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Distribution of Trace Metals (Cr, Cu, Ni, Pb, Zn, Sr, Ti, Mn and Fe) in the Vertical Section of Bottom Sediments in the Sevastopol Bay (Black Sea)

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Abstract
Purpose. The work is purposed at studying the elemental composition of the bottom sediments vertical section, and at evaluating the spatial-temporal variability and intensity of the polluting elements accumulation in the cores of the Sevastopol Bay bottom sediments based on the expedition research data.
Methods and Results. Sampling of the sediment surface layer (0–5 cm) and cores was carried out in May, 2016 at four stations in the Sevastopol Bay water area along the following fairway: in the apex of the eastern part near the Inkerman CHP, in the central part, in the Yuzhnaya Bay and in the western part of the Sevastopol Bay. The sediment columns were divided into the layers of 1–2 cm thickness. To determine macro- and micro-element concentrations, each sample was dried and homogenized. The total content of elements was determined by the X-ray fluorescence analysis (XRF) using a "Spektroskan MAKS-*G"* spectrometer. The organic carbon (C_{org}) concentration in a sample was defined by the spectrophotometric method after the organic matter had been oxidized by a sulfochromic mixture. To assess contribution of the anthropogenic sources to the bottom sediments pollution relative to the average composition of trace elements in the earth crust, such indicators as the enrichment factor and the geoaccumulation index were used. A significant at the 95%-level positive correlation (0.6–0.9) between the distribution of the studied metals and the sediments geochemical features was revealed using the example of the C_{org} concentrations.
Conclusions. Analysis of the obtained results of the EF parameter showed that the level of the bay bottom sediments enrichment with trace metals increased from moderate (4) and moderate-heavy (5) in the eastern apex to very heavy (27) and extremely heavy (90) ones in the Yuzhnaya Bay. It has been established that the maximum metal concentrations were associated with the periods of intense technogenic loads in the second half of the 20th century; as for Cu, Zn, Cr, and Fe, their concentrations continued to grow up to 2016. The content of lead and zinc in sediments decreased, while copper, on the contrary, increased up to 2016. Thus, the level of anthropogenic load on the Sevastopol Bay water area has not decreased, but even continues to grow.

Keywords: bottom sediments, organic carbon, heavy metals, enrichment factor, geoaccumulation index, Sevastopol Bay, Black Sea

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Introduction

Bottom sediments are an important component of the marine ecosystem and determine its state. Here, most of the organic and inorganic pollutants are accumulated, including the most dangerous and toxic, which during resuspension, dredging and dumping can pass into the water column, causing its secondary pollution. Bottom sediments are the habitat of numerous classes of benthic fauna, affect its species composition, bioaccumulation of the most hazardous substances, and disruption of the chain of biocenoses [1]. Unlike the water phase, which is characterized by high dynamic and seasonal variability, bottom sediments are a more static system, and their pollution level changes more slowly. Bottom sediments, which are a kind of depositing medium, are characterized by the ability to accumulate information about the ecological state of the entire study area [2]. The rates and volumes of bottom sediment formation, as well as contamination level of their layers, change throughout the existence of a water body, which makes it possible to trace both the impact of the changing anthropogenic load on the ecosystem over time and the change in those natural processes that occur in it [2].

Heavy metal compounds are among the most dangerous pollutants. It is known [3, 4] that the distribution and accumulation of metals are affected by the physicochemical characteristics of sediments. The connection between the concentrations of metals and the fractional composition of bottom sediments is explained by the increased absorption capacity and greater mobility of fine sediments, as well as the state of unstable equilibrium. It is known that when hydrodynamic conditions change, the silty fraction gets into the water in the form of a suspension [3]. As a result, an increase in the technogenic impact on bottom sediments, the processes of concentration and transfer of elements leads to the fact that the sediments themselves can act as secondary pollution sources.

The Sevastopol Bay is a vivid example of a semi-enclosed water area with complicated water exchange, which is located within the city limits and is subjected to long-term impact of various types of human activity [5]. As a result, its hydrological and hydrochemical regimes are violated, which leads to pollution of the water area and, consequently, bottom sediments. The natural characteristics of the bay are significantly transformed, the species composition of communities also changes, and the ability of the water area to assimilate pollutants decreases [5].

In coastal zones and water areas of a semi-enclosed type (which is the Sevastopol Bay), the sea bottom sediments are considered as a kind of pollution accumulators. The bottom sediments of the Sevastopol Bay have been studied for many years by employees of the Marine Hydrophysical Institute [3, 6–10] and the Institute of Biology of the Southern Seas [11–24].

