

EXPERIMENTAL AND FIELD RESEARCH

POLAROGRAPHY OF THE BOTTOM SEDIMENTS IN THE SEVASTOPOL BAY

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By the method of polarographic profiling performed with the help of an Au-Hg glass microelectrode, we obtained the first high-resolution vertical profiles of the distributions of oxygen, sulfides, oxidized and reduced forms of iron, reduced manganese, and iron monosulfide in pore waters of the bottom sediments in the Sevastopol Bay. It is shown that the regional features of the vertical distributions of the main polarographically active compounds are determined by the combination of several factors: the contents of organic carbon and iron and the sizes of particles of the sediments.

Introduction

The Sevastopol Bay is one of marine water areas subjected to strong permanent anthropogenic influence. On the one hand, the bay plays the role of a city-forming element of the geosphere. On the other hand, for a long period of time, it serves as a naval base with all typical industrial and economic infrastructures. The intense many-year investigations of the consequences of influence of the city and navy upon the ecosystem of the bay [1] are directed toward the analysis of the hydrological, hydrochemical, and biological characteristics of waters and the mean characteristics of the upper layer of bottom sediments [2]. In the present work, we consider the possibility of application of the method of polarographic profiling to the investigation of the processes running in bottom sediments.

The Sevastopol Bay is an estuary-type water area of about ~7 km in length with a mean width of ~1 km. Its mean depth is equal to 12 m and the maximum depth to 22 m [2]. The Sevastopol Bay is characterized by high rates of accumulation of sediments: 2.4 mm/yr [3]. The municipal sewage of the city plays the role of a source of large amounts of biogenic elements coming into the bay. The ecosystem of the Sevastopol Bay reached the eutrophic level, whereas some parts of the bay (e.g., the Yuzhnaya Bay) are characterized by the hypertrophic stage accompanied by the development of hypoxia in the bottom layers of water and the accumulation of organic carbon in the bottom sediments. The discharge of industrial wastes into the water area of the bay results in the accumulation of various metals in the sediments [2]. Under certain conditions, these sediments may turn into a source of secondary pollution of the entire water column. The variations in the physicochemical conditions (especially in the pH values and Eh), e.g., the oxidation of anaerobic sediments due to their periodic roiling (the Sevastopol Bay is a zone of intense navigation), may lead to changes in the degree of oxidation of the metals accumulated in the sediments. This, in turn, is accompanied by the changes in the migration ability of the metals, which become better accessible for the microorganisms [4, 5]. The exhaustion of the supply of oxygen in marine systems due to the restriction of its flow or as a result of the increase in the rate of its consumption leads to the formation of hydrogen sulfide and its interaction with metals.

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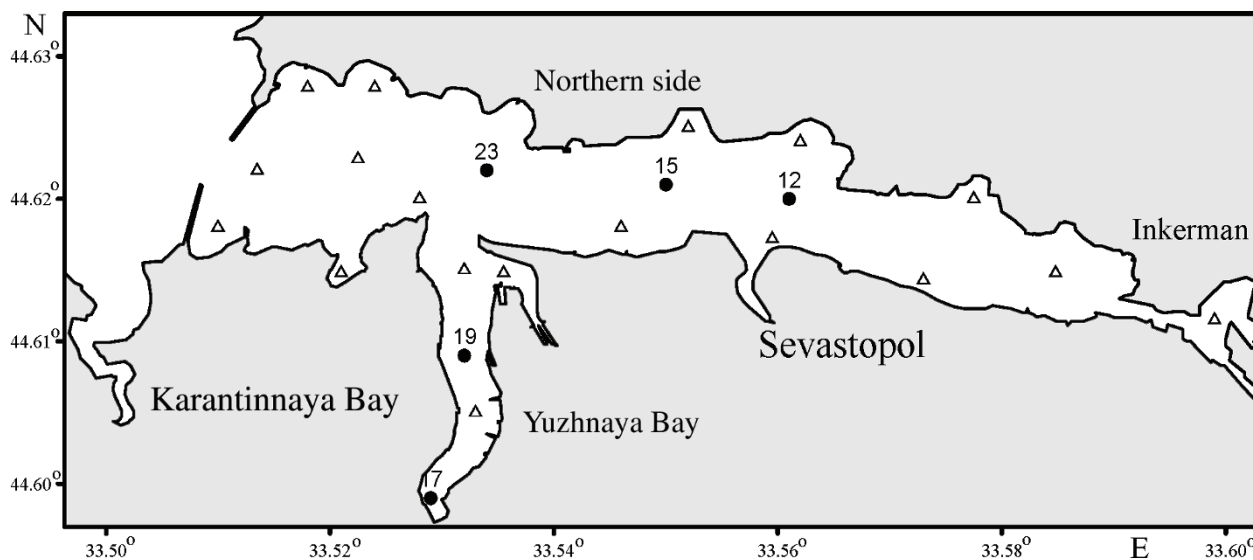


Fig. 1. Schematic diagram of location of the stations made for sampling (the dark circles mark the stations used for polarographic investigations).

As a result of the oxidation of hydrogen sulfide in variable flows of oxidizers and reducers, we observe the formation of intermediate compounds of sulfur (elemental sulfur, polysulfides, and thiosulfates), which may interact with metals and organic components [6, 7] to form compounds promoting the changes in the physico-chemical forms and mobilities of the metals.

The investigations of the composition of bottom sediments carried out earlier were, for the most part, realized after preliminary preparation of the samples and restricted to the determination of the characteristics of solid phases [1, 2, 8–10]. The method of polarographic profiling of sediments with the help of an Au–Hg glass microelectrode has been developed in the last decade. The main advantage of this method is connected with the possibility of analysis of the pore waters under the conditions maximally close to the natural conditions with high sensitivity and without destruction of the samples. The application of methods of this sort gives a good basis for understanding the dynamic processes running in the upper layer of sediments characterized by the presence of numerous reactions, including the mineralization of organic substances [6].

In the present work, for the first time, we use an Au–Hg glass microelectrode for the polarographic profiling of the bottom sediments in the Sevastopol Bay. In this case, we pose the problems of investigation of the possibilities of application of the proposed method, identification of compounds and plotting the profiles of their vertical distributions, and investigation of the geographic features of the vertical distributions of polarographically active compounds in the Sevastopol Bay.

