

## Features of Methane Distribution in the Euphotic Layer of the Northern Black Sea in Summer, 2018 (Based on the Data of the 102<sup>nd</sup> Cruise of R/V "Professor Vodyanitsky")

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**Purpose.** The main goal of the work was to assess the horizontal and vertical structure of methane (CH<sub>4</sub>) distribution, its emission to the atmosphere in the euphotic zone of the northern part of the Black Sea in summer, 2018 as well as to reveal its relationship with the chlorophyll *a* concentration.

**Methods and Results.** The CH<sub>4</sub> concentration in the surface layer was determined by the gas chromatographic method at 104 stations, including 45 stations at which the vertical profiles of the CH<sub>4</sub> content in the upper 0–50 m layer were done. The chlorophyll *a* concentration was defined by the fluorometric method. The CH<sub>4</sub> distribution in this region showed distinct spatial heterogeneity. The concentration of the dissolved in the surface water CH<sub>4</sub> varied within 0–39.2 nmol/l at all the stations. The average calculated value of the CH<sub>4</sub> seawater-air flux was 2.3 nmol/m<sup>2</sup>/day, and the average CH<sub>4</sub> saturation of surface water – 460 %. The major part of the sea area under study represented a source of methane emission to the atmosphere near-water layers, except for 15 stations where the CH<sub>4</sub> concentration in the surface layer was smaller than its equilibrium values. The calculated integral value of the CH<sub>4</sub> flux from the whole region under study (its area is equal to 88·10<sup>3</sup> km<sup>2</sup>) constituted 3.2 tons of CH<sub>4</sub> per day. Vertical distribution of CH<sub>4</sub> in the upper 50 m layer was different in the coastal and deep-sea areas. At the deep-sea stations, the maximum values were revealed in the sub-surface layers, whereas at the coastal stations (not deeper than 100 m), the highest CH<sub>4</sub> concentrations, up to 86 nmol/l, were observed mainly at the near-bottom horizons.

**Conclusions.** The average concentration of CH<sub>4</sub> in the deep-sea profiles was 2 times lower than that in the coastal ones. Sub-surface maximums of the CH<sub>4</sub> concentration coincided in general with the maximums of the chlorophyll *a* concentration. It was also found that the CH<sub>4</sub> highest concentration corresponded to the increased chlorophyll *a* content (0.58 mg/m<sup>3</sup>) in the Feodosiya Gulf surface water. The abnormally high concentration of CH<sub>4</sub> (269 nmol/l) at the bottom horizon, by an order of magnitude exceeding the average methane content in the adjacent areas, was revealed at the station near the Dnieper paleo-channel. Such an increased concentration is assumed to be caused by the methane emission from the gas seeps densely located in this region.

**Keywords:** methane, emission, chlorophyll *a*, euphotic layer, Black Sea.

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## Introduction

The CH<sub>4</sub> concentration in the oxygenated upper layers of the World Ocean often exceeds atmosphere equilibrium values. However, the methane formation in water during microbial methanogenesis is believed to require exclusively anaerobic conditions. This phenomenon is commonly called the “methane paradox”. It indicates that the oceans are the CH<sub>4</sub> source for the atmosphere.

According to the estimates available, the ocean makes a relatively small contribution to the budget for atmospheric methane compared to anthropogenic sources. The CH<sub>4</sub> emission into the atmosphere from all marine sources, including the open ocean, continental shelf, estuaries and seeps of the continental borderlands, is estimated at CH<sub>4</sub> 8.3–45.9 Tg per year [1]. Among the inland seas, the Black Sea is one of the most powerful methane reservoirs; many works have been devoted to the study of the biogeochemistry of the methane cycle in its water area [2–4]. The methane sources in the Black Sea are microbial production in bottom sediments and the water column, as well as methane gas emissions, which are widespread along the entire Black Sea shelf. Presence of a powerful anoxic zone in the Black Sea led to high rates of microbial production in the water column below the redox zone [5]. It was shown that methane of the anaerobic zone practically does not penetrate into the oxygen-containing water column, since its anaerobic oxidation rate is higher than the production rate. This is also indicated by the carbon isotopic composition of methane of aerobic stratum  $\delta^{13}\text{C}$  (–40.0 ... –66.6 ‰), which is on average by 20 ‰ different from the values obtained in the chemocline zone (–19.0 ... –48.5 ‰) [3]. On the other hand, in the studied areas of the upper, middle and lower parts of the continental slope and deep basin in the aerobic mass, a positive balance is observed in the microbial cycle of methane. Consequently, a number of researchers concluded that these are the methane formation processes in the aerobic water column that determine the flow of methane into the atmosphere from the deep Black Sea.

One of the first detailed studies of methane content profiles in aerobic waters of the Black Sea shelf was obtained during the works on the international project EROS-21 in August 1995 and in May 1997 on the northwestern shelf [5, 6]. More detailed studies were later conducted in 2002 in the northeastern part of the sea [7]. It was shown that there is a concentration maximum in the subsurface layer corresponding to the layer with conditional density of 14 kg/m<sup>3</sup>, below which there was a minimum of CH<sub>4</sub> content separating methane from the aerobic and anaerobic strata. The authors note that the CH<sub>4</sub> concentrations in the maximum layer are on average 1.5 times higher than the values of surface concentrations, however, the reasons for this distribution are not discussed.