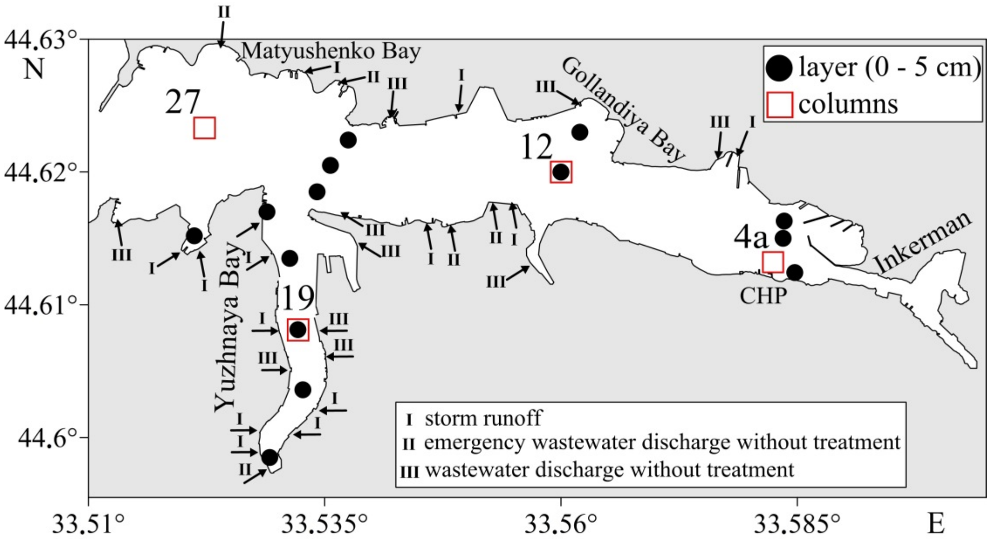
The main works were devoted to the study of the content and features of the accumulation of various pollutants of organic [14, 16] and inorganic origin [12, 17], including polyaromatic hydrocarbons [17], heavy metals in the surface layer of sediments [6, 23] and in them [10, 24], organochlorine compounds [18, 21, 22]. In [18–20] the estimates of sedimentation rates are given, and the data obtained were subsequently used in [10, 24] to interpret the heterogeneity of the distribution of metals in the Sevastopol Bay sediments. The effect of physicochemical characteristics of bottom sediments on the distribution of heavy metals is analyzed in [3, 6]. The geographical features of the vertical distribution of polarographically active compounds, including oxygen and sulfides, are studied in [8, 9].

Despite the fact that much attention is currently paid to the study of the spatiotemporal variability of the pollution level of bottom sediments in the Sevastopol Bay, pollution by heavy metals has been poorly studied. In [10] the authors considered only one column, and in [24] – two columns, which does not reflect the features of the spatial distribution of toxic metals in different parts of the bay water area according to the degree of technogenic load.

Therefore, the purpose of this work is to study the elemental composition of bottom sediments in a vertical section and to evaluate the spatial and temporal variability of the accumulation of polluting elements in the Sevastopol Bay bottom sediments according to expeditionary research data.

Materials and methods of research

In April 2016, using the Peterson bottom grab, 15 samples of the surface layer (0–5 cm) of bottom sediments were taken to study the spatial distribution of physical and chemical characteristics (Fig. 1). Sampling of columns in the Sevastopol Bay water area was carried out in May 2016 at four stations along the fairway: in the apex of the eastern part near the Inkerman CHP (station 4a), in the central part (station 12), in the Yuzhnaya Bay (station 19) and in the western part of the bay (station 27) (Fig. 1).



F i g. 1. Scheme of the stations for sampling bottom sediments in the Sevastopol Bay in 2016

The sampling was carried out by a diver using an acrylic tube 90 mm in diameter. After sampling, the soil column was transported to the laboratory, where it was divided into 1–2 cm layers using a manual extruder and an acrylic ring. Sediments were dark gray silt of liquid and semi-liquid consistency with inclusions of shell detritus. Before determining the concentrations of heavy metals, each sample was dried and homogenized. The total content of metals Cr, Cu, Ni, Pb, Zn, Sr and metal oxides TiO_2, MnO, Fe_2O_3 in the bottom sediments was determined by the X-ray fluorescence analysis (XRF) using the SPECTRO-SCAN MAX-G spectrometer of SPECTRON Research, Development and Production Facility (Russia) [1]. Several certified samples of soil composition were used to construct calibration graphs: typical chernozem (SChT set), soddy-podzolic sandy loamy soil (SDPS set), red earth soil (SRS set), and carbonate sierozem soil (SSC set). To check the correctness of the construction of calibration graphs, control samples were used – state standard samples DSZU 163.1-98 and DSZU 163.2-98. To assess the reproducibility and accuracy of measurements, the certified bottom sediment DSZU 16.3.1-98 was analyzed in eight repetitions. The minimum standard deviation was 0.003% for MnO, the maximum was 7.62% for Cr.

The granulometric composition of bottom sediments was determined by the combined method of decantation and dispersion. The separation of the silty-pelitic fraction (particle size up to 0.05 mm) was carried out by wet sieving, followed by determination of the dry mass by the gravimetric method. Coarse-grained fractions (particle size more than 0.05 mm) were separated by a grain-size method of dry sieving using standard sieves (GOST 12536-2014).

The organic carbon concentration (C_{org}) in the samples was determined by the spectrophotometric method after the oxidation of organic matter with a sulfochromic mixture (GOST 26213-91; introduced on June 30, 1993). The relative discrepancy of the method at C_{org} content of up to 3% in bottom sediments is 20%, at a content of 3–5% – 15%, and at more than 5% – 10%. To assess the reliability of the analyzes, the state standard sample (SSS) with a certified content of organic carbon C_{org} = 0.34% was used.

To assess the pollution of bottom sediments, such geochemical indices, providing the assessment of pollution level and the contribution of anthropogenic sources, as the enrichment factor and the geoaccumulation index were used.

The enrichment factor (EF) characterizes the level of an element concentration in the bottom sediments relative to its background content in the earth's crust. EF is applied to assess the presence and intensity of anthropogenic pollution of sediments relative to the average composition of the earth's crust according to the formula [25]

$$\mathrm{EF} = \frac{\left({}^{\mathrm{El}}/_{\mathrm{El_{ind}}}\right)_{\mathrm{sample}}}{\left({}^{\mathrm{El}}/_{\mathrm{El_{ind}}}\right)_{\mathrm{e.\,c.}}},$$

where El and El_{ind} are chemical element content and element indicator in a sample of bottom sediments (index "sample") and the upper part of the continental earth's crust (index "e.c.") (according to Vinogradov [26]), respectively.