Methods and Results

Sampling. The samples of the surface layer of bottom sediments were collected in October 2006 by using a DT-3 tubular bottom sampler on the drift stations in the central part of the bay and in the Yuzhnaya Bay (Fig. 1). After removing the bottom sampler to the deck of the ship, the columns of bottom sediments were placed into specially prepared glass cylinders by pressing performed with an aim guarantee the minimum possible deformation of the water–bottom-sediments boundary and the column of sediments inside the cylinder. The upper and lower end faces of the cylinder were sealed and the samples were delivered to the coastal laboratory for polarographic investigations.

Polarographic Profiling. In all electrochemical measurements, we use a standard three-electrode cell with DLK-60 potentiostat (Analytical Instrument Systems, Inc.). The Au–Hg working microelectrode was applied to determine the vertical profiles of polarographically active compounds in the pore waters of the sediments. It was made from a glass capillary filled with epoxy resin and a golden wire 100 μM in diameter placed inside the capillary. The end face of the electrode was polished and the frontal part of the golden wire was covered with a film of mercury [7, 11]. It was shown [7, 11] that this electrode can be successfully used for recording Fe(III), Fe(II), Mn(II), H_2S , and O_2 with the minimum limits of measurements varying from 5–10 μM /liter for iron and oxygen to 3 nM/liter for hydrogen sulfide. The saturated silver chloride electrode was used as the reference electrode and the role of the auxiliary electrode was played by the platinum electrode. The auxiliary and reference electrodes were placed into a layer of water directly above the surface of sediments. The working electrode moved in the vertical direction with the help of a micromanipulator with steps of 1 mm in the upper 0–6-mm layer of sediments and then with steps of 2 mm down to the maximum depth of profiling of the column of bottom sediments.

Our measurements were carried out by using cyclic scanning within the range of potentials (–0.1)–(–1.850) V with a period of preliminary preparation and stabilization of the electrode under a voltage of –0.1 V for 5 sec. The applied scanning rate equal to 2000 mV/sec enables us to guarantee high sensitivity and the minimum level of electric noises. Prior to and at the end of each profiling, the electrode was placed in seawater saturated with oxygen. Multiple realizations of the procedure of polarographic scanning make it possible to stabilize the working electrode and guarantee that its properties remain constant [7, 11]. In the cases where the sensitivity of the electrode decreased, we restored the mercury film on its working surface. The proposed mode of polarographic scanning does not allow one to get signals of Mn(II) and Fe(II) with maximum possible resolution and sensitivity. For this reason, the data on the distribution of Fe(II) are, in fact, qualitative and should be improved in the course of subsequent investigations.

Since the main aim of the present work is to study the possibilities of application of the proposed method, we do not recalculate the values of polarographic signals into the concentrations of the corresponding substances. Moreover, it is impossible to find the concentrations of iron monosulfide (FeS) and iron oxide-hydroxide (FeOOH) [12, 13] because the corresponding standard solutions do not exist and cannot be prepared.

It was assumed that the oxygen content can be overestimated because the procedure of sampling of the bottom sediments with the help of the DT-3 tubular bottom sampler can lead to a partial roiling and aeration of the surface layers of sediments. Furthermore, the concentration of oxygen in the sediments could increase for the time period between sampling and the realization of polarographic profiling. Nevertheless, the accumulated results (Figs. 2–6) and their subsequent analysis show that the characteristics of the distribution of oxygen are in very good agreement with the geochemical characteristics of sediments and the existing concepts concerning the correlations between the distributions of individual geochemical components.

Analysis of the Morphological and Geochemical Characteristics. After the procedure of polarographic profiling, we took samples from each column of the bottom sediments to determine the content of organic carbon [14] and perform the X-ray fluorescence analyses (Table 1) [15]. In addition, the results of analysis of the average content of organic carbon and the mean granulometric composition of the surface layer of bottom sediments obtained in the course of several expeditions in 2002–2006 were used to plot the maps of the space distributions of these characteristics in the Sevastopol Bay (Figs. 7 and 8).

The column of sediments taken at Station 17 (near the corner part of the Yuzhnaya Bay) had three layers. The upper layer (0–30 mm) was formed by a homogeneous dark mass, then we revealed a lighter intermediate layer (30–40 mm), and, finally, a new dark layer was observed at depths greater than 40 mm. The upper layer of sediments was characterized by the maximum, over the entire water area of the bay, content of organic carbon

equal to 7.27% (Table 1). The sediments taken at station 19 (in the Yuzhnaya Bay) represented a uniform mass of dark almost black color. The color of the column of sediments taken at station 23 (in the central part of the Sevastopol Bay, in front of the exit from the Artilleriiskaya Bay) varied from dark-gray to light-gray without pronounced boundaries between the individual layers. At station 15, the column of bottom sediments looked homogeneous, and its color varied from dark-gray to black. The column of sediments taken at station 12 had two layers each of which looked homogeneous. The boundary of the upper layer varied across the diagonal from 40 to 60 mm. The color of the upper layer varied from dark-gray to black. The lower layer was light-gray.

Table 1. Contents of Organic Carbon, Iron, and Manganese in the Bottom Sediments

| No. of station, layer | C _{org} , % | Fe, % | Mn, % |
|------------------------|----------------------|--------|--------|
| 12, upper layer | not determined | 4.0850 | 0.0411 |
| 12, lower layer | 4.17 | 3.7160 | 0.0388 |
| 15 | 4.91 | 4.0080 | 0.0335 |
| 17, upper layer | 7.27 | 3.5280 | 0.0361 |
| 17, intermediate layer | not determined | 3.6500 | 0.0374 |
| 17, lower layer | 4.97 | 3.5480 | 0.0322 |
| 19 | 5.24 | 4.6270 | 0.0425 |
| 23, light layer | 3.44 | 3.4090 | 0.0339 |
| 23, dark layer | 3.26 | 3.6950 | 0.0351 |

Results of the Polarographic Profiling of Bottom Sediments.

