

Organic Matter and Grain-Size Distribution of the Modern Bottom Sediments in the Balaklava Bay (the Black Sea)

N. A. Orekhova^{1,*}, E. I. Ovsyany¹, K. I. Gurov¹, M. A. Popov^{2,**}

¹*Marine Hydrophysical Institute, Russian Academy of Sciences, Sevastopol, Russian Federation*
*e-mail: natalia.orekhova@mhi-ras.ru

²*Kovalevsky Institute of Marine Biological Researches, Russian Academy of Sciences, Sevastopol, Russian Federation*
**e-mail: maricultura@mail.ru

The results of investigation of the bottom sediments sampled in the Balaklava Bay in February and June, 2015 are represented. The grain-size distribution, and the organic carbon (C_{org}) and calcium carbonate ($CaCO_3$) content have been studied. Noticeable change in the fractions' content that took place in course of the last 10 years is revealed. To a greater extent it is referred to the sand or gravel material, its quantitative characteristics and the features of its spatial distribution. As for the silt material in the Balaklava Bay sediments, its content, according to all the samples, grew, on the whole, from 58 to 66 %. The changes in the organic carbon abundance that took place in the bottom sediments in 2005–2015 were comparatively analyzed both for the Balaklava Bay and other water areas of the Heraklion Peninsula. A general tendency of the organic matter abundance to decrease in the bottom sediments of the bay was noted; it is treated as a result of some alteration in the anthropogenic pressure. The organic carbon mean concentration in the Balaklava Bay bottom sediments is two to three times lower than that in the other bays of the region which were subjected to permanent anthropogenic pressure. However, pollution of the Balaklava Bay with the untreated municipal, storm and industrial sewages leads to formation of the local bottom zones where the sediments are saturated with organic matter ($C_{org} > 2.5$ %). Such phenomena can exert a negative impact on the state of the marine environment ecology including, in particular, structural deviations in the macrozoobenthos community. Further decrease of the organic matter abundance is possible only in case the pollution basic sources are either completely removed or, at least, their influence is reduced. Such a condition is indispensable due to its extreme importance for implementing the state plan to turn the Balaklava Bay into a recreational area and a yacht marina.

Keywords: Balaklava Bay, bottom sediments, grain size, organic carbon, inorganic carbonate content.

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The issues of assessing the level of anthropogenic eutrophication of the Black Sea coastal waters remain relevant today. At the same time, the study of the impact

of bottom sediments organic enrichment on the processes occurring at the water-bottom interface, along with other factors (oxygen consumption for the oxidation of labile organic matter, redox conditions, grain size composition of the sediments, the lifetime condition of benthic community, etc.) is essential for determination of the role of sediments organic enrichment in the marine environment ecological condition.

Accumulation of organic matter (OM) in marine bottom sediments is typical for the marine shelf, especially for estuarine areas and semi-enclosed coastal waters with restricted water exchange, subject to constant anthropogenic pressure. Excessive OM accumulation negatively affects the ecological condition of coastal waters, which is manifested in the occurrence of benthic hypoxia/anoxia and fish mortality, the effect on macrobenthos, the increase in mobility of a number of metals during the occurrence of reducing conditions and their transition to the bottom waters, removal of nutrients, which contributes to the water eutrophication, etc. [1–3].

In this regard Sevastopol bays are studied very unequally: the research of bottom sediment OM in the Sevastopol Bay was carried out systematically for many years [4–6], in the other bays – occasionally. Such areas include the Balaklava Bay: in the 1940–90s the possibility of studying it was very limited, the bay ecosystem was subjected to significant anthropogenic impact. The change of the Balaklava Bay status and the reduction of man-induced load allow us to hope for the improvement of the marine environment ecological state. However, many problems associated with anthropogenic influence on its ecosystem remain unresolved to this day: the main sources of pollution are domestic, storm and industrial wastewater, which enters the water area of the bay without treatment, as well as river runoff and aeolian inflows [7, 8].

