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REDOX CONDITIONS OF BOTTOM SEDIMENTS AND MACROZOOBENTHOS CHARACTERISTICS IN THE KRUGLAYA AND KAZACHYA BAYS (SEVASTOPOL)

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A lack of systemic and environmentally efficient approach to exploitation of the Kruglaya and Kazachya bays (Sevastopol) resulted in their severe pollution. The conjunction of natural and anthropogenic factors led to deterioration of habitat conditions of benthic communities. The aim of this work was to carry out complex research of Kruglaya and Kazachya bays' ecosystems to study peculiarities of formation of redox conditions in bottom sediments and bottom water layer, as well as their effect on macrozoobenthos characteristics. Bottom sediments were sampled by diver in plexiglass tubes hermetically sealed at the top and bottom; it helped in preserving a fine structure of bottom sediments and bottom water layer. To study benthic communities, samples were taken in the same spot with a manual sampler. To obtain chemical composition of pore waters with high vertical resolution, the voltammetry analysis was carried out. Calculation of an oxygen flux at the boundary and in the upper layer of bottom sediments was performed according to the vertical profile of oxygen concentration in pore waters and geochemical analysis with applying the equation for the Fick's first law and considering concentration gradient and molecular diffusion of oxygen in pore waters. Standard hydrobiological methods were applied for the analysis of benthic material. When calculating the values of the Shannon diversity index (*H'*), the binary logarithm was used. The data analysis showed as follows: a high level of anthropogenic load and restricted water dynamics resulted in siltation of bottom sediments in the studied water areas, which obstructed oxygen penetration; the accumulation of organic carbon contributed to its active consumption. Stratification of a water column due to limited water exchange, high temperature of bottom water, accompanied by a decrease in oxygen solubility, and finely dispersed nature of bottom sediments contributed to the fact that the rate of oxygen input was lower than the rate of oxygen consumption for organic matter oxidation. This was followed by the development of oxygen deficiency zones and emergence of reduced compounds, in particular hydrogen sulfide. Importantly, suboxic conditions prevailed in the upper sediment layer, and anaerobic conditions prevailed below. Due to this, the main forms of macrozoobenthos were species tolerant to oxygen deficiency and organic pollution. Specifically, in some spots of the Kazachya Bay, polychaetes alone were recorded. At the same time, in the Kruglaya Bay mouth area, intense water dynamics and morphological peculiarities of bottom sediments contribute to saturation of the upper sediment layer with oxygen. Based on oxygen concentration data for the surface (0–5 mm) sediment layer (pore waters) and on geochemical peculiarities of bottom sediments (moisture and porosity), the oxygen flux at st. 4 (the Solenaya Bay) was calculated; the value was 0.73 $\mathrm{M \cdot m^{-2} \cdot year^{-1}}$. Considering oxygen concentration in bottom water layer (259 μM), the time for complete depletion of oxygen or its renewal is about 5 months if taking into account biogeochemical processes alone. Hence, it can be assumed that the ecosystems of the Kruglaya and Kazachya bays are in the stage of degradation. Their further exploitation without a developed systemic and rational approach will result in a critical deterioration of the ecosystems – the emergence and spread of environmental risk zones. It will reduce the recreational and socioeconomic attractiveness of these areas.

Keywords: sediments, pore water, oxygen, hydrogen sulfide, organic carbon, macrozoobenthos, coastal waters, Black Sea

Marine coastal ecosystems play an important role in human life (Harley et al., 2006). Those are involved in all spheres of economic activity and are largely subject to anthropogenic load, which affects their physicochemical and biological characteristics, as well as ecological state of the ecosystem in general (Cabral et al., 2019 ; Ducrotoy, 2021 ; Rabalais et al., 2009). Any external effects have a fairly quick response. Under favorable conditions, ecosystems are capable of recovering; however, under prolonged anthropogenic load and exposure to certain natural physical and physicochemical factors, natural balance is disrupted, and the system degrades (Rabalais et al., 2009). Out of coastal marine ecosystems, those with limited water exchange are the most susceptible to destruction. There, under certain conditions, water stratification occurs, sediments are silted, and pollutants and organic carbon accumulate in bottom sediments, which affects the state of benthic communities and results in formation of zones of ecological risk (Ovsyanyi & Orekhova, 2019 ; Orekhova et al., 2019a).

The bays of the Sevastopol region belong to the type of ecosystems, in which the accumulation of organic matter in bottom sediments prevails over destruction (Ignat'yeva et al., 2008 ; Orekhova & Konovalov, 2018b ; Orekhova et al., 2019b ; Osadchaya et al., 2003). Depletion of oxygen for the oxidation of organic matter and other reduced compounds leads to a shift in the processes, which occur due to anaerobic oxidation of organic matter, closer to the surface of bottom sediments (Orekhova & Konovalov, 2009, 2018a, 2018b). Thus, in the upper sediment layer, reduced forms of nitrogen, metals, and sulfur predominate, and anoxic zones with anaerobic conditions are formed. An increase in the content of reduced compounds, in particular the concentration of sulfides, results in a rise in their flux into bottom water layer (Orekhova & Konovalov, 2018b). In this case, anaerobic conditions are formed not only in bottom sediments, but also in water column (Berlinsky et al., 2003 ; Meysman et al., 2003). Such changes in physicochemical characteristics of ecosystems are reflected in their ecological status and, as a result, in the socioeconomic attractiveness of the region.

To study the ecological state of Sevastopol coastal waters, the Kazachya and Kruglaya bays were chosen, which have high social and recreational significance for the region.

Earlier studies of these bays (Zaika et al., 2011 ; Mironov et al., 2002, 2003 ; Mironova & Pankeeva, 2019 ; Sanitary and Biological Studies, 2018 ; Soloveva et al., 2019) showed as follows: over the last 10–15 years, their ecosystems have undergone certain changes due to an increase in anthropogenic load. However, there was no comprehensive study of the accumulation of organic matter in bottom sediments, as well as of redox conditions of the environment (including oxygen deficiency) in them and their effect on a benthic community. These investigations are relevant for the region due to an increase in the number of sources and flux of organic matter inputted into the water area of the bays.

MATERIAL AND METHODS

We used the data on the analysis of bottom water layer, pore waters, and bottom sediments sampled in two bays in September 2019.