According to [27, 28], the indicator element should be characterized by stable concentrations and the absence of vertical mobility, and should also be associated with fine sediment fractions. Metals such as Al, Fe, and Ti are the most widely used indicator elements [29–31].

In this work, Fe was applied as an indicator element of the lithogenic component due to its wide distribution in the lithosphere [32]. In addition, many

[1] NPO Spektron, 2016. Technique for Measuring the Mass Fraction of Metals and Metal Oxides in Powder Soil Samples Using X-ray Fluorescence Analysis M049-P/16. Saint Petersburg, 16 p.

authors involved in the study of bottom sediments in marine areas and estuaries also use Fe as an indicator element [33, 34].

The interpretation of the EF values was performed in accordance with [35–37]:

> 1 indicate no enrichment;

1–3 – insignificant enrichment;

3–5 – moderate enrichment;

5–10 – moderate-heavy enrichment;

10–25 – heavy enrichment;

25–50 – very heavy enrichment;

< 50 – extremely heavy enrichment.

Geoaccumulation index (I_{geo}) for assessing the pollution level of bottom sediments was originally defined by Müller [38] as

$$I_{\mathrm{geo}} = log_2\left(\frac{\mathrm{El_{sample}}}{1.5\cdot\mathrm{EL_{e.\ c.}}}\right),$$

where $\mathrm{El_{sample}}$ and $\mathrm{El_{e.c.}}$ are chemical element content in a sample of bottom sediments and in the upper part of the continental earth's crust (according to Vinogradov [26]), respectively.

A factor of 1.5 is used due to possible variations in the background values for this metal in the environment, as well as very small anthropogenic impacts [29, 39].

Depending on the value of the geoaccumulation index, the following gradations of bottom sediment pollution are distinguished:

$I_{\mathrm{geo}} \le 0$ – practically unpolluted sediments;

$0 \le I_{\mathrm{geo}} \le 1$ – unpolluted – moderately polluted;

$1 \le I_{\mathrm{geo}} \le 2$ – moderately polluted;

$2 \le I_{\mathrm{geo}} \le 3$ – moderately to strongly polluted;

$3 \le I_{\mathrm{geo}} \le 4$ – strongly polluted;

$4 \le I_{\mathrm{geo}} \le 5$ – strongly to extremely polluted sediments;

$5 < I_{\mathrm{geo}}$ – extremely polluted sediments [38].

To assess the geochronology of bottom sediment stratification at stations 19, 27 we used the results of studying the vertical distribution of ^{137}Cs, $^{239+240}$Pu and ^{90}Sr in the sediments of the Sevastopol Bay presented in [18–20]. To estimate the age of the sediment at stations 12, 19, an accumulation rate of 2.4 mm/year was applied, and for station 27 – 4.6 mm/year. The accumulation rate data were used to calculate the date of the sediment layer deposition using the following formula [18]:

$$\text{Year} = 2016 - \frac{\text{sediment layer depth, cm}}{\text{sediment accumulation rate, cm•year}^{-1}},$$

Thus, a sediment layer of 0–1 cm at stations 12 and 19 accumulated over four years, and at station 27 in the Konstantinovsky ravelin area – for two years.

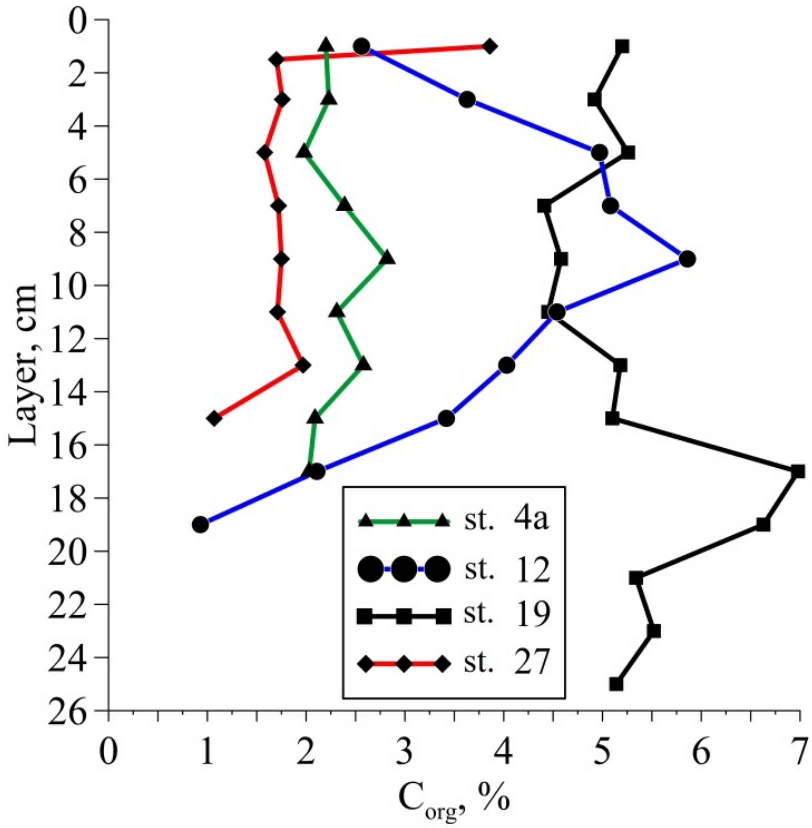
Correlation coefficients, as well as their reliability, were calculated using the Statistica program. The reliability level of the obtained correlation coefficients chosen in the work was 95%.