The first studies of the Balaklava Bay bottom sediments were carried out by professor A. Verigo in 1885. Plasticine black sediments were studied in the upper part of the bay. They were used as therapeutic mud as an analogue to the one of the Saki and Odessa estuaries. The content of mineral salts, amine bases, fatty acids was determined [9]. The beginning of modern sediment studies was initiated by the Institute of Marine Biological Research (IMBR) in the 1990s [10]. The data on physical-chemical indicators of bottom sediments, the composition and quantitative characteristics of macrozoobenthos were obtained, as well as water area ecological status was assessed. The studies performed by Marine Hydrophysical Institute (MHI) in 2005 provided the assessment bottom sediments contamination with metals and consideration of accumulation and distribution of organic carbon (C_{org}) features in the surface layer (0–5 cm) [11]. In 2006, a comprehensive study of the Black Sea coastal water sediments was carried out with the participation of IMBR, including the OM of Balaklava Bay [12]. Currently, due to the decision of the Russian Federation Government on the development of Balaklava Bay as an international center for yacht tourism [13], the assessment of the condition and marine environment ecological recovery are of great importance.

The main purpose of this work is to study C_{org} distribution features in the surface layer and in the bottom sediments, assessment of level of bottom sediments enrichment with organic matter in the modern period and the trends of its changes over the time.

The region of works, materials and methods of research

Balaklava Bay, located in the southwest of the Heracleean Peninsula, is a semi-enclosed area of estuary type with restricted water exchange. The bay has S-shaped configuration: in the central part, the knee-like narrowness divides it into two approximately water areas – the northern and southern basins, which have different morphometry and hydrodynamics, the primary production amount and pollution level [7, 14].

As already noted, the Balaklava Bay was subjected to a prolonged anthropogenic load [7, 11]. Sources of bottom sediment industrial pollution were the wastewaters from “Metalist” shipyard discharged into the upper part of the bay without treatment, as well as pollution resulting from the dock repair of ships. The Balaklavka River, the catchment area of which is 27 km², flows into the apex part of the bay. Hydrometric and hydrochemical observations on the river are not carried out. The river is fed mainly by rainwater. During the low water period the river dries out and serves as a collector for wastewater discharge. Balaklavka River runoff is formed by a slope flush from the catchment area (mainly from residential area and the territory of Balaklava mine department) and municipal wastewater in the amount of $\geq 8 \cdot 10^3$ m³/day. They are discharged without any treatment into Megalo-Yalo Bay near the Balaklavsky Cape. Under certain hydrodynamic situations [8] these wastewaters, which are actually discharged onto the water surface (10 m depth), enter the southern basin of the bay, affecting the processes of sedimentation, accumulation of pollutants and organic carbon. Discharge of pollutants into the Balaklavka River is estimated at 18.5 tons/year, which include 1.84 tons/year of suspended matter and 2.3 tons/year of organic substances [15]. Currently the bay is used mainly as a yacht marina and a harbor for fishing boats. In their mooring sites local water pollutions with oil products is observed.

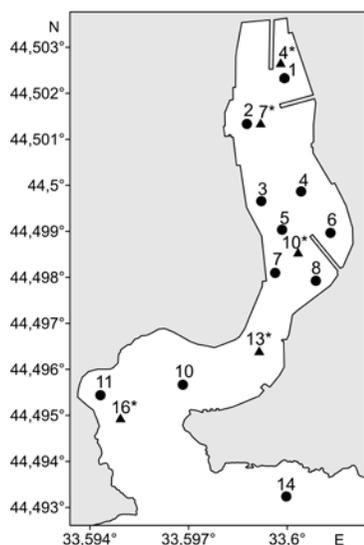


Fig. 1. Scheme of the sampling stations (February, June 2015): ● – bottom sediments from the surface (0–5 cm); ▲ – sediment columns