The Kazachya Bay is located in the southwestern Heracles Peninsula (Fig. 1) (Mironov et al., 2002 ; Ovsyanyi & Orekhova, 2019). This water area is characterized by free water exchange with the deep sea and is one of the objects of the nature reserve fund of the Sevastopol region (Mironov et al., 2003). Until recently, it was considered one of the cleanest Sevastopol bays (Mironov et al., 2003). To date, its coast is actively used as a recreational area: sandy and pebble beaches are located in the top of the bay. However, active construction on the bay coast and development of a new residential zone with the appropriate infrastructure, with year-to-year rising area and population, led to a significant increase in anthropogenic load on its ecosystem (Soloveva et al., 2019).

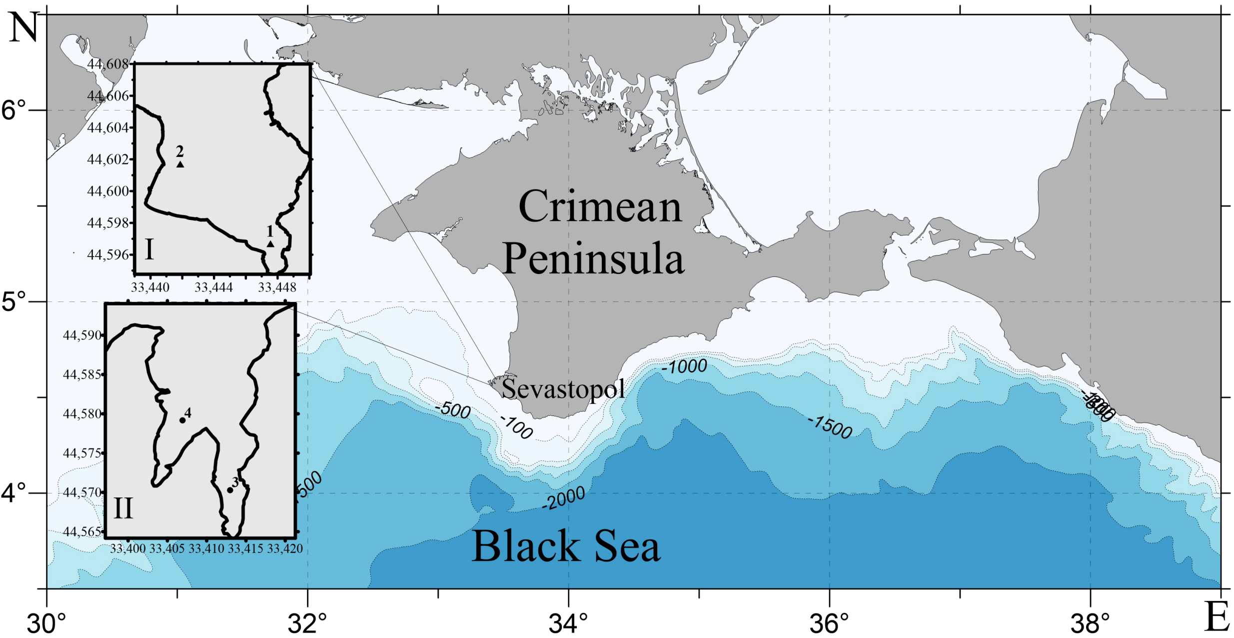

Fig. 1. Scheme of sampling stations in the bays of the Sevastopol region: I, the Kruglaya Bay; II, the Kazachya Bay

The Kruglaya Bay, the shallow one, is located in the northern Heracles Peninsula between Dvoinaya and Streletskaya bays (Fig. 1); it is of the semi-enclosed type (Mironova & Pankeeva, 2019), with limited water exchange (Zaika et al., 2011). During cold season, the bay waters are well aerated due to their dynamics and vertical convective mixing. During warm period, because of a seasonal thermocline determining the two-layer structure of waters, vertical water stratification and weak ventilation of bottom layer at a relatively high temperature are characteristic (Zaika et al., 2011). An increase in temperature promotes intensive oxygen consumption when it is involved in various biological and chemical processes (Zaika et al., 2011). The Kruglaya Bay is a recreational area as well, with resting places, city beach, and entertainment centers. At the same time, there is an emergency runoff of sewage water; therefore, during summer, sanitary and epidemiological indicators often do not meet the standards (Sanitary and Biological Studies, 2018). Intensive construction of the microdistrict, arrangement of the beach area, and a rise in the number of small boats on the eastern coast resulted in an increase in anthropogenic load on the bay ecosystem (Sanitary and Biological Studies, 2018). All this negatively affects its ecological state. There can be an additional source of organic matter and pollutant input into the bay due to water exchange with the adjacent area: contiguous semi-enclosed bays with numerous permanent, local, emergency, and unauthorized wastewater discharges (Kuftarkova et al., 1999). The maximum load on the bay waters falls on summer.

The samples were taken by diver in plexiglass tubes hermetically sealed at the top and bottom. Depth of the tube immersion was limited by the nature of the sediments. The columns sampled were transferred in a strictly vertical position to preserve a fine structure of bottom sediments and bottom water layer. At each point, bottom sediment columns were sampled in one replication. To study benthic communities, samples were taken in the same spot in duplicate, with a manual sampler with an area of 0.025 m^2. Water temperature in the samples was of +22…+24 °C.

In the Kruglaya Bay, bottom sediment columns were sampled in the apex (st. 1; N44.597°, E33.448°; Fig. 1) and in the mouth area (st. 2; N44.602°, E33.442°; Fig. 1). The sampling points were chosen considering different sedimentation conditions and sources of organic matter input. The shallow (sampling depth of 0.5 m) bay apex is most exposed to anthropogenic load, and due to the remoteness from the bay mouth, water stagnation often occurs there. Moreover, in the bay apex, there are sources of pollution: runoff from storm sewers and permanent outlets of untreated domestic wastewater (Kuftarkova et al., 2008). This contributes to organic matter accumulation and oxygen consumption in bottom sediments and bottom water layer. In the bay mouth area (st. 2), the depth is of 10 m; an underwater coastal abrasion slope is located there (Mironova & Pankeeva, 2019). In this area, active hydrodynamic effect, peculiarities of bottom topography, and absence of significant and permanent sources of organic matter contribute to the saturation of bottom water layer and sediment surface with oxygen.