Station 17. In Fig. 2, we present the vertical profiles of the intensity of polarographic signals for Station 17. The polarograms recorded in the upper 2-mm layer of bottom sediments contain two irreversible peaks, corresponding to the reduction of O₂ to H₂O₂ at -0.3 V and H₂O₂ to H₂O at -1.3 V. In addition, we observe several irreversible signals within the range (-0.6)–(-0.3) V indicating the presence of FeOOH with different degrees of crystallization and Fe(III) as a component of various organic complexes [12, 16]. At a depth of 2 mm, the signal of oxygen disappears and the peak of Fe(III) turns into the main signal. The maximum intensity of this peak is recorded at a depth of 6 mm and then it decreases to the background values. The signal attributed to Fe(II) exhibits a complex vertical structure. Against the background of insignificant general decrease in the intensity of this signal with depth, we observe narrow layers of its local minimum at a depth of 30 mm and its maximum at a depth of 78 mm (Fig. 2a). The reversible signal of hydrogen sulfide at about -0.7 V [6, 7] is formed at a depth of 2 mm and reaches its maximum level for this station at a depth of 10 mm. In deeper layers of the sediments, we detect the formation of a local minimum of the hydrogen-sulfide signal, up to its complete vanishing at a depth of 28 mm. In the 28–36-mm layer, the content of hydrogen sulfide again increases with depth but then decreases down to complete vanishing at a depth of 48 mm (Fig. 2b). The signal of FeS in the form of two peaks at -1.15 and -0.9 V appears at a depth of 8 mm but remains weak down to 30 mm. Moreover, its level chaotically changes with depth.

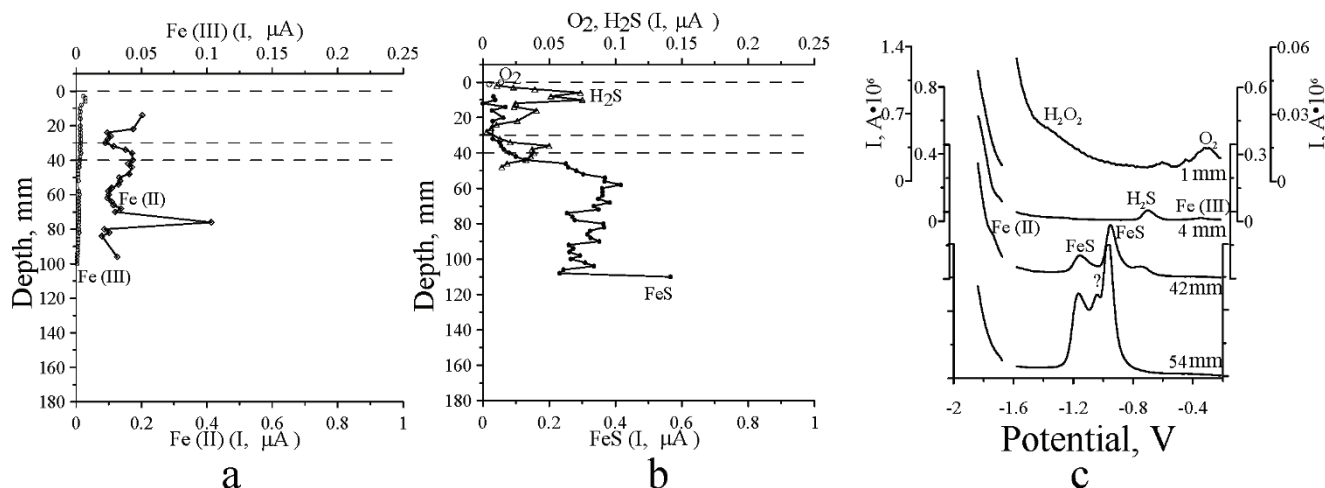


Fig. 2. Vertical distributions of Fe(II) and Fe(III) (a), O_2 , H_2S , and FeS (b) and their signals in the polarograms (c) (Station 17).

At depths greater than 30 mm, the signal of FeS monotonically increases, reaches its maximum value at a depth of 60 mm, and then decreases, but continues to be the main signal in the polarograms down to the maximum depth of profiling equal to 110 mm. Note that there exists one more peak corresponding to a potential of -1.05 V. This peak appears at a depth of 46 mm and its maximum value is attained at 82 mm. In view of the depth of appearance of this signal and the character of its vertical distribution, one may assume that it is related to iron or manganese sulfides and, possibly, their complex compounds. The available data do not enable us to identify this signal and, hence, we do not consider it in what follows.

Station 19. At Station 19 (just as at Station 17), the signals of oxygen are observed solely in the upper 2-mm layer of the bottom sediments. However, in this case, their maximum level on the surface of sediments is more than 1.5 times higher. The signal related to FeOOH manifests itself at a depth of 3 mm. Its intensity increases with depth and attains its maximum value at a depth of 22 mm. In deeper layers, the analyzed intensity decreases to the background level attained at 32 mm. As in the case of Station 17, the signal of Fe(II) does not have any visible vertical structure. The signal of hydrogen sulfide appears at a depth of 10 mm, reaches its maximum value at a depth of 20 mm, then decreases down to a depth of 50 mm, and finally, remains almost constant down to the maximum depth of profiling (Fig. 3b). It is worth noting that the maximum content of hydrogen sulfide at Station 19 is three times higher than at Station 17. Moreover, unlike Station 17, the concentration of hydrogen sulfide in the deepest layers of the bottom sediments at Station 19 does not vanish and even remains as high as 50% of the maximum value for Station 17. The signal of FeS appears at a depth of 24 mm, i.e., in the layer corresponding to the maximum concentrations of hydrogen sulfide. It should be emphasized that the maximum values of the signal of FeS at Station 19 are more than 15 times lower than at Station 17. No signal was detected at a potential of -1.05 V.

Station 23. At Station 23, as in the cases of Stations 17 and 19, oxygen is detected only in the upper 2-mm layer of the bottom sediments but its concentration on the surface of sediments is 5–8 times higher (Fig. 4b). The signals of FeOOH are absent. The signal of Fe(II) is present and exhibits a trend to intensification with the appearance and growth of the FeS content. The signal of hydrogen sulfide is detected at a depth of 10 mm, then it sharply increases, and reaches its maximum at 14 mm. In deeper layers of sediments, we observe a local minimum of the concentration of hydrogen sulfide at a depth of 40 mm and its maximum at a depth of 60 mm.

