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Characteristics of Bottom Sediments in the Coastal Areas of the Crimean Peninsula

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Abstract: The aim of this work was to assess the influence of physical, chemical, and hydrochemical factors on the characteristics of bottom sediments in various areas of the shelf of the Crimean Peninsula. The data obtained during the cruises of the RV "Professor Vodianitsky" in the fall of 2018 and summer of 2019 were analyzed. Hydrochemical analyses of the bottom waters were carried out using standard hydrochemical methods. Profiles of dissolved oxygen, hydrogen sulfide, and oxidized and reduced forms of iron in pore waters were obtained, and the geochemical characteristics of bottom sediments were determined. The features of their spatial and vertical distributions were considered. Pelite-aleuritic sediments with inclusions of sandy material and shell detritus prevailed in the coastal zone of the Crimean shelf. The organic carbon content varied from 0.5–0.6% in the gravel–sand sediments of the Kerch pre-strait area to 2.5–2.7% in the northwestern part. The prevalence of suboxic conditions was noted, and the main processes in the sediment upper layer were controlled mainly by reactions involving iron. In some areas of the southern coast of Crimea and the Kerch pre-strait area from the Sea of Azov, the development of anoxic conditions in the surface layer of bottom sediments was recorded.

Keywords: bottom sediments; pore waters; voltammetry; oxygen; hydrogen sulfide; granulometric composition; organic carbon; Black Sea

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1. Introduction

Coastal ecosystems are characterized by high productivity and biodiversity, which is why they account for more than 90% of the world's seafood and mariculture production [1]. In addition, they are attractive for recreational purposes and play a significant role in the social and economic spheres [2,3].

Bottom sediments are one of the convenient tools for assessing the state of marine ecosystems [4]. Representing a quasistationary system, they are an integral indicator of all the pollution entering the marine environment. At the same time, unlike regular monitoring of the hydrological parameters of waters, studies of the characteristics of bottom sediments are usually carried out intermittently [5]. This is why the study, assessment of the state and prognosis of the oxygen deficiency development in the bottom sediments of marine ecosystems are relevant.

Significant anthropogenic pressure on coastal waters contributes to the influx of additional amounts of organic matter and nutrients, thus leading to intensive sedimentation and rapid changes in the geochemical characteristics of the environment [6]. Such changes are negative and lead to the degradation of coastal marine ecosystems.

The main processes that determine the characteristics and conditions of bottom sediments and the state of the ecosystem as a whole are controlled, among other things, by reactions involving organic matter and its production or degradation (oxidation).

The sequence of organic matter oxidation reactions (Table 1) is thermodynamically predetermined. First, oxygen is used as an oxidizer of organic matter, which ultimately leads to its exhaustion [7–9]. As a result, oxygen deficiency develops in the bottom sediments and then in the water column, which leads to hypoxia/anoxia and the formation of environmental risk zones [10].

Table 1. Oxidation reactions of organic matter in bottom sediments.

Eq. No	Process Name	Reaction Scheme	Redox Conditions
(1)	Aerobic oxidation	$C_{106}H_{175}O_{42}N_{16}P + 150\ O_2 \rightarrow 106\ CO_2 + 16\ HNO_3 +$ $+ H_3PO_4 + 78\ H_2O$	Oxic
(2)	Nitrate reduction	$C_{106}H_{175}O_{42}N_{16}P + 104\ HNO_3 \rightarrow 106\ CO_2 + 60\ N_2 +$ $+ H_3PO_4 + 138\ H_2O$	Suboxic
(3)	Manganese reduction	$C_{106}H_{175}O_{42}N_{16}P + 260\ MnO_2 + 174\ H_2O \rightarrow 106\ CO_2 +$ $+ 8\ N_2 + H_3PO_4 + 260\ Mn(OH)_2$	Suboxic
(4)	Iron reduction	$C_{106}H_{175}O_{42}N_{16}P + 236\ Fe_2O_3 + 410\ H_2O \rightarrow 106\ CO_2 +$ $+ 16\ NH_3 + H_3PO_4 + 472\ Fe(OH)_2$	Suboxic
(5)	Sulfate reduction	$C_{106}H_{175}O_{42}N_{16}P + 59\ H_2SO_4 \rightarrow 106\ CO_2 + 16\ NH_3 +$ $+ H_3PO_4 + 59\ H_2S + 62\ H_2O$	Anoxic
(6)	Methanogenesis	$C_{106}H_{175}O_{42}N_{16}P + 59\ H_2O \rightarrow 47\ CO_2 + 59\ CH_4 +$ $+ 16\ NH_3 + H_3PO_4$	Anoxic

After the oxygen concentration decreases below the threshold value (<1% sat.) [11], the main oxidant changes, nitrates/nitrites, MnO_2, and FeOOH, act as oxidants of organic matter (Table 1). After the exhaustion of these compounds, sulfate reduction processes accompanied by the formation of reduced forms of sulfur and methanogenesis processes occur [11].

In addition to the content and reactivity of organic matter (and the concentration of organic carbon proportional to it), the granulometric composition is an important factor determining the features of biogeochemical processes and changes in redox conditions in bottom sediments.

Ultimately, the geochemical composition of sediments (granulometric composition, organic carbon content, porosity), the oxygen concentration in the bottom waters, and features of the hydrology and hydrodynamics of the water column determine the oxygen downflux, as well as the concentration and depth of its penetration into the bottom sediments [12,13].

Currently, the hydrology and hydrodynamics of the Crimean Peninsula shelf zone have been sufficiently studied [14–17]. Based on a complex analysis of the hydrological data and instrumentally measured currents, the concepts of thermohaline and kinetic fields for individual sections of the shelf and for different seasons were expanded. The studies of [14–17] presented the vectors of instrumentally measured currents at various horizons; their position was compared with the elements of climatic water circulation. The vectors of instrumentally measured currents, including those in the bottom water layer of interest in the summer of 2018, were studied [17].