In the Kazachya Bay, samples were taken in the central areas of the eastern branch (st. 3; N44.570°, E33.413°; Fig. 1) and of the western one – in the Solenaya Bay (st. 4; N44.579°, E33.407°; Fig. 1). Sampling depths were of 3.5 and 13.6 m for st. 3 and st. 4, respectively. The water exchange is not limited (Mironov et al., 2003), but these areas are under significant anthropogenic load due to dense settlement of the shores and location of infrastructure facilities (Ovsyanyi & Orekhova, 2019).

The voltammetry analysis with the use of a glass Au/Hg microelectrode was carried out to obtain a chemical profile of pore waters with high vertical resolution (1–5 mm) (Brendel & Luther, 1995 ; Orekhova & Konovalov, 2009). This method allows to quantify electrochemically active compounds in pore waters, primarily oxygen, sulfides and other reduced forms of sulfur, and reduced forms of iron and manganese; the method error does not exceed 10 % (Orekhova & Konovalov, 2018b).

Organic carbon content (C_{org}; % dry weight) in bottom sediments was determined by coulometry on an AN-7529 express analyzer according to a technique adapted for marine sediments (Ljutsarev, 1986). The method error does not exceed 10 % (about ± 0.2 % dry weight).

The calculation of an oxygen flux at the boundary and in the upper layer of bottom sediments was carried out according to the data of voltammetry and geochemical analyses with applying the equation for the Fick's first law considering concentration gradient and molecular diffusion of oxygen in pore waters (Hyacinthe et al., 2001):

$$J = -\varphi D_s dC/dZ \,, \tag{1}$$

where J is the flux, mol·($year^{-1}$·m^{-2});

φ is porosity;

D_s is the coefficient of molecular oxygen diffusion taking into account the viscosity, m^2·$year^{-1}$;

dC/dZ is the concentration gradient, mol·m^{-4}.

Molecular oxygen diffusion coefficients in pore waters were taken from (Meysman et al., 2003). When calculating these coefficients, temperature of bottom water layer, which was measured immediately at the time of sampling, was taken into account.

Considering the high rate of sedimentation processes in the coastal zone, short time for diagenetic processes of bottom sediments compaction, high intensity of intra-annual dynamics of bottom sediments, and high rate of redox biogeochemical processes, the effect of advective currents was not taken into account.

Benthic samples were washed through a sieve with a 1-mm mesh and fixed in ethanol. Further processing of the fixed material was carried out under laboratory conditions. Species were identified according to the guides (Opredelitel', 1968, 1969, 1972). Bivalves were weighted after their dissection and removing the fixative solution from the mantle cavity. At each station, biomass (g·m^{-2}) and abundance (ind.·m^{-2}) of a separate species were calculated from the total benthic sample. The values of the Shannon diversity index (*H'*) (the binary logarithm was used) and Pielou evenness index were calculated in the Diverse application of the PRIMER-5 package.

RESULTS

The height of the column sampled in the Kruglaya Bay apex (st. 1) was of 25 cm. Sediment is represented by gray and dark gray silted sand. The sediment surface in the sampling area was covered with a layer of vegetation. Based on the works of Mironova and Pankeeva *et al.* (Mironova & Pankeeva, 2019 ; Pankeeva et al., 2019), it can be assumed that this is a community of seagrasses and green algae, mainly Cladophora species on silty sediments.

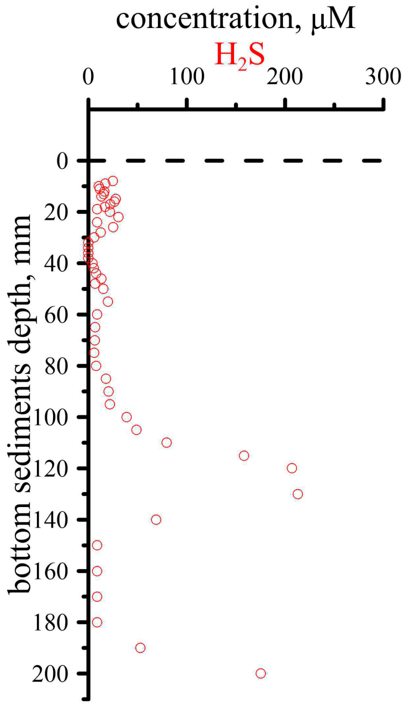

Fig. 2. Vertical profile of hydrogen sulfide in pore waters of bottom sediments sampled in the Kruglaya Bay (st. 1)

The finely dispersed nature of sediment and the organic matter content of about 1.97 % contributed to active oxygen consumption. Thus, in bottom water layer, oxygen saturation of 56 % was observed; directly above the surface of seagrasses and on the sediment surface, it dropped down to 19 %, which corresponds to hypoxia (Zaika et al., 2011). In the layer down to 7 mm, no voltammetrically active compounds were detected (Brendel & Luther, 1995 ; Orekhova & Konovalov, 2009), which may indicate the occurrence of processes with oxidized forms of nitrogen in this depth interval (Orekhova & Konovalov, 2009). Below, hydrogen sulfide appears, with non-uniform distribution (Fig. 2). In the depth interval of 8–30 mm, hydrogen sulfide concentration varies within 9–31 μM. This is followed by the interval of 32–40 mm, in which hydrogen sulfide concentration is below the detection limit (3 μM) or there is no hydrogen sulfide. In the layer of 42–140 mm, hydrogen sulfide concentration increases with depth, reaching a maximum of 207 μM at 120 mm, and then decreases. In the depth interval of 150–180 mm, hydrogen sulfide concentration is constant and amounts to 9 μM; it sharply increases from 190 mm, reaching 175 μM at 200 mm. Further profiling was not performed.

At st. 2 (see Fig. 1), sediment is represented by sand; the height of the column sampled is of 9 cm. Free water exchange, bottom peculiarities (Mironova & Pankeeva, 2019), and absence of organic matter sources contribute to oxygenation of bottom water layer. In bottom water layer and in upper sediment layer, oxygen saturation of 100 % was recorded.

In the central area of the eastern Kazachya Bay (st. 3, Fig. 1), a significant predominance of silty material contributed to organic carbon accumulation (to date, its content reaches ≈ 7 %). High content of organic matter leads to oxygen consumption in bottom water layer and on the sediment surface for its oxidation (Orekhova & Konovalov, 2009). Oxygen concentration in bottom water layer (10 cm above the sediment surface) corresponded to saturation of 65 %. Such oxygen concentration at a sampling depth of 3.5 m indicates the development of oxygen deficiency.

