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Original article

Accumulation of Heavy Metals and Distribution of the Areas of Technogenic Loads in Balaklava Bay: Results of Long-Term Research

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Abstract
Purpose. The purpose of the study is to define the spatial distribution of heavy metal concentrations in bottom sediments and identify areas of technogenic load in Balaklava Bay in 2005–2019, using different geochemical coefficients and indices.
Methods and Results. The samples of the surface layer of bottom sediments (0–5 cm) were collected using a Peterson bottom grab in 2005, 2015, 2018 and 2019 and analyzed. The bulk content of elements was determined by the method of X-ray fluorescence analysis using a Spectroscan MAKS-G spectrometer. In order to assess the contribution of anthropogenic sources to bottom sediment pollution relative to the background content of metals in the coastal zone of the Crimean Peninsula shelf, the following indicators were applied: element concentration levels in sediments, total pollution indices, enrichment factors and geoaccumulation index. According to estimates of the degree of bottom sediments pollution in Balaklava Bay obtained from 2005 to 2019, the pollution level varied from low for elements such as V, Cr and Ni, to high for Cu, Zn and Pb. The most polluted areas were noted in the northern part of the basin, specifically in its central and apex parts. Bottom sediments in the Balaklava Bay basin southern part remained unpolluted throughout the period under study.
Conclusions. It has been shown that the elevated level of pollution in the bottom sediments of the northern part of the bay is the result of a complex impact of natural and anthropogenic factors. However, the proximity of the polluted areas to municipal and storm water runoffs and yacht marinas suggests that the anthropogenic contribution exceeds the natural one. Furthermore, the increase in the values of the studied indices and parameters indicates that this contribution is growing over time.

Keywords: Balaklava Bay, bottom sediments, heavy metals, contamination factors, enrichment factor, geoaccumulation index

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Introduction

Bottom sediments represent a relatively stable yet complex multicomponent system capable of accumulating various chemical substances, particularly heavy metals, and acting as a source of secondary pollution in water bodies through physicochemical processes such as desorption, diffusion and resuspension, as well as biological processes such as bioturbation and bioirrigation [1, 2]. Once heavy metal compounds enter an aquatic environment, they undergo various transport and transformation processes, which are influenced by multiple factors. The danger posed by heavy metals as pollutants is exacerbated by their long-term redistribution across components of the marine ecosystem, with accumulation occurring in hydrobionts at different levels of the food chain [3–5].

Monitoring the levels of pollutants and heavy metals in bottom sediments is highly relevant for the coastal areas of the Black Sea, particularly the Crimean Peninsula, which is renowned for its resorts. Of particular interest are observations of self-purification and secondary pollution processes in water bodies subjected to anthropogenic pressure. Balaklava Bay is a characteristic example of a semi-enclosed water area exposed to prolonged and intensive anthropogenic impact.

While studies of Balaklava Bay were sporadic in the 20th and early 21st centuries, the bay is now being examined in detail and on a regular basis by researchers from Marine Hydrophysical Institute (MHI) of the Russian Academy of Sciences and Institute of Biology of the Southern Seas (IBSS) RAS [6–18]. The increased interest in researching Balaklava Bay in recent years is linked to its use as an active yacht marina, which has led to greater anthropogenic pressure on the bay ecosystem and consequently a decline in its ecological state. To date, the oceanographic, hydrological and hydrochemical characteristics [6–8] of the bay waters and the adjacent part of Megalo-Yalo Gulf have been thoroughly investigated, as have wave dynamics and water circulation using mathematical modeling [9–11]. Important studies on the physicochemical [12–16] and radiochemical [17] properties of bottom sediments have also been conducted over the past decade. Studies [12–15] have examined the granulometric composition of sediments and their dynamics [16] in detail. The accumulation patterns of various organic [13, 15, 18] and inorganic [14, 17] pollutants have also been investigated. Research [14, 15] has focused on identifying correlations between the accumulation of different elements and the physical (granulometric composition and moisture content) and chemical (organic matter and carbonate content) characteristics of bottom sediments.

However, a comprehensive study of the spatial variability of microelement pollution levels in bottom sediments, or an assessment of temporal changes in this pollution, has not yet been conducted in Balaklava Bay. It is crucial to evaluate spatial and temporal variations in the intensity of anthropogenic pollution in order to determine the rate and direction of changes in the anthropogenic load on the ecosystem.

According to [19], the total content of heavy metals (Cr, Cu, Ni, Pb, Zn) in the bottom sediments of Balaklava Bay in 2005 was 558 mg/kg, which is higher than the levels found in Sevastopol Bay (431 mg/kg) [19], the coastal areas of Crimea (281 mg/kg) [20] and Turkey (260 mg/kg) [21], as well as in the northeastern part of the Black Sea (163 mg/kg, excluding Ni) [22]. By way of comparison, the total microelement content of bottom sediments in some Mediterranean coastal areas ranged from 30–163 mg/kg [23–25], while the levels in Al-Harar Lagoon in the Red Sea and the South China Sea shelf were 136 mg/kg [26] and 125 mg/kg [27], respectively. However, the values obtained in Balaklava Bay are comparable to those in Tokyo Bay (536 mg/kg) [28] and Boston Harbor (689 mg/kg) [29], but significantly lower than in New York Harbor (1270 mg/kg) [30] or in sediments from industrial centers such as Birmingham, UK (1090 mg/kg) [31], Baoji, China (1296 mg/kg) [32], and Seoul, South Korea (4494 mg/kg) [33].

Current regulatory standards for permissible metal levels in bottom sediments do not account for regional variations in pollutant accumulation. Such an assessment can be performed using geochemical indices, such as the Enrichment Factor (*EF*) and the Geoaccumulation Index (I_{geo}), which reflect the concentration of an element in sediments relative to its background level [34–36]. According to [37], since anthropogenic anomalies are polyelemental, cumulative pollution indices must be calculated. The Pollution Load Index (*PLI*) and the Degree of Contamination (C_{deg}) are two widely used indices for assessing pollution in coastal sediments worldwide [38–40]. In this study, the following metals were selected to calculate cumulative pollution indices: V, Cr, Ni, Cu, Zn, Pb, Sr, Fe, Mn and Ti. This selection is based on previous research into sediments from Balaklava [14, 15] and Sevastopol Bays [19], as well as the Crimean shelf [20], in which these metals were analyzed.

