DOI: 10.22449/2413-5577-2022-1-42-54

Redox Conditions and Characteristics of Bottom Sediments in the Bays of the Sevastopol Region

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Abstract

The paper aims at assessing redox conditions in the bottom sediments of Kamyshovaya Bay in comparison with those in other bays of the Sevastopol region, and at studying the geochemical characteristics of bottom sediments and the chemical composition of pore waters. The data obtained during expedition research onboard the R/V *Victoria* in July 2021 were analyzed. Using the polarographic method of analysis with the use of a glass Au-Hg microelectrode, experimental data were obtained on the vertical distribution of oxygen, hydrogen sulfide, oxidized and reduced forms of iron in the pore waters of Kamyshovaya Bay in summer. Geochemical characteristics of bottom sediments were determined, such as particle size distribution and organic carbon content. The peculiarities of their spatial and vertical distribution were considered. The particle size distribution of sediments in the bay varies. In the upper part of the bay, sediments are represented by shell gravel and sand, and in the central and southern parts, aleurite and pelite silts prevail. The content of organic carbon in the surface layer of Kamyshovaya Bay bottom sediments ranges from 0.3 to 2.2 % dry mass, with an average value of 1.2 % dry mass, which is lower than in other bays of the Sevastopol region. It was found that the main characteristics of pore waters were determined by processes involving dissolved forms of iron (Fe (II, III), FeS) and hydrogen sulfide. In the upper layer of sediments, suboxic conditions were noted, which indicates the development of oxygen deficiency and formation of ecological risk zones for the bay ecosystem.

Keywords: bottom sediments, pore waters, oxygen, polarographic analysis, particle size distribution, organic carbon, Black Sea, Kamyshovaya Bay

Acknowledgements: the work was carried out under state assignment on topic no. 0555-2021-0005 “Complex interdisciplinary research of oceanologic processes, which determine functioning and evolution of the Black and Azov Sea coastal ecosystems” and supported by RFBR grant no. 20-35-90103.

For citation: Kurinnaya, Yu.S., Gurov, K.I., Zabegaev, I.A. and Orekhova, N.A., 2022. Redox Conditions and Characteristics of Bottom Sediments in the Bays of the Sevastopol Region. *Ecological Safety of Coastal and Shelf Zones of Sea*, (1), pp. 42–54. doi:10.22449/2413-5577-2022-1-42-54

Окислительно-восстановительные условия и характеристики донных отложений бухт Севастопольского региона

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Аннотация
Цель работы – оценить окислительно-восстановительные условия в донных отложениях Камышовой бухты в сравнении с другими бухтами Севастопольского региона, изучить геохимические характеристики донных отложений и химического состава поровых вод. Проанализированы данные, полученные в ходе экспедиционных исследований на НИС «Виктория» в июле 2021 г. С помощью полярографического метода анализа с использованием стеклянного Au-Hg-микроэлектрода получены натурные данные вертикального распределения кислорода, сероводорода, окисленных и восстановленных форм железа в поровых водах Камышовой бухты в летний сезон. Определены геохимические характеристики донных отложений: гранулометрический состав, содержание органического углерода. Рассмотрены особенности их пространственного и вертикального распределения. Гранулометрический состав осадков в бухте разнообразен. В верховье бухты отложения представлены ракушечным гравием и песком, а в центральной и южной частях преобладают алевритовые и пелитовые илы. Содержание органического углерода в поверхностном слое донных отложений Камышовой бухты изменяется от 0.3 до 2.2 % сухой массы при среднем значении 1.2 % сухой массы, что ниже, чем в других бухтах Севастопольского региона. Установлено, что основные характеристики поровых вод определялись процессами с участием растворенных форм железа (Fe (II, III), FeS) и сероводорода. В верхнем слое отложений отмечены субкислородные условия, что указывает на развитие дефицита кислорода и формирование зон экологического риска экосистемы бухты.

Ключевые слова: донные отложения, поровые воды, кислород, полярография, гранулометрический состав, органический углерод, Черное море, Камышовая бухта.

Благодарности: работа выполнена в рамках государственного задания ФГБУН ФИЦ МГИ по теме № 0555-2021-0005 «Прибрежные исследования», а также при поддержке проекта РФФИ № 20-35-90103 «Факторы, определяющие потоки кислорода и сероводорода на границе вода – донные отложения в морских экосистемах».