A similar distribution of methane in the photic layer of the World Ocean has been repeatedly noted by different researchers [8–11]. In 1998, the presence of archaea at different horizons in samples of aerobic water was detected by *in situ* hybridization [12]. The obtained values of methanogenesis in the aerobic waters of the Black Sea and other meromictic water bodies were quite high, sometimes exceeding the methanogenesis rate in the anaerobic zone [6]. These data comparison with the methane distribution over the horizons indicated that zones favorable for the anaerobic process of microbial methanogenesis should exist in the aerobic water column.

For a long time, methane generation was believed to occur in anaerobic microniches – the conglomerates of organic particles and zooplankton intestines [13]. In direct radioisotope experiments with zooplankton, it was shown that the intensity of methanogenesis was proportional to the number of copepods. However, it is worth noting that under natural conditions, many species of zooplankton actively migrate in the water column during the day, which should complicate the stable concentration maxima formation.

Recent studies have shown that the methane appearance in water may be associated with the destruction of various methylated molecules contained in dissolved organic matter,

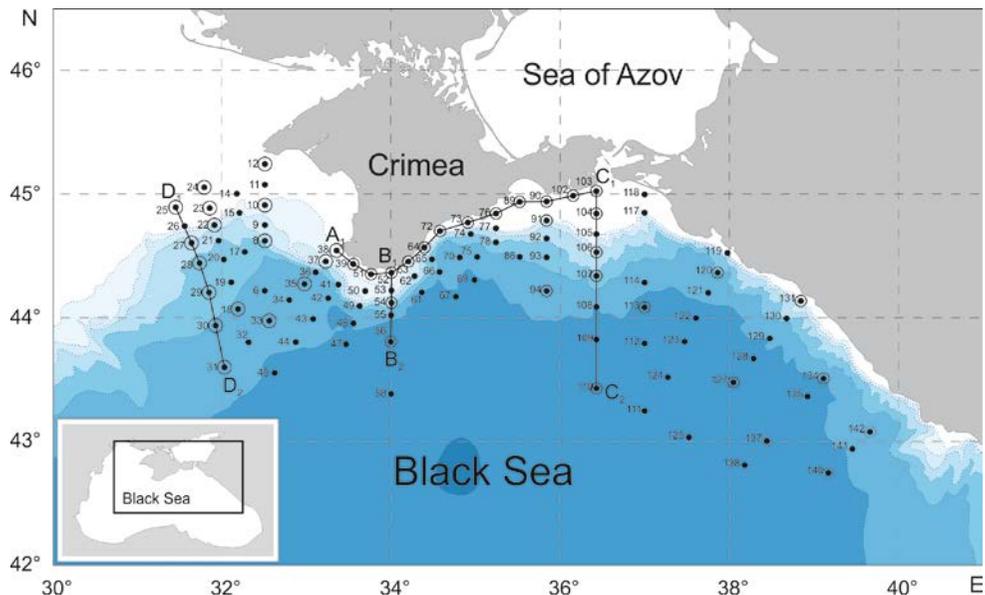
as well as metabolic products of several phytoplankton types [14]. The  $\text{CH}_4$  formation mechanism from methylated substances is still not fully understood. There are the following two types of its formation supposed: abiogenic [15] and biogenic due to the metabolism of bacteria [16] or phytoplankton [17]. It was shown that in freshwater reservoirs, the  $\text{CH}_4$  concentrations correlate with phytoplankton biomass and primary production [18], and this is explained by the archaean methanogenesis fixed in anaerobic niches on the surface of phytoplankton cells. Regardless of which mechanisms are responsible for the marine “methane paradox,” it has been shown that the  $\text{CH}_4$  production in oxidized surface waters is in some way related to primary production [19].

The present research is aimed to assess the horizontal and vertical structure of the of methane ( $\text{CH}_4$ ) distribution, its emission to the atmosphere in the euphotic zone of the northern part of the Black Sea in summer, 2018 as well as to reveal its relationship with the chlorophyll *a* concentration.

### Materials and Methods

The research was carried out on the 102<sup>nd</sup> cruise of the R/V *Professor Vodyanitsky* in June – July 2018 in the northern Black Sea (Fig. 1). Water samples were taken from the surface layer and in the water column to 50 m depth. The lower boundary of the euphotic zone was determined as the Secchi disk visibility depth multiplied by 3.

The  $\text{CH}_4$  concentration in the surface water layer was measured at 104 stations, at 45 of which vertical profiles of  $\text{CH}_4$  distribution to 50 m depth were also determined (Fig. 1). Water samples from horizons of 10, 15, 20, 30, 40 and 50 m were taken using 10-liter Niskin bathometers of a Rosette-type probing complex equipped with a hydrophysical probe by Sea-Bird Electronics, Inc. (USA) with temperature, salinity and pressure sensors.