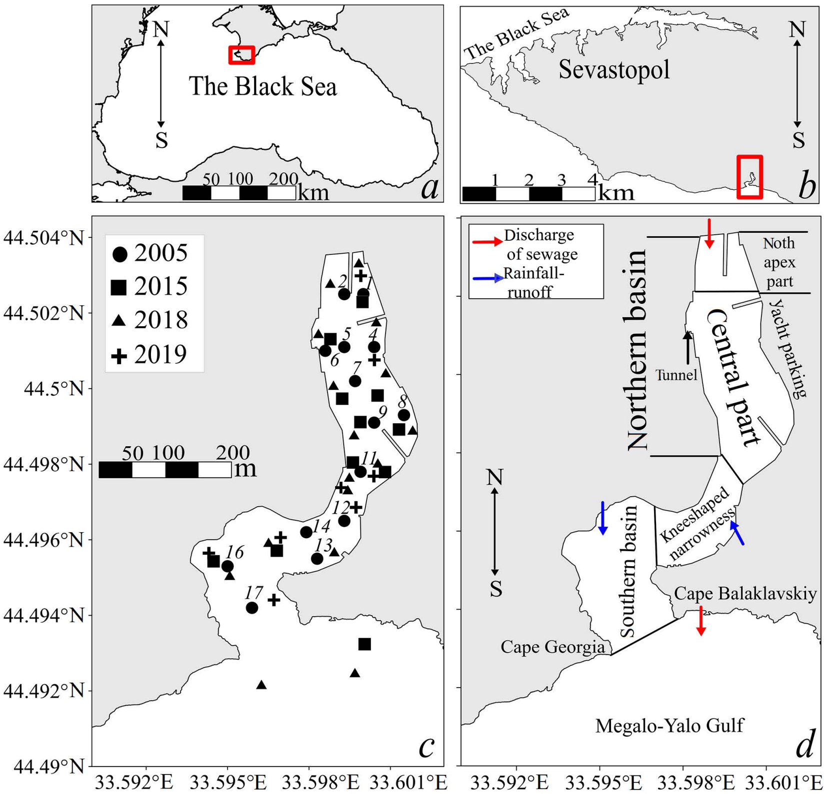
This paper aims to identify features of microelement and heavy metal accumulation in the bottom sediments of Balaklava Bay, and to assess the spatial distribution of areas of technogenic loads between 2005 and 2018, using various geochemical indices.

Materials and methods

The study used data obtained during field expeditions carried out by Marine Hydrophysical Institute (MHI) in Balaklava Bay in 2005, 2015, 2018, and 2019 (Fig. 1). Data on the granulometric composition of the sediments and their organic carbon (C_{org}) content in Balaklava Bay was obtained from previous studies [12, 14, 15].

Based on the bottom morphometry, shoreline configuration and hydrodynamic features of the water masses and bottom sediments, the bay water area was divided into several zones: a shallow northern basin with an isolated apex in the innermost part of the bay; a central section; a southern basin; and a knee-shaped narrowness connecting the latter two zones [7].

Surface sediment samples (from the 0–5 cm layer) were collected using a Petersen grab sampler (coverage area: 0.025 m^2). For metal analysis, the top 5 cm of sediment was subsampled from the central part of the grab using a plastic spoon and placed into pre-labeled zip-lock polyethylene bags. The samples were then transported to the laboratory, where they were oven-dried at 105°C until they reached constant weight and were homogenized.



F i g. 1. Location of the Sevastopol region under study (highlighted in red rectangle) (*a*), its enlarged image (red rectangle marks Balaklava Bay) (*b*), scheme of the bottom sediment sampling stations in Balaklava Bay (*c*), zoning of the bay water area and location of the main storm and sewage water runoffs (*d*)

The total content of chemical elements (Fe, Mn, Ti, V, Cr, Ni, Cu, Zn, Sr, Pb) was determined using X-ray fluorescence (XRF) spectroscopy on a Spectroscan Max-G spectrometer (*Spectron*, Russia). This method enables the total concentration of elements (from Be to U) to be determined in various natural substances in the range of 0.0001–100% [1]. Calibration curves were constructed using certified reference soil samples, including typical black soil, sod-podzolic sandy loam, red soil and carbonate gray soil. The calibration was validated using certified reference materials (CRMs) DSZU 163.1-98 and DSZU 163.2-98. To assess the reproducibility and accuracy of measurements, the certified bottom sediment (DSZU 163.1-98) was analyzed eight times. The minimum standard deviation was 0.003% for MnO and the maximum was 7.62% for Cr.

[1] NPO Spektron, 2016. *Methodology for Measuring the Mass Fraction of Metals and Metal Oxides in Powdered Soil Samples by X-ray Fluorescence Analysis M049-P/16*. Saint Petersburg: NPO Spektron LLC, 18 p. (in Russian).

To evaluate the intensity of microelement accumulation in the surface sediment layer between 2005–2015 and 2015–2018, the percentage increase in concentration was calculated using the following formula:

$$\Delta = (C_{\text{end}} - C_{\text{start}})/C_{\text{start}} \cdot 100,$$

where Δ is the increase in concentration, %; C_{start} and C_{end} are the initial and final metal concentrations (mg/kg), respectively.

For the period from 2005 to 2015, the increase in concentration was calculated as the difference between concentrations in 2015 and 2005. For the period from 2015 to 2018, the increase in concentration was calculated as the difference between the concentration in 2018 and 2015.

The Pollution Load Index (*PLI*), which is a cumulative indicator of sediment pollution by metals, was calculated according to [35]:

$$PLI = \sqrt[n]{CF_1 \cdot CF_2 \cdot CF_3 \cdot \ldots \cdot CF_n},$$

where $CF_{1,2,3,\ldots}$ are the contamination factors for each metal; *n* is the number of metals analyzed (here, n = 10). $PLI > 1$ indicates polluted sediments; $PLI \le 1$ indicates unpolluted sediments.

Degree of Contamination (C_{deg}), which assesses overall pollution levels, was calculated according to [34]:

$$C_{\text{deg}} = \sum_{i=l}^{n} CF,$$

where C_{deg} at a low level – less than 10, at a moderate level – in the range of 10–20, at a significant level – 20–40, at a very high level it is 40 or more.

The Enrichment Factor (*EF*), first introduced in [40], quantifies the normalized accumulation level of an element in bottom sediments relative to its background concentration. This enables the evaluation of anthropogenic contributions. Initially, EF calculations initially used average metal concentrations in the upper continental crust as a reference. However, crustal averages often fail to accurately represent regional geochemical baselines. To improve accuracy, we adopted average values of metal concentrations for the coastal region of Crimea [20], obtained by the authors using methodology [1] (consistent with the analytical protocol of the present study).

The Enrichment Factor (*EF*) is calculated using the following equation:

$$EF = \frac{(\text{EL}/\text{EL}_{\text{ind}})_{\text{sample}}}{(\text{EL}/\text{EL}_{\text{ind}})_{\text{background}}},$$

where $(\text{EL}/\text{EL}_{\text{ind}})_{\text{sample}}$ is the ratio of the target element concentration to the concentration of the indicator element (titanium was selected for this study) in the sediment sample (mg/kg); $(\text{EL}/\text{EL}_{\text{ind}})_{\text{background}}$ is the ratio of the background concentrations of the target element to titanium (mg/kg) in the coastal regions of the Crimean Peninsula [20]. The rationale for selecting titanium as the indicator element is also explained by the fact that it is s a major constituent of soils and sediments, and is highly resistant to weathering and anthropogenic influences [41]. The *EF* is commonly used in marine and estuarine sediment studies as an indicator of pollution [42–46].