On the sediment surface, oxygen concentration decreases down to 100 μM (saturation of 40 %); below, all oxygen is depleted (Fig. 3a). No voltammetrically active compounds were found in the depth interval of 1–20 mm (Orekhova & Konovalov, 2009, 2018b), which allows to suggest the occurrence of biogeochemical processes of organic matter mineralization mainly with nitrates/nitrites involved. Mosaic signals corresponding to reduced iron and manganese with concentrations of about 2 and 3 μM, respectively (Fig. 3a), may indicate the occurrence of processes with these compounds involved. Below, hydrogen sulfide appeared (Fig. 3a). With depth, concentration of sulfides varied within 36–346 μM; other components were not detected.

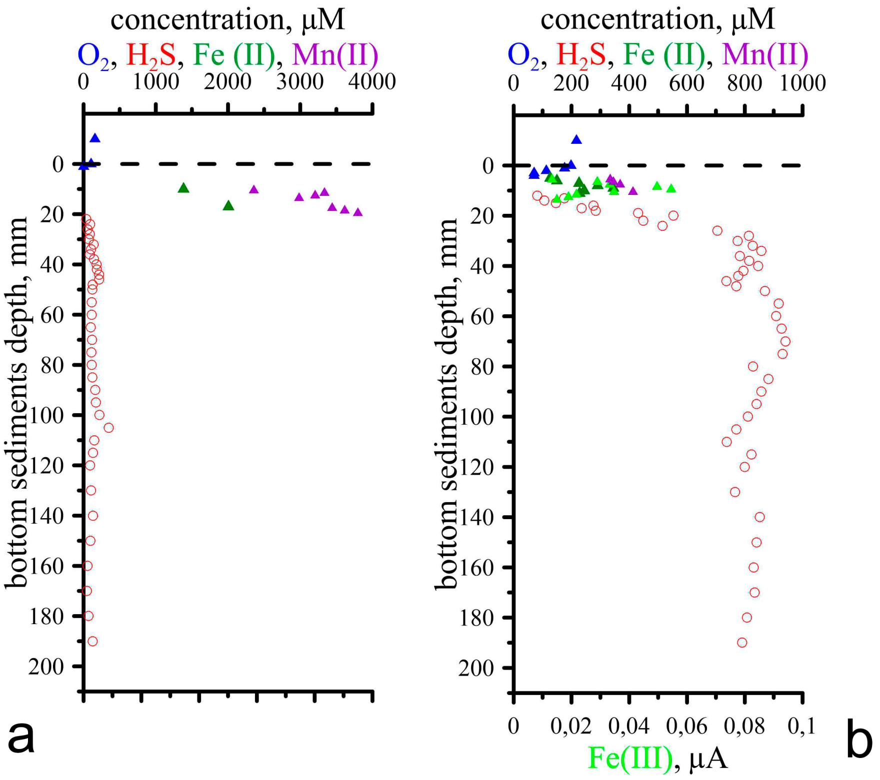

Fig. 3. Vertical profile of the chemical composition of pore waters of bottom sediments sampled at stations 3 (a) and 4 (b) in the Kazachya Bay

A sampling depth in the Solenaya Bay (st. 4, Fig. 1) located in the western Kazachya Bay, was of 13.6 m. The column height was of 34 cm; sediment was mainly represented by a finely dispersed fraction. However, the appearance of sampled sediment differed from the previous ones: in the upper 2-mm layer, a fluff layer was recorded; in the depth interval of 2-20 mm, gray-brown sand was found; and below, homogeneous dark gray silted sand was registered.

In bottom water layer, oxygen concentration corresponded to saturation of 97 %. On the sediment surface, oxygen concentration decreases down to 200 μM (saturation of 80 %). It penetrated into the sediment down to 4 mm (Fig. 3b). From 5 mm, Fe(III) appears; its intensity [due to the formation of colloidal solutions, Fe(III) concentration cannot be determined analytically (Brendel & Luther, 1995)] increases with depth, reaching a maximum at 9 mm, and then decreases; from 14 mm, its signal disappears. In the layer of 5–11 mm, signals are recorded corresponding to reduced forms of iron and manganese. Iron and manganese concentrations averaged 230 and 365 μM, respectively (Fig. 3b). From 11 mm, hydrogen sulfide appears; its concentration is 82 μM; it increases up to 942 μM with depth. In hydrogen sulfide distribution, two "depth intervals" can be distinguished: 12–110 mm (there, concentration of sulfides first increases, reaching a maximum value (942 μM) at 70 mm, and then decreases) and 120–200 mm (it is a layer of insignificant increase and decrease in sulfide concentration, but the value varies within 767–852 μM).

Based on the data on oxygen concentration in the surface (0–5 mm) sediment layer (pore waters), as well as on material on geochemical composition of bottom sediments, the oxygen flux at st. 4 was calculated: 0.73 $M \cdot m^{-2} \cdot year^{-1}$. Considering oxygen concentration in bottom water layer (259 μM), the time for complete depletion of oxygen is about 5 months if taking into account biogeochemical processes alone.

Table 1 shows the data on oxygen concentration on the sediment surface, depth of emergence of hydrogen sulfide and its concentration, and quantitative indicators of the benthic community in the water areas studied. Table 2 contains the data on macrozoobenthos characteristics (abundance, biomass, Shannon index, and Pielou evenness index) of the Kruglaya and Kazachya bays.

Table 1. Geochemical characteristics of bottom sediments and macrozoobenthos abundance

Station	Oxygen concentration on the sediment surface, μM	Depth of hydrogen sulfide emergence, mm	Mean hydrogen sulfide concentration in bottom sediment column ± *SD*, μM	Hydrogen sulfide concentration range, μM	Macrozoobenthos abundance, $ind. \cdot m^{-2}$
St. 1 (the Kruglaya Bay)	< 20	8	31 ± 30	< DL…213	2,480
St. 2 (the Kruglaya Bay)	238	–	–	–	360
St. 3 (the Kazachya Bay)	< 20	20	126 ± 42	< DL…346	40
St. 4 (the Kazachya Bay)	177	11	696 ± 196	< DL…941	80

Note: *SD* denotes standard deviation; < DL is below the detection limit (3 μM).

