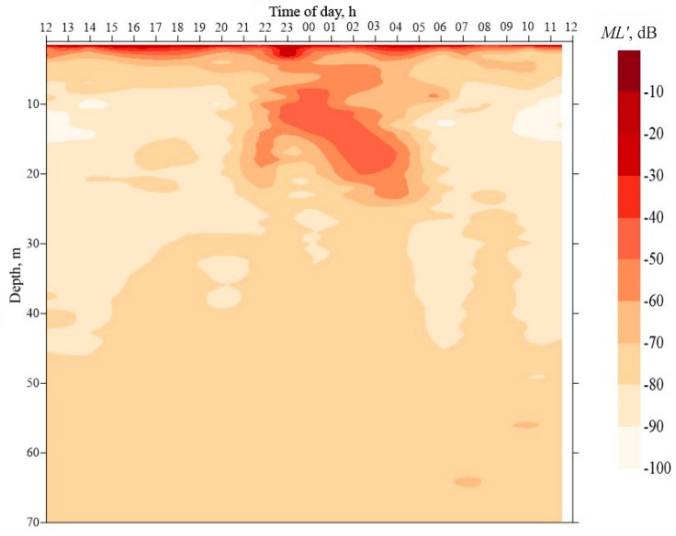
F i g. 2. SSL echograms and the corresponding profiles of the volume backscattering coefficient *SV'* at different time at stations *123* and *220*

Hydroacoustic studies of SSL dynamics. The echograms obtained from the observation results and the corresponding profiles of the vertical distribution of the *SV'* volume backscattering strength are shown in Fig. 2. For shallow water station 123 records for 59 s, for station 220 – for 2 min 28 s (Fig. 2, *b*, *d*, *f*) are presented. For both stations, the step of volume backscattering strength *SV'* values in depth was 3 cm. The echograms show that against the background of a general background signal corresponding to approximately – 80 dB, more intense signals up to – 20 dB were observed (Fig. 2). It is assumed that the background signal is a non-migratory component, which can be represented by mineral and organic suspension, bacterio- and phytoplankton. The migrating component consists of fish and zooplankton echoes.

The vertical SSL distribution in the water column was not constant and varied depending on the considered area and time of day. The diurnal dynamics of SSL for shallow station 123 and deep-water station 220 is shown in Fig. 3 and 4, respectively. In the near-surface layer in the daytime at both stations, sparce sound scattering layers were observed. They were formed by single objects (fish), which are displayed by extended, most often horizontal echo responses (Fig. 2, *a*, *b*). At the same time, denser SSL, probably formed by mixed accumulations of fish and zooplankton, were clearly observed outside the UQL. At night, in accordance with the diurnal rhythm of fish and zooplankton migration, the intensity of echo signals from many marine organisms that rose to the sea surface significantly increased, while in the morning hours, the reverse migration, directed to the underlying layers began (Fig. 3, 4).



F i g. 3. Vertical distribution of the sound-scattering coefficient of *ML'* layer (acoustic index of the fish and plankton total biomass) depending on time at station *123*



F i g. 4. Vertical distribution of the sound-scattering coefficient of *ML'* layer (acoustic index of the fish and plankton total biomass) depending on time at station *220*

T a b l e 1

CH_4 concentration at different horizons, stock $V(CH_4)$, emission at the atmosphere – water interface $F(CH_4)$ and diurnal turnover at the coastal station *123*