The *EF* values were interpreted according to [46] using the following classification: *EF* values not exceeding 1 indicate no accumulation; *EF* values in the range 1–3 indicate insignificant accumulation; *EF* values in the range 3–5 indicate moderate accumulation; *EF* values in the range 5–10 indicate moderately heavy accumulation; *EF* values in the range 10–25 indicate heavy accumulation; *EF* values in the range 25–50 indicate very heavy accumulation; *EF* values exceeding 50 indicate extremely heavy accumulation.

The Geoaccumulation Index (I_{geo}), originally proposed by G. Müller [36], was calculated as:

$$I_{\text{geo}} = \log_2\left(\frac{\text{El}_{\text{sample}}}{1,5 \cdot \text{El}_{\text{background}}}\right),$$

where $\text{El}_{\text{sample}}$ and $\text{El}_{\text{background}}$ are the concentrations of the element in the sediment (mg/kg) and the background concentration of the element [20] (mg/kg), respectively. The correction factor of 1.5 accounts for natural variations in background levels and minimal anthropogenic influences [47]. Depending on the value of the geoaccumulation index, the following pollution classes are distinguished: $I_{\text{geo}} \leq 0$: practically unpolluted; 0–1: unpolluted to moderately polluted; 1–2: moderately polluted; 2–3: moderately polluted; 3–4: heavily polluted; 4–5: heavily to extremely polluted; more than 5: extremely polluted [36].

Statistica software was used to compute the correlation coefficients and their significance levels. A 95% confidence level was applied to evaluate the reliability of the correlations.

Results and discussion

Granulometric composition of bottom sediments. The surface layer of the bottom sediments in Balaklava Bay is predominantly composed of fine-grained silt sediments. Coarse-grained gravel-sand material accumulates only locally near the shoreline, primarily due to the elevated concentrations of shell gravel and detritus found there.

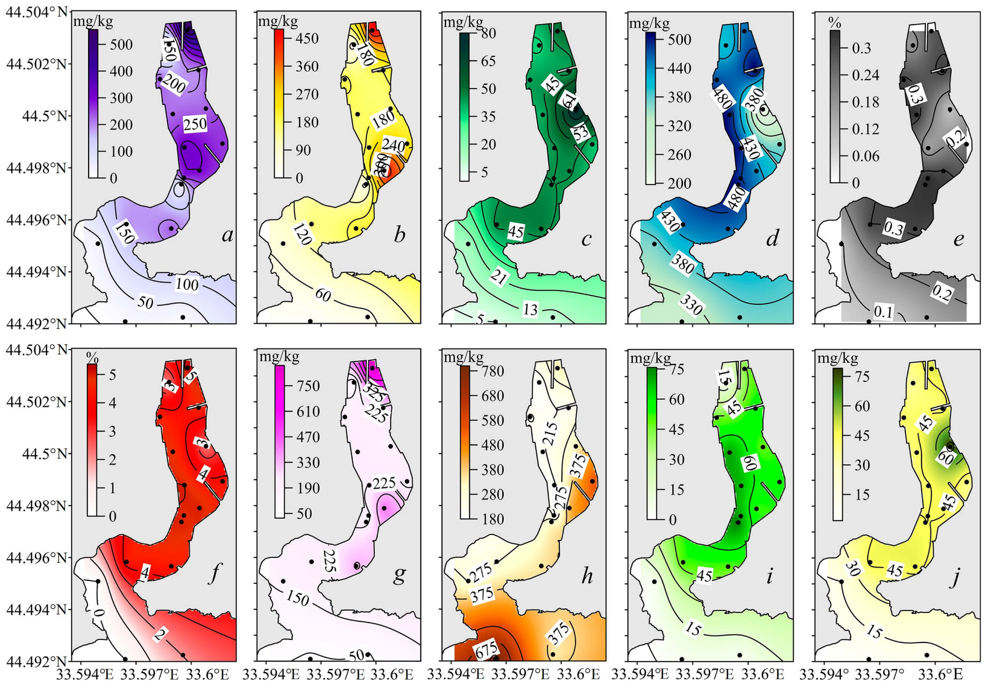
Studies [12, 14, 15] have shown that the granulometric composition of the bottom sediments in Balaklava Bay changed considerably between 2005 and 2018. Firstly, the proportion of fine silty material in the bottom sediments of the bay increased: the average proportion of the silty fraction was 58% in 2005, increasing to 66% in 2015 and reaching 76% in 2018. This indicates a clear siltation of the bay. Additionally, the ratio of silty sediment fractions changed significantly, with an increase in the proportion of pelitic material (averaging 13% in the bay in 2005, 50% in 2015 and 62% in 2018), particularly in the northern part of the basin: the ratio of pelitic to silty fraction (in %) was 19/58 in 2005; 71/17 – in 2015 and 81/11 – in 2018.

The increased accumulation of silty material in the northern part of Balaklava Bay is due to a combination of natural and anthropogenic factors. Natural factors include the isolation of this part of the bay from open-sea wave action and weak hydrodynamics and water circulation, while anthropogenic factors include the input of terrigenous material and organic matter with stormwater and municipal wastewater discharges.

In contrast, the average content of gravel-sand material decreased from 42% in 2005 to 34% in 2015, declining further to 23% by 2018.

Distribution of metals in surface sediment layer. The analysis of the spatial distribution features of the microelements studied in the surface layer of the bottom sediments of Balaklava Bay was carried out based on data from 2018. The sampling stations are shown in Fig. 1, *c*.

Concentrations of heavy metals showed considerable variability: 0.1–0.3% (Ti), 0.3–3.8% (Fe), 5–76 mg/kg (V), 5–80 mg/kg (Ni), 40–123 mg/kg (Cr), 148–399 mg/kg (Mn),10–483 mg/kg (Cu), 15–560 mg/kg (Pb), 183–803 mg/kg (Sr), 38–869 mg/kg (Zn). The spatial distribution of heavy metals in the 0–5 cm sediment layer is presented in Fig. 2.



F i g. 2. Spatial distribution of Pb (*a*), Cu (*b*), Ni (*c*), Mn (*d*), Ti (*e*), Fe (*f*), Zn (*g*), Sr (*h*), V (*i*), Ni (*j*) contents in the bottom sediments of Balaklava Bay (2018)

The maximum concentrations of Fe, Cu, Pb, and Zn were recorded in the sediments of the northern basin, particularly in the apex part. Mn and V accumulated preferentially along the western shore of the northern basin (Fig. 2). Elevated levels of Cr and Ni were observed near the eastern shore in the central part of the northern basin. Meanwhile, Ti accumulated predominantly in the knee-shaped narrowness area, and Sr concentrations peaked in the sediments of the southern basin and the bay mouth.