Для цитирования: Окислительно-восстановительные условия и характеристики донных отложений бухт Севастопольского региона / Ю. С. Куринная [и др.] // Экологическая безопасность прибрежной и шельфовой зон моря. 2022. № 1. С. 42–54. doi:10.22449/2413-5577-2022-1-42-54

Introduction

Bottom sediments are a thermodynamically non-equilibrium system with a certain energy reserve, generally determined by the content of the organic matter (OM) and the processes of its transformation [1]. In the *water-bottom* interface, significant gradients of substance concentration are observed with the formation of the flows of substances, which depend on the conditions and characteristics of

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[1] Volkov. I.I.. 1979. *Ocean Chemistry. Vol. 2: Geochemistry of Bottom Sediments*. Moscow: Nauka, 536 p. (in Russian).

both the bottom water layer and the bottom sediments themselves. To the greatest extent, this applies to oxygen and hydrogen sulfide, which are the determining substances in the study of the formation of environmental redox conditions, as well as the components that determine the possibility and conditions for the existence of benthic organisms [1]. It should be noted that hydrogen sulfide is a catalytic poison resulting in respiratory depression and death of benthic organisms [2].

It is known that dissolved oxygen from the surface layer of water enters the bottom layer of water and bottom sediments due to the processes of advection and diffusion. If the rate of its consumption in the oxidation process exceeds the rate of its intake, oxygen deficiency goes poorly. [3]. Nevertheless, the course and intensity of biogeochemical processes associated with the involvement of oxygen primarily depend on the geochemical characteristics of bottom sediments (organic carbon content and particle size distribution of sediments) [4]. The consumption of oxygen for the respiration of microorganisms, as well as its involvement in biogeochemical processes with OM and other reduced compounds, results in the predominance of the process of OM anaerobic oxidation.

Consequently, the reduced forms of nitrogen, metals, and sulfur appear in the upper layer of bottom sediments, and anoxia areas are formed [5]. Thus, the chemical composition of pore waters reflects the biogeochemical processes occurring in bottom sediments [6].

The increase in the number of coastal ecosystems, in the bottom sediments and near-bottom water layer of which oxygen deficiency is observed, is primarily associated with an increase in the OM flow due to anthropogenic activity [7].

Kamyshovaya Bay is a typical example of a marine coastal ecosystem subject to anthropogenic impact. On its shores, the Sevastopol Sea Fishing Port, an oil terminal, two permanent and one emergency sewage outlets, storm drains, a cement plant, a boiler station, and multi-storey buildings are located [8, 9]. The breakwater at the entrance to the bay hinders water exchange with the open part of the sea and contributes to the accumulation of pollutants, including organic carbon, in bottom sediments.

For many years, researchers of the Institute of Biology of the Southern Seas of the Russian Academy of Sciences (IBSS, Sevastopol) have been studying the ecosystem of Kamyshovaya Bay. In [9, 10], the main hydrological characteristics of waters and geochemical characteristics of sediments were studied, and the content of chloroform-extractable substances (CES) and hydrocarbons in the surface layer of bottom sediments of the bay was estimated. It was established that the natural humidity in the bottom sediments of Kamyshovaya Bay varied from 28 to 52 %, its value was close to that of Sevastopol Bay. Oxidized conditions (Eh from +276 mV) in the sands of the mouth of the bay gave way to reduced conditions (Eh up to −59 mV) in the silts of the central part, while pH varied from 7.3 to 8.3. Nevertheless, most of the surface layer of bottom sediments is characterized by oxidized conditions. Pollution of bottom sediments with CEV and oil products was observed in the central part of the bay, while the values of their concentrations here were substantially lower than in other bays of the Sevastopol region [9, 10].