Table 2. Macrozoobenthos characteristics (abundance, biomass, Shannon index, and Pielou evenness index) of the water area studied

Class	Species	St. 1		St. 2		St. 3		St. 4	
		N	M	N	M	N	M	N	M
Bivalvia	*Chamelea gallina* (Linnaeus, 1758)	–	–	40	7.52	–	–	–	–
	Mytilaster lineatus (Gmelin, 1791)	80	0.012	120	0.04	–	–	–	–
	Abra segmentum (Récluz, 1843)	1,640	220.8	–	–	–	–	–	–
	Cerastoderma glaucum (Bruguière, 1789)	80	63.6	–	–	–	–	–	–
	Lucinella divaricata (Linnaeus, 1758)	–	–	–	–	–	–	40	0.012
Gastropoda	*Tritia neritea* (Linnaeus, 1758)	40	6.68	–	–	–	–	–	–
	Tritia pellucida (Risso, 1826)	80	33.44	–	–	–	–	–	–
Crustacea	*Ampelisca diadema* (Costa, 1853)	–	–	40	0.32	–	–	–	–
Insecta	*Chironomus* sp.	40	0.016	–	–	–	–	–	–
Harpacticoida		40	0.004	–	–	–	–	–	–
Polychaeta	*Capitella capitata* (Fabricius, 1780)	40	0.008	–	–	–	–	–	–
	Heteromastus filiformis (Claparède, 1864)	40	0.004	–	–	40	0.008	–	–
	Notomastus lineatus (Claparède, 1863)	40	0.004	–	–	–	–	–	–
	Nephtys hombergii Savigny in Lamarck, 1818	–	–	–	–	–	–	40	3.12
	Cirriformia tentaculata (Montagu, 1808)	–	–	160	3.04	–	–	–	–
	Glycera alba (O. F. Müller, 1776)	40	1.56	–	–	–	–	–	–
Ascidiacea		320	17.64	–	–	–	–	–	–
In total		2,480	343.77	360	10.88	40	0.008	80	3.132
Shannon index (log$_2$ based)		1.93	1.56	1.75	1.06	–	–	1.0	0.04
Pielou evenness index		0.46	0.39	0.88	0.53	–	–	1.0	0.04

Note: N denotes abundance, ind.·m^{-2}; M, biomass, g·m^{-2}.

Macrozoobenthos maximum abundance (2,480 ind.·m^{-2}) was recorded in the Kruglaya Bay apex; in its upper layer of bottom sediments, hypoxic conditions were noted. In the bay mouth area, with the maximum oxygen concentration (238 μM) on the sediment surface and with no hydrogen sulfide, macrozoobenthos abundance was an order of magnitude lower (360 ind.·m^{-2}) due to a decrease in bivalve abundance and absence of gastropods, ascidians, insects, and harpacticides (Table 2). In the Kazachya Bay, abundance of hydrobionts was significantly lower; the minimum value (40 ind.·m^{-2}) was registered at the minimum oxygen concentrations on the sediment surface (Table 1).

In the Kruglaya Bay, bivalve molluscs predominated in terms of abundance and biomass. *Mytilaster lineatus* was recorded at both stations; at st. 2, it was the most abundant bivalve species (Table 2). At this station, *Chamelea gallina* predominated in terms of biomass, wherein at st. 1, the species was not found. Gastropods were not recorded. In the bay apex (st. 1), the predominant species in terms of abundance and biomass was the detritus feeder *Abra segmentum*. The same values of abundance were observed for the filter feeders *Mytilaster lineatus* and *Cerastoderma glaucum*. Gastropods were represented by two species: *Tritia neritea* and *Tritia pellucida*.

In the bay apex, ascidians and four polychaetes with the same abundance values were recorded as well: *Capitella capitata*, *Heteromastus filiformis*, *Notomastus lineatus*, and *Glycera alba* (biomass-dominant species). In the bay mouth area, ascidians were absent, and polychaetes were represented by one species: *Cirriformia tentaculata*.

The results of our research show low values of species diversity and abundance for molluscs in the Kazachya Bay. At st. 4, only the bivalve *Lucinella divaricata* was found; gastropods were not recorded. High biomass values in the Kazachya Bay were noted for polychaetes (Table 2) represented by two species of the same abundance: *Heteromastus filiformis* at st. 3 and *Nephtys hombergii* at st. 4. At st. 3, no other representatives of benthic fauna were registered.

DISCUSSION

The results of geochemical analysis provide a basis for understanding the ongoing biogeochemical processes (Volkov, 1973 ; Mitropol'skii et al., 1982 ; Rozanov & Volkov, 2009 ; Khimiya okeana, 1979 ; Orekhova & Konovalov, 2009). Pore waters are an integral part of bottom sediments (Rozanov & Volkov, 2009). The study of their characteristics allows to assess redox and acid-base properties of bottom sediments, content of mobile forms of metals, and possibility of their binding and transition into a solid form of sediments or into the water column (Kuftarkova et al., 1999 ; Mironov et al., 2003).

According to our material and the data of Soloveva *et al.* (2019), mean organic carbon content in bottom sediments of the Kruglaya Bay is 1.67–1.97 %, which is more than 2 times higher than mean organic carbon content in the New Black Sea sediments (0.71 %) and bottom sediments of the Black Sea shelf (Mitropol'skii et al., 1982). Such organic carbon content in bottom sediments contributes to active oxygen consumption and development of its deficiency.

A significant rise in anthropogenic load on the Kazachya Bay water area and its coast resulted in an increase in organic carbon content. According to (Ovsyanyi & Orekhova, 2019), C_{org} content in 2015 averaged 2.74 % (35 % higher than in 2002). To date, C_{org} concentration is about 5.8 %

(the range is 4.32–7.86 %), which is comparable to organic carbon content in bottom sediments of the Sevastopol Bay (Inkerman area, the Yuzhnaya Bay) – the most anthropogenically stressed water area of the Sevastopol region (Orekhova et al., 2019b).