In addition to the hydrological regime, the features of the spatial and vertical distributions of oxygen in the water column of the coastal regions of the Crimea have been studied [18–20]. Analysis of the published papers shows that modern studies on the vertical distribution of oxygen in the water column focused on estimates of the suboxic zone boundary positions [21,22] and were carried out mainly in the deep-water areas of the Black Sea. The study of oxygen concentrations in the bottom waters of the coastal regions of the Crimea is currently paid little attention.

The geochemical characteristics of bottom sediments have not been studied in such detail. Earlier studies are reflected in the works of [23,24]. Currently, the geochemical characteristics of bottom sediments arouse great interest within the framework of studying the features of the accumulation and spatial distribution of various pollutants in the water areas of the Crimean shelf [2,4,25] and closed and semi-closed lagoons [26,27]. Some works [28,29] are devoted to the study of the vertical profiles of the key redox species in pore waters of the bottom sediments obtained by voltammetry. In [30,31], the redox conditions in the bottom waters were evaluated using various geochemical indices.

However, the comprehensive investigation of the influence of different characteristics of the bottom waters and bottom sediments on the bottom sediment chemical composition in the Crimean coastal waters has been paid little attention.

The purpose of this work was to assess the influence of geochemical (granulometric composition, organic carbon content) and hydrochemical (oxygen concentration in the bottom waters) factors on the formation and characteristics of the chemical composition of bottom sediment pore waters in various areas of the Crimean Peninsula shelf.

2. Materials and Methods

During the cruises on the RV "Professor Vodyanitsky" in the autumn of 2018 and summer of 2019, complex studies were carried out, including an analysis of the hydrochemical characteristics of the water column and geochemical characteristics of bottom sediments in the coastal areas of the Crimean Peninsula (Figure 1).

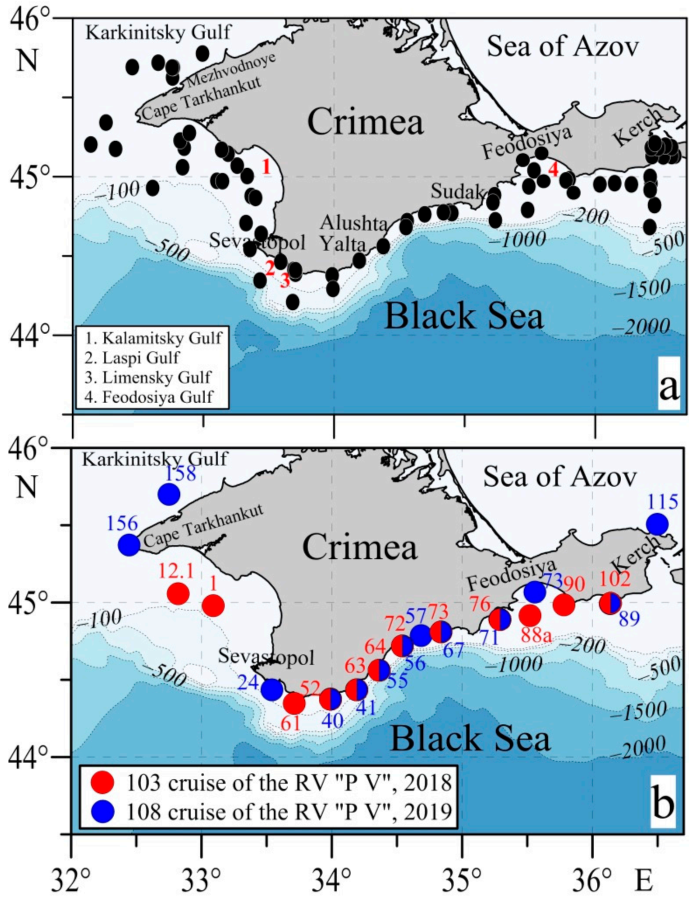

Figure 1. Scheme of sampling stations (**a**) bottom sediments surface layer and bottom water layer; (**b**) columns of bottom sediments.

Samples from the bottom waters were taken for chemical analysis using bathometers.

The dissolved oxygen content in the water was determined using the Winkler volumetric titration method with the Carpenter modification [32]. The accuracy of the technique is ±0.010 mL/l (±0.4 μM).

Samples of the surface sediment layer (0–5 cm) were taken using a Peterson dredger (coverage area of 0.1 m^2). To study the vertical structure of the sediments, columns of bottom sediments were selected using a sampler device with an acrylic tube (inner diameter of 60 mm) and a vacuum seal. This sampling method makes it possible to preserve the fine structure of the bottom sediment surface layer and the bottom waters.

The granulometric composition of bottom sediments was determined by the mass content of particles with different sizes, expressed as a percentage, relative to the mass of a dry soil sample taken for analysis. At the same time, a combined method of decantation and dispersion was used. The aleurite and pelite fractions (≤0.1 mm) were separated by wet sieving, followed by determination of the dry mass gravimetrically. Coarse-grained fractions (>0.1 mm) were separated by the sieve method of dry sieving using standard sieves (GOST 12536-2014).

The content of organic carbon (C_{org}) was determined coulometrically on an express analyzer AN 7529 using a technique adapted for marine bottom sediments [33,34]. The value of the standard deviation for samples with a C_{org} content of <0.5% was 0.028, and that for samples with a C_{org} content of >1.5% was 0.083.

To obtain the chemical profile of pore waters, voltammetry with a glass Au-Hg microelectrode was used [35–37]. An electrode saturated with silver chloride was used as a comparison electrode, and a platinum electrode was used as an auxiliary. Profiling of bottom sediment columns was carried out with a vertical resolution from 1 to 10 mm. The error of the method was 10%. To analyze the physicochemical characteristics in the laboratory, the columns were divided into 1–2-cm thick layers using a hand extruder and an acrylic ring.