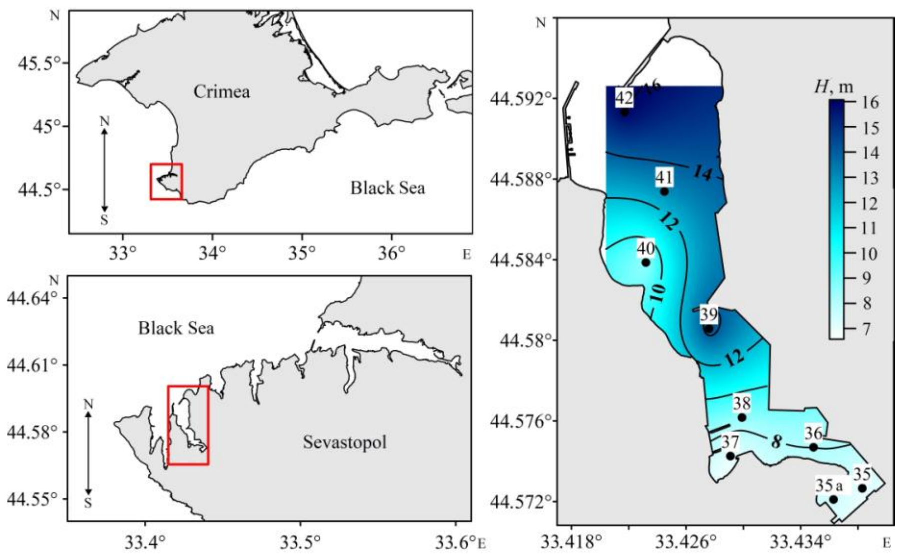
Since 2014, the cargo turnover of the fishing port of Kamyshovaya Bay has decreased, as well as the number of ships entering the port. By 2017, the cargo turnover dropped to 300 thousand tons from 2.5 million tons [10]. Nevertheless, the level of pollution of bottom sediments remains, although in some areas it has been slightly reduced [11]. At the same time, no studies on the features of the spatial and vertical distribution of organic carbon (C_{org}) in the bottom sediments of Kamyshovaya Bay, as well as the vertical distribution of oxygen, hydrogen sulfide and other key components of pore waters, have been previously conducted. Similar studies were carried out for such bays of the Sevastopol Region as Balaklava Bay [12], Sevastopol Bay [4, 13], Omega [13], and coastal regions of the Crimean shelf [14, 15].

This work aims at the assessment of the redox conditions in the bottom sediments of Kamyshovaya Bay and other bays of the Sevastopol Region, studies of the geochemical characteristics of bottom sediments and chemical composition of pore waters.

Materials and methods

Bottom sediment samples to study the physicochemical characteristics of sediments and chemical composition of pore waters were taken in July 2021. A total of nine samples of the surface layer of bottom sediments and two cores were taken (Fig. 1).

Sample taking and preparation of bottom sediments were carried out in accordance with regulatory documents (GOST 17.1.5.01-80; ISO 5667-19:2004). Samples of the upper layer of sediments (0–5 cm) were taken using a Petersen grab. Bottom sediment cores for studying the vertical structure of the sediment



F i g . 1 . Map of bottom sediment sampling stations were taken using Plexiglas tubes, hermetically sealed from above and below. This method of sampling made it possible to preserve the fine structure of the surface layer of bottom sediments and the bottom water layer.

To obtain the chemical profile of pore waters, the polarographic method of analysis was used with a glass Au–Hg microelectrode [4, 16, 17]. A silver chloride electrode saturated with silver chloride was used as a reference electrode, and a platinum electrode was used as an auxiliary one. Profiling of bottom sediment cores was carried out with a vertical resolution of 1 to 10 mm. The main advantage of the method is the ability to analyze the composition of the pore waters of bottom sediments under conditions as close to natural ones as possible, without disrupting the sample and additional sample preparation, with high sensitivity (in particular, O_2 – 5 μM, H_2S – 3 μM). The method error makes 10 %. Using this method, it is possible to study the dynamic processes occurring in the upper layer of sediments, where great varieties of reactions take place, including the mineralization of OM [4, 16, 17]. In the laboratory, to analyze the physicochemical characteristics, the cores were separated into layers 1–2 cm thick using a manual extruder and an acrylic ring.