The samples of bottom sediments for studying spatial distribution of geochemical parameters (the content of C_{org} , chloroform bitumen and carbonate content ($CaCO_3$)) were taken at the stations (Fig. 1) February 2015 from the surface layer (0–5 cm) using the Petersen dredge. In June 2015, the sediment columns were taken to study the vertical distribution features. Sampling, preparation and analysis of samples were carried out using standard methods in accordance with regulatory documents (GOST 17.1.5.01-80, ISO 5667-12:1995, ISO 5667-19:2004, ISO 14235-1998, ISO 10693-1995, ISO 11277:1998, GOST R 11465-2011) taking into account methodological recommendations of UNEP [16]. C_{org} and carbonate content are measured in % of dry matter mass.

The results and their discussion

Bottom sediments of the bay are represented by silt sediments, sandy silts and sediments with coarse-grained stone gravel and shell material with low silt content. Silt sediments in the upper layers (0–5 cm) are semi-liquid, with a “fluffy” layer (0–2 cm), with moldy (putrid) odor and/or with H₂S smell (3–5 cm) (Fig. 2). They are saturated with water, their natural water content varied from 150 to 92 %. Silty sediments were characterized by a high content of organic carbon, ≥ 2.5 % (Fig. 3, *a*). Sands with shell gravel had 30–37 % of natural water content, the maximum CaCO₃ content (up to ~ 99%) and minimum content of C_{org} (less than 0.5 %) (Fig. 3, *b*).

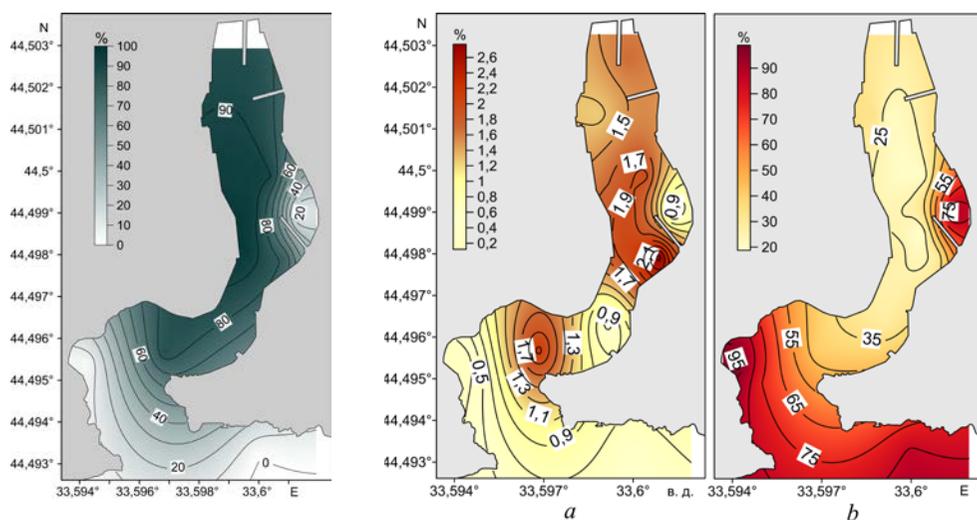


Fig. 2. Distribution of the aleuritic fraction (%) in the Balaklava Bay bottom sediments (2015)

Fig. 3. Distribution of C_{org} (%) – *a* and CaCO₃ (%) – *b* in the surface layer (0–5 cm) of the Balaklava Bay bottom sediments (2015)

When analyzing the sediment columns, loose fine-grained black and dark gray sediments were found in the lower segments of samples with the inclusion of shell detritus and separate shells. In addition to mollusks and detritus, the presence of human activity products (fragments of plastic film, melted metal particles, wood chips, etc.) is characteristic of bottom sediments in layers below 5–6 cm. Precipitation in a segment deeper than 5–7 cm has a pronounced smell of oil products and sometimes also a rainbow “oil” gleam.