H, m	Time												
	07:00	09:00	11:00	13:00	15:00	17:00	19:00	21:00	23:00	01:00	03:00	05:00	07:00
CH_4, nmol/l													
0	3	1	0.8	7	5	5	2	6	8	16	0,9	3	4
5	1	15	0.8	31	1	11	3	4	2	13	2	11	5
10	9	4	0.8	30	27	9	3	11	8	21	4	7	1
15	14	5	0.9	20	21	18	4	6	9	14	5	12	19
20	39	1	0.8	8	27	15	9	2	8	12	15	21	15
25	14	0.8	0.8	12	30	25	14	5	13	15	17	20	21
30	20	0.8	17	44	37	14	10	3	20	13	11	31	18
35	17	0.6	1	19	28	10	11	6	20	21	16	25	15
39	5	5	2	15	22	15	6	22	32	22	23	19	5
$V(CH_4)$, μmol/m^2													
0 - 39	580	154	106	930	993	600	308	320	606	732	456	740	518
$F(CH_4)$, μmol/m^2·day													
0	0.25	-0.15	-0.24	1.32	0.93	1.87	0.61	2.39	1.64	3.40	-0.24	0.52	0.62
Daily turnover, %													
0 - 39	0.04	-0.10	-0.23	0.14	0.09	0.31	0.20	0.75	0.27	0.46	-0.05	0.07	0.12

N o t e. Here and in Table 2, different concentrations of CH_4 are shown in color.

Diurnal CH_4 content dynamics in the water column. At coastal station *123*, 13 soundings were carried out (Table 1). The CH_4 distribution in the water column during the 24-hour period was non-uniform, the CH_4 range concentration was 0.8–44 nmol/l. The CH_4 concentration maxima changed their location during the day, while being in the middle-depth layers in the 20–30 m range. The exception was the night hours between 21:00 and 03:00, when the CH_4 content maxima were in the bottom layer. For several soundings in the 5–10 m layer below the sea surface, elevated CH_4 concentrations (31 nmol/l), lower than the main underlying maxima (44 nmol/l), were found. The surface horizon for all soundings was characterized

by relatively low CH_4 concentration values, which were in the 0.8–16 nmol/l range. Low methane (0.6–17 nmol/l) concentrations, without pronounced maxima, were also found in the entire water column in the morning hours from 09:00 to 11:00.

Table 2

CH_4 concentration at different horizons, stock $V(CH_4)$, emission at the atmosphere – water interface $F(CH_4)$ and diurnal turnover in the upper 100-m layer at the deep-water station *220*

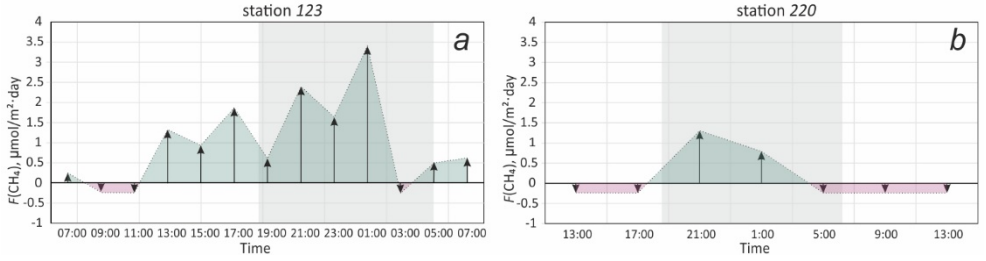
H, m	Time						
	13:00	17:00	21:00	01:00	05:00	09:00	13:00
CH_4, nmol/l							
0	0.2	0.2	7	5	0.2	0.2	0.1
10	0.2	0.2	9	4	3	0.2	0.2
20	11	43	24	16	0.2	0.1	0.2
30	13	14	41	4	0.2	0.3	2
40	2	35	84	3	0.2	1	1
50	0.2	3	43	8	0.2	0.2	0.2
60	0.1	2	9	49	3	0.2	0.2
70	0.2	0.1	4	14	0.2	0.1	0.2
80	0.1	1	6	0.1	0.2	0.1	2
90	0.1	1	0.1	4	1	0.2	0.1
100	11	2	0.1	5	0.2	0.1	3
$V(CH_4)$, μmol/m^2							
0 - 100	384	1016	2273	1122	87	30	94
$F(CH_4)$, μmol/m^2·day							
0	-0.24	-0.24	1.31	0.79	-0.24	-0.24	-0.24
Daily turnover, %							
0 - 100	-0.06	-0.02	0.06	0.07	-0.27	-0.79	-0.25