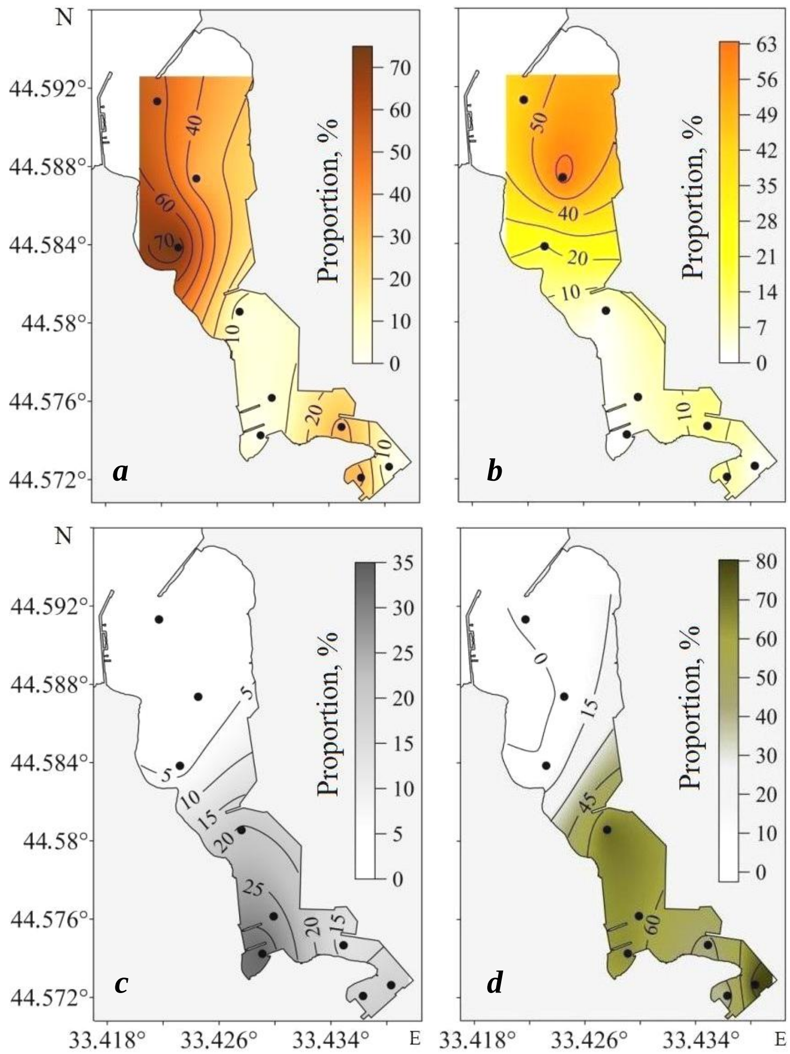
The particle size distribution of bottom sediments was determined by the mass content of particles of various sizes expressed as a percentage, in relation to the mass of the soil dry analysis. In this case, a combined method of decantation and dispersion was used. The aleurite and pelite fraction (≤ 0.05 mm) was separated by wet sieving followed by gravimetric determination of the dry mass. Coarse fractions (> 0.05 mm) were separated by dry screening using standard sieves (GOST 12536-2014).

The content of C_{org} was determined by the coulometric analysis using *AN-7529* express analyzer according to the method adapted for sea bottom sediments [18].

Results and discussion

The particle size distribution of sediments in the bay is diverse (Fig. 2, Table 1). It is established that the average size of sediment particles in Kamyshovaya Bay (1.5 mm) is higher than the average particle size in Sevastopol (0.23 mm), Kazachya (0.45 mm) [19], and Balaklava (0.46 mm) [20] Bays.

In the head of the bay (stations 40–42), sediments are represented by shell gravel and detritus, as well as sand (Fig. 2, *a*, *b*). In this part of the bay, the maximum concentration of coarse-dispersed gravel and pebble material (34–76 %) and the minimum concentration of fine-dispersed pelite-aleuritic silts (1–2 %) are observed. Toward the apex, the proportion of coarse-grained shell material decreases, while the proportion of fine-grained pelite silts increases. In the bay central part (stations 37–39), sediments consist mainly of aleuritic and pelitic silts (Fig. 2, *c*, *d*), and the proportion of the clay fraction in this area makes on average 94 %. Sediments in the southern part of the bay are characterized by the presence of shell detritus (up to 33%), as well as the maximum content of pelite material (81 %) in the apex station (station 35a).