Results and discussion

According to studies [3, 6, 8] the bottom sediments of the Sevastopol Bay are mainly represented by a finely dispersed silty fraction: sandy aleurite-pelitic and silted shell rocks. The features of the spatial distribution of the fractional composition of the Sevastopol Bay sediments are associated with the features of the Chernaya River flood character, which determines the qualitative and spatial heterogeneity of the terrigenous material entering the bay. Accumulation of coarse-grained material in the inner part is determined by avalanche sedimentation [40], and at the exit from the bay and along the coastline, by abrasion activity [6]. In the central part, the inflow rates of terrigenous material weaken, which leads to the accumulation of finely dispersed fractions [6]. In addition, the authors found that the proportion of the clay fraction in the surface layer (0–5 cm) of the bay bottom sediments increased by an average of 1.5 times from 60.5% in 2001 to 83.4% in 2016, which indicates siltation of the bay. The revealed fact can contribute to the accumulation of various kinds of substances, including pollutants, since fine silts have a greater accumulative capacity than sand and gravel sediments.

An analysis of the spatial distribution of heavy metals in the surface layer, based on the data obtained in 2016, made it possible to identify zones of their increased content for various parts of the bay. It is noted that the maximum concentrations of the studied elements are observed mainly in the bottom sediments of the Yuzhnaya Bay in its northern (Co, Zn, Fe, Ti, V) and southern (Cu and Pb) parts, as well as in the central and eastern parts of the Sevastopol Bay (Ni, Cr). In the western part of the bay and at the exit from it, the concentrations of metals are minimal. The nature of the spatial distribution of the studied elements in the surface layer of the bay bottom sediments served as a determining factor in choosing stations for column sampling. The correlation analysis between the concentration of pollutants in the layer (0–5 cm) and the geochemical characteristics of the sediment revealed a statistically significant positive correlation with the organic carbon content (r = 0.5–0.9) for Pb, Zn, Cu, and with silt fraction – for Ni (r = 0.6).

Bottom sediments at station 4a were represented by silty sands with inclusions of shells and shell detritus. C_{org} content varied from 1.98% in 4–6 cm layer to 2.8% in 8–10 cm layer (Fig. 2). The main factor determining both the hydrological and hydrochemical features of the waters of this area and the features of the formation and composition of bottom sediments is the proximity of the combined heat and power (CHP) plant. The outflow of fresh warm waters and the features of the bottom topography also contribute to the formation of a concentration gradient between the bottom and surface layers. As a result, this leads to the development of hypoxia in the water column, and in bottom sediments – to the accumulation of organic carbon and other pollutants and the appearance of anaerobic conditions [41].



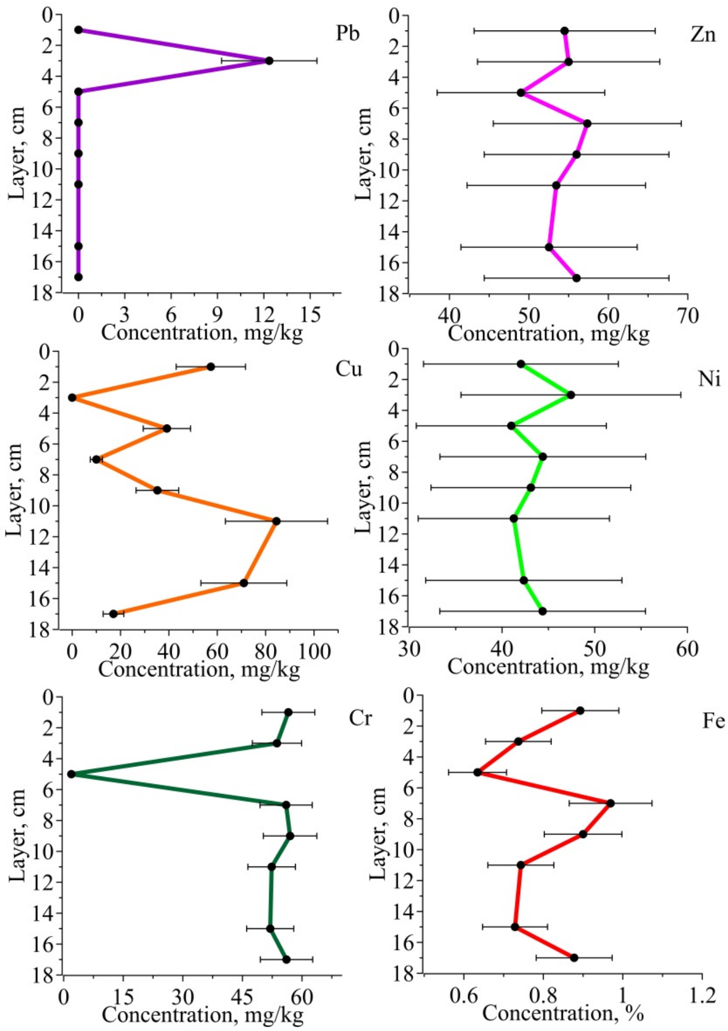
F i g. 2. Vertical distribution of C_{org} concentrations in the bottom sediments of the Sevastopol Bay

Features of the vertical distribution of metals at station 4a are given in Fig. 3. It was determined that the maximum concentrations of such elements as Pb, Zn, Ni, and Fe are noted at the 2–4 cm and 6–8 cm horizons. It is noted that for Pb and Ni in 0–4 cm level a decrease of concentrations is observed, and for Cu, Zn, Cr and Fe concentrations, on the contrary, an increase is noted. An average positive correlation (0.5) with C_{org} content was observed for Zn, Cr, Ti and Fe (Fig. 4). In general, the analysis of the vertical distribution of metals at station 4a showed that the concentrations of metals, except for Cu, are lower than those for the coastal areas of the Crimean Peninsula [42].