According to the data obtained, in bottom sediments of the Kruglaya Bay, the main processes of organic matter mineralization [their sequence is determined by the thermodynamic characteristics of the system and is described in detail in (Orekhova & Konovalov, 2009)] were carried out with oxidized forms of nitrogen involved (equation 2) in the upper 7-mm layer and sulfates involved (equation 3) in a layer of 8–200 mm in the bay apex (st. 1):

$$C_{106}H_{175}O_{42}N_{16}P + 104HNO_3 \leftrightarrow 106CO_2 + 60N_2 + H_3PO_4 + 138H_2O\,, \tag{2}$$

$$C_{106}H_{175}O_{42}N_{16}P + 59H_2SO_4 \leftrightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 59H_2S + 62H_2O\,. \tag{3}$$

This was facilitated by the presence of a permanent source of organic matter, shallow depth, high temperature of bottom water layer (+24 °C), and limited water exchange.

Hydrogen sulfide distribution obtained may indicate a non-uniform organic matter accumulation due to a shift in the load level in different periods, redeposition resulting from turbidity, *etc.*

In the bay mouth area (st. 2), the absence of a permanent source of organic matter and water dynamics (Zaika et al., 2011 ; Kuftarkova et al., 2008) contributed to the fact as follows: during the period studied, there was enough oxygen to oxidize all organic matter. In the upper layer of bottom sediments (0–20 mm), aerobic conditions were recorded, and the main processes of organic matter oxidation were carried out with the oxygen involved (equation 4) (Orekhova & Konovalov, 2009):

$$C_{106}H_{175}O_{42}N_{16}P + 150O_2 \leftrightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 78H_2O\,. \tag{4}$$

Chemical composition of pore waters and geochemical characteristics of bottom sediments, *inter alia* organic carbon accumulation, as well as water circulation affect characteristics of benthic communities. As known, benthic diversity largely depends on redox conditions of the environment, presence of oxygen / hydrogen sulfide (Zaika et al., 2011), and organic matter content.

Despite the state corresponding to hypoxia in bottom water layer and an insignificant oxygen content (< 20 μM) on the sediment surface, the Kruglaya Bay apex was characterized by the highest macrozoobenthic diversity. In addition to bivalves, polychaetes and ascidians were noted. At the same time, two out of five recorded mollusc species in the Kruglaya Bay, *Abra* and *Cerastoderma*, are resistant to organic pollution (Tikhonova, 2010 ; Tikhonova & Rubtsova, 2012). This fact also indicates a fairly high level of organic pollution. The decrease in macrozoobenthos abundance at st. 2 is determined by geological and geomorphological structure of the underwater relief [it is an underwater coastal abrasion slope composed of psephite deposits with outcrops of bedrock (Mironova & Pankeeva, 2019)] and rather intensive water circulation in this area (Zaika et al., 2011). However, polychaetes are found there as well; a decrease in abundance and biomass (by almost an order of magnitude) of bivalves, absence of gastropods, and presence of crustaceans are registered. The polychaete *Cirriformia tentaculata* recorded in the bay mouth area is less resistant to organic pollution than species previously noted in other bay areas. They are found in spots at some distance from the source of organic matter, in so-called intermediate zones (Dean, 2008). Absence of ascidians in the Kruglaya Bay is characteristic of this water area: 2000 to 2009, they were not found as well (Mironov et al., 2003 ; Sanitary-Biological Investigations, 2009).

Thus, the greatest macrozoobenthic diversity in the Kruglaya Bay is confined to the apex station with silty and sandy bottom sediments (st. 1). In terms of its composition, this area has always significantly differed from other coastal areas (Mironov et al., 2003). On sandy and pebble sediments (st. 2), the diversity and quantitative parameters of macrobenthos are lower than in the mouth area, which also coincides with the data of earlier studies (Mironov et al., 2003). Species composition at the stations corresponds to that in earlier periods.

The Kruglaya Bay water area is distinguished by fluctuations in abundance and biomass, as well as a variability in the predominant species. Specifically, at st. 1 in 1999 and 2002–2004, the mollusc *C. glaucum* prevailed; in 2000 and 2004, *H. acuta*. In the recent period, a variety of crustaceans and polychaetes has been recorded in macrozoobenthos (Mironov et al., 2003). In 2001, a sharp decrease in species abundance was revealed in this area, with polychaetes predominating among four species registered (Mironov et al., 2003). During that period, significant abundance of *M. lineatus* juveniles was observed there (Mironov et al., 2003), as in the present study. It was noted earlier that at st. 1, the level of pollution of marine sediments with petroleum products is still not high enough to exert a depressing effect on species sensitive to this pollutant (Mironov et al., 2003). Besides pollutants, a wave effect has a significant impact on the formation of the community; however, in the points studied at st. 2, it is less notable, and at st. 1, it is practically absent. The latter favorably affects the development of malacofauna (including filter feeders); the accumulation of silt particles in bottom sediments contributes to an increase in the diversity and abundance of detritus feeders (Mironov et al., 2003).

In the Kazachya Bay, despite the better water exchange (Mironov et al., 2002) than in the Kruglaya Bay, the presence of permanent sources of organic matter led to its significant accumulation. Due to high organic carbon concentrations (4.32–7.86 %), oxygen is not the main component during its oxidation, and anaerobic conditions prevail in bottom sediments. There, hydrogen sulfide concentration in bottom sediments is significantly higher than in other bays of the Sevastopol region (Orekhova et al., 2019a ; Orekhova & Konovalov, 2018b). However, different conditions of sedimentation and sources of organic carbon determine as follows: at st. 3 in the upper sediment layer, suboxic conditions are observed, and the main biogeochemical processes are carried out with nitrates/nitrites involved (equation 2) in the 20-mm sediment layer. Below, sulfate reduction occurs, and one of its products is hydrogen sulfide (equation 3). In pore waters of bottom sediments at st. 4, the maximum hydrogen sulfide concentrations (about 900 μM) were noted; however, aerobic conditions were recorded in the upper 4-mm layer, which is probably due to the influx of “fresh” oxygen-enriched waters because of ventilation. Below, anaerobic conditions prevail, with their development resulting from sulfate reduction (equation 3). Moreover, for the Kazachya Bay area, the presence of reduced forms of iron and manganese was registered (Fig. 3) in the upper layer (0–20 mm), which may be associated with their local input *prior* to sampling.