F i g . 2 . Distribution of gravel (*a*), sand (*b*), aleurite and pelite (*c*), pelite and aleurite (*d*) fractions in bottom sediments

The increased proportion of finely dispersed material in the central part and especially in the southern shallow part of the bay is primarily determined by the peculiarities of the morphometry of the bay and a large number of moorings and piers acting as wave shadows resulting in the accumulation of material, as well as by the features of hydrodynamics and weak water exchange. Thus, all the rain and municipal wastewater material accumulates here.

This was reflected in the distribution of organic carbon in the surface layer of bottom sediments of Kamyshovaya Bay (Fig. 3, *a*; Table 1), which varied from 0.3–0.4 % dry wt. at the stations near the bay outlet up to 2–2.2 % dry wt.

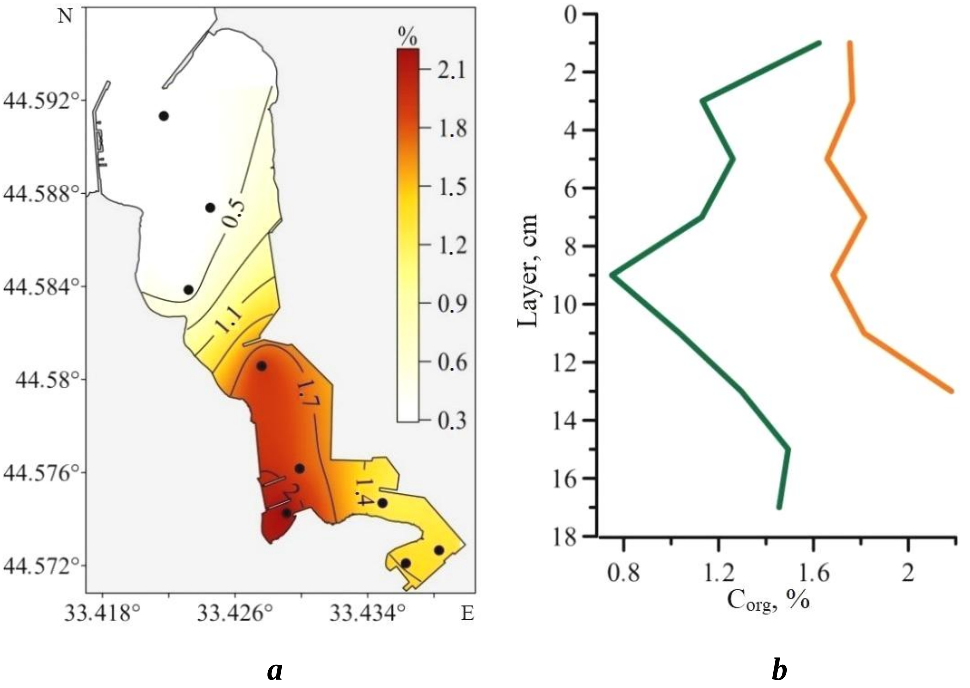
T a b l e 1 . Particle size distribution of bottom sediments and organic carbon content

Station number	Fractions, %				C_{org}, %
	Gravel (10–1 mm)	Sand (< 1–0.1 mm)	Aleurite-pelitic (< 0.1–0.05 mm)	Pelite-aleuritic (< 0.05–0.001 mm)	
42	53.4	44.2	1.3	1.1	0.3
41	33.8	63.6	1.2	1.4	0.3
40	75.8	19.3	3.1	1.8	0.4
39	5.1	2.3	20.7	71.9	1.9
38	5.0	5.1	27.0	63.0	1.3
37	0	1.1	33.7	65.2	2.2
36	33.0	12.1	12.9	42.0	1.2
35	32.8	11.0	17.0	39.2	1.8
35a	0	1.3	18.1	80.6	1.4

at the stations in the central bay with a gradual decrease in its apex. The average C_{org} content in the bottom sediments of Kamyshovaya Bay (1.2 % dry wt.) was lower compared to other bays of the Sevastopol Region: Omega (1.4 % dry wt.), Balaklava (1.97 % dry wt.) [20], Kazachya (2.7 % dry wt.) [21], Sevastopol (3.7 % dry wt.) and Streletskaya (4.3 % dry wt.) Bays [21]. This can indicate the absence of a permanent source of OM in the bay. The maximum values of the organic carbon content were observed in the places of accumulation of finely dispersed material (Fig. 2; 3, *a*). As for the samples of the sediments surface layer, a high positive correlation (0.91) between the concentrations of C_{org} and the content of pelite-aleuritic material was observed.