An analysis of the obtained EF values revealed that for bottom sediments at station 4a a moderate accumulation of Cr, Zn, and Ni is noted, while for Cu it is moderately severe and severe (1–11). At the same time, for Cr, Zn, and Ni, a slight decrease in accumulation has been observed recently, while for Cu, on the contrary, an increase has been noted (Table). Judging by the values of I_{geo} parameter, sediments at station 4a can be considered practically unpolluted, the average value of I_{geo} amounted to 1.45.

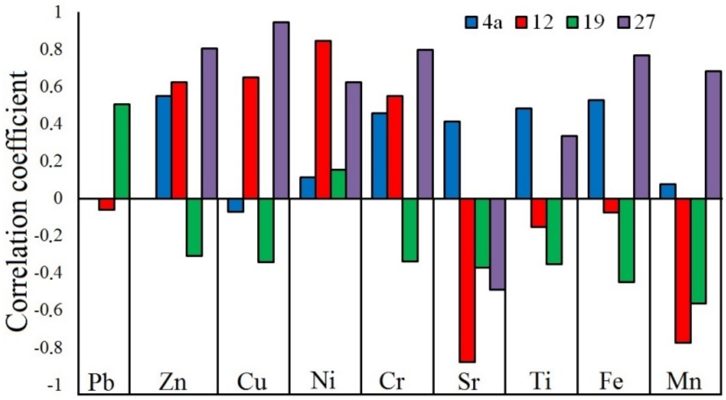
Calculated values of the enrichment factor (EF) for trace metals in the sediments of the Sevastopol Bay

No. of station	EF in the sediment layer, cm												
	0–2	2–4	4–6	6–8	8–10	10–12	12–14	14–16	16–18	18–20	20–22	22–24	24–26
							For Pb						
4a	-	4,9	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	4,8	10.3	2.4	22,5	21,0	8.9	5.9	-	-	-
19	58,9	71,4	64,1	72,7	63.0	58,9	69,2	144,0	137,7	110,9	100,3	135.7	58,9
27	63,1	-	-	-	-	-	-	-	5.2	-	-	-	-
							For Zn						
4a	3,4	4,2	4,3	3,3	3,5	4,0	4.0	3.6	-	-	-	-	-
12	9,3	4,9	5,7	5,9	6.1	5,9	5.7	4.9	3.2	2.5	-	-	-
19	6,7	6,4	6,3	6,2	6,2	6,5	7.3	7.6	7.0	7.1	7.3	7.5	6.7
27	7,1	4,1	4,1	4,1	4.1	5.2	5.0	4.9	8.5	-	-	-	-
							For Cu						
4a	6,4	-	6,1	1,0	3,9	11,2	9,6	1,9	-	-	-	-	-
12	8,0	10,6	15,7	19,2	21,6	13,1	16,3	5,2	0,8	14,1	-	-	-
19	32,6	17,9	25,5	33,2	89,7	22,4	19,6	24,3	22,1	32,4	20.5	30,4	32,6
27	23,3	2,8	2,8	4,4	-	9,3	10,0	3,2	-	-	-	-	-
							For Cr						
4a	3,5	4,1	0,2	3,2	3,5	3,9	4.0	3.6	-	-	-	-	-
12	4,0	3,5	3,4	3,5	3,5	3,1	4,3	3.4	2.5	3.0	-	-	-
19	2,6	2,4	2,7	3,3	2,8	2,6	2,8	3.3	3.5	3.2	3,0	3.4	2.6
27	2,9	3,9	3,7	3,4	3,1	4,6	4,0	4,0	4,8	-	-	-	-
							For Ni						
4a	3,8	5,2	5,2	3,7	3,8	4,5	4,7	4.1	-	-	-	-	-
12	3,3	3,3	3,3	3,9	4,0	2,5	4,7	3.7	2.3	1,3	-	-	-
19	2,4	2,1	2,5	3,4	2,8	2,5	2,3	3,9	3,9	3.4	2,9	4.4	2.4
27	2,7	3,1	3,4	3,0	2,3	5,1	4,1	3.4	3.4	-	-	-	-