A clear relationship emerged between sediment granulometry and metal accumulation. The highest elemental concentrations were consistently recorded at stations dominated by fine-grained silty material. Conversely, the lowest concentrations were recorded in the southern basin, where gravel-sand deposits containing only a 20–30% silt fraction prevail [15]. The table below shows the correlation coefficients between the studied parameters.

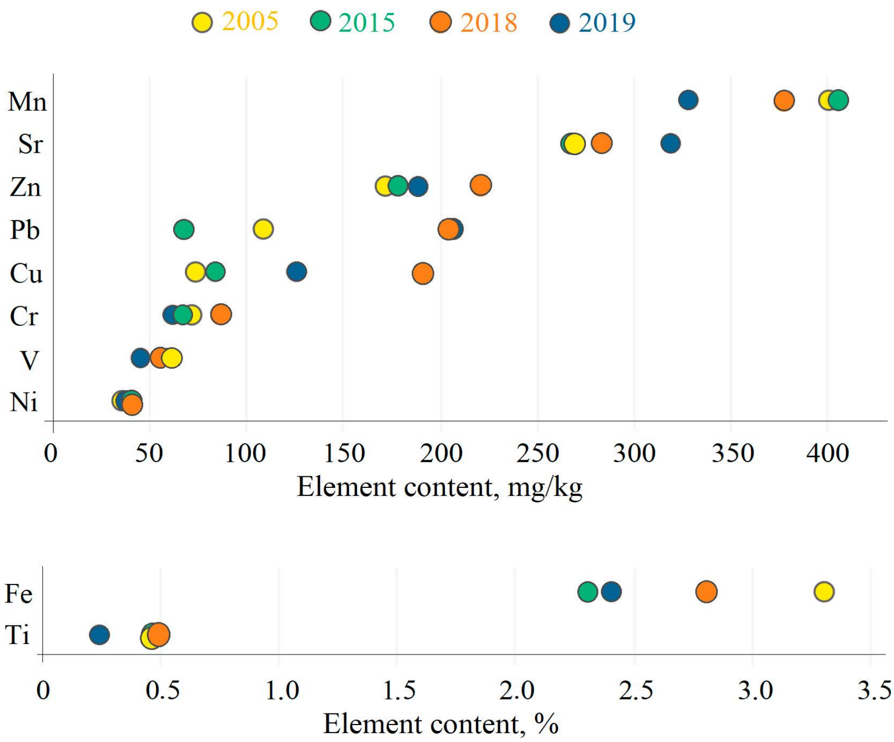
Pearson correlation coefficients between concentrations of heavy metals, fractional content of particle size distribution fractions and C_{org} content. Correlation coefficients statistically significant at the 95% level are marked in red

Parameters	Fe	Mn	Cr	V	Cu	Ni	Zn	Pb	Sr	Ti
Gravel	−0.2	−0.7	−0.3	0.0	0.0	0.2	−0.1	0.0	0.5	−0.3
Sand	−0.8	−0.5	−0.6	−0.7	−0.5	−0.8	−0.4	−0.6	0.6	−0.7
Silt	0.8	0.7	0.7	0.7	0.4	0.6	0.4	0.5	−0.7	0.7
Aleurite	0.4	0.1	0.5	0.4	0.6	0.6	0.4	0.4	−0.2	0.4
Pelite	0.7	0.7	0.6	0.6	0.3	0.5	0.3	0.5	−0.7	0.7
C_{org}	0.7	0.1	0.6	0.7	0.6	0.9	0.5	0.7	−0.1	0.5
Fe	1	0.8	0.9	0.9	0.7	0.6	0.6	0.8	−0.4	0.8
Mn		1	0.8	0.6	0.4	0.1	0.3	0.4	−0.6	0.8
Cr			1	0.8	0.8	0.4	0.7	0.8	−0.2	0.9
V				1	0.5	0.7	0.3	0.7	−0.4	0.7
Cu					1	0.5	0.9	0.9	−0.1	0.5
Ni						1	0.4	0.6	−0.4	0.4
Zn							1	0.8	−0.1	0.4
Pb								1	−0.2	0.6
Sr									1	−0.4
Ti										1

Correlation analysis revealed that all the studied heavy metals, except Sr (r = −0.4), showed direct correlations with Fe (r = 0.6…0.9). All the metals also correlated with both the silt fraction content and organic carbon content (C_{org}) (r = 0.3…0.7 for silt and r = 0.1…0.9 for C_{org}), with the exception of Sr (r = −0.7 and r = −0.1, respectively). However, statistically significant correlations (at 95% confidence level) were absent between silt content and Cu, Zn, as well as between C_{org} content and Mn, Ti, Zn. The difference in correlation patterns between metals and total silt versus pelitic material fractions reflects the specific features of trace element accumulation in different fine-grained sediment fractions [48–50]. No correlation was found between metal concentrations and gravel fraction content (r = −0.3…0.0), except for Mn (r = −0.7), while the correlation for Sr (r = 0.5) was statistically insignificant. This can be explained by the low gravel content, its uneven distribution within the sediment samples and the poor sorption capacity [50].

Similar positive correlations have been documented between heavy metal concentrations, C_{org} silt fraction content and Fe in sediments in various regions of the World Ocean, including the Red Sea [26, 38], the Bohai Sea [27], the Pacific Ocean [44], the South China Sea [45], the Atlantic Ocean [46], among others.

Comparative analysis of metal concentrations over the study period. A comparative analysis of mean concentrations of the studied elements in 2005, 2015, 2018, and 2019 is presented in Fig. 3.



F i g. 3. Average values of metal concentrations based on the data for 2005, 2015, 2018 and 2019

The study revealed that concentrations of Zn, Cu, Cr, and Ti in 2018 were higher than in 2005 (171–220 mg/kg for Zn, 73–190 mg/kg for Cu, 71–86 mg/kg for Cr, and 0.46–0.48% for Ti), followed by a decrease in 2019 (188 mg/kg for Zn, 125 mg/kg for Cu, 61 mg/kg for Cr, and 0.23% for Ti). The lowest average Pb concentration in the bay sediments was recorded in 2015 (67 mg/kg), while the highest values occurred in 2018 and 2019 (204 mg/kg). Maximum average concentrations for Mn, V, and Fe were observed in 2005 (400 mg/kg, 60 mg/kg, and 3.3%, respectively), with minima recorded in 2019 (327 mg/kg, 44 mg/kg, and 2.4%, respectively). Sr showed an inverse pattern, with the lowest value (268 mg/kg) in 2005 and the highest (318 mg/kg) in 2019. The average Ni concentration remained relatively stable throughout the study period, ranging from a minimum of 35 mg/kg in 2005 to maxima of 40 mg/kg in 2015 and 2018.