Except for the spatial variability of the content of organic carbon in the surface layer of bottom sediments, its vertical profile was also studied for stations 35a and 39 (Fig. 3, *b*, Table 2). It was established that for the central bay (station 39), the C_{org} value in the 0–10 cm layer remained practically unchanged (within 0.1 %), while in the 12–14 cm layer it increased, reaching the maximum – 2.2 % dry wt. This nature of the vertical C_{org} can indicate that the level of the man-caused impact on the bottom sediments of Kamyshovaya Bay has not changed in recent years.

For the apex of the southern part of the bay (station 35a), the C_{org} concentration in the 0–10 cm layer decreased from 1.6 % to 0.7 % dry wt., and then increased to 1.5 % dry wt. in the 16–18 cm layer. Elevated C_{org} concentrations in the upper layers of the apex point to the presence of OM sources in this area, probably of anthropogenic origin.



F i g . 3 . Peculiarities of spatial (*a*) and vertical (*b*) distribution of C_{org} in bottom sediments of the bay (green line – St. 35a, orange line – St. 39)

T a b l e 2 . Vertical distribution of organic carbon in bottom sediments

Station number	C_{org}, %, in sediment layer, cm								
	0–2	2–4	4–6	6–8	8–10	10–12	12–14	14–16	16–18
35	1.62	1.13	1.26	1.13	0.75	1.04	1.30	1.49	1.46
39	1.75	1.76	1.66	1.82	1.68	1.81	2.18	–	–

Analysis of the pore waters of bottom sediments showed the development of oxygen deficiency in the upper layer of sediments at station 39 (67 % sat., 163 μM). A similar situation is observed in Sevastopol (122 μM) [13] and Kazachya (126 μM) Bays. As a comparison, the oxygen concentration in the upper layer of sediments in the coastal areas of the Crimean Peninsula shelf varied on average from 200 to 300 μM [4, 15]. Oxygen at station 39 penetrated the sediment to a depth of 2 mm (Fig. 4, *a*). In general, the insignificant depth of oxygen penetration into the sediment can be explained by the finely dispersed nature of the sediments in Kamyshovaya Bay.

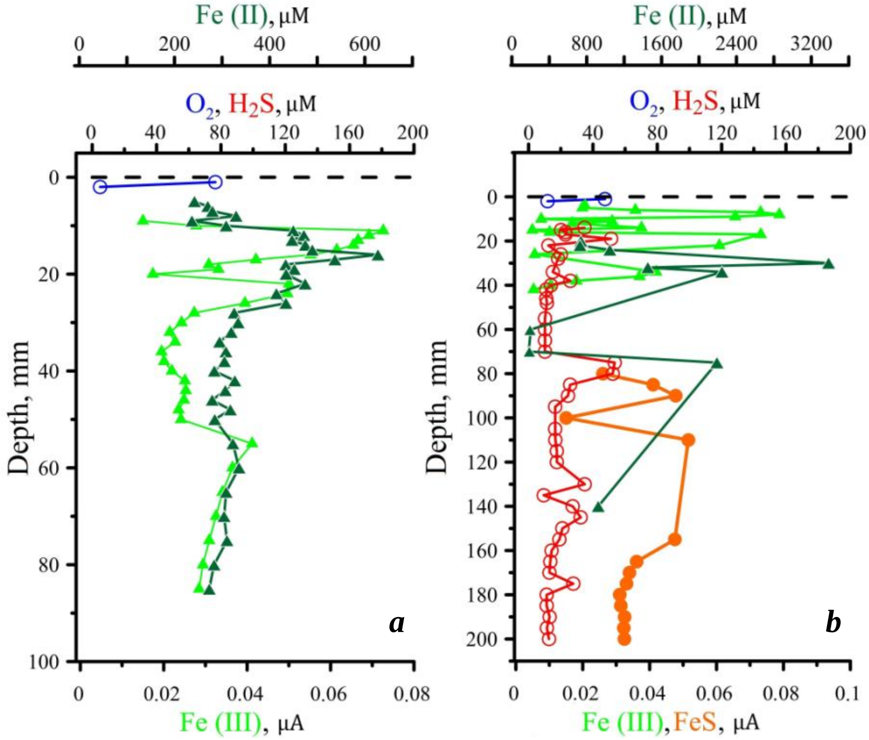


Fig. 4. Vertical profiles of pore waters of Kamyshovaya Bay at Stations 39 (*a*) and 35a (*b*) in July 2021

