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# Influence of Organic Matter Content in Bottom Sediments in Crimean Water Areas with Intensive Water Exchange on Zinc, Chromium, and Nickel Accumulation

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**Abstract**
The paper analyzes the data obtained during field studies in water areas with intensive water exchange: Kalamita Bay (2011, 2012), Feodosiya Bay (2006), and the Kerch Strait (2007, 2008). The content of heavy metals (Zn, Ni, Cr) in the bottom sediments of the studied water areas was determined using X-ray fluorescent spectroscan MAKS-G. Spatial heterogeneities in the distribution of Zn, Ni, Cr in the bottom sediments of Kalamita Bay, Feodosiya Bay, and the Kerch Strait were assessed, with the organic matter content taken into account. A comparative analysis was carried out of the organic matter content in the bottom sediments of the studied water areas. The organic matter not only forms the type of sediments, but also determines their ability to accumulate various substances, including macro- and micronutrients. It is shown that the bottom sediments of Feodosiya Bay and the Kerch Strait contain increased levels of organic carbon. Correlation relations between the contents of heavy metals and organic carbon as one of the main sediment-forming components of the bottom sediments were calculated using the method of constructing matrices of pair correlations. A high level of correlations between Zn, Ni, Cr and organic carbon contents (0.7–0.8) was determined in the bottom sediments of Kalamita Bay and the Kerch Strait. In the bottom sediments of Feodosiya Bay, high correlation coefficient with $C_{org}$ content (0.9) was observed only for Zn. The hydrodynamic regime of water areas with intensive water exchange (especially in the Kerch Strait) determines the spatial heterogeneity of the particle size distribution of bottom sediments, especially the fine fraction and the organic matter associated with it, which also affects the behaviour of the studied metals.

**Keywords**: Kalamita Bay, Feodosiya Bay, Kerch Strait, bottom sediments, organic carbon, heavy metals

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# Влияние содержания органического вещества в донных отложениях акваторий Крыма с интенсивным водообменом на накопление цинка, хрома и никеля

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**Аннотация**
Проанализированы данные, полученные в ходе экспедиционных исследований в прибрежных акваториях Крыма с интенсивным водообменом: Каламитском (2011, 2012 гг.), Феодосийском (2006 г.) заливах и Керченском проливе (2007, 2008 гг.). Содержание тяжелых металлов (Zn, Ni, Cr) в донных отложениях исследуемых акваторий определяли рентгенофлуоресцентным методом с использованием прибора «Спектроскан МАКС-*G*». Оценены пространственные неоднородности в распределении Zn, Ni, Cr в донных отложениях Каламитского и Феодосийского заливов, Керченского пролива с учетом содержания органического вещества. Осуществлен сравнительный анализ содержания органического вещества в донных отложениях исследуемых акваторий, которое не только формирует тип осадков, но и определяет их способность к накоплению различных веществ, в том числе макро- и микроэлементов. Показано, что в донных отложениях Феодосийского залива и Керченского пролива повышено содержание органического углерода, цинка и хрома. Выполнен расчет коэффициентов корреляции между содержанием тяжелых металлов и органического углерода как одного из основных осадкообразующих компонентов донных отложений с применением методики построения матриц парных корреляций. Высокий уровень корреляционных связей содержания Zn, Ni, Cr с содержанием органического углерода (0.7–0.8) определен для донных отложений Каламитского залива и Керченского пролива. В донных отложениях Феодосийского залива высокое значение коэффициентов корреляции с содержанием $C_{орг}$ (0.9) наблюдается только для Zn. Гидродинамический режим акваторий с интенсивным водообменом (особенно в Керченском проливе) определяет пространственную неоднородность распределения мелкодисперсной фракции донных отложений и связанного с ней органического вещества, что также влияет на особенности поведения исследуемых металлов.