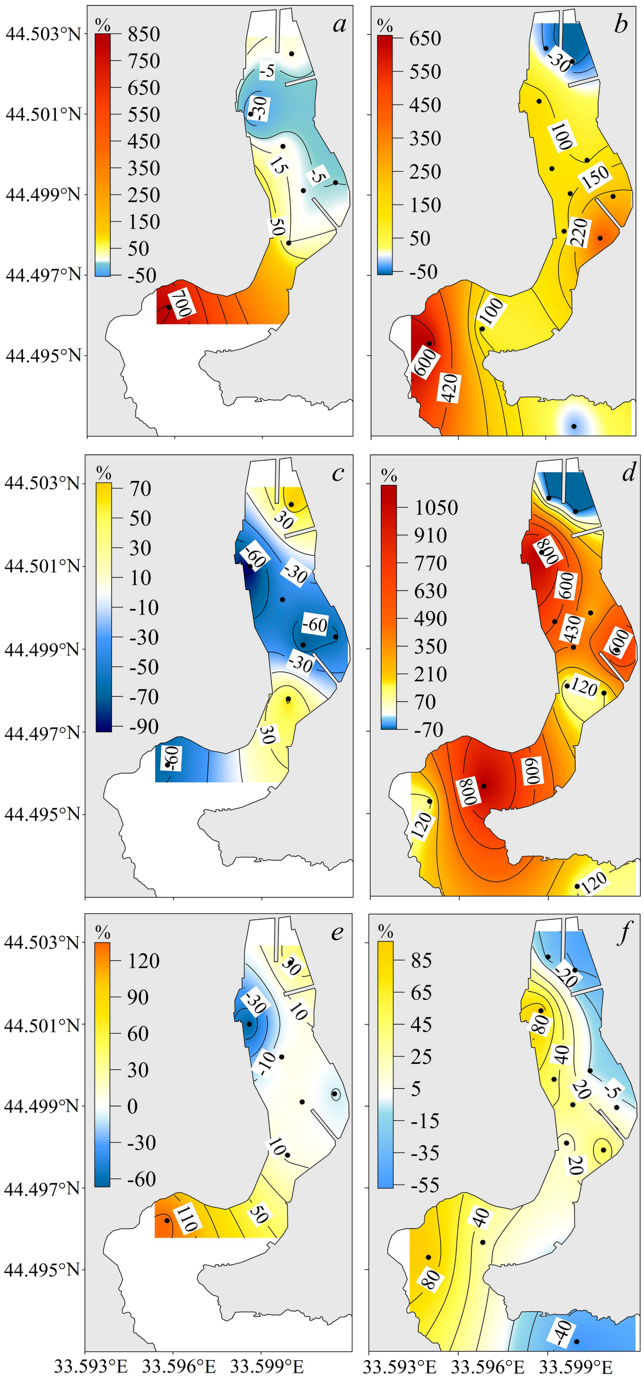
For comparison: the total content of trace elements (Cr, Cu, Ni, Pb, Zn) in Balaklava Bay sediments was 558 mg/kg in 2005 [19]. However, following numerous dredging and cleanup operations in the northern basin between 2005 and 2015, concentrations decreased to 414 mg/kg by 2015. Nevertheless, the year-round presence of numerous boats and yachts in the bay, along with hull maintenance and painting activities near quay walls, combined with multiple sources of stormwater runoff and wastewater discharges (including untreated effluents), led to deteriorating conditions by 2018, resulting in an increased total content of studied trace elements reaching 763 mg/kg.

Assessment of sediment pollution levels. Growth rate values. The spatial distribution features of the estimated growth rates for Cu, Pb, and Zn are presented in Fig. 4. Analysis reveals that during 2005–2015, all the studied elements showed negative growth rates (–5% to –30%) in the central part of the northern basin (Fig. 1, *d*), likely attributable to dredging operations conducted during this period.

Concentrations have increased positively (by 15–150%) in the northern apex part and the southern part of the northern basin. For copper (Fig. 4, *a*), concentrations have also increased in the southern basin. In the northern part of the bay, this is explained by the location of the ship berths and repair facilities that were operational until 2015. In the southern part of the northern basin, it is explained by the features of water circulation and sedimentation in the bay. In the southern basin, it is explained by the additional contribution of terrigenous material that comes with stormwater runoff.

Between 2015 and 2018, the situation changed dramatically. Throughout the water area of the bay, except for the northern part, three zones can be identified where each of the selected trace elements showed significant concentration increases (Fig. 4, *b*, *d*, *f*). The first zone is the western shore of the northern basin. An increase of 100–150% was observed for Cu in this zone, 430–1200% for Pb and 30–90% for Zn. This increase in trace element concentrations is apparently explained by the significant accumulation of the pelite-aleurite fraction (up to 0.05 mm), whose concentrations in this area increased from 2–19% in 2005 to 84–87% in 2018.

The second zone is the southeastern part of the northern basin. The increase here is due to the combined influence of stormwater runoff, the dense location of small craft berths and the features of water circulation that determine the inflow and accumulation of fine-grained sediments in this area [5, 14]. The increase amounts to 150–440% for Cu, 160–760% for Pb, and 10–50% for Zn.



F i g. 4. Spatial distribution of the values of increase in trace element concentrations: *a*, *b* – copper; *c*, *d* – lead; *e*, *f* – zinc in the bottom sediments of Balaklava Bay in 2005–2015 (*a*, *c*, *e*) and 2015–2018 (*b*, *d*, *f*)

The third zone comprises the northwestern part of the southern basin. Research results show that, for Cu and Zn, concentration growth values were lower in 2015–2018 than in 2005–2015. On the contrary, a significant increase in Pb concentration was noted, rising from 65% in 2005–2015 (Fig. 4, *c*) to 130–1150% in 2015–2018 (Fig. 4, *d*). The main sources of pollutant input into the bottom sediments of this zone are stormwater runoff from the northern part of the southern basin and municipal wastewater discharged into the bay exit.