In the bottom sediments of the Kazachya Bay, oxygen deficiency in the upper sediment layer and high hydrogen sulfide concentrations in bottom sediment column led to the fact that the benthic community was not characterized by high abundance and diversity, and polychaetes were the predominant class (Table 2). According to (Mironov et al., 2002 ; Belan & Moshchenko, 2009), *Capitella capitata* is a recognized positive indicator species of organic pollution, resistant to oxygen deficiency and reaching its maximum abundance under severe environmental pollution; *Heteromastus filiformis* is an indicator species of eutrophic waters (Losovskaya, 2011).

In recent years, changes have been observed in the macrozoobenthic community of loose sediments in the Kazachya Bay. According to AZTI Marine Biotic Index (AMBI), in 2003 and 2009, at most of the stations studied in the bay, the “undisturbed” state of benthic communities was recorded, while in 2006, “slightly disturbed” state was registered (Tikhonova & Alyomov, 2012). On sandy sediments, 13 Gastropoda taxa and 11 Bivalvia taxa were found. The ratio of gastropods was 55 and 75 % in 2011–2012 and 2018–2019, respectively; the ratio of bivalves was 45 and 25 %. In 2018–2019, there was a slight decrease in Mollusca abundance: Gastropoda, two times; Bivalvia, four times (Makarov, 2020). In terms of abundance, gastropods *Hydrobia acuta* (Draprnaud, 1805) prevailed: 55 and 70 % in 2011–2012 and 2018–2019, respectively; in terms of biomass, bivalves *Cerastoderma glaucum* (Bruguière, 1789) prevailed: 54 %. The mean abundance of molluscs decreased on average by three times compared to the values of 2011–2012, but the species composition was typical for loose sandy sediments (Makarov, 2020). These data differ from the values obtained in our study. The disparities revealed can be associated with the nature of bottom sediments (loose sandy sediments and silty sediments), sampling depth (coastal samples from a depth of 0.1 m and samples from a depth of more than 13 m), mosaicity of the benthic community distribution, and different oxygen regimes. Similar rearrangements in the benthic community were registered not only on loose sediments of the Kazachya Bay, but also in the epiphyton of *Zostera* seagrass. The number of species in 1970–1971 and 2006–2007 was the same – 13. Species composition for the indicated period practically did not differ. In 2006–2007, instead of *Steromphala divaricata* (Linnaeus, 1758), the species of the same genus was recorded – *Steromphala adriatica* (Philippi, 1844); instead of *Mytilus galloprovincialis* Lamarck, 1819 juveniles, a closely related Mytilidae species was noted – *M. lineatus*. However, mollusc mean abundance and mean biomass decreased significantly. Specifically, in 1970–1971, the mean abundance of Mollusca was 6,182 ind.$\cdot$kg^{-1}, while in 2006–2007, only 257 ind.$\cdot$kg^{-1} (it decreased by almost 25 times). The mean biomass in the early 1970s was 44.2 g$\cdot$kg^{-1}, while in the early 2000s, 8 g$\cdot$kg^{-1} (it decreased by more than 5 times). Moreover, there was a change in the predominant species. In the early 2000s, in terms of abundance and biomass, *Tricolia pullus* (Linnaeus, 1758) prevailed. In the early 1970s, *Rissoa membranacea* (J. Adams, 1800) definitely prevailed, and *Tricolia* was a non-abundant species (Makarov, 2018).

It can be assumed that the changes occurring in the macrozoobenthic community in the Kazachya Bay are caused not only by the anthropogenic factor (hypoxia development due to a recent increase in anthropogenic load on the water area because of the massive construction on the bay coast), but also by long-term fluctuations in abundance of the species themselves, characteristic of this region (Makarov, 2018), and active water dynamics in winter.

Moreover, there is a gradation of a particular species belonging to a certain group in terms of sensitivity to pollution: sensitive, indifferent, and stable ones (Mironov et al., 2003). Sensitive species are those found only in bottom sediments with the I–III pollution levels [these levels were determined by the content of chloroform extractable substances in them (Mironov et al., 2003)] or those characterized by a pronounced decrease in the frequency of occurrence with an increase in the pollution level of bottom sediments. Macrozoobenthic species characterized by the opposite tendency (an increase in the frequency of occurrence with an increase in the pollution level) are attributed to the ecological group of stable. According to this scale, the species recorded in the Kruglaya Bay water area are classified as stable ones (*A. segmentum*, *C. glaucum*, *T. neritea*, *T. pellucida*, and *C. capitata*), sensitive ones (*C. gallina* and *A. diadema*), and indifferent ones (*M. lineatus* and *H. filiformis*). For the Kazachya Bay, one sensitive species was recorded (*L. divaricata*), as well as two indifferent ones (*H. filiformis* and *N. hombergii*).

For the Kruglaya Bay, the Shannon indices calculated for abundance were 1.93 and 1.75 (Table 2). For the Kazachya Bay, the values were much lower: 0 and 1.0. Comparison of values obtained with those of previous studies shows that they are commensurate in Kruglaya Bay: earlier, the index varied 1.14 to 2.14 (Mironov et al., 2003). In the Kazachya Bay, the index is currently significantly lower. Earlier, it averaged 2.04–2.41 and reached 3.47 at some stations (Mironov et al., 2003). The results obtained can be associated with the mosaicity of the benthic community distribution over the bay water area (in the bay apex, the index values are lower), with a small number of samples analyzed, and with changes in habitat conditions. According to the classification of the state of the macrozoobenthic community for loose sediments considering the Shannon index (Water Framework Directive, 2009), it can be assessed as bad for the Kazachya Bay and moderate for the Kruglaya Bay. The Shannon indices calculated for biomass in the bays were low: the values did not exceed 1.56, and at some stations those were close to 0 (Table 2). The Pielou evenness index was rather low in the Kruglaya Bay, which indicates the predominance of particular species in the benthic community (Table 2). One species was recorded in the Kazachya Bay (st. 3), which makes it impossible to calculate the index. At st. 4, the Pielou evenness index is 1.

Analysis of species diversity in the water areas studied shows as follows: the formation of the benthic community, along with concentration of oxygen, hydrogen sulfide, and organic matter in bay bottom sediments, is influenced by habitat conditions of hydrobionts as well: presence of a food base, speed of currents, intensity of organic matter input, granulometric composition of bottom sediments, and wave processes (Neyman & Karpinsky, 2013).