**Fig. 1.** Scheme of the stations in the 102<sup>nd</sup> cruise of the R/V “Professor Vodyanitsky”. Circles denote the stations where the 0–50 m vertical profiles were done, black dots – the stations of surface water samples, solid lines – the latitudinal sections  $D_1D_2$ ,  $B_1B_2$ ,  $C_1C_2$  and the along-coastal section  $A_1C_1$

The  $\text{CH}_4$  content was measured by phase-equilibrium degassing [20] on an HP 5890 chromatograph with a packed column and a flame ionization detector under the following

conditions: the carrier gas is nitrogen, space velocity – 30 ml/min, temperature of the detector – 225 °C and of the injector –120 °C, the column is steel stuffed, the column length is 1 m, the inner diameter is 2 mm, the sorbent is Porapack Q 80/100 mesh (*Serva*). Surface water samples at each station were taken in duplicate. The methane determination error did not exceed 7 %.

Calculation of methane emission from water to atmosphere  $F$  was carried out according to the described procedure [21] according to the following equation

$$F = k(C_{\text{CH}_4} - C_{\text{eq}}), \quad (1)$$

where  $k$  is the exchange rate coefficient;  $C_{\text{CH}_4}$  are the observed concentrations of dissolved methane in surface water (nmol/l);  $C_{\text{eq}}$  is the equilibrium  $\text{CH}_4$  concentration in the surface layer of sea water with atmospheric air (nmol/l).

To calculate the equilibrium methane concentration in water, the equation from [22] was used:

$$\begin{aligned} \ln C_{\text{eq}} = & \ln \text{CH}_4 + A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100) + \\ & + S[B_1 + B_2(T/100) + B_3(T/100)^2], \end{aligned} \quad (2)$$

where  $\text{CH}_4$  is the atmospheric methane concentration (*ppm*);  $T$  is the absolute temperature (K);  $S$  is the salinity (‰),  $A_n$  and  $B_n$  are the constants (nmol/l). Hydrological data ( $T$ ,  $S$ ) were obtained using an SBE 911plus CTD probe. For each station, the equilibrium concentration value was calculated taking into account temperature and salinity data measured in situ. The methane concentration in the atmosphere for all stations was taken equal to 2 ppm.

The exchange rate coefficient  $k$  depends on wind speed and water temperature. The coefficient was calculated according to the equation from [21]:

$$k = 0,31u^2(\text{Sc}/660)^{-1/2}, \quad (3)$$

where  $u$  is the wind speed (m/s);  $\text{Sc}$  is Schmidt number, also calculated from [21]:

$$\text{Sc} = 2039,2 - 120,31T + 3,4209T^2 - 0,40437T^3, \quad (4)$$

where  $T$  is the surface water temperature (K) *in situ*.

The integral  $\text{CH}_4$  flux from the sea surface was estimated taking into account the mean emission values and the area of the studied water area. This area was calculated in the *Surfer 8* program as the area of a polygon whose vertices were the boundary stations (Fig. 1).

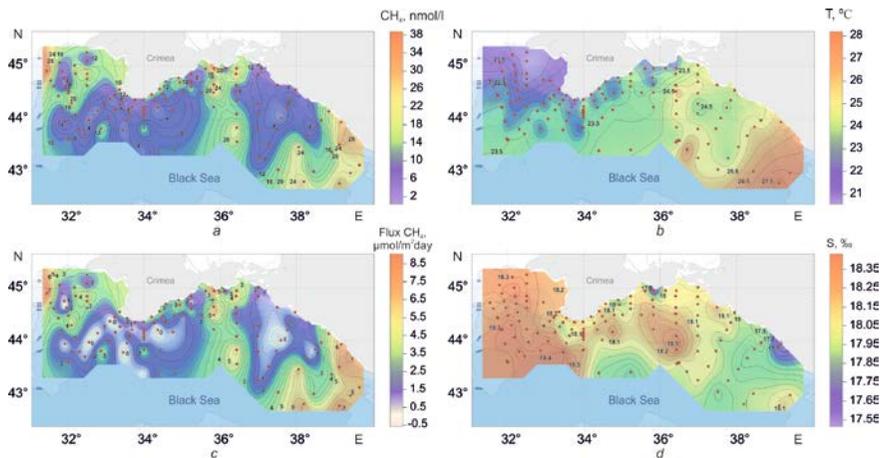
To determine the chlorophyll *a* (*Chl a*) concentration, the fluorimetric method was used [23]. The 0.3–0.6 l bathometric water samples immediately after sampling were passed through Whatman GF/F glass filters with a working surface of 22 mm at a vacuum of no more than 0.2 atm. The pigments were extracted with 90 % aqueous acetone.

The concentration of suspended matter ( $C_{\text{susp}}$ , mg (dry)/l) in surface water samples was determined by the method of “membrane filtration” [24]. Nucleopore filters with 0.45  $\mu\text{m}$  pore size were dried in an oven at 60 °C, weighed on a Sartorius microanalytical balance with 0.1 mg sensitivity and then 4–5 L of water was filtered through them. Filters with precipitated suspension were also dried and weighed. According to the difference in mass and volume of filtered water,  $C_{\text{susp}}$  was determined. The average relative error in determining the suspended matter concentration was 7 %.

For statistical data processing, construction of maps and graphs, computer programs *MS Excel*, *Surfer* and *Gidrolog* were used [25].