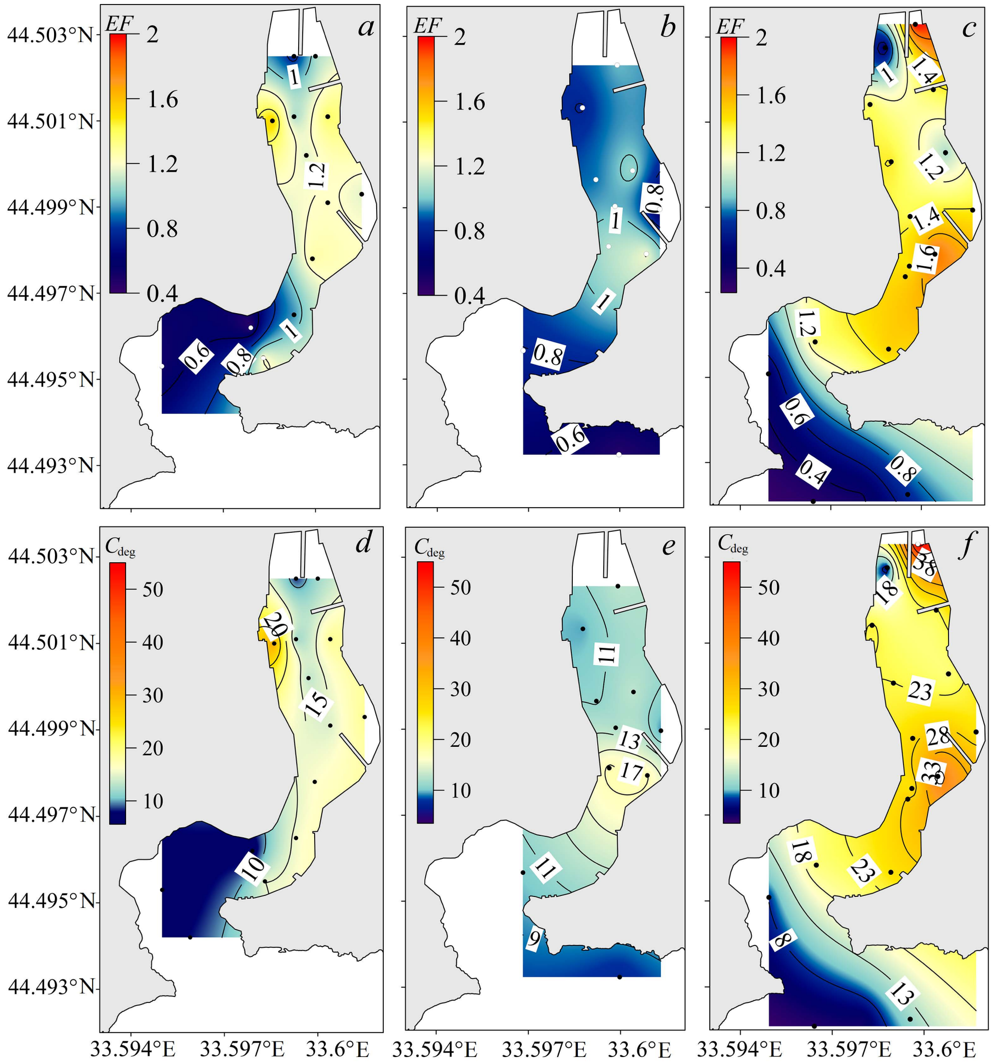
The significant increase in the growth rates of Pb and Cu content in the central part of the bay indicates intensive siltation, which is partly a natural process caused by the regulated nature of the bay and the inflow of untreated wastewater. The deterioration of the natural environment is also due to the increasing number of small vessels, boats and other means of marine transport, as well as painting and cleaning work conducted in the bay.

Integrated pollution indices (*PLI*, C_{deg}). The integrated pollution indices (*PLI* and C_{deg}) were calculated for each sampling station. The spatial distribution of these indices in the bay surface sediment layer over different years is presented in Fig. 5.

According to the *PLI* and C_{deg} values, the total pollution level of the bottom sediments in 2005 was classified as unpolluted to moderately polluted, with values of 1.0 and 13.9 respectively. The minimum values were recorded in the southern basin and the knee-shaped narrowness (0.5–0.9 and 6–8), while the maximum values occurred in the sediments of the northern basin (0.7–1.6 and 12–30). By 2015, the average bay-wide index values had decreased to 0.86 and 12; however, they increased again to 1.2 and 23 by 2018. Notably, the C_{deg} index for northern basin sediments averaged 27 (indicating significant pollution), with a local maximum of 54 (high pollution level) in the northern apex area.

While the maximum *PLI* index values were observed in the sediments of the central part of the northern basin in 2005, anthropogenic anomalies had completely spread across the entire water area of the northern basin and the knee-shaped narrowness by 2018. This redistribution of the index values is determined by the specific water circulation patterns of the water in the northern basin [10] and the dynamics of the bottom sediments within the bay [16]. Additionally, Balaklava's main recreational infrastructure (cafes, restaurants, hotels, and residential buildings) and primary ship berthing facilities are located on the eastern shore of the northern basin.

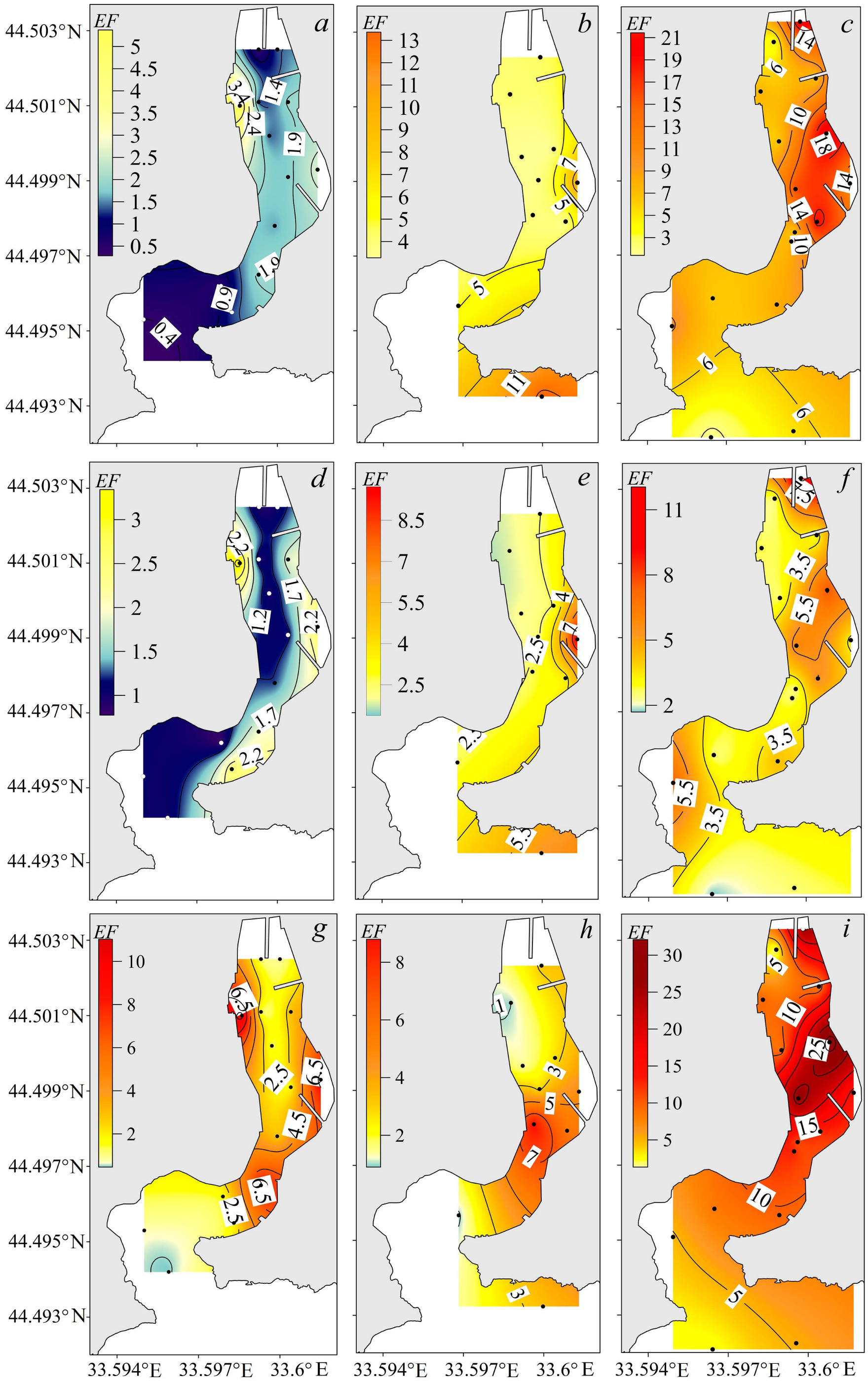
The maximum *PLI* index values recorded in the northern apex in 2018 differ from previous results and can be attributed to the relocation of sampling stations closer to potential pollution sources, such as the mouth of the Balaklavka River. The minimum index values observed in 2015 were likely the result of dredging operations and bay bottom cleaning measures carried out between 2005 and 2015. Excluding the 2015 calculations and comparing values from 2005 and 2018 reveals that the overall pollution level of Balaklava Bay bottom sediments has increased by an average factor of 1.5.