When studying the grain-size composition of bottom sediments a significant change of their fractional ratios over the last 10 years was observed. To a greater degree it concerns sand and gravel material, its quantitative characteristics and features of spatial distribution. Silt material content in the sediments of Balaklava Bay in all samples increased, on average, from 58 to 66 %, fine material is still concentrated in the western and north-western parts of the northern basin (Fig. 2). At the same time, an increase in the proportion of silt sediments enriched with organic matter in the northwestern part of the southern basin should be noted (Fig. 2; 3, *a*). This can be considered as a result of pollution by municipal wastewaters.

A separate question of the man-induced impact on the bay bottom sediments is the impact the Balaklava mine department production activity, which extracts marble-like limestone using open pit mining. A crushing-and-preparation plant with a design capacity of $4.5 \cdot 10^6$ tons/year is located within the boundaries of Balaklava, and loading terminal is located on the territory adjacent to the apex of the Balaklava Bay. These objects are the main sources of fine dust. According to the estimate obtained in [17], the emission of pollutants (dust) into the atmosphere is about 1.400 tons/year. Under effect of wind and water slope erosion loose limestone enters the water area of the bay. In the bottom sediments this is manifested in the form of light interlayers in 12–14 cm segment (stations 4* and 7* in Fig. 1), as well as in the study of river alluvium in the lower course of the Balaklavka River.

The results of C_{org} and carbonate content studies in the bottom sediments of the Balaklava Bay showed that C_{org} accumulation level in it is significantly lower than in other areas of the Heraklean Peninsula, but higher than in the open waters of the Southern Coast of Crimea (SCC) (Table). It should also be noted that average C_{org} content in the Balaklava Bay over the past 10 years has decreased noteworthy and in 2015 it amounted to 1.40 % due to the changes in anthropogenic load. Hydrodynamics of water (upwelling) and hydrochemical regime (lack of persistent hypoxia in the bottom waters) [7] also affect the accumulation of organic matter, which provides the possibility of oxidative destruction of newly formed organic matter in contrast to Sevastopol Bay, where hypoxia and anoxia occur regularly.

Organic matter C_{org} and $(CaCO_3)$ content in the bottom sediments of the Crimea coastal areas (0–5 cm layer)

Water area	Quantity of stations	C_{org} , %		$CaCO_3$, %		Source
		Mean	Range	Mean	Range	
Balaklava Bay, 2005	15	2.40	0.66–4.83	40.1	18.8–82.9	[11]
The same, 2015	16	1.40	0.15–2.80	42.2	18.4–99.1	Present work
Sevastopol Bay, 2003–2005 including Southern Bay	62	4.40	0.97–11.6	34.5	18.9–68.6	[4–6]
	16	5.40	2.71–7.22	27.6	18.7–38.9	
Sevastopol Bay, 2015–2017 including Southern Bay	35	3.36	0.5–7.24	34.0	22.5–87.3	Present work
	11	5.03	3.3–7.45	32.7	27.5–42.0	Present work
Streletskaia Bay, 1982–1985	8	3.02	0.27–5.42	No data	No data	[19]
	5	4.29	3.00–6.36	57.8	51.4–61.6	Present paper
Kazachia Bay, 2002	12	1.80	0.11–4.55	78.0	44.1–99.9	[20]
	6	2.74	0.39–6.08	54.2	38.0–98.5	Present paper
Limenskiy Gulf (SCC), 2012	12	0.51	0.23–1.08	38.8	20.1–47.7	[21]

At the same time, the impact of discharge of untreated municipal wastewaters on C_{org} content at their transport to the southern basin became more significant, $> 2\%$. The same level remains in the silty sediments of the northern basin deep part $> 2.5\%$ (Fig. 3, *a*). This testifies that local sources of accumulation exist as a consequence of anthropogenic influence.