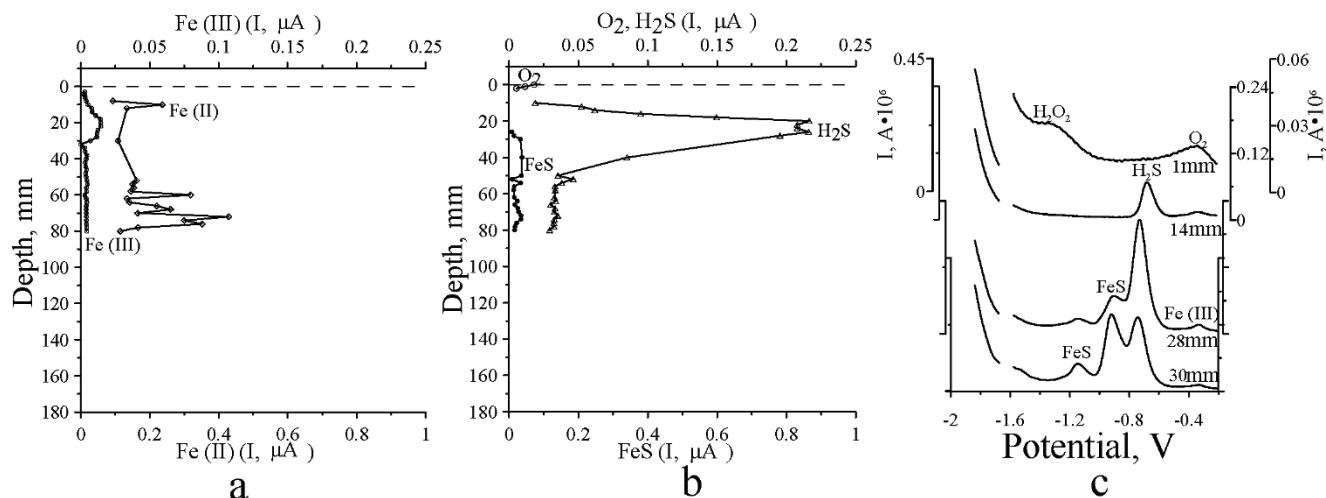


Fig. 3. Vertical distributions of Fe(II) and Fe(III) (a), O_2 , H_2S , and FeS (b), and their signals in the polarograms (c) (Station 19).

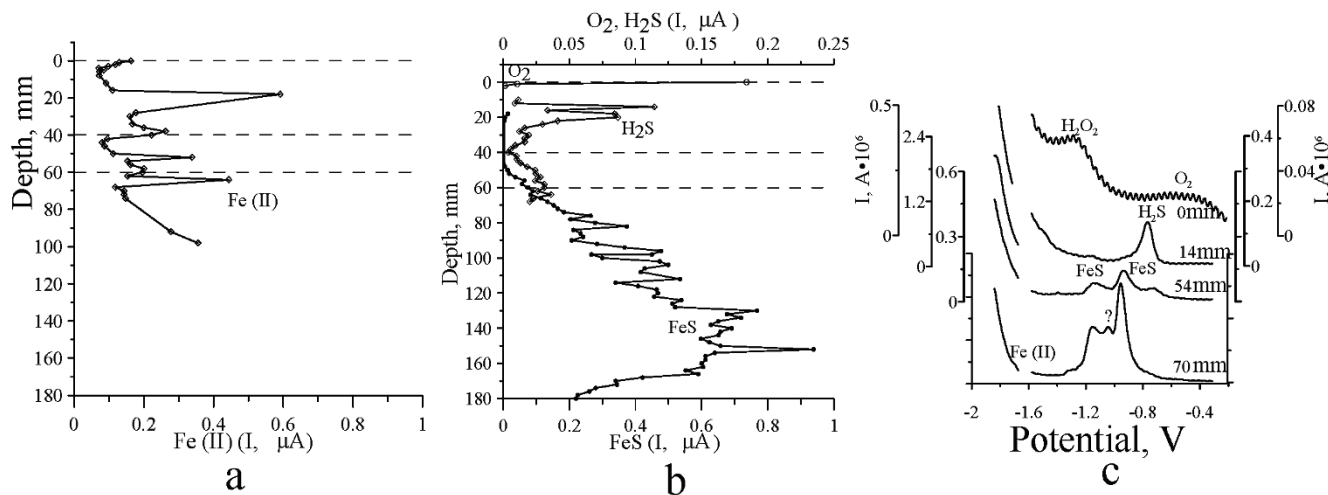


Fig. 4. Vertical distributions of Fe(II) (a), O_2 , H_2S , and FeS (b), and their signals in the polarograms (c) (Station 23).

Then the hydrogen-sulfide signal weakens and disappears at a depth of 70 mm. The signal of FeS appears at a depth of 48 mm, increases with depth, attains its maximum at 130–160 mm, and then decreases. As in the case of Station 17, a signal corresponding to a potential of -1.05 V appears somewhat deeper (at a depth of 62 mm) than the signal of FeS. Its variations with depth are similar to the variations of the signal of FeS. The maximum intensity of this signal is attained at a depth of 152 mm. Then the signal begins to decrease but remains significant even at the maximum depth of profiling equal to 180 mm. As characteristic features of the vertical distribution of the intensity of polarographic signals at Station 23, one can mention the maximum, over all analyzed stations, concentration of oxygen on the surface of sediments and a smooth almost linear increase in the signal of FeS in a broad, as compared with the other stations, layer (50–135 mm) (Fig. 4b).

Station 15. In Fig. 5, we present the vertical distributions of the intensity of polarographic signals obtained in profiling the column of bottom sediments at Station 15 (Fig. 1).