3. Results

3.1. Northwestern Region

The waters of the North West Shelf (NWS) are under intense anthropogenic pressure. The supply of a large amount of nutrients (nitrogen, silicon, phosphorus) with river runoff and their active consumption by phytoplankton for photosynthesis lead to active consumption of oxygen in the bottom waters for the oxidation of organic matter [18]. As a result, oxygen deficiency zones occur and anoxic conditions develop, first in the bottom sediments, and then in the bottom water layer. The dynamics of the NWS waters in winter are determined by the influence of the Rim Current; in other seasons, they are determined mainly by the influence of wind currents. In [38], it was shown that under north, northeastern and eastern winds, cyclonic circulation prevails in the NWS, the Rim Current propagates along the western coast of the Crimea and the Danube runoff is directed to the south. Under southern and southwestern winds, anticyclonic circulation forms, and the runoff of the Danube River spreads over the entire shelf. The scheme of surface layer water transport in the NWS was also presented in [39]. The study of [17] presented the vectors and quantitative characteristics of bottom currents according to the data of cruise 103 of the RV Professor Vodyanitsky. The current velocities in the bottom water layer in the seaward part of the Kalamitsky Gulf reached 10 cm/s.

In this work, the Black Sea NWS includes the Karkinitsky and Kalamitsky Gulfs, as well as an extended section of the coastal zone from Cape Tarkhankut to Cape Khersones. Further, in this work, these water areas will be referred to as the northwestern region, which is explained by their geographical position relative to the Crimean coast.

The oxygen concentration in the bottom waters of the northwestern region in the summer of 2019 varied from 164 to 287 µM (from 50 to 94% sat.) (Figure 2c). The minimum concentrations were noted in the seaward part of the Kalamitsky Gulf, in the Sevastopol area (depths of 80–90 m) and in the area of Mezhvodnoye village (15–26 m). The maximum values were noted in the southwestern seaward part of the Karkinitsky Gulf (depths of 15–40 m).

The surface layer of the sediment in the northwestern region was formed mainly by silty material (up to 72%) (Figure 2a), consisting mostly of a pelite-aleuritic fraction (60%). Coarse-grained gravel–sand material was distributed fragmentarily in shallow water in the northern part of the Kalamitsky Gulf and in the area of Cape Tarkhankut. At some stations, the sediment material consisted of large shells, and the proportion of the >1 mm fraction reached 65–85%.

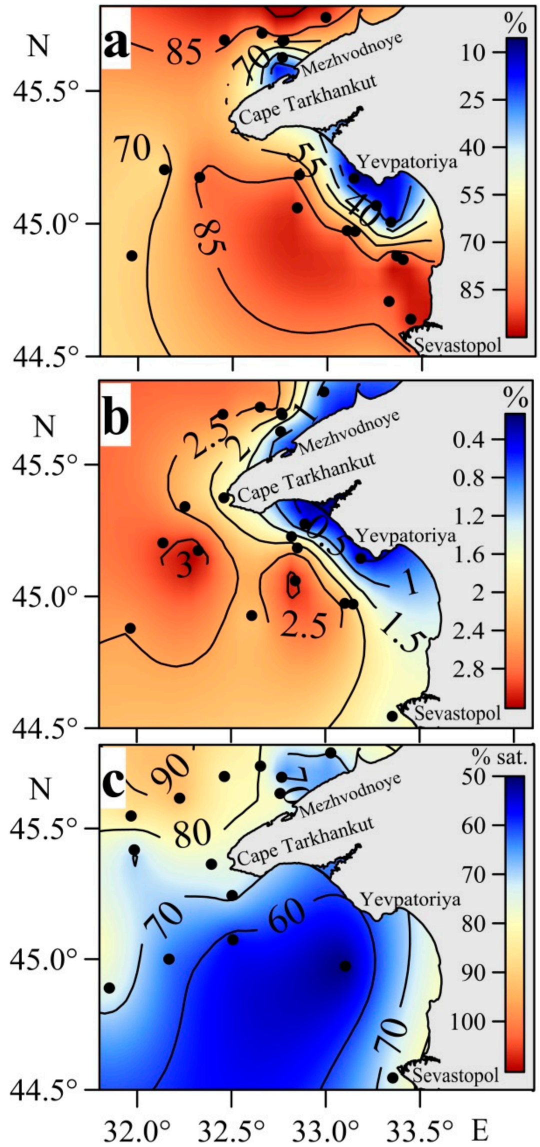

Figure 2. Spatial distribution of the clay fraction (**a**) and C_{org} (**b**) in the sediment surface layer, and (**c**) oxygen saturation in the bottom waters of the northwestern region.

The content of C_{org} in the sediment surface layer (Figure 2b) varied from 0.3–0.8% dry. wt. at stations located near the coast of Yevpatoriya and around Cape Tarkhankut, to 2.4–3.3% dry. wt. in fine-grained silty sediments of the seaward part of the Kalamitsky Gulf and the open southwestern part of the Karkinitsky Gulf. On average, the content of C_{org} in the sediment surface layer in the northwestern region was 2.0% dry. wt.

In the area of the Karkinitsky Gulf (St. 158) (Figure 3b), the bottom water layer (depth ~27 m) was weakly saturated with oxygen (62% sat., 185 μM) (Figure 2c). The chemical composition of pore waters was determined by the processes involving sulfates, the reduction products of which are hydrogen sulfide and its derivatives (Table 1). The average concentration of hydrogen sulfide was 163 μM. The processes of organic matter oxidation were also controlled by the processes involving dissolved forms of iron (Table 1), were the average concentration of Fe(II) was 441 μM. The decrease in the oxygen concentration in the bottom water layer and the development of suboxic conditions in the upper layer of bottom sediments at stations located near the coast probably resulted from an additional supply of organic matter with urban and storm runoff from the northern coast of the Karkinitsky Gulf. This also led to increased siltation of the coastal zone, since it is quite shallow and has limited water exchange [39].