C_{org} spatial distribution in the surface layer of bottom sediments is characterized by considerable heterogeneity (Fig. 3, *a*), which is determined by such factors as bay morphometry, hydrodynamic features and grain-size characteristics, primary production, localization of pollution sources and the level of anthropogenic pressure. Thus, in the marine part of the northern basin the maximum C_{org} concentrations ($\geq 2\%$) are located in the area of aleurite-pelitic silt distribution, which is determined by organic matter feature to be accumulated in fine sediments (Fig. 3). Here an increased primary production is also observed [18].

The minimum C_{org} ($\leq 1.5\%$), observed in the apex part of the bay are the result of the bottom sediments “dilution” when the loose limestone rocks get into the basin during their extraction. A separate analysis of dark and light interlayers showed differences in C_{org} and $CaCO_3$ concentrations: in the limestone of light interlayers C_{org} content is by 1–2 orders of magnitude lower and the carbonate content is two times higher than in the bay bottom sediments. The same carbonate enrichment is also characteristic of the Balaklavka River mouth alluvium (Tavricheskaya Embankment) compared with the sediments taken upstream.

Intensive accumulation of biogenic carbonates is characteristic of the southern basin in the part adjacent to the open sea, where sediments formed by shell rock are found. The mass fraction of $CaCO_3$ here reaches 99% (Fig. 3, *b*).

In marine bottom sediments the general nature of OM vertical distribution is determined by the processes of its accumulation and destruction. It is expressed by a consistent decrease of C_{org} content from the upper to the lower horizons [22]. But such a “classic” nature of the vertical distribution is not always observed in the bays due to the impact of certain natural factors and anthropogenic impact.

In order to assess the features of OM vertical distribution, three columns of bottom sediments from the bay apex part (station 7*), the central part of the northern basin (station 10*) and from the southern basin (station 16*) (Fig. 1, 4) were analyzed. C_{org} vertical distribution is similar at all studied stations (Fig. 4, *a*). Its general direction in 15–17 cm sediment layer (Fig. 4, *a*) is similar to the “classic” distribution — a decrease in concentration from the upper to the lower layers, which is especially pronounced at the deepwater stations 10* and 16*. However, in 5–13 cm segment a noticeable increase of C_{org} concentrations with intermediate fluctuations and a maximum in 10–11 cm layer is observed. Obviously, this is a phenomenon of man-induced type — a long-term and intense pollution of bottom sediments with oil products. This is indicated by both visual signs noted above (a pronounced specific odor and the nature of sediments) and the maximum concentrations of chloroform bitumen (A_{chl}). At the same time, the carbonate distribution is antibatic: at the maximum values of C_{org} the carbonate content of sediments decreases, which is a natural result of hydrocarbon pollution. Therefore, it is hardly possible to consider such an increase of C_{org} concentrations only as a result of productivity growth, although this area of the bay is characterized by an increased level of primary production [18].

Based on the sedimentation rate of the Balaklava Bay ($5.3 \text{ mm}\cdot\text{year}^{-1}$) [23], the time period of C_{org} concentrations increase in the sediments for 5–16 cm segment over 1950–1990 period can be estimated at a qualitative level. As it was a period of active man-induced pollution, as well as on the basis of the above-described state of bottom sediments in this segment, it can be argued that C_{org} accumulation in this period is primarily due to oil pollution, which is confirmed by the features of bitumen distribution (Fig. 4, *b*).

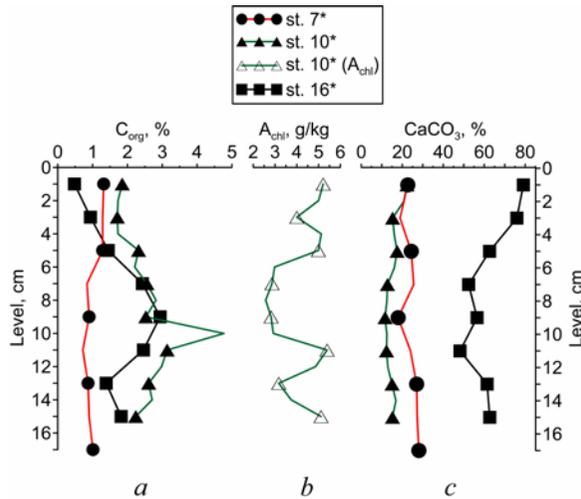


Fig. 4. Vertical distribution of the organic carbon – *a*, the chloroform bitumen – *b* and the inorganic carbon (content) – *c* (Balaklava Bay, 2015)