At deep-water station 220, 7 soundings were carried out (Table 2). The CH_4 distribution in the water column during the specified period, as well as at the coastal station, was uneven. The CH_4 distribution profile during the first probing at 13:00 on June 13 was characterized by the presence of a maximum (13 nmol/l) at the 30 m depth, which deepened to 40 m by 21:00 and increased to 84 mol/l. In the morning and afternoon hours of June 14, the CH_4 concentrations were close to or below the equilibrium values (2.5 nmol/l) in the entire studied layer from the surface to 100 m.

CH_4 flows at the water–atmosphere interface. At station *123* in the period from 13:00 to 01:00, the CH_4 flows were directed from the water to the atmosphere, the maximum (3.4 μmol/m^2·day) was recorded at 01:00 (Fig. 5, *a*). In the morning, the flows were significantly lower (0.5 μmol/m^2·day) compared to the daytime and evening hours (05:00–07:00, June 9) or even directed from the atmosphere into the water (09:00–11:00, June 8).

At deep-water station 220, a generally similar trend was observed: the CH_4 flows from water to the atmosphere in the evening and night hours (0.8–1.3 μmol/m^2·day)

and CH_4 runoff from the atmosphere to water in the morning and afternoon periods (13:00 –17:00, June 13, and 5:00–13:00, June 14). However, the CH_4 flow value and emission time interval into the atmosphere at the deep-water station were significantly less compared to the shallow-water station (Fig. 5, *b*).



F i g. 5. Diagram of the diurnal dynamics of CH_4 fluxes to the atmosphere for the coastal *123* (*a*) and deep-water *220* (*b*) stations

Discussion

Comparison of the diurnal dynamics of CH_4 vertical distribution at two stations showed high variability of CH_4 concentration in the water column at each of them. The maximum CH_4 concentration (84 nmol/l) was noted at a deep-water station in the 40 m layer at 21:00, while it was not stable in time and migrated deep into the water column. The values decreased to a level below equilibrium with the atmosphere (2.5 nmol/l) 8 hours after the maximum CH_4 concentration detection in the entire studied water column (0–100 m from the sea surface). This indicates a high mosaicity of the spatial distribution of production processes, which can be affected both by the microbial link spread responsible for CH_4 generation in the water column and by hydrophysical processes of mixing due to horizontal currents. The stable thermohaline stratification observed for both stations indicates the absence of vertical mixing during monitoring (Fig. 1).

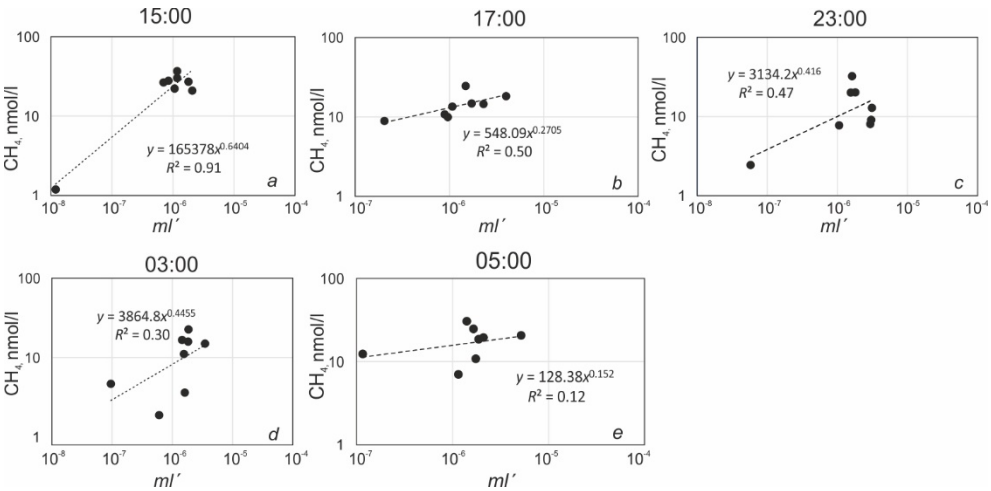
Deep-water regions, far from the shelf zone, are especially interesting from the viewpoint of the methane cycle processes in its aerobic layer. According to the current paradigm, methane from the anaerobic zone of the Black Sea scarcely penetrates into the overlying aerobic layer. This is indicated by its anaerobic oxidation rates, which are much higher than the rates of production, as well as the CH_4 carbon isotopic composition of the aerobic stratum $\delta 13C$ (– 40.0 ... – 66.6‰), which differs by an average of 20‰ from the values obtained in the chemocline zone (– 19.0 … – 48.5‰) [40]. The effect of bubble gas emissions on the upper aerobic layer in deep water areas under normal geological conditions is excluded [26]. In this regard, it is assumed that it is the processes of "aerobic production" of CH_4 that form the observed concentration CH_4 maxima and determine its flow into the atmosphere from the deep-water Black Sea area.