**Ключевые слова**: Каламитский залив, Феодосийский залив, Керченский пролив, донные отложения, органический углерод, тяжелые металлы

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## Introduction

The Crimean coastal water areas are subject to a complex impact as a result of the effluence of the organic matter of anthropogenic and natural origin into the coastal areas. Regardless of its genesis, the organic matter specifically plays an important role in the formation of the type of sediments and their ability to accumulate various substances coming with sedimentary material, including macro- and microelements. The spatial distribution of microelements and heavy metals in bottom sediments is determined by their content of organic and inorganic carbon and their granulometric composition [1]. In previous works, individual features of the spatial distribution of microelements and heavy metals in the surface layer of bottom sediments of the studied water areas of Kalamita Bay [2], Feodosiya Bay [3], and the Kerch Strait [4] were considered.

The aim of this work is to evaluate the effect of organic carbon content in bottom sediments of the Crimean coastal water areas with intensive water exchange on the peculiarities of the spatial distribution of zinc, nickel, and chromium.

## Materials and Methods

We analyzed the data obtained during field studies in the water areas of Kalamita Bay (2011, 2012), Feodosiya Bay (2006), and the Kerch Strait (2007, 2008) (Fig. 1).

Figure 1 shows the location of bottom sediment sampling stations in the areas under study. Sampling was carried out using Peterson samplers according to state standards GOST 17.1.5.01-80 and DSTU ISO 5667-19:2007 [1)]. The upper layer of sediments (0–5 cm) was studied. The studied metals (total forms) were determined by the X-ray fluorescence method of analysis using spectroscan MAKS-G [2)]. To assess the reproducibility and accuracy of measurements of the content of zinc, nickel, and chromium, the analysis of certified bottom sediment state standard DSZU 163.1-98 was used in eight replicates [1)].

The organic carbon concentration in the sample was determined by the spectrophotometric method after the oxidation of the organic matter with a sulfochromic mixture (state standards DSTU ISO 14235-2005 [3)]; DSTU 4289:2004 [4)]. The error estimate of the organic matter content for the as-deposited sediments is up to 3 % with its content not exceeding 2.5 % [3), 4)].

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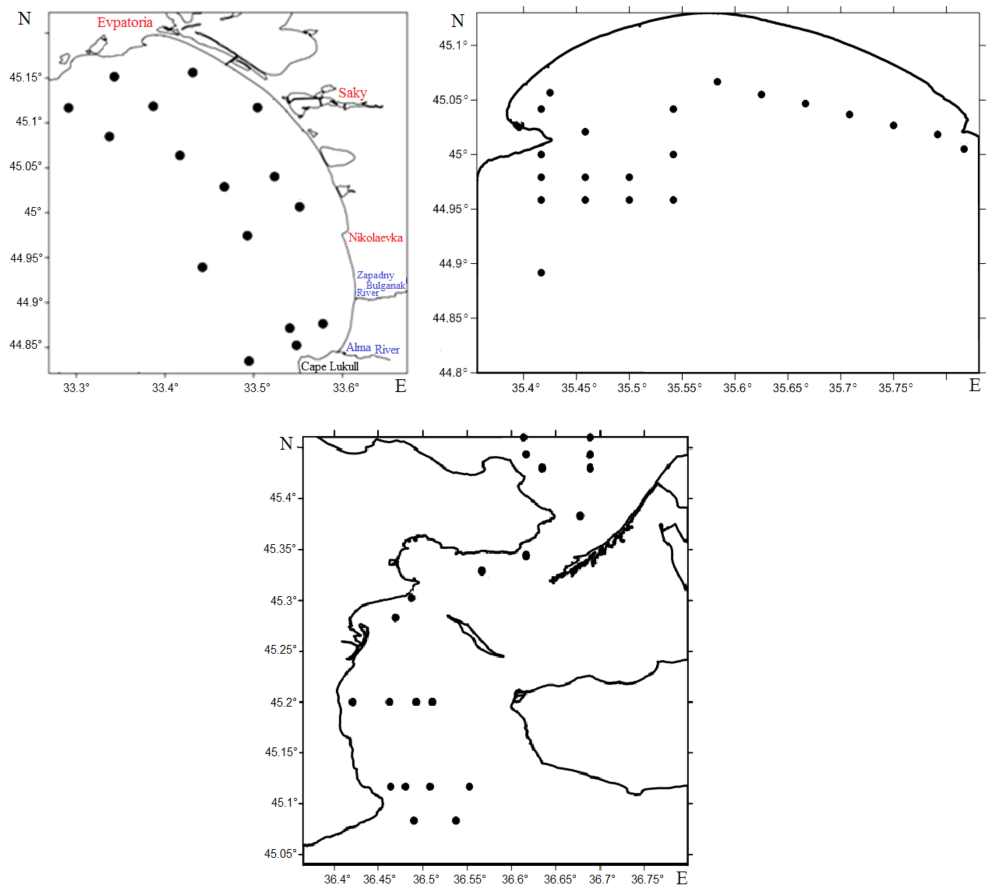
[1)] State Standard, 1980. *General Requirements for Sampling of Bottom Sediments of Water Objects for their Pollution Analysis*. Available at: https://docs.cntd.ru/document/1200012787 [Accessed: 25 May 2020] (in Russian).