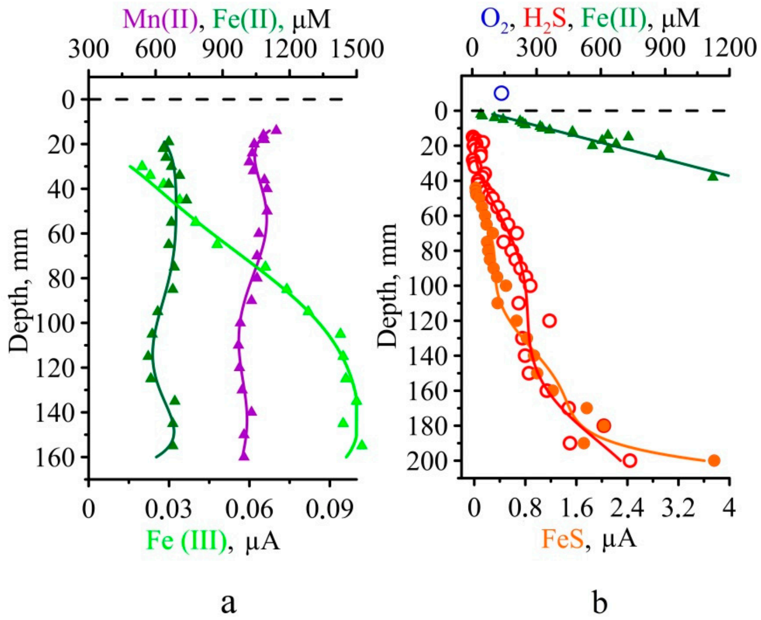

Figure 3. Vertical distribution of pore water components of bottom sediments in the northwestern region: (**a**) St. 12.1; (**b**) St. 158.

In the area of Kalamitsky Bay (St. 12.1, depth ~60 m), the finely dispersed nature of the sediment and the high content of C_{org} (2.7% dry wt.) led to oxygen deficiency and the development of suboxic conditions. In the upper layer (0–10 mm), the oxidation of organic matter occurred due to nitrates/nitrites, which are inactive in the potential range used [35]. Below, high concentrations of Fe(II) and Mn(II) were noted (Figure 3a), which averaged 676 μM and 1039 μM, respectively. High concentrations of these components might be explained by the occurrence of ferromanganese nodules in these areas [40], which was also confirmed by modern data in [31].

3.2. Southern Coast of Crimea and Feodosiya Gulf

The region of the southern coast of Crimea (SCC) includes a section of the coast from Cape Aya to the Feodosiya Gulf. A large number of sanitary-resort and health infrastructure facilities are concentrated along the shore. The Feodosiya Gulf is characterized by a more intense anthropogenic impact, including the industrial–agrarian–recreational type of economic development of the territory, especially in its western part [41]. The modern state of the Feodosiya Gulf ecosystem is significantly affected by the maritime complex facilities and the discharge of storm- and wastewater [42].

In the coastal zone of the SCC, the direction of currents in 75% of cases coincides with the direction of the coastline. In 80–90% of cases, their speed does not exceed 20 cm/s, and only in 2% of cases is their speed more than 40 cm/s. The maximum velocities are noted for the southwestern and northeastern currents [43]. According to the data of [17], the velocities of bottom currents in the SCC region vary from 10 cm/s in the shallow Feodosiya Gulf (10–20 m) to 20–30 cm/s in the deep-water areas (50–100 m).

Under the action of wind, a two-layer structure of flows periodically forms in shallow coastal water, and a countercurrent is observed under the drift current [43]. In the area of Alushta, a countercurrent is observed between the Rim Current and the coast [44]. This nature of coastal current structures has certain ecological consequences. When wastewaters are discharged at a distance of less than 4 km from the coast, pollutants return to the beach zone and accumulate in the bottom water layer. On the contrary, when the outlet is over

10 km from the coast at a depth of more than 100 m, the transverse circulation in the Rim Current leads to their further sinking and moving away from the coast [44]. In addition, according to the studies presented in [45], under the action of prolonged northeast winds, the Sea of Azov waters saturated with suspended matter spread along the entire SCC, reaching Cape Khersones.

The granulometric composition of the bottom sediments of the SCC is diverse. In the Sevastopol region, the surface layer (0–5 cm) was poorly represented by the gravel fraction (2%), and the proportion of sandy material was about 1%. The silty material prevailed (94%) (Figure 4a), formed mainly by the pelite-aleuritic fraction (77%). The content of C_{org} averaged 2.4% dry. wt.

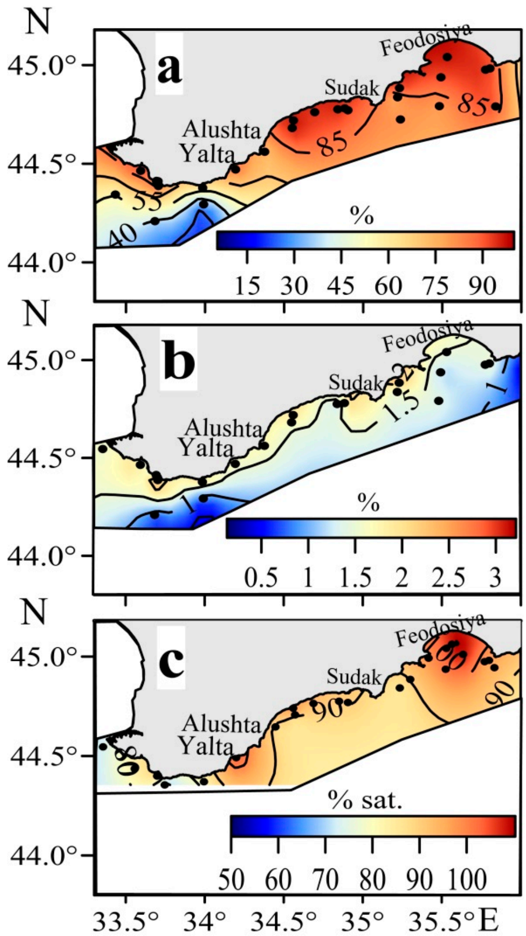

Figure 4. Spatial distribution of the clay fraction (**a**) and C_{org} (**b**) in the sediment surface layer, and (**c**) oxygen saturation in the bottom waters of the SCC region.

To the southeast of Sevastopol, the sediment became coarser. The content of the gravel fraction at the stations located near the shore in the Limensky Gulf and the Laspi Gulf reached 10–23%, and the content of silty material reached 66–72%. The content of C_{org} in the bottom sediment surface layer in this area reached 2.7% dry. wt.