The diurnal dynamics of the vertical distribution of the *ML'* layer strength, reflecting the total biomass of various hydrobionts and non-living suspension in the water column, is characterized by the thickening of sound scatterers in the upper water layers at night and scattering during the daytime (Fig. 4, 5). This is in line corresponds to the trend of the diurnal SSL variation in the water column shown earlier [26]. For deep-water station 220 high CH_4 concentrations were also

obtained in the evening and at night (Table 1). It is important to point out that, in this case, the CH_4 concentration maximum was deeper than the UQL and by 01:00 was divided into two maxima (16 and 49 nmol/l) in the 20 and 60 m layers.

At shallow station 123 for 24 h, except for soundings at 09:00 and 11:00, the entire water column was characterized by CH_4 values exceeding the equilibrium concentrations. The diurnal dynamics at the shallow and deep-water stations was different. The CH_4 concentration maxima found at different depths during the period under consideration changed their location quite chaotically. It is known that, at shallow water shelf stations, the vertical CH_4 distribution structure is significantly affected by its diffusion and bubble flows from bottom sediments [41].

It is also possible that the CH_4 formation occurs directly in the water column, as in deep-sea regions. The dependence of CH4 concentration in water on the sound scattering coefficient of the layer *ml'*, which is a relative characteristic of the total biomass and suspended matter amount, is shown in Fig. 6 for individual soundings at shallow station 123.



F i g. 6. Dependence of the seawater CH_4 concentration on the sound-scattering coefficient of layer *ml'* at different time at the shallow water station *123*

Overall, the low coefficients of determination and the periodic nature of the dependence of the parameters do not indicate the presence of a relationship between SSL and CH_4 concentration at the shallow water station. Uncertainty can be introduced by additional unaccounted factors: the presence of additional bottom CH_4 sources outside the considered area [41–43], as well as the time lag between the studied parameters as a result of vertical and horizontal migration of living organisms in the water column.

CH_4 emission into the atmosphere. The surface water layer (0–1 m) at both stations was characterized by lower CH_4 concentrations compared to the underlying layers, which is probably determined by methane redistribution at the water–atmosphere interface. The daily range of CH_4 concentrations in

the surface layer was 0.8–16 nmol/l and 0.2–7 nmol/l in the shallow and deep-water areas, respectively. The calculated values of the diurnal specific CH_4 flow at the atmosphere–water interface for both studied stations are fractions of a percent of the CH_4 reserves in the water column (Tables 1, 2). This indicates that the atmospheric CH_4 emission is not a significant factor in its redistribution in water.

In the diurnal dynamics of methane flows into the atmosphere at both stations, the increased emission values are noted at night and the lower values are noted during daytime, up to CH_4 runoff from the atmosphere into water in the deep sea area (Fig. 5).