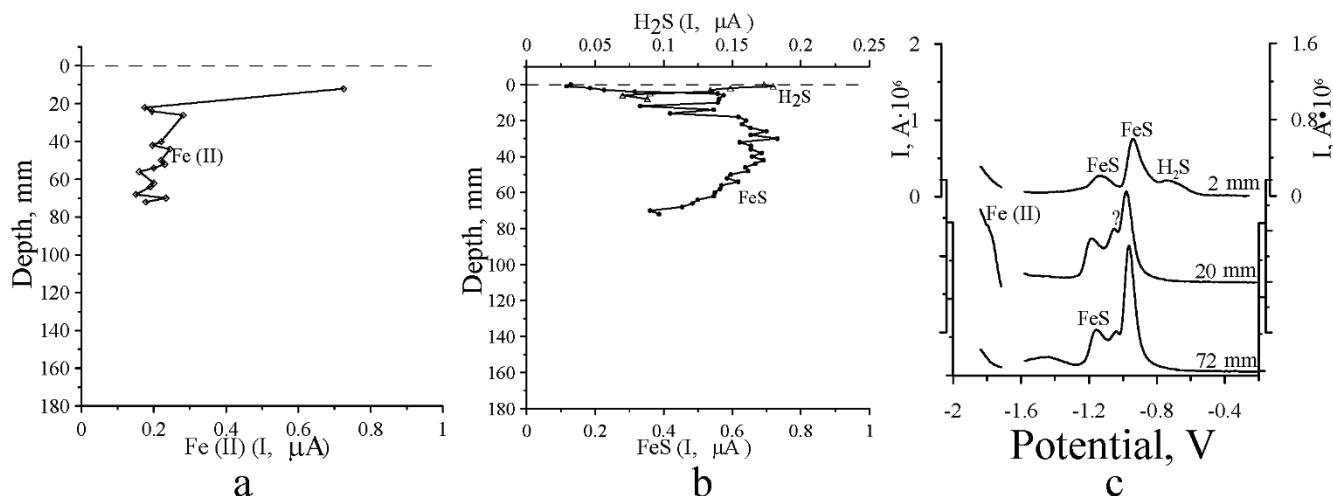


Fig. 5. Vertical distributions of Fe(II) (a), H_2S and FeS (b), and their signals in the polarograms (c) (Station 15).

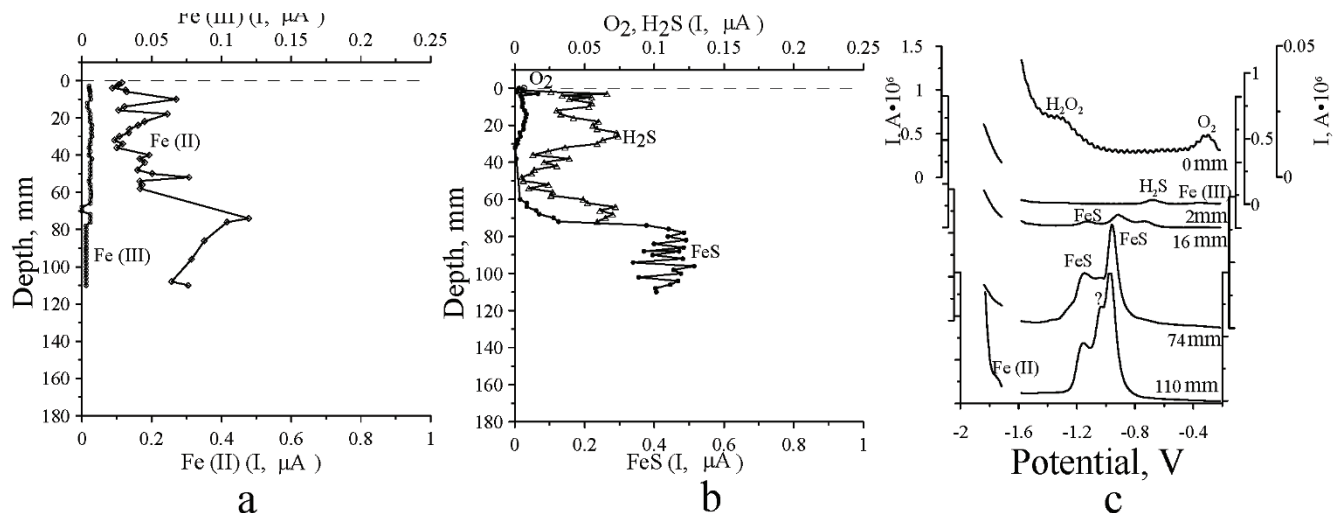


Fig. 6. Vertical distributions of Fe(II) and Fe(III) (a), O_2 , H_2S , and FeS (b), and their signals in the polarograms (c) (Station 12).

In this column, we detected the presence of an air gap at a depth of 72 mm. Hence, the procedure of profiling was carried out only for the upper part of the column. The main specific feature of the analyzed polarograms is the absence of signals of oxygen and FeOOH even on the surface of sediments. Instead of oxygen, we detect the presence of hydrogen sulfide and iron monosulfide (Fig. 5). Further, the intensity of the signal of hydrogen sulfide is maximum in the upper 2-mm layer. Then this signal sharply decreases and disappears at a depth of 8 mm. A fairly intense signal of FeS is recorded even on the surface of sediments. Its intensity sharply increases with depth, reaches its maximum value at a depth of 26 mm, and then decreases. As in the cases of all stations with significant contents of FeS, the signal corresponding to a potential of -1.05 V appears and attains its maximum value at a depth greater than the corresponding depth for the signal of iron monosulfide by about 10 mm. As at Station 17, the signal of Fe(II) decreases with depth.

Station 12. In Fig. 6, we present the vertical distributions of polarographic signals for Station 12 (in the central part of the Sevastopol Bay in front of the exit from the Kilen Bay).