## Results

**Hydrology.** The hydrological parameters measured during June – July 2018 corresponded to a typical summer hydrophysical structure. The seasonal thermocline was located at 10–25 m depth; the temperature at the cold intermediate layer horizons was 7.8–8.2 °C. There was an increase in surface water temperature in the direction from northwest to southeast from 20 to 28 °C, respectively. The most pronounced feature in the temperature distribution in the upper layer was its increase, associated with the non-synchronization of surveys in different areas of the works. In early June, relatively low values were determined in the northwest and closer to the Kalamitskiy Gulf border, where the temperature reached 20.5 °C (Fig. 2, *b*). At the end of June, surface water warmed up to 28 °C, but at the same time, a region of relatively low temperature was observed in the central part of the Caucasian polygon (Fig. 2, *b*).



**Fig. 2.** Map of the methane – *a*, temperature – *b*, estimated sea-air methane fluxes – *c* and salinity – *d* distribution

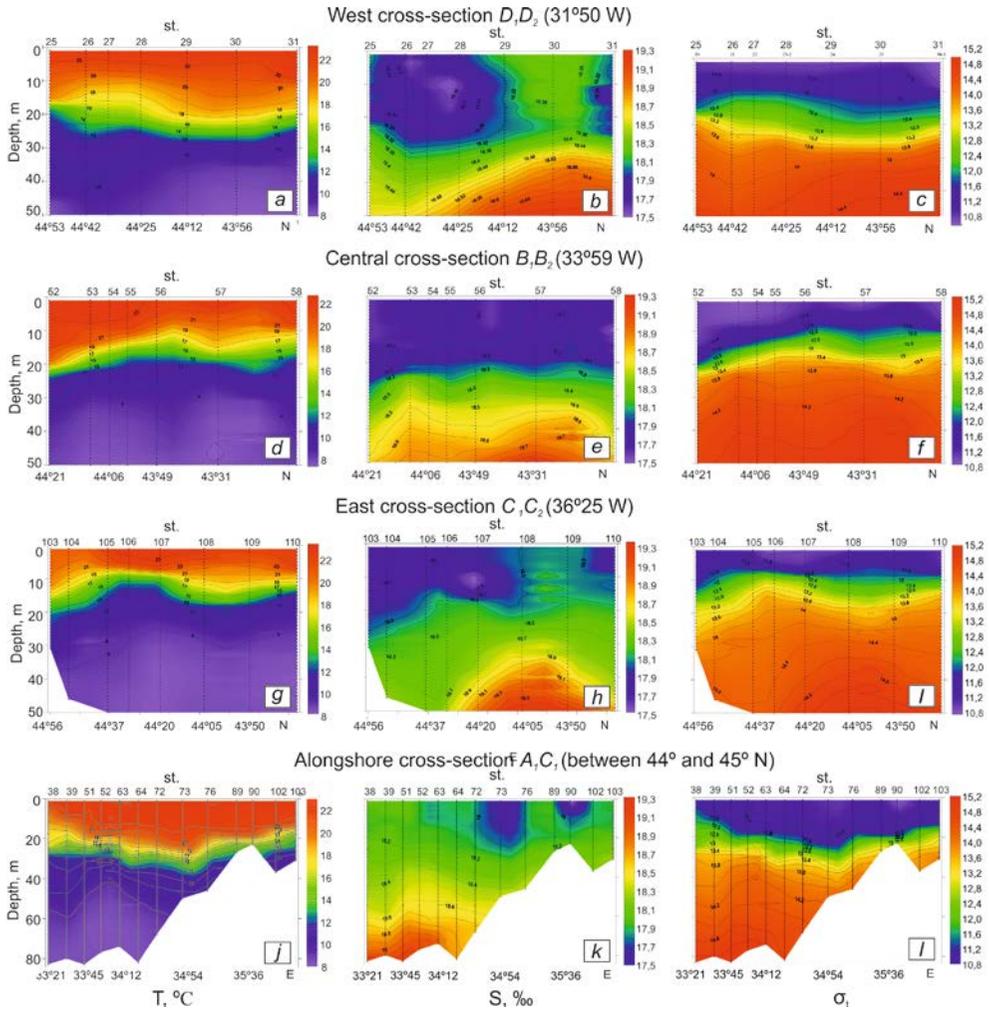
The surface water layer salinity varied in the range 17.5–18.5 ‰ (Fig. 2, *d*). The lowest salinity waters were traced in the form of a localized spot in the east of the survey, in the central part of the anticyclonic meander of the Black Sea Rim Current. The lower salinity values (below 17.6 ‰) were also observed in the shoreland: off the southern coast of the Kerch Peninsula, in the Feodosiya Gulf and in the Caucasus coast area.

**Methane and its fluxes from the water surface.** In the studied period, the surface water dissolved CH<sub>4</sub> concentration for all the stations varied in the range 0–39.2 nmol/l (average 11.5 nmol/l). The highest CH<sub>4</sub> content in the surface layer was noted in the northwestern part of the sea at the shallow water station No. 25 and in the Feodosiya Gulf at st. No. 90, where the concentration was 39.2 and 38.5 nmol/l, respectively. Relatively high concentrations of 26 nmol/l were also observed off the Caucasus coast (Fig. 2, *a*).