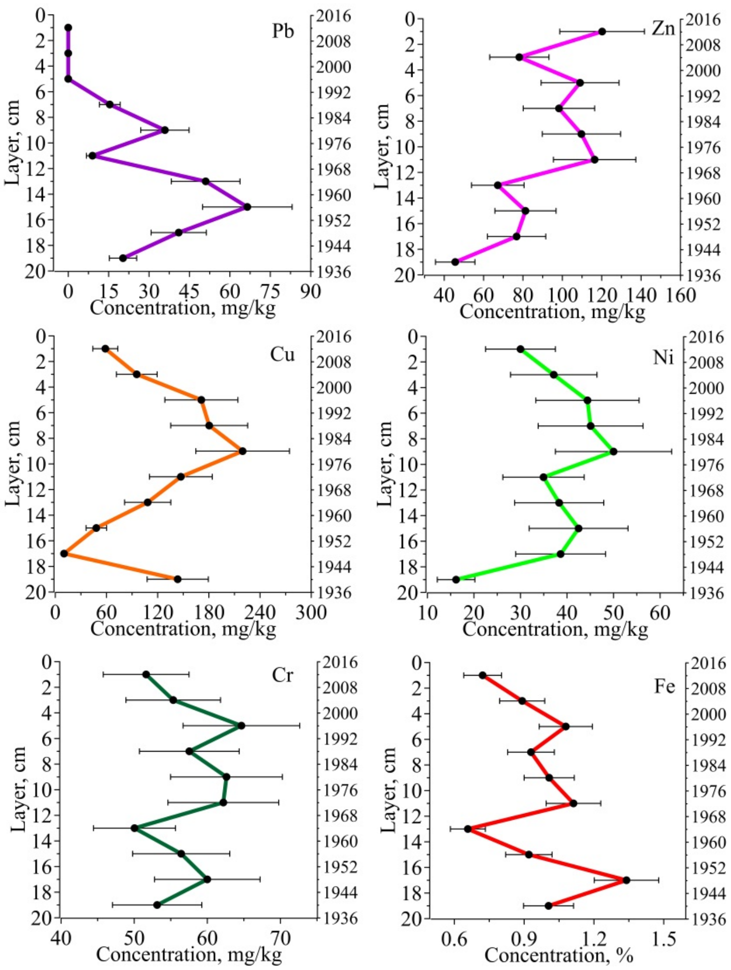


F i g. 3. Vertical distribution of metals: lead, zinc, copper, nickel, chromium (mg/kg) and iron (%) in the bottom sediments of the Sevastopol Bay (station 4a)

Station 12 is located in the central part of the Sevastopol Bay abeam the Gollandiya Bay (Fig. 1). The sediments are represented by dark gray and black silts with inclusions of shell detritus and the smell of petroleum products. Two long-term periods can be distinguished in the vertical distribution of C_{org} concentration: 1) intensive accumulation of organic matter in the period from the early 1940s to the mid-1980s. In the 20th century, C_{org} concentration increased from 0.93% in the 18–19 cm layer to 5.86% in the 8–10 cm layer; 2) a decrease in the rate of organic matter accumulation in bottom sediments in the period from the mid-1980s of the 20th century until the sampling in 2016, the C_{org} concentration decreased by almost 2.5 times (from 5.86 to 2.56%).



F i g. 4. Correlation coefficients of metal concentrations with the C_{org} content



F i g. 5. Vertical distribution of metals: lead, zinc, copper, nickel, chromium (mg/kg) and iron (%) in the bottom sediments of the Sevastopol Bay (station 12)

Vertical metal profiles at station 12 are demonstrated in Fig. 5. For most elements, the vertical distribution is not uniform and there are several concentration peaks.

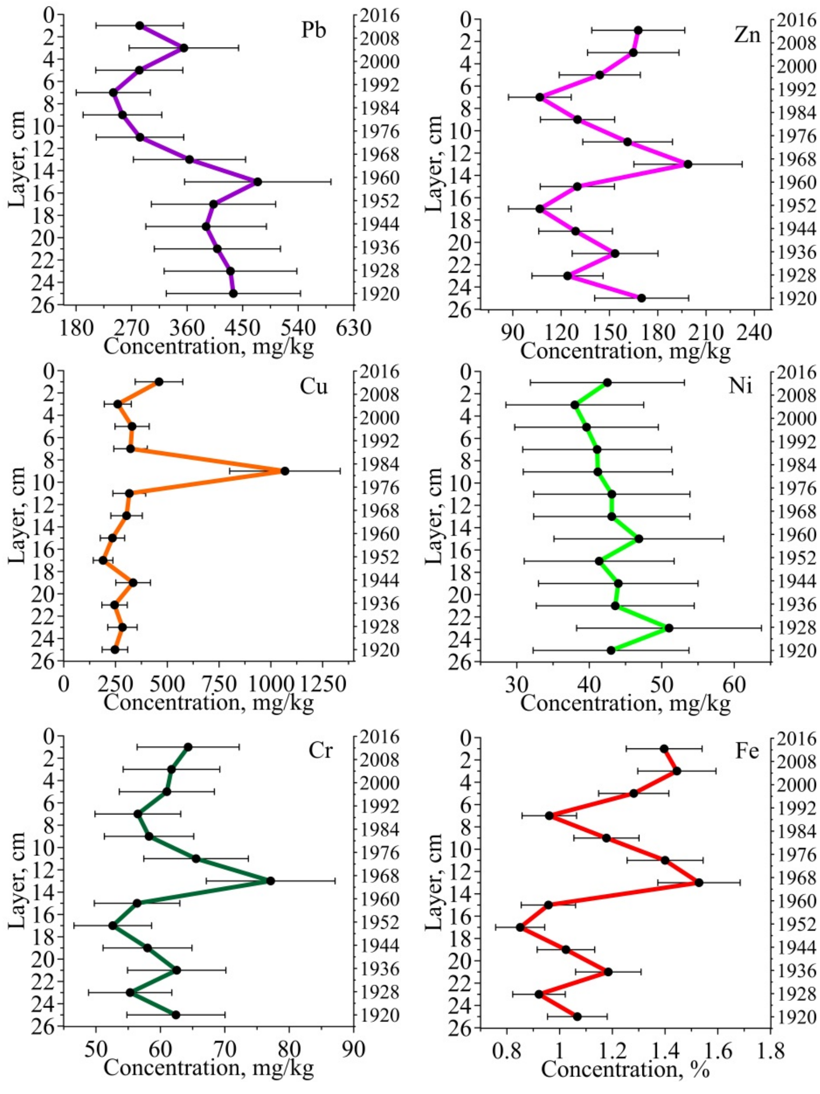
For Ni, Cu, Cr, Fe, and Pb, an increase in the concentration in the lower sediment layers (8–18 cm) and a decrease in its values in the period from the mid-1980s are observed (0–10 cm) for Ni, Cu, Pb and since the mid-1990s (0–6 cm) for Fe and Cr. The maximum concentrations of Ni (50 mg/kg) and Cu (220 mg/kg) were noted for 8–10 cm layer, which also agrees well with the vertical distribution of C_{org} content. As a result, the maximum correlation values of 0.8 and 0.7, respectively, were noted for these elements (see Fig. 4). For such elements as Fe, Cr, and Ni, the concentrations do not exceed the values obtained for the sediments of the Crimean shelf; for Cu – they exceed them along the entire length of the column; for Pb – in 8–10 and 12–20 cm layers; for Zn – in 0–2 and 4–12 cm layers. It was determined that Zn is the only metal whose concentrations at station 12 have continued to grow since the 1940s, and the level of its enrichment has changed from insignificant to moderate-heavy.