In the northeast direction from Yalta to Sudak, the sediment was represented mainly by silty material (72–95%) (Figure 4a), with an increase in the pelitic fraction from 55% to 89%. The increased proportion of gravel–sand material in the SCC was determined mainly by the contribution of shell material. Thus, the maximum values were noted both near the coast and at the stations located on the continental slope (100–300 m). The content of C_{org} in this area averaged 1.5% dry. wt. (Figure 4b).

The maximum proportion of silty material was noted in the Feodosiya Gulf (Figure 4a), the content of which decreased from the central part (97%) to the seaward part (79%). The content of the gravel fraction was minimal (1–2%) and slightly increased to 8% in the offshore part due to an increase in the proportion of shells and shell detritus. The average content of C_{org} in the central part of the gulf was 1% dry. wt., and in the seaward part it was 1.4% dry. wt. (Figure 4b). Thus, the C_{org} content in the bottom sediments of the Feodosiya Gulf was, on average, lower in comparison with the shallow water stations in the SCC region.

In the Sevastopol region (St. 24, depth ~80 m), the saturation of bottom waters with oxygen was 84% (275 μM), but there was no oxygen on the sediment surface. The main components of the pore water in this region were oxidized forms of iron.

In the area of the SCC from Yalta to Sudak (depths of 20–80 m), intense water dynamics provided the oxygen saturation of the bottom waters (up to 105% sat.; Figure 4c). The main processes of organic matter oxidation in the upper layer of sediments took place with the participation of oxygen. In the lower layers, the main biogeochemical processes proceeded mainly with the participation of dissolved forms of iron and sulfates (Table 1).

In the area of Yalta (St. 41, depth ~35 m), the penetration of oxygen in bottom sediments up to 14 mm (Figure 4a) determined the oxic conditions. Below, the conditions changed to anoxic, and the main components of the pore waters were reduced forms of iron and sulfides. In addition, the high concentration of Fe(II) (up to 500 μM) limited the sulfide flux into the upper layer of the sediments.

In the area of Alushta (St. 57, depth ~50 m), despite the oxygen saturation of the bottom waters (93% sat., 293 μM), hydrogen sulfide was already present in the surface of the sediments. This led to the rise of anoxic conditions. The main components of the pore waters were the reduced forms of iron and sulfur. The concentration of hydrogen sulfide varied from 1 to 392 μM, with an average value of 140 μM. The average concentration of Fe(II) was 472 μM (Figure 5b).

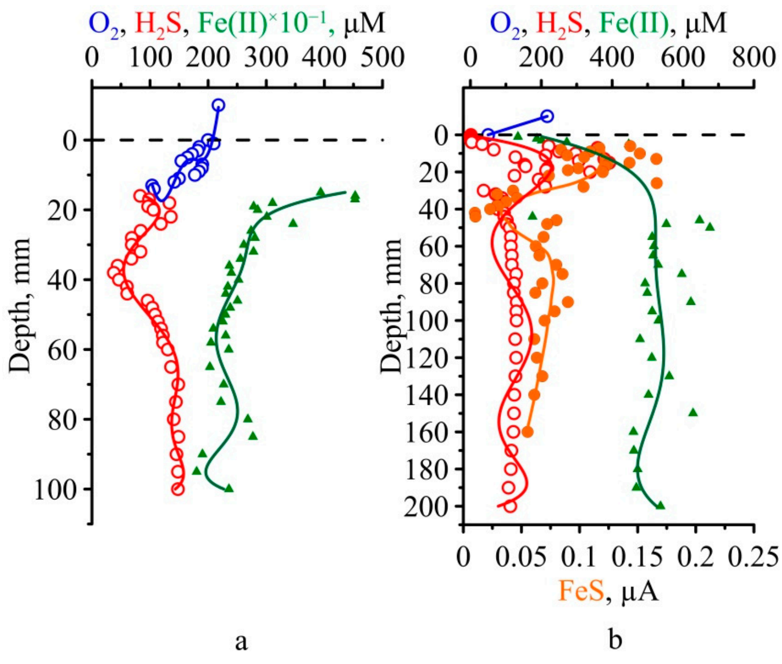

Figure 5. Vertical distribution of pore water components of bottom sediments in the SCC region: (**a**) St. 41; (**b**) St. 57.

Despite the sufficient oxygen saturation of the bottom waters (up to 110% sat.) (Figure 4c), there was no oxygen in the surface of sediments in the Feodosiya Gulf (St. 73, depth ~21 m). The main components of pore waters were reduced forms of iron and sulfur (Figure 6a). The average concentration of Fe(II) was 1123 μM, and the maximum concentration reached up to 2100 μM. This is probably the result of a significant anthropogenic contribution; for example, port manufacture [41,42]. The concentration of hydrogen sulfide varied from 110 to 368 μM, with an average value of 270 μM. The presence of hydrogen sulfide is also determined by the anthropogenic contribution of stormwater and municipal wastewater [42], which are additional sources of nutrients and organic matter.