The main component of pore waters was iron (Fig. 4, *a*). The concentration of Fe (II) increased with depth, reaching its maximum (628 μM) in the 16 mm layer, and then decreasing. The maximum content of Fe (III) was observed in the 11 mm layer, with the features of the vertical distribution similar to those of Fe (II). No hydrogen sulfide was recorded at this station. Thus, suboxygen conditions were observed in the surface layer of bottom sediments. The main biogeochemical processes proceeded with the participation of iron (Fe (II, III)).

In the bottom sediments surface layer in the apex part (station 35a), the oxygen content decreased to 48 μM (20 % sat.). The chemistry of pore waters was determined by processes including dissolved forms of iron (Fe (II, III)) and hydrogen sulfide (Fig. 4b). The pore water predominant component was hydrogen sulfide. In general, its distribution was uniform, with the maxima in the 19 and 75 mm layers (with the values of 51 and 53 μM, respectively). The peak of hydrogen sulfide in the upper part of the core can indicate a 'fresh' source of the organic matter. At the same time, the content of hydrogen sulfide in the pore waters of this area was lower compared to its content in other bays of the Sevastopol Region. Thus, in Balaklava Bay, the maximum concentrations of hydrogen sulfide reached 73 μM [12], in Omega – 213 μM, in Kazachya – 941 μM, in Yuzhnaya – 1,538 μM [13]. As a comparison, on the western coast of the Crimean Peninsula, the concentration of hydrogen sulfide in bottom sediments reached 276–435 μM [15]. At the same time, the pore waters of bottom sediments in the apex part of Kamyshovaya Bay were characterized by a high content of Fe (II) with a maximum concentration of 3,384 μM in the sediments upper layer (0–30 mm). The obtained values are significantly higher than in Balaklava (861 μM) and Kazachya (2,005 μM) Bays, and are close to the value obtained at the station in the Yalta Region (4,500 μM) [15], but lower than in Yuzhnaya Bay (8,292 μM). Based on the vertical profile of the pore waters components, it can be concluded that suboxygen conditions are still observed in the upper part of the sediment (0–10 mm), but anaerobic conditions predominate below.

Conclusions

New field data on the chemical composition of pore water (vertical distribution of oxygen, hydrogen sulfide, oxidized and reduced forms of iron) and geochemical characteristics of bottom sediments (particle size distribution, organic carbon content) for Kamyshovaya Bay are obtained and analyzed.

It is established that the chemistry of pore waters is determined by processes involving dissolved forms of iron (Fe (II, III)) and hydrogen sulfide. Suboxygen conditions are observed in the upper layer of sediments, which indicates the formation of zones of ecological risk in the ecosystem of the bay.

In the head of the bay, sediments are represented by shell gravel and sand, and in the central and southern parts by aleurite and pelite silts. The content of organic carbon in the surface layer of the bottom sediments of Kamyshovaya Bay varies from 0.3 to 2.2 % dry wt., which is lower than in other bays of the Sevastopol Region.

The analysis of the obtained results suggests the absence of significant permanent sources of OM. Nevertheless, despite the previously observed general decrease in the man-caused impact on the ecosystem of the bay in recent years, the content of OM increases. Apparently, the increase in the content of OM against the background of a decreasing man-caused impact is explained by the influence of such natural factors as the influx of terrigenous material with storm drains, the morphology of the apex of the bay, its weak water exchange with other parts of the water area and with the open sea.

The continuation of such trends can lead to a change of the currently observed suboxygen conditions in bottom sediments by anaerobic ones. The risk of suffocation phenomena will increase resulting in the appearance of lifeless spaces in the water area.

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Submitted 29.10.2021; accepted after review 20.12.2021;
revised 4.02.2022; published 25.03.2022

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All the authors have read and approved the final manuscript.