According to EF estimates, in the bottom sediments at station 12 a moderate enrichment of Zn (5), Cr (3), Ni (3), and heavy enrichment of Cu (12) (Table) are noted. The analysis of I_{geo} parameter values showed that bottom sediments at station 12, with the exception of Cu and Pb (moderate pollution), are almost unpolluted with the metals under study.

Station 19 is located in the central part of the Yuzhnaya Bay. It is known that the Yuzhnaya Bay is considered one of the most polluted bays [6, 12, 24]. The dense location of moorage cites, as well as sites for the repair of military and civilian ships along its shores, a large number of municipal and storm water sources, including emergency ones and without treatment, poor water exchange and a long coastline have led to negative changes in the Yuzhnaya Bay ecosystem. Bottom sediments in this area are represented by finely dispersed pelitic silts with minor inclusions of shell detritus, coal admixture, and a pronounced smell of petroleum products. The intensive supply of organic matter with sewage and storm runoffs and isolation from wind and wave action led to the fact that bottom sediments began to accumulate intensively and retain various pollutants, including heavy metals. In addition, the intense supply of organic matter with urban and storm runoff leads to active oxygen consumption in the bottom water layer and the development of anaerobic conditions in the upper layer of bottom sediments [9].

The vertical distribution of C_{org} at station 19 is not uniform. In 16–26 cm layer, an increase in the concentration of organic carbon is observed, which, apparently, refers to the period of industrialization in the USSR in the 1930–40s. From the 1950s to the 1980s, the concentration decreased from 6.98 to 4.41%, and then, from the end of the 1990s, it gradually began to increase to 5.2% by 2016.

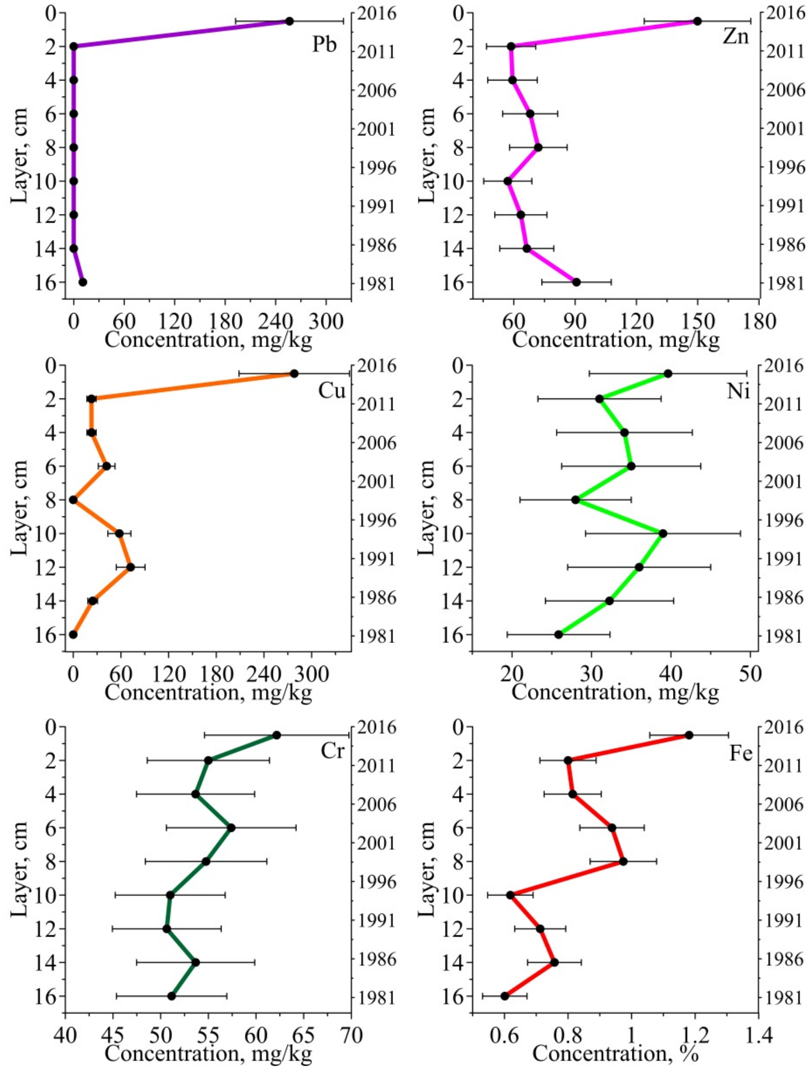
In the vertical profile of sediments at station 19 (Fig. 6) for the studied elements, peaks of maximum concentrations appear in various segments: for Zn (200 mg/kg), Cr (77 mg/kg), Fe (1.5%) in a layer of 12–14 cm, and for Pb (475 mg/kg) and Ni (47 mg/kg) in the 14–16 cm layer. Such heterogeneities are related to certain layers of the bottom sediments. According to the estimates proposed in [18–20], these concentrations presumably date back to the 1960s–1970s, and belong to the period of industrial growth in the USSR. At present, the concentrations of all studied heavy metals, with the exception of Pb, continue to grow. It was found that the level of maximum concentrations of Pb, Cu and Zn at station 19 exceeds significantly the values obtained for the bottom sediments of the Crimean shelf [42].