F i g. 5. Distribution of total pollution indices *PLI* (*a*, *b*, *c*) and C_{deg} (*d*, *e*, *f*) in the bottom sediments of Balaklava Bay in 2005 (*a*, *d*), 2015 (*b*, *e*) and 2018 (*c*, *f*)

The consistently low *PLI* (less than 1) and C_{deg} (less than 10) index values observed in southern waters (Fig. 5) and at the bay exit from 2005 to 2018 are explained by the unique water circulation patterns in the open part of the bay, which is exposed to storm wave activity [9–11], as well as by the granulometric composition of sediments at the sampling stations [12, 14, 15].

Enrichment Factor. This study presents *EF* calculations for Zn, Cu and Pb, as these elements showed the highest average values across the bay during the study period (2005, 2015, 2018): 2–10, 2–4 and 3–12, respectively. Fig. 6 shows the spatiotemporal variability of *EF* values in surface sediments of Balaklava Bay.



F i g. 6. Distribution of the *EF* for copper (*a*, *b*, *c*), zinc (*d*, *e*, *f*) and lead (*g*, *h*, *i*) in the bottom sediments of Balaklava Bay in 2005 (*a*, *d*, *g*), 2015 (*b*, *e*, *h*) and 2018 (*c*, *f*, *i*)

Analysis revealed that the *EF* values of all the studied elements increased from 2005 to 2018, with average multiplication factors of 7, 3 and 4 for Cu, Zn and Pb, respectively.

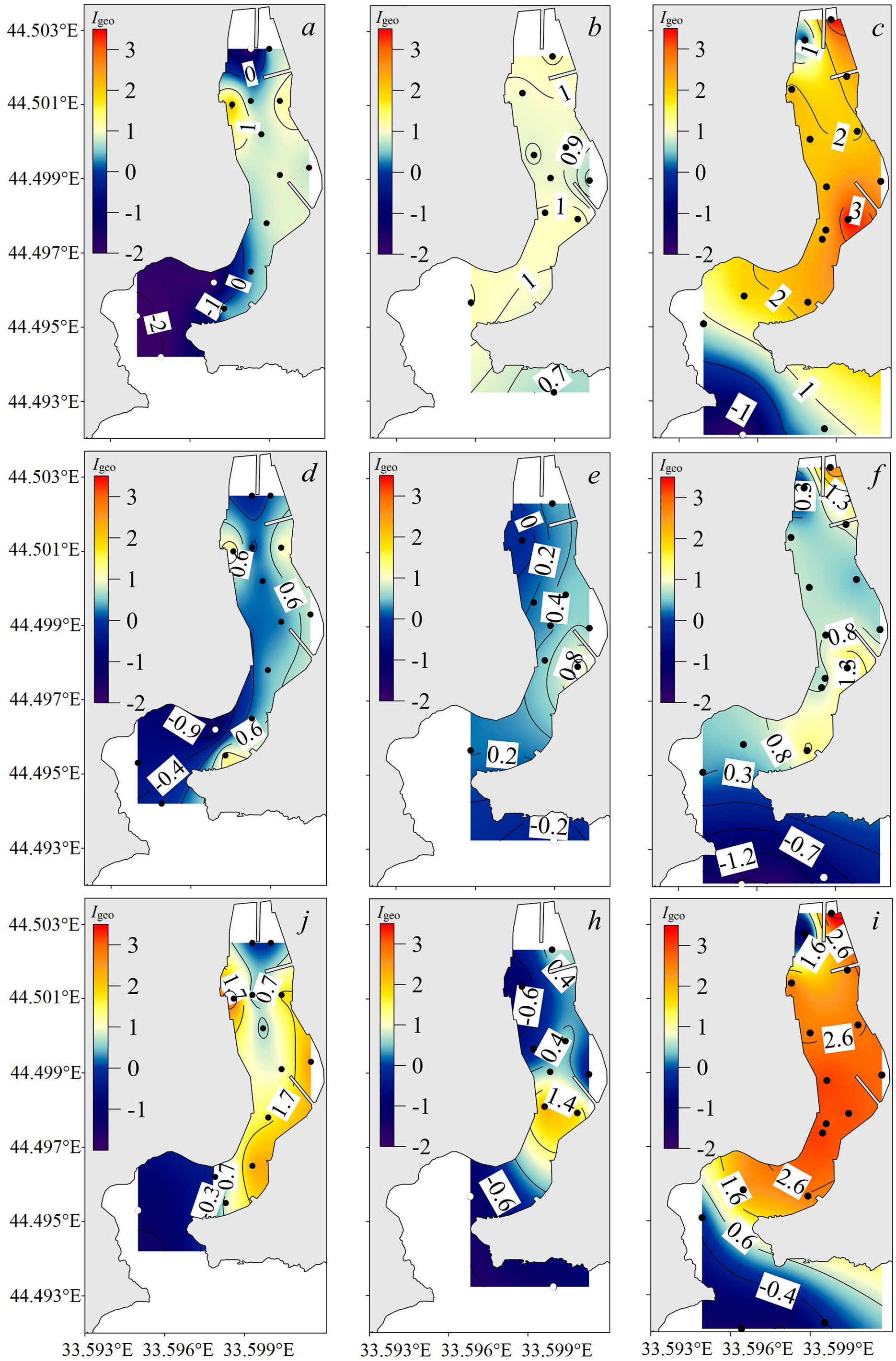
In 2005, the *EF* values ranged from 0.3–5.4 for Cu (Fig. 6, *a*), 0.8–3.4 for Zn (Fig. 6, *d*) and 0.5–11.1 for Pb (Fig. 6, *g*). No enrichment was observed in the southern basin and northern apex of the bay, while local maxima indicating moderate Zn enrichment, moderately severe Cu enrichment and severe Pb enrichment were noted near the tunnel outlet. Moderately severe Pb enrichment was also noted in the central bay area (9.2) and the knee-shaped narrowness (*EF*=8.3). By 2015, the *EF* values for Cu and Zn had increased by factors of 3.4 and 2.4, respectively, while Pb showed little change (3.2 in 2005 vs 3.5 in 2015). Overall, the bay-wide Cu enrichment level increased to moderate, reaching severe levels at some stations in the central area (*EF*=10.3) and the bay exit (*EF*=13.4) (Fig. 6, *b*). Zn maintained minor enrichment in the central area, with local maxima of moderately severe enrichment in the central bay (*EF*=9.9) and the bay exit area (*EF*=6.5) (Fig. 6, *e*). Pb enrichment ranged from minor/moderate in the central areas and at the outlet, to severe (*EF*=8.5) in the knee-shaped narrowness (Fig. 6, *h*). By 2018, only minor enrichment levels persisted at stations near the bay exit for all metals and in some central and southern basin areas for Zn. The maximum EF values were recorded in the central bay areas and corresponded to heavy (*EF*=10…22) Cu enrichment (Fig. 6, *c*), moderately heavy (*EF*=5.5…7.7) Zn enrichment (Fig. 6, *f*) and very heavy (*EF*=27.6…32.6) Pb enrichment (Fig. 6, *i*).