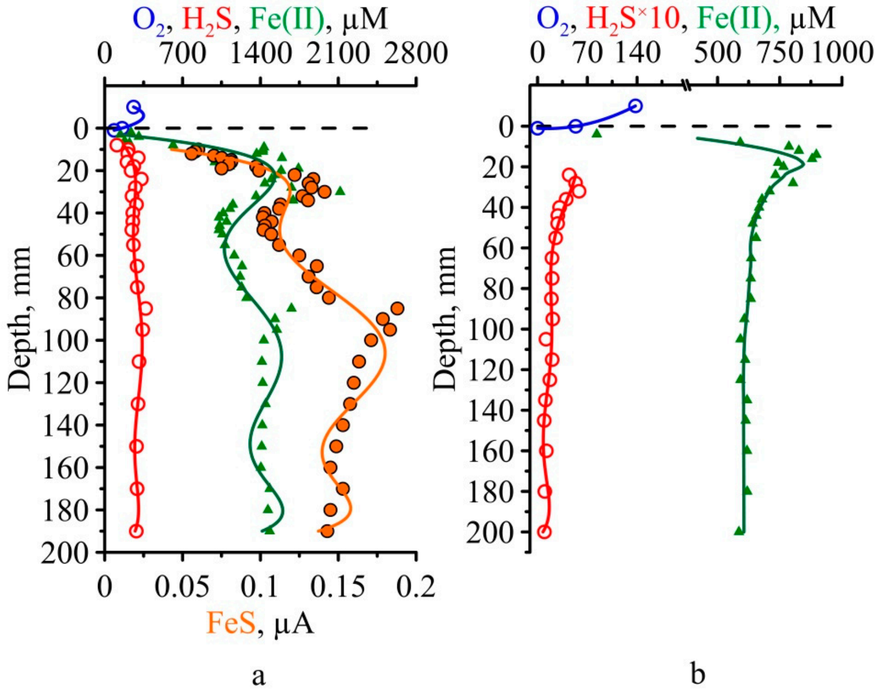

Figure 6. Vertical distribution of pore water components of bottom sediments in the Feodosiya Gulf: (**a**) St. 73; (**b**) St. 88a.

In the seaward part of the Feodosia Gulf (St. 88 a, depth ~32 m), Fe(II) was also the main component of the pore water, but its concentrations were lower and averaged 655 µM (Figure 6b). This may indicate that, farther from the central part of the gulf, the anthropogenic load is significantly reduced. The average concentration of hydrogen sulfide was also an order of magnitude lower than in the central part of the Feodosia Gulf and amounted to 2.5 µM. The processes of organic matter oxidation in bottom sediments in this area were controlled by reactions involving iron (Table 1).

Thus, despite the active water dynamics, the low content of C_{org}, and the saturation of the bottom waters with oxygen, the determining factor in the occurrence of anoxic conditions in the Feodosia Gulf bottom sediments was probably the predominance of the silty fraction (up to 97%).

3.3. Kerch Pre-Strait Area

In the late 1980s–early 1990s, the Kerch pre-strait area from the Black Sea was subjected to strong anthropogenic impact, which led to siltation of the upper layer of bottom sediments. Some of the main factors influencing the ecosystem of this area, in addition to shipping and active fishing, are soil dumping, dredging, and the transfer of suspended matter from the Kerch Strait [46,47]. These factors negatively affected the chemical composition of sediments and benthic communities [42,48].

Coarse-grained material prevailed in the surface layer (0–5 cm) of the bottom sediments of the Kerch pre-strait from the Black Sea, and the content of the >10 mm fraction reached 47% (Figure 7a). The silty material averaged 28% of the sediment mass and was formed by the aleuritic-pelite (6%) and pelite-aleuritic (22%) fractions. The content of C_{org} averaged 0.7% dry. wt. (Figure 7b).

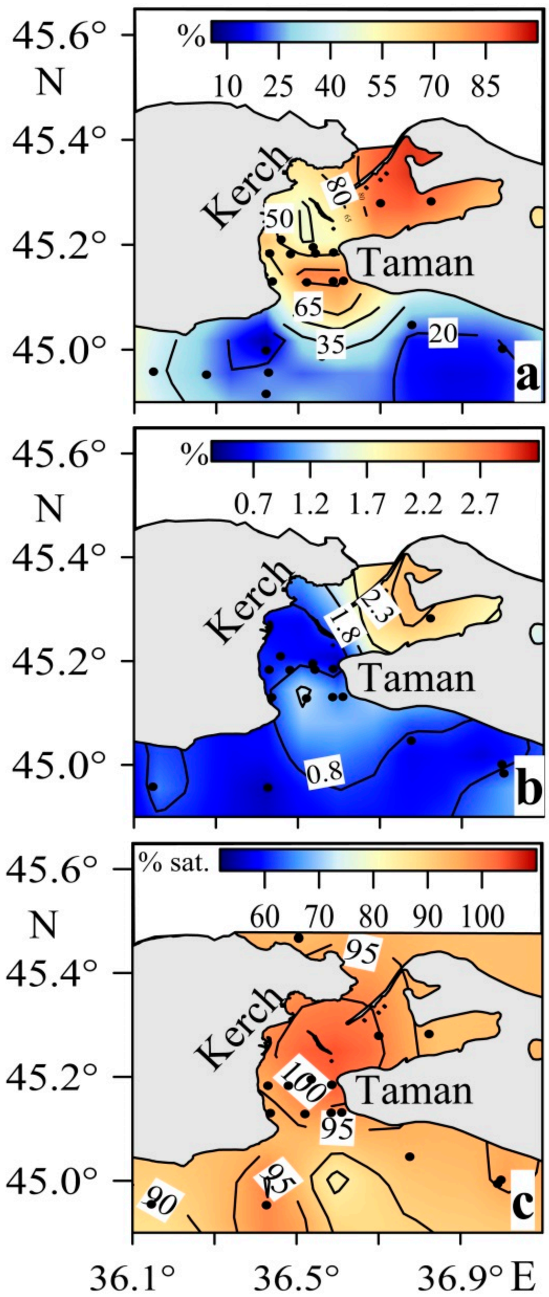

Figure 7. Spatial distribution of the clay fraction (**a**) and C_{org} (**b**) in the sediment surface layer, and (**c**) degree of oxygen saturation of the bottom water layer of the Kerch pre-strait region.

In the region of the Kerch pre-strait from the Sea of Azov (St. 115, depth ~10 m), the oxygen concentration in the bottom water layer was 217 µM (91% sat.) (Figure 7c), and on the sediment surface (0 mm), it decreased to 133 µM (Figure 8a). The predominant components of the pore waters were the reduced forms of iron and manganese. The Fe(II) concentration reached 2700 µM (Figure 8a), with an average value of 803 µM. Two layers of Mn(II) concentrations were noted: 1–15 mm and 36–76 mm (Figure 8a). The concentration of Mn(II) in the 1–15 mm layer increased from 236 to 854 µM (average value of 538 µM), and in the 36–76 mm layer, it decreased from 1042 to 658 µM (average value of 853 µM). Iron monosulfide (FeS) was also noted.