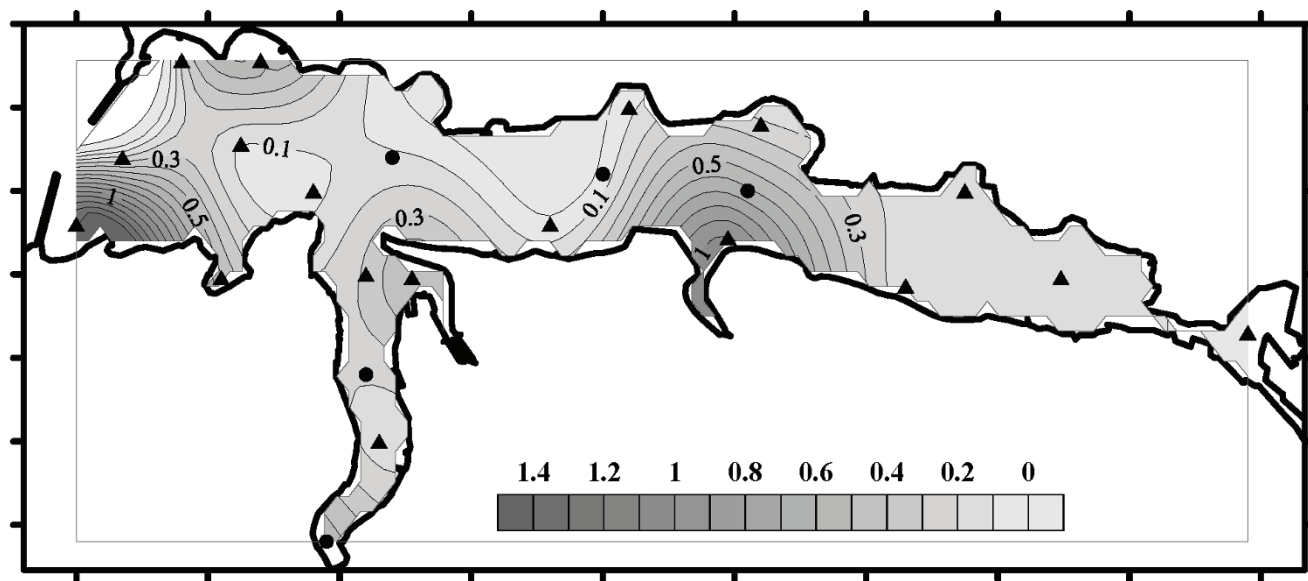


Fig. 7. Average granulometric composition of the bottom sediments (mm).

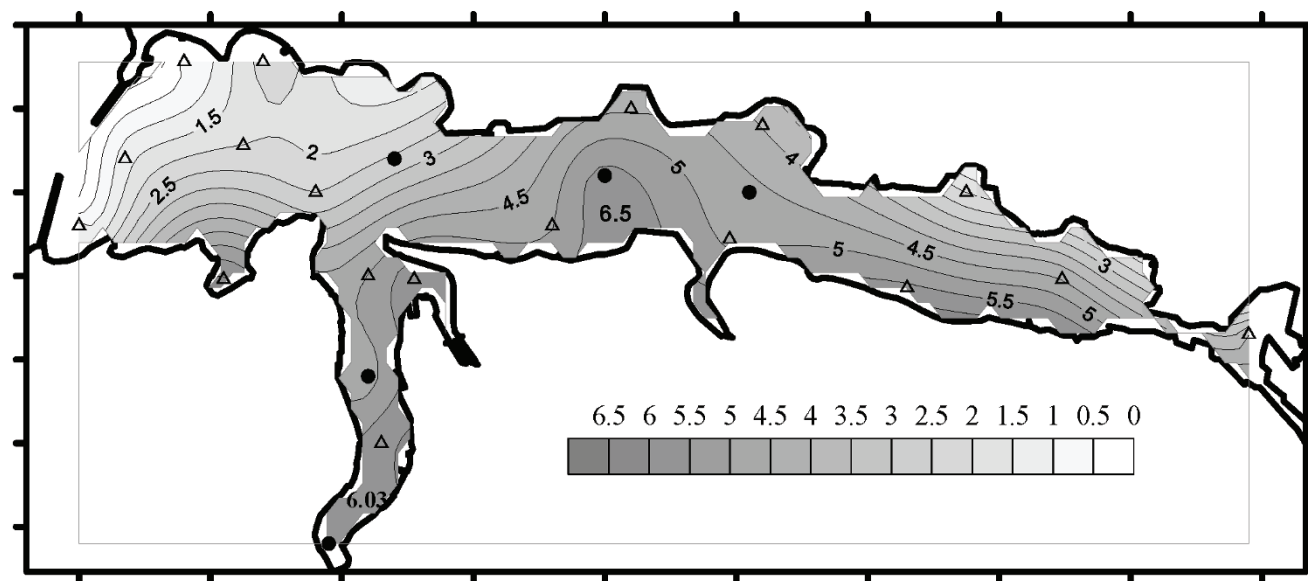


Fig. 8. Content of organic carbon (%) in the bottom sediments of the Sevastopol Bay.

The length of the column is equal to 110 mm. At this station, the signal of oxygen was present only on the sediment surface. At a depth of 2 mm, we already detected the signals of Fe(II), FeOOH, and H₂S. The signal of FeOOH was recorded over the entire length of the column but its intensity was low as compared with Station 17 and, especially, Station 19 (without clearly pronounced features of the vertical distribution). The vertical distribution of hydrogen sulfide was similar to its distributions observed at Stations 17 and 23 both by the maximum content of the compound and by the presence of two maxima at depths of 26 and 66 mm and a local minimum at a depth of 48 mm (Fig. 6b). The intensity of the signals of FeS observed at depths of 2–60 mm sharply increases at depths greater than 60 mm, reaches its maximum at 80 mm, and then slightly decreases. The signal

of Fe(II) is present along the entire profile but does not exhibit any trends or correlations with the vertical distributions of the other geochemical characteristics. At depths greater than 60 mm, parallel with a sharp increase in the FeS content, the signal of Fe(II) becomes almost three times more intense. The signal corresponding to -1.05 V appears at a depth of 74 mm and its vertical distribution relative to the signal of FeS varies in exactly the same way as for the other stations with high contents of FeS.

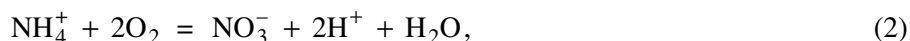
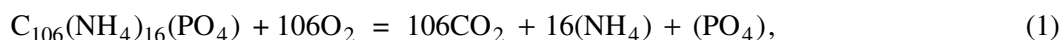
Discussion