Conclusion

The diurnal dynamics of the vertical distribution of CH_4 dissolved in water was studied at a deep-water station in the northeastern Black Sea and at a shallow water station in the Yalta Bay. For both stations, the vertical profiles of CH_4 concentration were characterized by high variability of values. In the water column (0–39 m) at the shallow water station throughout the monitoring, CH_4 concentrations that significantly exceeded the equilibrium values with the atmosphere (2.5 nmol/l), were observed. Concentration maxima (< 44 nmol/l) were found in the subsurface layers, which changed depth several times during the day and were located mainly under the thermocline. At the deep-water station, in the vertical distribution of CH_4 in the 0–100 m layer, profiles with the CH_4 concentration maximum presence (< 84 nmol/l) were observed only in the interval from 17:00 to 01:00. During the rest of the time, CH_4 concentrations in the water column at the deep-water station did not exceed the equilibrium values with the atmosphere.

The diurnal range of CH_4 concentrations in the surface layer was 0.8–16 and 0.2–7 nmol/l for the shallow and deep-water areas, respectively. The calculated values of CH_4 flows at the water – atmosphere interface during the day varied in the range of – 0.1 ... 3 μmol/m^2·day. At both stations, the maximum CH_4 flows into the atmosphere were recorded at night. It is shown that the atmospheric emission of CH_4 is not a significant factor in its redistribution in water, since the calculated values of the diurnal specific CH_4 flow at the atmosphere – water interface are fractions of a percent of its reserves in the water column.

A similar nature of the CH_4 and SSL concentration field distribution in the aerobic layer of the deep-sea station was established. For certain time intervals, significant coefficients of determination between the CH_4 concentration and the sound scattering coefficient of the layer *ml'* as a biomass amount characteristic were obtained. Determining the detailed mechanism of the relationship between sound-scattering layers and CH_4 concentration fields requires additional research.

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About the authors:

Tatyana V. Malakhova, Senior Research Associate, Radiation and Chemical Biology Department, FSBSI FRC A.O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences (2 Nakhimov Ave., Sevastopol, 299011, Russian Federation), Ph.D. (Biology), **SPIN-код: 4625-9702**, t.malakhova@imbr-ras.ru

Yuriy G. Artemov, Senior Research Associate, Radiation and Chemical Biology Department, FSBSI FRC A.O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences (2 Nakhimov Ave., Sevastopol, 299011, Russian Federation), Ph.D. (Geogr.), **SPIN-код: 3880-5421**, yu.g.artemov@gmail.com

Alena I. Khurchak, Leading Engineer, Radiation and Chemical Biology Department, FSBSI FRC A.O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences (2 Nakhimov Ave., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0001-9769-0279**, **SPIN-код: 4826-7330**, alenamyra@mail.ru

Lev V. Reshetnik, Leading Engineer, Radiation and Chemical Biology Department, FSBSI FRC A.O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences (2 Nakhimov Ave., Sevastopol, 299011, Russian Federation), **SPIN-код: 2515-3599**, lev3012@gmail.ru

Alexandr V. Fedirko, Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya Str., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0002-8399-3743**, **SPIN-код: 2496-1715**, vault102@gmail.com

Viktor N. Egorov, Chief Engineer, Radiation and Chemical Biology Department, FSBSI FRC A.O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences (2 Nakhimov Ave., Sevastopol, 299011, Russian Federation), Dr.Sci. (Biology), Academician of the Russian Academy of Sciences, **ORCID ID: 0000-0002-4233-3212**, **SPIN-код: 6595-6759**, egorov.ibss@yandex.ru

Contribution of the co-authors:

Tatyana V. Malakhova – aim setting of the research, analyzing and summarizing the research results, paper preparation

Yuriy G. Artemov – analyzing and summarizing the research results, paper preparation

Alena I. Khurchak – field works, gas chromatographic analysis of samples, paper preparation

Lev V. Reshetnik – field works, paper preparation

Alexandr V. Fedirko – field works, paper preparation

Viktor N. Egorov – analyzing and summarizing the research results, paper preparation

The authors have read and approved the final manuscript.
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