The methane flux from the water surface to the atmosphere at all stations was calculated for the corresponding water temperature and wind speed of 2 m/s. The calculation showed that for most stations the phenomenon of the so-called “methane paradox” was observed, in which methane saturation of the surface water layer exceeded equilibrium values. During the study period, it varied between 0–1519 %, averaging 460 %, and the average value of the calculated value of the CH<sub>4</sub> flux from water to the atmosphere was 2.3 μmol/m<sup>2</sup>/day. The highest methane emission, reaching 9.2 μmol/m<sup>2</sup>/day, was determined in the same areas where its increased content was detected. At several deep-sea

stations, the methane concentration in water was below equilibrium values; accordingly, the calculated atmospheric flux assumed a negative value (Fig. 2, c).

**Cross-sections.** To study the vertical distribution of methane in the euphotic layer, three latitudinal sections were made (Fig. 1): west  $D_1D_2$ , which stretched from the Dnieper paleo-channel (station No. 25) to the center of the western halistatic zone (station No. 31); east  $C_1C_2$  – from the Kerch Strait (station No. 103) to the eastern halistatic zone (v. 110) and the central  $B_1V_2$  connecting station No. 52 and 56. The  $A_1C_1$  section was also completed for all coastal stations not deeper than 100 m.

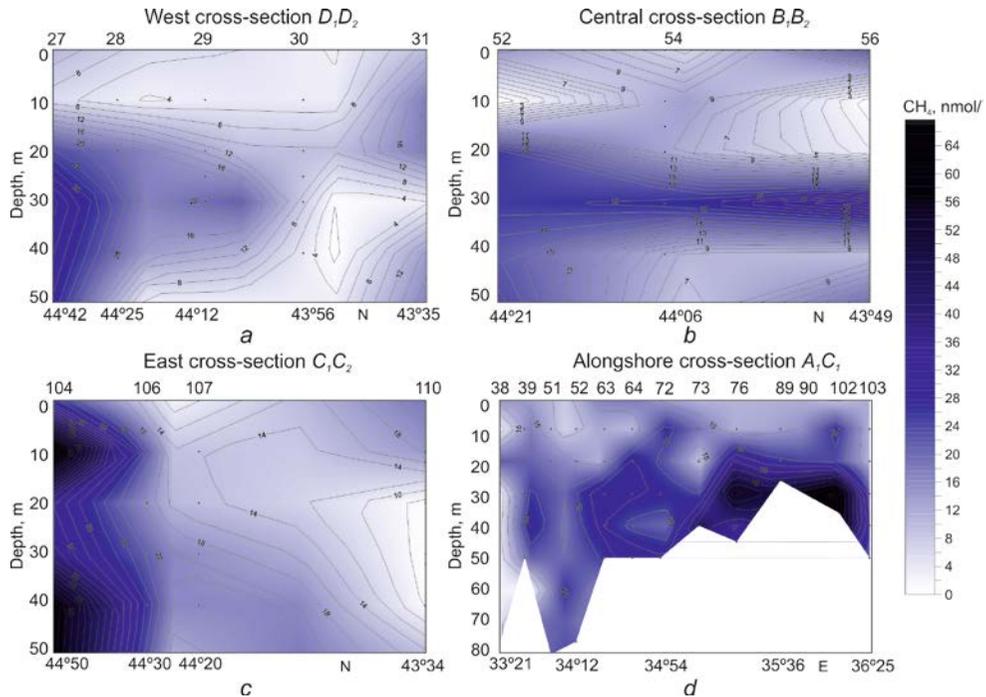


**Fig. 3.** Vertical distribution of temperature (a, d, g, j), salinity (b, e, h, k) and  $\sigma_t$  (c, f, i, l) along three latitudinal cross-sections: west  $D_1D_2$  – a, east  $C_1C_2$  – b, central  $B_1B_2$  – c and section  $A_1C_1$  – d for the coastal stations not deeper than 100 m

At the deepwater stations of the east (stations No. 108, 109) and west (station No. 30) cross-sections, the rise of more saline deep waters to the surface was noted (Fig. 3, b, 3, h). The maximum rise up to 3-4 m was observed in the east of the studied area, where a spot of abnormally cold waters was located on the surface. The surface water layer desalination in

the northeastern part of the polygon at station No. 90 in the Feodosiya Gulf and at station No. 73, located 7 miles from the coast between Sudak and Alushta (Fig. 3, *k*).

In the vertical distribution of methane in the upper 50-meter layer in the eastern, central and western cross-sections, its increased content in the subsurface layers is noted. In the  $B_1B_2$  section, the maximum layer was located under the thermocline, where the  $CH_4$  concentrations reached 24 nmol/l and in the  $D_1D_2$  and  $C_1C_2$  sections, – 34 nmol/l (Fig. 4).