The values of the oxygen flux calculated (0.73 $\mathrm{M \cdot m^{-2} \cdot year^{-1}}$) at water – bottom sediments boundary and time of hypoxia development in bottom water layer in the Solenaya Bay area (st. 4) indicate the following: while maintaining the level of anthropogenic load with no water dynamics there, anoxia conditions in bottom water layer can develop in 5 months. This will undoubtedly result in the appearance of reduced forms of components (metals, nutrients, and sulfur) in the upper sediment layer and worsen habitat conditions of benthic communities.

Conclusion. Stratification of a water column due to limited water exchange, high temperature of bottom water layer, accompanied by a decrease in oxygen solubility, finely dispersed nature of bottom sediments, and high content of organic carbon (up to 7 % in bottom sediments of the Kazachya Bay and up to 2 % in bottom sediments of the Kruglaya Bay) contribute to the fact that the rate of oxygen consumption for organic matter oxidation exceeds the rate of its input. This is accompanied by the development of zones of oxygen deficiency on the surface of bottom sediments and reduced forms of compounds, in particular hydrogen sulfide, in their column.

In the upper sediment layer of the areas studied, suboxic conditions prevail; below, anaerobic ones. This led to the fact that the main forms of macrozoobenthos are species tolerant to oxygen deficiency and organic pollution. Specifically, in the investigated spots of the Kazachya Bay, polychaetes alone were present. The maximum hydrogen sulfide concentrations (up to 900 μM) in bottom sediments of the Solenaya Bay (the Kazachya Bay) are probably due to the presence of an additional source of organic matter there. The calculated time for complete depletion of oxygen in the upper sediment layer (where it was recorded), taking into account biogeochemical processes alone at this station, is about 5 months.

Species diversity of the benthic community in bottom sediments of the studied bays indicates that the determining factors in its formation are not only concentrations of oxygen, hydrogen sulfide, and organic matter in bottom sediments, but also presence of a food base, speed of currents, intensity of organic matter input, granulometric composition of bottom sediments, wave processes, *etc.*

Hence, it can be assumed that a lack of systemic and environmentally efficient approach to exploitation of the Kruglaya and Kazachya bays resulted in their severe pollution, which contributed to the deterioration of habitat conditions of benthic communities. The development of hypoxic conditions on the sediment surface and hydrogen sulfide emergence in the upper sediment layer may indicate that the ecosystems of the Kruglaya and Kazachya bays are in the stage of degradation.

Their further exploitation without reducing anthropogenic load will result in the emergence and spread of environmental risk zones. This will worsen the recreational and socioeconomic attractiveness of these areas.

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ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫЕ УСЛОВИЯ ДОННЫХ ОТЛОЖЕНИЙ И ХАРАКТЕРИСТИКИ МАКРОЗООБЕНТОСА БУХТ КРУГЛОЙ И КАЗАЧЬЕЙ (Г. СЕВАСТОПОЛЬ)

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Отсутствие системного и экологически рационального подхода при эксплуатации бухт Севастопольского региона (бухт Круглой и Казачьей) привело к значительному их загрязнению. Комбинация ряда естественных и антропогенных факторов обусловила ухудшение условий существования бентосных сообществ. Целью данной работы было провести комплексные исследования экосистем бухт Круглой и Казачьей для изучения особенностей формирования окислительно-восстановительных условий в донных отложениях и придонном слое вод, а также их влияния на характеристики макрозообентоса. Пробы донных отложений отбирал водолаз трубками из оргстекла, герметично закрываемыми сверху и снизу, что позволило сохранить тонкую структуру донных отложений и придонного слоя вод. Для изучения бентосных сообществ в этом же месте отбирали пробы с помощью ручного пробоотборника. Для получения химического состава поровых вод с высоким вертикальным разрешением использовали полярографический метод анализа. Расчёт потока кислорода на границе и в верхней части донных отложений выполняли по данным вертикального профиля концентрации кислорода в поровых водах и геохимического анализа, используя уравнение для первого закона Фика с учётом градиента концентраций и молекулярной диффузии кислорода в поровых водах. Для анализа бентосного материала применяли стандартные гидробиологические методы. При расчёте значений индекса разнообразия Шеннона (*H’*) использовали логарифм по основанию 2. Анализ полученных данных показал, что высокий уровень антропогенного воздействия и ограниченная динамика вод привели к заиливанию донных отложений исследуемых акваторий, что затрудняло поступление кислорода в них, а накопление в осадках органического углерода обусловили активное его расходование. Стратификация водной толщи за счёт ограниченного водообмена, высокая температура придонного слоя вод, сопровождающаяся снижением растворимости кислорода, и мелкодисперсный характер донных отложений способствовали тому, что скорость поступления кислорода была меньше скорости его потребления на окисление органического вещества; это сопровождалось развитием зон дефицита кислорода и появлением восстановленных соединений, в частности сероводорода. Отмечено, что в верхнем слое донных отложений преобладали субкислородные условия, ниже — анаэробные. Это привело к тому, что основными формами макрозообентоса являлись виды, толерантные к дефициту кислорода и к загрязнению органическими веществами. Так, на некоторых участках бухты Казачьей присутствовали только полихеты. При этом отмечено, что в районе выхода из бухты Круглой интенсивная динамика вод и морфологические особенности дна способствуют насыщению верхнего слоя отложений кислородом. На основании данных о концентрации кислорода в поверхностном (0–5 мм) слое осадка (в поровых водах), а также данных о геохимических характеристиках (влажность, пористость) донных отложений рассчитан поток кислорода на ст. 4 (бухта Солёная); его величина составила 0,73 $М·м^{-2}·год^{-1}$. Принимая в расчёт концентрацию кислорода в придонном слое вод (259 мкМ), можно сказать, что время развития аноксии с учётом только биогеохимических процессов составляет около 5 месяцев. Таким образом, можно предположить, что экосистемы бухт Круглой и Казачьей находятся в стадии деградации. Дальнейшая их эксплуатация без выработанного комплексного и рационального подхода приведёт к критическому ухудшению их экосистем — к появлению и распространению зон экологического риска, что снизит рекреационную и социально-экономическую привлекательность данных районов.

Ключевые слова: донные отложения, поровые воды, кислород, сероводород, органический углерод, макрозообентос, прибрежные акватории, Чёрное море