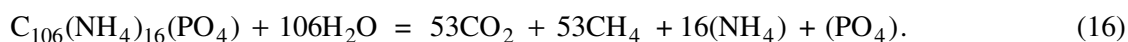
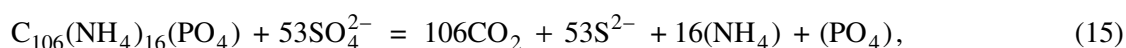
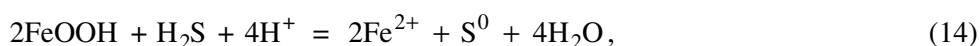
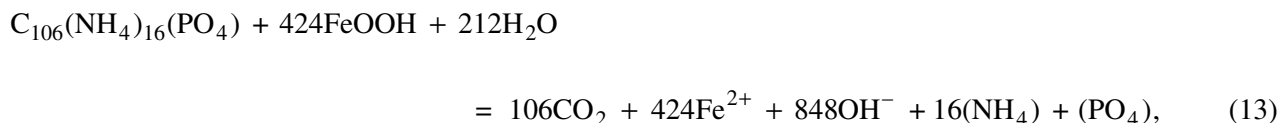
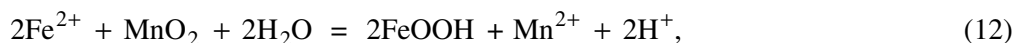
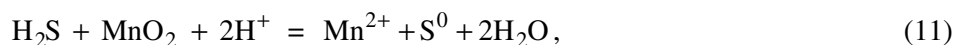
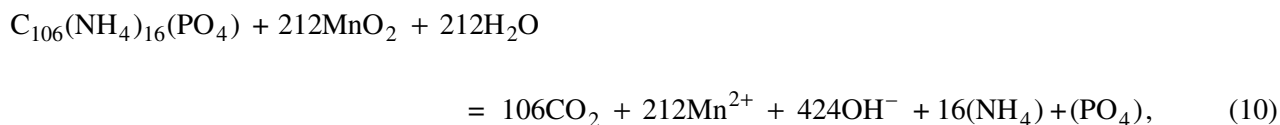
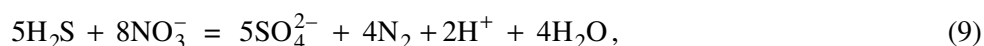
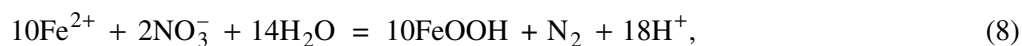
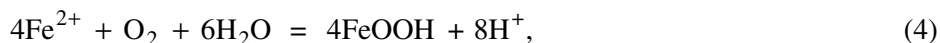
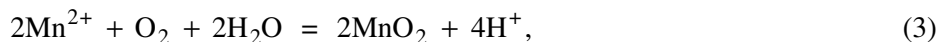
The surface layer of the bottom sediments in the Sevastopol Bay is represented mainly by sandy aleurite-pelites and, to a lesser degree, by silted shell rocks. The aleurite-pelitic silts are fluid-plastic fine-grained formations of black color indicating that reducing conditions are realized in the sediments [2, 17]. The smell of hydrogen-sulfide was detected for these samples [2]. However, there are no qualitative and quantitative data of the analyses of the contents and distributions of oxygen, reduced sulfur, and reduced and oxidized forms of iron and manganese. The granulometric composition of the bottom sediments in the Sevastopol Bay is characterized by the absence of coarse-grained fractions (Fig. 7). The medium-grained sediments were discovered in the regions close the exit of the bay. However, almost all water area of the bay is represented by fine-grained fractions [1, 2, 8]. This morphological composition, even in the absence of anthropogenic pressure and for low levels of the primary and export production, leads to the formation of bottom sediments characterized by insignificant contents or even by the absence of oxygen due to low rates of its diffusion. Depending on the flows of organic carbon, iron, manganese, and oxidized forms of nitrogen (nitrates and nitrites), one may observe the formation of geochemical structures containing hydrogen sulfide and other forms of reduced sulfur, which would lead to catastrophic changes in the structure of the ecosystem.

High contents of organic carbon are typical of the bottom sediments in the Sevastopol Bay, especially of the surface layer of corner regions and small bays on the south side of the water area (Fig. 8). This fact reflects high rates of the production of organic carbon and its inflow from the coastal sources [2]. The intense consumption of oxygen, especially in summer, is a natural result of the high content of organic carbon [1]. This leads to the development of hypoxia in the bottom layers of water and to the appearance and accumulation of the reduced forms of iron, manganese, and sulfur.

The comparative analysis of the morphology, granulometric composition (Fig. 7), and vertical structure of the bottom sediments, as well as the content of organic carbon (Fig. 8) shows that the most complex structure of the sediments is observed in the region with the maximum content of organic carbon (Station 17). The periodic inflows of organic substances of the anthropogenic origin with municipal sewage waters and storm discharges lead to the active consumption of oxygen and the development of anaerobic conditions. Under these conditions, we observe the formation of sediments of dark color typical of various compounds of reduced sulfur. As we move from the regions with high contents of organic carbon, the geochemical processes of diagenesis lead to the formation of the classical structure of sediments (Station 23) with gradual increase in the content of reduced sulfur in deeper layers. Moreover, the deep layers of sediments have lighter colors due to the elevated content of carbonates, reduced content of organic carbon, and the transformation of dark metal monosulfides (FeS) into lighter pyrites (FeS₂).

The geochemical composition of the marine bottom sediments and pore waters is formed as a result of the following principal biogeochemical processes:





The sequence of these processes is determined by the intensity of the flows of oxygen and particulate organic substances and the presence (and contents) of iron and manganese. Sulfates are also macrocomponents of seawater and, as a rule, complete the chain of natural oxidizers and lead to the formation of hydrogen sulfide [reaction (15)]. The redox disproportionation of the organic substances and formation of methane [reaction (16)] become possible only in the case of complete exhaustion of the supply of sulfates.

Reactions (1)–(6) run in the presence of oxygen. In this case, oxygen and FeOOH are the main polarographically active substances. In deeper layers of the sediments, we observe the processes of denitrification in which the role of the main oxidizer is played by nitrates [reactions (7)–(9)]. Since nitrates are electrochemically inactive in the analyzed range of potentials, one can expect solely the formation of the signals of FeOOH in the course of polarographic profiling of these layers. As soon as the supply of nitrates is exhausted, MnO₂ and

FeOOH turn into the main oxidizers [reactions (10)–(14)] and one can expect the appearance of the signals of Fe^{2+} , FeOOH, and Mn^{2+} in the polarograms. The possibility of realization of the processes of reduction of FeOOH [reaction (14)] and oxidation of Fe^{2+} [reaction (13)] results in the situation characterized by the presence of several signals of FeOOH in these layers of the sediments. These signals reflect the degree of crystallization and the nature of complexes formed with the participation of Fe^{3+} [12]. The onset of redox geochemical processes with the participation of sulfates [reaction (15)] is characterized by the appearance of the signals of reduced sulfur (elemental sulfur, hydrogen sulfide, and iron monosulfide) in the polarograms. Depending on the intensity of reduction of sulfates and the amount of reactive iron, hydrogen sulfide, iron monosulfide, or pyrite may turn into the main product of the geochemical processes.