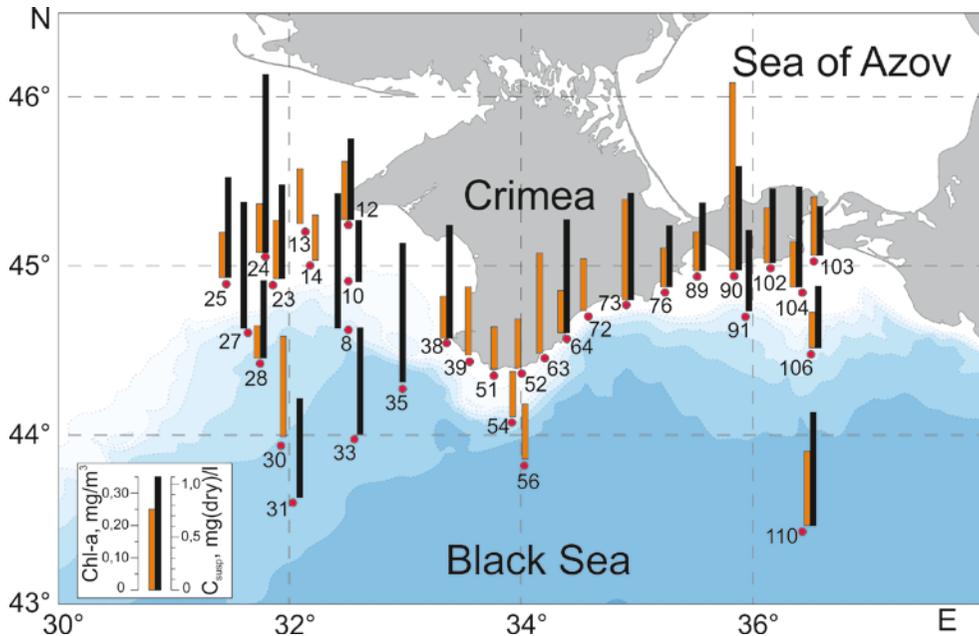


**Fig. 4.** Vertical distribution of the dissolved methane (nmol/L) along three latitudinal sections: western  $D_1D_2$  – *a*, eastern  $C_1C_2$  – *b*, central  $B_1B_2$  – *c* and section  $A_1C_1$  – *d* for the coastal stations not deeper than 100 m

An abnormally high  $CH_4$  concentration, 269 nmol/l in the near-bottom horizon, which is 10 times higher than the mean methane content in adjacent areas, was determined at station 25.

In the alongshore cross-section  $A_1C_1$ , the high  $CH_4$  concentrations, reaching 86 nmol/L, were observed in the bottom layers of the eastern area. At station No. 90, where some water desalination was observed, the surface maximum of methane content reaching 38.5 nmol/l was also defined (Fig. 4, *d*).

**Chlorophyll *a* and suspended matter in the surface layer.** At six stations of the western shelf off the coast of Crimea (stations No.12–14, 23–25), as well as at most stations along the coastal strip of the peninsula from Cape Chersonesus to the Kerch Strait (Fig. 5), low *Chl a* values typical for the summer period were obtained in the surface layer. They varied in the range of 0.12–0.31 mg/m<sup>3</sup>, on average  $0.17 \pm 0.05$  mg/m<sup>3</sup>. The exception was station No. 90, where the studied pigment content on the water surface was 0.58 mg/m<sup>3</sup>, being unusually high at this time of the year.



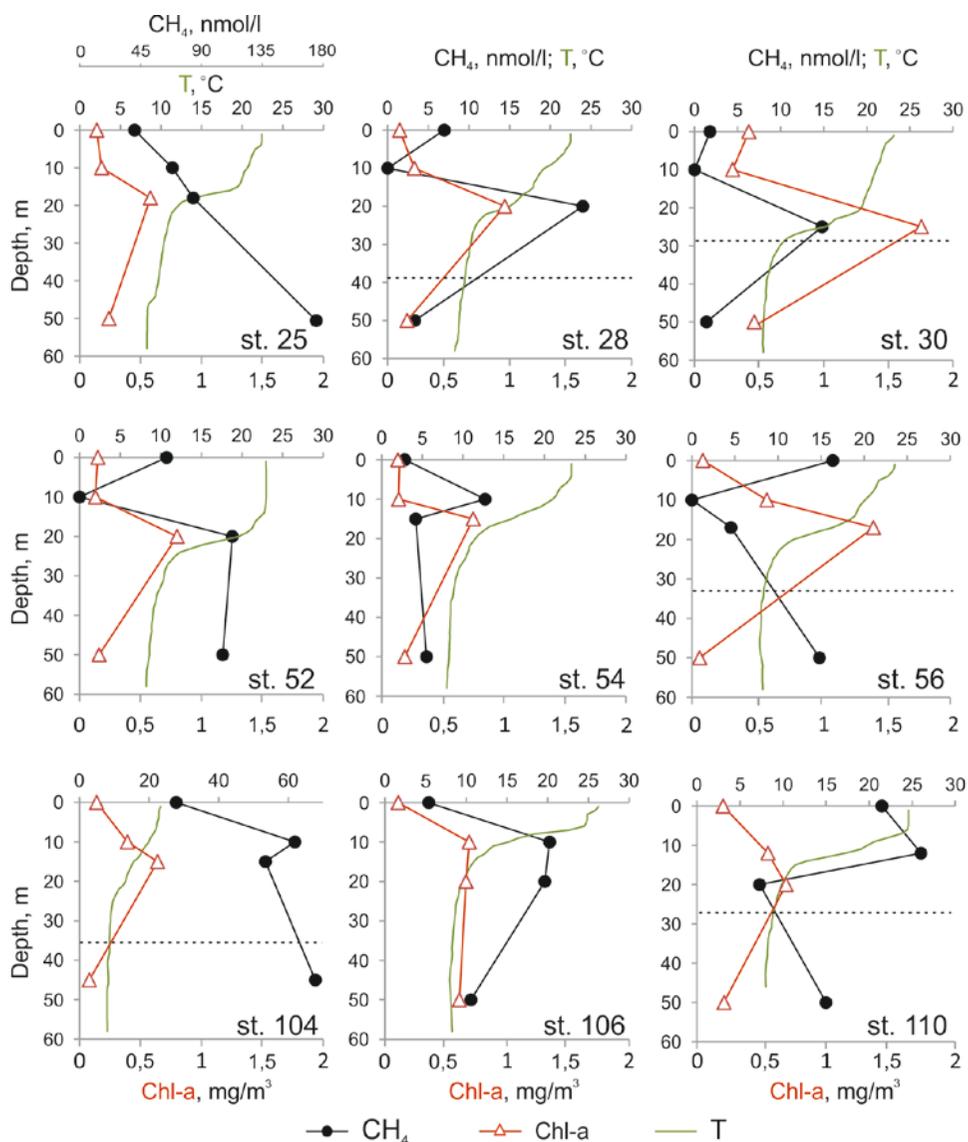
**Fig. 5.** Map of the *Chl-a* and suspended matter  $C_{susp}$  (black columns) spatial distribution in surface water