Despite the decrease of the total level of the bay bottom sediments enrichment with C_{org} which took place during the last 10 years, local OM accumulations can have a significant impact on the bottom biological communities.

Based on the estimates of the threshold level, the achievement of which has a negative effect on the macrofauna state causing structural changes [2, 3], we can conclude that the observed level of OM accumulation ($C_{\text{org}} > 2.5 \%$) led to a change in the structure of the bay benthic community. Macrozoobenthos species resistant to pollutants are the dominant ones. At the same time, low abundance and biomass are observed in the most polluted parts of the bay – in the estuarine part of the southern basin and in the central part of the northern basin [24].

Conclusion

According to the results of a comparative analysis of data on C_{org} content in modern sediments of the Balaklava Bay for 2005–2015, a trend for a decrease of organic matter content was determined. The cause is both a change in anthropogenic load level and nature and features of hydrophysical processes that form the image of the Balaklava Bay marine environment. Unlike the Sevastopol Bay where hypoxia and anoxia appear regularly, no cases of low oxygen concentrations ($< 2 \text{ ml}\cdot\text{dm}^{-3}$) in the bay were revealed. This is a consequence of the absence of organic matter significant accumulation and disposal in the bottom sediments. The impact of hydrodynamic regime and upwelling, contributing to the ventilation of bottom

waters and maintaining the level of oxygen concentrations in the bottom zone above the critical one, which provides the oxidative destruction of newly formed organic matter, is also not excluded.

However, the inflow of untreated municipal, storm and industrial wastewater into the bay leads to the formation of increased OM concentrations in the sediments and to a negative impact on the macrofauna state causing structural rearrangements in the benthos community. Therefore, without the implementation of systematic environmental measures for eliminating the main pollution sources of the Balaklava Bay, the hazard of eutrophication and organic matter accumulation remains.

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About the authors:

Natalia A. Orekhova – Head of Marine Biogeochemistry Department, FSBSI MHI (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), Ph.D. (Geogr.), **ORCID ID: 0000-0002-1387-970X**; **ResearcherID: I-1755-2017**; natalia.orekhova@mhi-ras.ru

Evgeniy I. Ovsyany – Research Associate, Marine Biogeochemistry Department, FSBSI MHI (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0002-6093-5102**, EugeneOvsyany@yandex.ru

Konstantin I. Gurov – Senior Engineer-Researcher, Marine Biogeochemistry Department, FSBSI MHI (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0003-3460-9650**, **ResearcherID: L-7895-2017**, gurovki@gmail.com

Mark A. Popov – Research Associate, Aquaculture and Marine Pharmacology Department, FSBSI IMBI (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), Ph.D. (Geogr.), **ORCID: 0000-0003-0220-1298**, markp@bignir.net

Contribution of the co-authors:

Natalia A. Orekhova – participation in the discussion of the article materials; discussion of the study results; analysis and generalization of the research results, editing and supplementing the text of the article, formulation of the conclusions

Evgeniy I. Ovsyany – scientific supervision of the research, setting out the objectives and tasks of the research; analysis of literature data, analysis of materials on the research theme; formulation of the conclusions

Konstantin I. Gurov – collection and systematization of data, analysis and preparation of initial conclusions, qualitative analysis of the results and their interpretation, construction of tables, graphs, diagrams

Mark A. Popov – collection of available materials on the research, qualitative analysis of the results and their interpretation

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