The results of our polarographic investigations make it possible to study the specific space features of the vertical chemical structure of pore waters of the bottom sediments in the Sevastopol Bay. High contents of organic carbon are responsible for the fact that oxygen penetrates into the sediments at most by 2–3 mm. Note that the maximum concentration of oxygen on the surface of sediments was observed at Station 23 characterized by the minimum content of organic carbon (Fig. 8). At the stations with the highest contents of organic carbon, the amount of oxygen was minimum (Station 17) or it was completely absent (Station 15). The absence of oxygen on the surface of the bottom sediments at Station 15 is determined by the combination of at least two factors: the high content of organic carbon, which results in high rates of the consumption of oxygen, and the fine-grained structure of sediments, which restricts the diffusion flow of oxygen from the bottom layer of waters into the sediments.

The absence of oxygen at depths starting from 3 mm creates the conditions for the participation of nitrogen, iron, manganese, and sulfur in redox processes [reactions (6)–(15)] and for the appearance of the corresponding signals in the polarograms (Figs. 2–6). The relationship between the intensities of signals and the character of their vertical distribution depend on several factors, the most important of which are the contents of organic carbon, iron, and manganese. If the amount of iron is significant, then iron sulfides (FeS and FeS_2) are the main products of the diagenesis of organic substances in the marine sediments. Hydrogen sulfide can be present in trace amounts determined by the kinetics of the process of sulfate reduction and the formation of iron sulfides. In the absence of significant amounts of iron and manganese, sulfides are the main final products of the oxidation of organic substances in marine media, and the sulfates required for reaction (15) turn into a macrocomponent. This situation is observed, e.g., in the abyssal sediments of the Black Sea [18].

The Sevastopol Bay serves as a naval base for several centuries since the appearance of the city itself. As a result, the contents of various metals in the bottom sediments in the bay exceed their background levels [8]. Moreover, iron is a macrocomponent and its concentration varies within the range 3.4–4.6% (Table 1). For this content of reactive iron, one may expect the formation of significant amounts of Fe(II), which binds hydrogen sulfide to form FeS. The accumulated data confirm this assumption. Hydrogen sulfide is present only in the upper part of the column of sediments (Figs. 2–6). In deeper layers of sediments, we observe an increase in the FeS content and a decrease in the concentration of hydrogen sulfide up to its complete vanishing. Thus, the iron content of the bottom sediments in the Sevastopol Bay is sufficiently high to bind the entire produced hydrogen sulfide in iron sulfides. The maximum in the profile of the vertical distribution of hydrogen sulfide is always located over the boundary of the onset of stable growth of the signal of FeS (Figs. 2–6). The closer the onset of stable growth of the intensity of the signal of FeS to the sediment surface, the higher the peak of hydrogen sulfide. At Station 15, where the increase in the FeS content begins from the water–bottom boundary, the maximum content of hydrogen sulfide is detected on the surface of sediments and oxygen is absent. The signal of hydrogen sulfide abruptly weakens with depth up to its complete vanishing in the upper 10-mm layer of sediments (Fig. 5). It is possible to assume that the depth of the onset of stable growth of FeS depends on the content of organic substances and the sizes of particles in the sediments. The high contents of organic substances and fine-grained sediments at Station 15 (Figs. 5, 7, and 8) restrict the flow of oxidizers from the bottom layer of waters and the

upper part of sediments. Note that stable conditions for sulfate reduction and the formation of FeS are preserved in deeper layers of the bottom sediments. In coarse-grained sediments (Station 19, Figs. 3 and 7), the seasonal variations of the intensity of flows of oxygen and organic carbon result in significant contents of the oxidized forms of iron in the upper part of sediments, elevated contents of hydrogen sulfide in deeper layers, and the maximum depth of stable growth of the FeS content.

The accumulated data on the content and vertical distribution of FeS enable us to make several assumptions, which are of great importance for understanding the evolution of ecosystem of the Sevastopol Bay and prediction of possible changes in its state. First, the inflow of organic substances into the bottom sediments of the bay exceeds the assimilation potential of the analyzed ecosystem. This leads to the accumulation organic matter in the bottom sediments [2, 8], exhaustion of the supply of oxidizers even in the uppermost layers of sediments, and the intense production of hydrogen sulfide, which makes sediments unsuitable for the existence of benthos communities. The displacement of these sediments creates the sites of secondary pollution. Second, the vertical distribution of FeS is characterized by the presence of a maximum. This enables us to assume that the amount of produced sulfides increases as a result of the increase in the inflow of organic carbon, that, at present, the iron content is sufficient for binding the entire produced amounts of hydrogen sulfide, and that, in the historical past, there was a period when the inflow of organic carbon into the sediments was much weaker. Third, the exhaustion of the supply of iron (its flow into the sediments weakens, whereas the inflow of organic carbon increases) will lead both to a sharp increase in the content of free hydrogen sulfide in the sediments and to its penetration into the bottom layers of water.

CONCLUSIONS

The accumulated experimental data show that Au–Hg microelectrodes can be efficiently used for the polarographic investigations of the vertical distributions of the main components participating in the early diagenesis of bottom sediments in the Sevastopol Bay. The procedure of polarographic profiling of the bottom sediments enables one to successfully record the signals and study the vertical distributions of oxygen, oxidized and reduced iron, reduced manganese, and reduced sulfur (including hydrogen sulfide and iron monosulfide) in the sediments.

The profiles obtained in the present work correspond to the main processes running in the sediments and specifying their structure and composition. The regional distinctions in the vertical distributions of the investigated geochemical components of the bottom sediments in the Sevastopol Bay are determined, first of all, by the relationships between the flows of oxygen, iron, and organic substances, as well as by the granulometric composition of the sediments. Thus, the elevation of the content of organic carbon results in a more intense consumption of oxidizers in the upper part of sediments and in the production of hydrogen sulfide. On the other hand, the presence of large amounts of iron creates the situation in which hydrogen sulfide is nothing but an intermediate product completely transformed into iron monosulfide in deeper layers of sediments. As a delayed result of this process, we can mention the accumulation of sulfides, which may serve as a source of secondary pollution in the course of dredging of the bay accompanied by the displacements of the bottom sediments.

The increase in the amount of organic matter in the bottom sediments can exceed the assimilation potential of iron (relative to the possibility of binding of the produced hydrogen sulfide), which would lead to catastrophic changes in the state not only of the bottom sediments but also of the bottom layers of water in the bay.

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