The study revealed that, while elevated *EF* values were observed in close proximity to the main sources of substance input into bottom sediments in 2005, by 2018 these values had become distributed throughout the entire bay area.

The spatial distribution patterns of metal accumulation zones in the bay bottom sediments are explained by the combined influence of natural and anthropogenic factors. In particular, the increase in silt fraction content from 58% in 2005 [12] to 66% in 2015 [14] and further to 76% in 2018 [15] enhanced the sediments’ sorption capacity, thereby accounting for the overall increase in metal accumulation across the entire bay area. Furthermore, the concentration of local pollution sources in the central part of the bay indicates its intensive use as a yacht marina and growing anthropogenic pressure on the aquatic environment.

A comparison of the values obtained for Balaklava Bay with those recorded in the coastal areas of Crimea [20] showed significantly higher levels of contamination (with Pb concentrations exceeding the reference values by an order of magnitude). These findings demonstrate the severe pollution of the bay bottom sediments and the substantial anthropogenic impact on this marine ecosystem.

Geoaccumulation index. Following the same approach as for the *EF* parameter, the I_{geo} index was applied to visualize heavy metal pollution in Balaklava Bay bottom sediments, focusing on Zn, Cu, and Pb (Fig. 7). This selection was primarily motivated by the fact that, for other studied trace elements, $I_{geo} \leq 0$ indicated practically uncontaminated sediments.



F i g. 7. Distribution of I_{geo} parameter for copper (*a*, *b*, *c*), zinc (*d*, *e*, *f*) and lead (*g*, *h*, *i*) in the bottom sediments of Balaklava Bay in 2005 (*a*, *d*, *g*), 2015 (*b*, *e*, *h*) and 2018 (*c*, *f*, *i*)

The geoaccumulation index of the 2005 samples revealed that the sediments ranged from nearly uncontaminated (−2.1…−0.2) in the southern basin to moderately polluted (2.1–3.2) in the northern basin (Fig. 7, *a*, *d*, *g*). The average I_{geo} values were 0.0 for Cu, 0.2 for Zn and 0.8 for Pb. By 2015, the average I_{geo} value had increased to 0.9 for Cu and 0.3 for Zn, while decreasing to 0.1 for Pb. This shift was also evident in the sediments of the southern basin, where Cu and Zn accumulation rose to moderate levels.

Local decreases in Pb I_{geo} values were traced to dredging activities in the northern basin, near the tunnel outlet (3.2 in 2005 versus –1.1 in 2015), and in the municipal beach/small craft mooring area (2.5 in 2005 versus –0.5 in 2015).

By 2018, the I_{geo} values for Cu and Pb had increased markedly, averaging 1.7 and 1.8, respectively, while the rise in Zn was modest, from 0.3 to 0.5. Although the average I_{geo} value indicated moderate pollution, specific stations in the northern basin were heavily contaminated (3.0–3.8) (Fig. 7, *c*, *f*, *j*).

As previously noted, the elevated pollution levels in the northern basin stem from a combination of natural and anthropogenic influences. Comparative data from Crimean coastal sediments [20] showed significantly lower averages: –1.44 for Cu, –0.4 for Zn and 0.03 for Pb. The spatial correlation of peak contamination with municipal/stormwater outfalls and yacht moorings demonstrates anthropogenic dominance over natural factors. Consistent upward trends in all calculated indices (PLI, C_{deg}, EF, I_{geo}) confirm that this anthropogenic contribution is progressively intensifying.

Conclusion

Balaklava Bay was used as a case study to investigate the distribution features of trace elements in bottom sediments, assess the spatial distribution of enrichment and pollution zones, and evaluate changes in anthropogenic pressure between 2005 and 2019. Various geochemical coefficients and indices were employed for this study.

To assess the anthropogenic contribution to sediment pollution in relation to the average composition of trace elements in Crimean coastal shelf areas, the study used contamination and enrichment factors, as well as integrated pollution and geoaccumulation indices.

The research established that the level of sanitary-toxicological hazard posed by sediment pollution in Balaklava Bay shifted from acceptable/moderately hazardous to hazardous/severe during the study period.

Elevated concentrations of the studied elements were consistently observed in samples that were dominated by fine-grained silty material. A comparative analysis of metal concentrations revealed an increasing trend for Cu, Zn, Sr and Pb from 2005 to 2019, whereas Mn, V and Fe showed an opposite, decreasing pattern.

The pollution assessment indicated low levels of accumulation and enrichment for V, Cr and Ni, which did not exceed background values for Crimean coastal areas. Localized exceedances of background levels were noted for Fe, Mn, Sr and Ti, primarily in the fine-grained silts of the northern basin. Pollution levels for Cu, Zn and Pb varied widely, ranging from low levels in the sediments of the southern basin and the bay mouth areas, to high levels in the waters of the northern basin.

The study confirmed that elevated pollution levels in sediments of the northern basin result from a combination of natural and anthropogenic factors. However, the spatial correlation between contamination hotspots and municipal/stormwater discharge points and yacht mooring areas demonstrates that anthropogenic contributions outweigh natural influences. Increasing index values clearly indicate the progressive intensification of this anthropogenic impact. This comprehensive analysis reveals the spatial dynamics of sediment pollution and its temporal evolution in the bay ecosystem under growing anthropogenic pressure.

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Yulia S. Gurova – data processing, analysis and interpretation of data, participation in the discussion of the paper materials, paper correction, formulation of the conclusions

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The authors declare that they have no conflict of interest.