In the three studied sections (D<sub>1</sub>D<sub>2</sub>, B<sub>1</sub>B<sub>2</sub>, C<sub>1</sub>C<sub>2</sub>), the surface *Chl a* concentration at stations located at a depth of up to 1200 m did not exceed 0.15 mg/m<sup>3</sup>; at deepwater stations located at a depth of up to 1600 m (station No. 30) and more than 2000 m (stations No.56, 110), values of 0.17–0.31 mg/m<sup>3</sup> were obtained.

The suspended matter concentration in the surface layer was in the range of 0.46–1.72 mg(dry)/l at station No. 24 and 103, respectively (Fig. 5).

**The vertical distribution of *Chl a* and methane in the water column.** In Fig. 6 shows the vertical profiles of the methane, *Chl a* and temperature distribution at nine stations of the studied cross-sections. It was shown that at all stations a subsurface maximum of *Chl a* content located in the thermocline zone was found. At the deep sea stations No. 30 and 56 of the west and central cross-sections at 17–25 m depth, *Chl a* concentrations exceeding 1 mg/m<sup>3</sup> were noted. Shape of the vertical distribution of *Chl a* (single-mode profile) is typical for the summer season, when the highest stratification of waters during the year is observed. The presence of a deep maximum of *Chl a* may be associated with an increase in its intracellular content, which occurs as a result of the adaptation of algae to low light intensity [26]. A change in the species composition of phytoplankton can also be observed with depth. It is a consequence of changes in temperature, intensity and spectral composition of light and the availability of nutrients [27].

For the coastal stations No. 25, 52 and 104, the methane concentration increase from the surface to the bottom is characteristic, while in most of the others the maximum was located in the subsurface layer and spatially coincided with the maximum of the *Chl a* content (Fig. 6).



**Fig. 6.** Vertical profiles of CH<sub>4</sub> concentration, *Chl-a* and temperature distribution in the upper 50 m layer. Dotted line marks the euphotic zone depth. At the stations where the euphotic zone depth is not indicated, work was carried out at night. The temperature and CH<sub>4</sub> scales coincide for all the stations, except for station 25

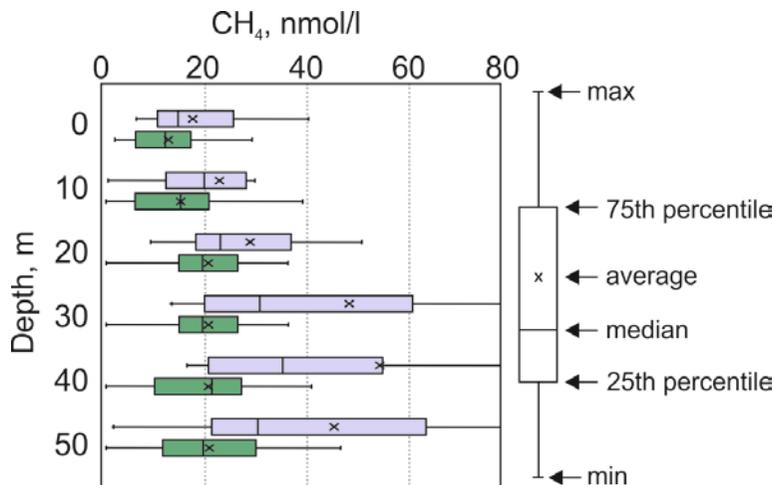
### Discussion

The methane content in the surface water layer of the studied areas, which did not exceed 39.2 nmol/L, turned out to be on average 4 times less than the technologically loaded Sevastopol Bay during the same observation season [28]. Most of the studied sea area was the methane income source into the drive layers of the atmosphere, with the exception of 15 stations out of 104, where the CH<sub>4</sub> concentration in the surface layer was below equilibrium values. The calculated integral CH<sub>4</sub> flux for the summer season

from an area of 88,000 km<sup>2</sup> was 3.2 tons per day, taking into account that the mean value of methane emission to the atmosphere was 2.3 μmol/m<sup>2</sup>/day.