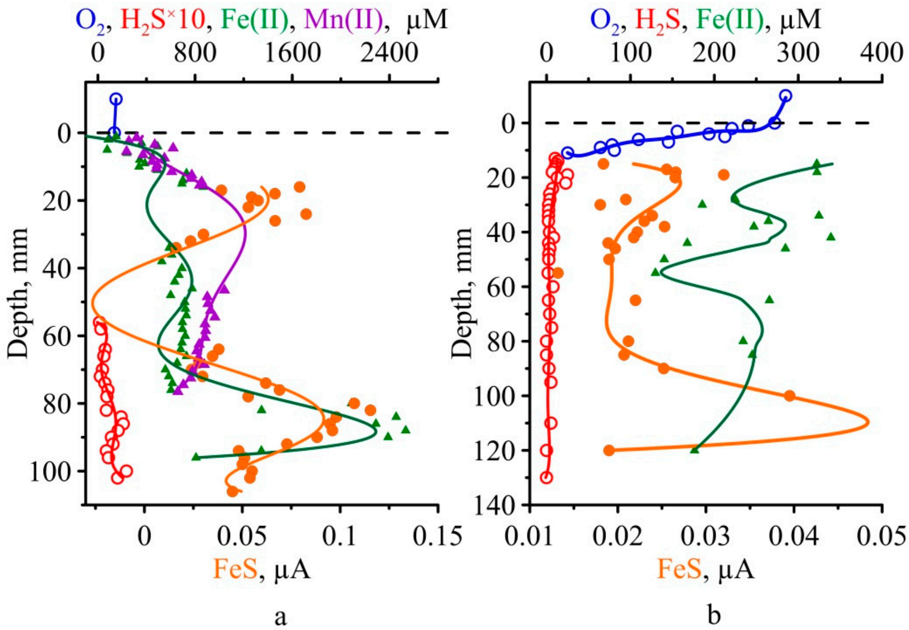

Figure 8. Vertical distribution of pore water components of bottom sediments in the Feodosiya Gulf: (**a**) St. 115; (**b**) St. 89.

In the region of the Kerch pre-strait from the Black Sea (St. 89), the oxygen concentration in the bottom water layer was 282 μM (88% sat.), which is quite typical for this depth (45 m). On the sediment surface, its concentration reached 272 μM (Figure 8b), and it penetrated the sediment up to 11 mm deep. Below, the main components of the pore waters were reduced forms of iron. The Fe(II) concentration varied between 130 and 628 μM, with an average value of 288 μM. The presence of iron monosulfide, which is a product of the interaction between reduced forms of sulfur and iron (Table 1), was also noted. Its formation, apparently, contributed to the binding of sulfides; the average concentration of H_2S was 6 μM. As a result, the oxic conditions in the upper layer of the bottom sediments in this area and the low content of C_{org} (less than 1% dry wt.) were determined by intense water dynamics [17] under the influence of the Rim Current and the granulometric composition of the sediment.

4. Discussion

The depth affects both the formation of the hydrochemical structure of waters and the features of the formation of sediments [21,22,49]. The analysis of the results obtained made it possible to confirm the established ideas that oxygen saturation in the water column may decrease with the depth (Figure 9a). The Current data show that the average oxygen saturation of the bottom waters varied from 73% sat. in the northwestern region and 79% sat. in the SCC to 96% sat. in the region of the Kerch pre-strait.

It was also confirmed that, with increasing depth, the proportion of the fine-grained clay fraction increases (Figure 9c). The exception is shallow-water areas (for example, the Feodosia Gulf, Karkinitsky Gulf, the shallow part of the northwestern region), in which finer-grained sediments are formed. In addition, in [49], it was noted that, depending on the hydrodynamic regime, sediments of different particle sizes can accumulate at the same depth. One of the characteristic examples of such dependence is the pre-strait zone of the Kerch Strait. In some of its sections, both coarse-grained shell and fine-grained silty sediments accumulate. As a result, an average (0.55) linear dependence of the accumulation of the fine-grained pelitic fraction on the depth was noted for the Black Sea coastal areas.

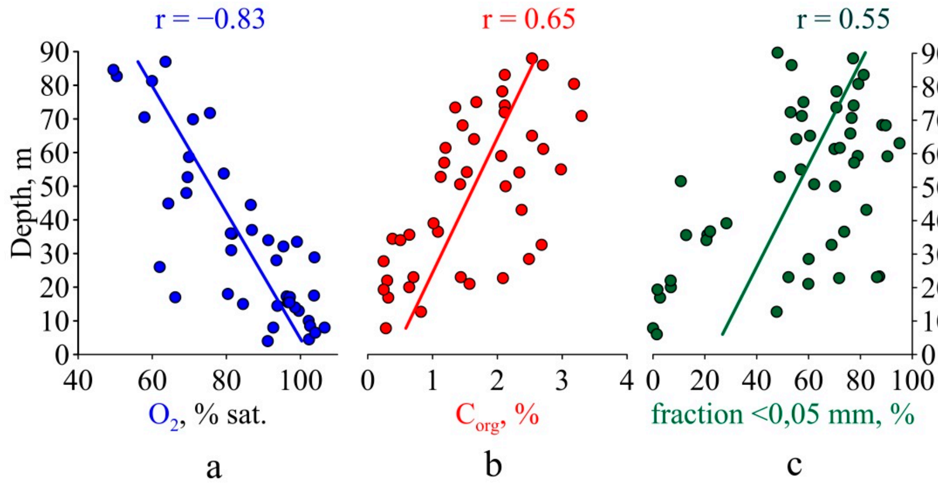

Figure 9. Dependence of the value distribution on depth: (**a**) the oxygen saturation of the bottom waters; (**b**) the content of C_{org} in the surface layer of the sediment; (**c**) the proportion of the pelite-aleuritic fraction in the surface layer of the sediment.

For the coastal areas, a positive (0.63) linear correlation dependence of the oxygen concentration on the proportion of the coarse-grained fraction (> 0.1 mm) in the surface (0–5 cm) sediment layer was obtained. This confirms the well-established notion that the average sediment size determines the oxygen flux, as well as the concentration and depth of its penetration into bottom sediments [12,13,50,51].