F i g. 6. Vertical distribution of metals: lead, zinc, copper, nickel, chromium (mg/kg) and iron (%) in the bottom sediments of the Sevastopol Bay (station 19)

According to EF estimates, bottom sediments of the Yuzhnaya Bay are characterized by an extremely heavy level of Pb enrichment (59–144), very heavy and heavy Cu enrichment (18–90), and moderate heavy enrichment of Zn (6–7). According to the value of I_{geo} parameter, it can be said that the sediments are strongly contaminated with lead (3.3–4.3), moderately to strongly contaminated with copper (1.4–3.9), and moderately contaminated with zinc (−0.2–0.7).

Station 27 is located in the western part of the Sevastopol Bay abeam the Matyushenko Bay. The station is located on the fairway, so it is remote from the direct flow of storm and domestic wastewater. Since the station is located near the exit from the bay, the water exchange with the open sea here is the most intensive in the Sevastopol Bay. Increased values of wave heights for different wind directions [43], the presence of eddy formations [12] and, as a result, high abrasion activity in the coastal zone [6] determine the special lithodynamic regime of this area. As a result, bottom sediments at station 27 are represented by clay silts with shell and shell detritus (the content of the fraction with a particle size of more than 1 mm was 3–35%).



F i g. 7. Vertical distribution of metals: lead, zinc, copper, nickel, chromium (mg/kg) and iron (%) in the bottom sediments of the Sevastopol Bay (station 27)

The vertical distribution of C_{org} at station 27 is fairly homogeneous with an average content of 1.7%. The exception is the upper (0–1 cm) fine-grained layer of silt, in which C_{org} concentration was 3.86%. Apparently, this content of organic matter is explained by the increased sorption capacity of fine-grained pelitic silts. Such features of the geochemical composition of sediments directly determine the vertical distribution of metals in the sediment (Fig. 7), and the correlation coefficient with the vertical distribution of C_{org} is average for Mn (0.7) and Ni (0.6) and high for Cu (0.9), Zn, Cr and Fe (0.8) (see Fig. 4).

The location of concentration maxima in the upper layer (0–1 cm) of sediments is typical for Pb, Zn, Cu, Cr, Ni, and Fe (Fig. 7). The values obtained in this work significantly exceed the values in the coastal regions of Crimea [42]: for Pb by 11 times; for Cu by 9 times; and for Zn by 2 times. At the same time, already in the 1–2 cm layer, the concentrations of such elements as Pb, Zn, Cu, and Fe are an order of magnitude lower. An analysis of the vertical distribution of metals showed that, if we do not take into account the upper layer of the sediment, a decrease in concentrations has been observed in recent years for Pb, Zn, and Cu, and an increase for Cr, Ni, and Fe. With the exception of the upper layer, for which a heavy enrichment of metals was noted (average EF = 20), all elements are characterized by moderate (3.4) enrichment (Table), and the pollution level is insignificant (average $I_{geo} = -0.95$).

Conclusions

The features of the vertical distribution of a number of heavy metals (Pb, Zn, Cu, Ni, Cr and Fe) in bottom sediments of various parts of the Sevastopol Bay were studied. When studying the vertical distribution of heavy metals in the bottom sediments of the Sevastopol Bay, for each sediment column, the maximum, minimum, and average concentrations of these elements were considered in comparison with their content in the bottom sediments of the Crimean Peninsula shelf.

The geochronology of heavy metal distribution in bottom sediments was carried out based on the results of a study of the vertical profiles of ^{137}Cs, $^{239+240}Pu$ and ^{90}Sr in the Sevastopol Bay sediments. It was determined that the peaks of metal concentration maxima refer to periods of intense technogenic loads in the second half of the 20th century, and the concentrations of Cu, Zn, Cr, and Fe continued to grow until 2016. It was noted that the intensity of metal accumulation is determined by the location of sources of lithogenic and biogenic components (storm and municipal wastewaters), as well as close proximity to sources of pollutants. In addition, a significant positive correlation of the studied metal distribution with the geochemical properties of sediments was established at 95% confidence level using the example of C_{org} concentrations. To assess the contribution of anthropogenic sources to pollution of bottom sediments relative to the average composition of elements in the earth's crust, such indicators as the enrichment factor and geoaccumulation index were applied in the work. An analysis of the obtained values of EF parameter revealed that in the bay bottom sediments the enrichment level increases from moderate (4) and moderate heavy (5) in the apex eastern part of the Sevastopol Bay to very heavy (27) and extremely heavy (90) in the Yuzhnaya Bay. I_{geo} values indicate that bottom sediments in the eastern and western parts are almost uncontaminated, moderately contaminated with copper and lead in the central part, and moderately to strongly contaminated with copper and strongly contaminated with lead in the Yuzhnaya Bay. In addition, if the level of accumulation of lead and zinc decreases, then the one of copper, on the contrary, grows until 2016.

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