It is known that for relatively shallow shelf stations, the structure of the vertical distribution of methane can be significantly affected by its fluxes from bottom sediments [19]. In this regard, in order to assess the regularities of the vertical distribution of methane, all the stations studied in this respect were divided into two conditional groups: stations, the depth of which reached the anaerobic zone ( $\sigma_t > 16.2$ ), and the open shelf stations ( $\sigma_t < 16.2$ ). The first group includes 27 stations with depths of 161–2,110 m, the second group includes 21 stations with depths of 28–140 m.

The studies in 2002 [7] showed that methane in the aerobic zone of the Black Sea is unevenly distributed. In surface water masses, layers enriched in methane were observed. They were separated from deep waters, where the concentration exceeded the surface by 2–3 orders of magnitude, with zones of low methane content. These data show that methane diffusing from the anaerobic zone due to the concentration gradient was oxidized at the upper boundary of the redox zone, and individual layers of the aerobic zone had their own source of methane production [7]. As in previous studies, the same concentration subsurface maxima of CH<sub>4</sub> were found: in the first group, at 68 % of the stations, in the second – at 33 %, while at the majority of offshore stations, an increase in concentration was observed from the surface to the bottom (Fig. 7). The maximum methane content in both groups of stations was located at depths of 20–40 m. Fig. 7 shows the vertical distribution profiles of dissolved methane in the water column for two groups of stations. It was shown that, on average, the methane concentration for deep-water profiles was two times lower compared to shallow ones.



**Fig. 7.** Box-plots of methane concentration in the water column at the deep-sea (green) and shallow (lilac) stations

Anomalously high methane concentrations reaching 269 nmol/l at the bottom were observed in the northwestern Black Sea near the Dnieper paleo-channel (station No. 25 in Fig. 1). It is likely that such methane concentrations in the bottom horizons of the water column are associated with its release from the vultures widespread in this region [2]. It is

known that earlier on the Bulgarian shelf in the bottom waters unusually high concentrations of methane were found, reaching 7070 nmol/L (depth 55 m), which the authors attribute to its coming from seeps [3]. The plume of dissolved CH<sub>4</sub> in the bottom layers of well-stratified waters can extend more than 400 m from the place of bubble gas ejection, and the concentration decreases from 7800 to 250 nmol/l when removed from the seep, as shown in studies in the North Sea [29]. The distance from the station No. 25 to the nearest seeps registered in previous cruises, was about 4.2 km [1]. Possibly, new centers of gas unloading could appear in this area.

The increased concentrations at coastal stations No. 52 and 104 in the bottom layer may be also associated with diffusion from bottom sediments.

Previously, studies carried out in the coastal regions of Crimea in the summer of 2017 on the 96<sup>th</sup> cruise of the R/V *Professor Vodyanitsky* showed that the nature of the vertical distribution of CH<sub>4</sub> and *Chl a* in the water column coincided: their concentrations increased with increasing depth [30]. The stations were located at a depth not exceeding 62 m, and all samples for determining *Chl a* were taken within the euphotic zone. Then the maximum concentration of the studied pigment at a depth where 1 % of PAR penetrates, was recorded. It coincides with previously published data for the Black Sea. [28].

### Conclusion

The article presents data on the methane (CH<sub>4</sub>) content in the euphotic water layer of the northern and northeastern Black Sea in the summer 2018. The CH<sub>4</sub> distribution in this area showed a pronounced spatial heterogeneity. The surface layer dissolved CH<sub>4</sub> concentration for all stations varied in the range 0–39.2 nmol/l. The mean value of the calculated CH<sub>4</sub> flux from water to the atmosphere was 2.3 μmol/m<sup>2</sup>/day, and the average methane saturation of surface water was 460 %. At several deep-sea stations, the CH<sub>4</sub> concentration in water was below equilibrium values, and its fluxes were negative.

A different character of the vertical CH<sub>4</sub> distribution is determined for the coastal and deep-sea areas in the upper 50 m layer. The latitudinal cross-sections studied showed maxima in the subsurface layers; along the coastal cross-section, high CH<sub>4</sub> concentrations, reaching 86 nmol/l, were mainly observed in the bottom layers. It was shown that, on average, the maxima methane concentration values for deep-water profiles are 2 times lower compared to shallow ones.

An abnormally high methane content reaching 269 nmol/l at the bottom was determined at a station located in the northwestern Black Sea in the Dnieper paleo-channel area. This may indicate methane releases from seeps that are widespread in the area.

The similar character of the distribution of CH<sub>4</sub> and *Chl a* in the euphotic zone of the studied Black Sea area is shown. The subsurface CH<sub>4</sub> concentration maxima generally coincided with the location of the *Chl a* content maxima. It was also found that the increased *Chl a* concentration (0.58 mg/m<sup>3</sup>) in the surface layer of the Feodosiya Gulf corresponded to the maximum CH<sub>4</sub> concentration.

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