A significant correlation between the content of the clay fraction and C_{org} content was found in the studied water areas. This was primarily determined by the relationship with the content of pelite-aleuritic material (the correlation was 0.7), while the correlation with the aleuritic-pelite fraction was weak (0.2). However, despite the noted relationship between the pelite-aleuritic fraction and C_{org} content, the effect of the depth was more pronounced (Figure 8b). This stronger relationship is explained by the fact that in modern sediments in the coastal areas of the Black Sea, organic carbon also accumulates in silty sands with inclusions of shell detritus (1.7–2.1% dry wt.). In earlier works, it was noted that for coarse-grained sediments in the Crimea coastal regions, the content of C_{org} did not exceed 1% [39,52,53]. The data obtained in this work indicate a significant excess of the studied values. Similar dynamics were previously displayed in [52] on the example of the Kerch Strait.

The increase in the rates of C_{org} input and accumulation in medium- and coarse-grained sediments apparently, indicates an intensification of anthropogenic pressure on marine natural ecosystems, even in the case of open water areas with high water dynamics.

As a result of an increase in the supply of organic matter to bottom sediments, oxygen is consumed for its oxidation. A decrease in the supply of oxygen from the bottom water layer in this case can lead to an oxygen deficiency. The depletion of oxygen for the oxidation of organic matter and other reduced compounds leads to a shift in the processes occurring due to the anaerobic oxidation of organic matter closer to the sediment surface. Thus, reduced forms of nitrogen, manganese, iron, and sulfur become predominant in the upper layer of sediments, and oxygen-free zones with anaerobic conditions are formed [9–11]. An increase in the content of reduced compounds, in particular, the concentration of sulfides, in the surface layer of sediments will further lead to an increase in their flow into the bottom water layer. In this case, anaerobic conditions are formed in bottom sediments and in the water column [11]. Such changes in the physical and chemical characteristics of sediments affect the ecological state of the ecosystem and, as a result, the socio-economic attractiveness of the region.

Relationships between the distribution of C_{org} in sediments and H_2S concentrations in the pore waters of bottom sediments in the coastal areas of the Crimean Peninsula shelf were determined (Figure 10). For the surface layer (0–5 cm), a significant positive correlation (0.67) was established at the 95% confidence level (Figure 10a). With depth, the content of organic carbon in the cores increased, which was also seen in the data on the concentrations of hydrogen sulfide. The values of the correlation dependence of the studied parameters varied from 0.7 to 0.99, which indicates a strong relationship between the geochemical characteristics of the sediments and the chemical composition of the pore water (Figure 10b).

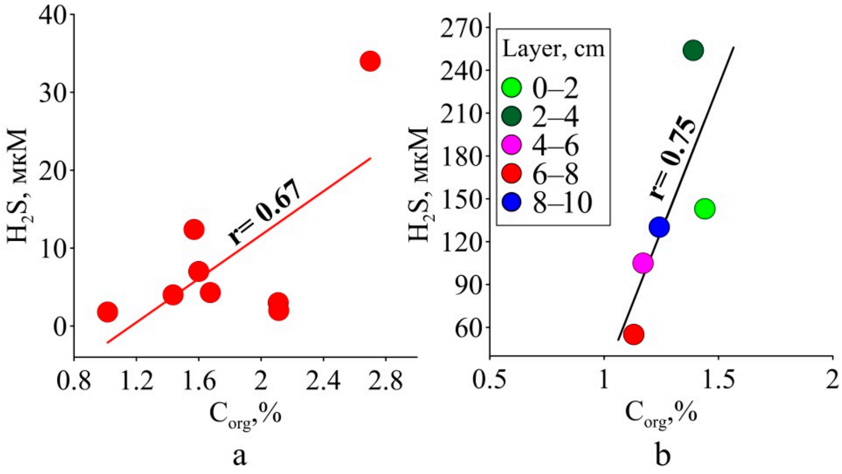

Figure 10. Relationship between H_2S concentrations in pore water and C_{org} in: (**a**) 0–5 cm layer and (**b**) bottom sediment cores.

5. Conclusions

The analysis of the results obtained in this work made it possible to conclude that in the northwestern region (Karkinitsky and Kalamitsky Gulfs), there was a lack of oxygen in the bottom sediment surface layer, as well as oxygen deficiency in the bottom water layer. In the SCC area, intensive hydrodynamics contributed to the saturation of the bottom waters with oxygen (up to 105% of sat.). At most stations, oxygen penetrated into the sediment up to 20 mm. The main processes of the organic matter oxidation in the sediment upper layer occurred with the participation of oxygen. However, despite the saturation of the bottom water layer with oxygen, in the area near the Feodosiya Gulf, hydrogen sulfide was already present in the surface layer of sediments, and the main processes in the bottom sediments proceeded with the participation of iron and hydrogen sulfide. In the Kerch pre-strait area from the Black Sea side, oxic conditions prevailed in the bottom water layer and the sediment upper layer, and from the Sea of Azov side, the absence of oxygen was noted in the upper layer of bottom sediments and the main processes proceeded with the participation of reduced forms of iron and manganese. In the southwestern part of the Kerch Strait, suboxic conditions were noted.

The presence of positive linear correlation dependences of the oxygen concentration on the proportion of the coarse-grained fraction (>0.1 mm), and of the hydrogen sulfide concentration on the C_{org} content in the surface layer (0–5 cm) of the sediment and sediment columns, indicate a strong relationship between the geochemical characteristics of sediments and the chemical composition of the pore water. This confirms the early assumptions that the average particle size of the sediment determines the oxygen flux, concentration, and depth of its penetration into bottom sediments, while the intensive supply and accumulation of organic carbon, on the contrary, lead to the depletion of oxygen for its oxidation and contribute to the appearance of high hydrogen sulfide concentrations.

It is noted that in areas with an aerobic environment, the main factor determining the redox conditions is the water dynamics. This factor affects the saturation of bottom waters with oxygen. However, the limitation of water exchange and changes in the conditions and rates of sedimentation in these zones can contribute to the formation of oxygen-deficient zones.

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