[2)] [*Methods for the Measurement of the Mass Fraction of Metals and Metal Oxides in Powder Soil Samples by X-ray Fluorescence Analysis. M049-П/02*]. Saint Petersburg: OOO "Spektron", 2002, 16 p. (in Russian).

[3)] State Standard, 2007. *Soil Quality. Determination of Organic Carbon by Sulfochromic Oxidation* (*ISO* 14235-1998, *IDT*). Kiev: Derzhspozhivstandart Ukrainy, 10 p. (in Ukrainian).

[4)] State Standard, 2005. *Soil Quality. Methods for Determination of Organic Matter*. Kiev: Derzhspozhivstandart Ukrainy, 14 p. (in Ukrainian).




F i g . 1 . Bottom sediment sampling areas in the coastal water areas of Crimea: *a* – Kalamita Bay (August 2011; September 2012); *b* – Feodosiya Bay (2006, 22 stations); *c* – the Kerch Strait (December 2007; March 2008). The points denote stations

The absence or presence of a correlation between the content of heavy metals and the content of organic carbon was determined by the method of constructing matrices of pair correlations (Table 1) in the program *Statistika* 6.0 [5].

**Results and Discussion**

Kalamita and Feodosiya Bays as well as the Kerch Strait, as coastal water areas of Crimea with intensive water exchange, are subject to the influence of natural, climatic, and anthropogenic factors.

Due to its geographical location, **Kalamita Bay** is influenced by the deep-water part of the Black Sea. It is a transitional link from the open part of the sea to the northwestern shelf and successfully avoids such phenomena as bottom hypoxia and

T a b l e 1 . Coefficients of correlation between $C_{org}$ and studied metals

| Element, mg/kg | $C_{org}$ | | |
|---|---|---|---|
| | Kalamita Bay | Feodosiya Bay | Kerch Strait |
| Zn | 0.8 | 0.9 | 0.7 |
| Ni | 0.8 | 0.5 | 0.7 |
| Cr | 0.7 | 0.3 | 0.8 |

subsequent fish kills. The absence of abundant freshwater runoff and significant industrial infrastructure on the shores of West Crimea, as well as undisturbed water exchange with the deep part of the sea, make the waters of the bay more similar to the waters of the open sea.

**Feodosiya Bay** is one of the least studied areas of the Black Sea coast in terms of the structure and dynamics of waters and their hydrochemical composition under the conditions of modern anthropogenic impact. This region had been used for a long time as a training area for the USSR naval forces, which excluded the possibility to obtain any field data in the field studies of civil ships. At the same time, the Feodosiya region is of great recreational importance. The arc of Feodosiya Bay coast is framed by a beach strip [3].

**The Kerch Strait** is a heavy shipping area. The work of ports significantly affects the ecological situation in the region. Offshore cargo transshipment points in the southwestern part of the strait also make their negative contribution [6].

According to previously published data [7], the geochemical background of the abovementioned metals is increased in bottom sediments, regardless of the hydrodynamic situation in coastal waters. And in accordance with [7] and[5)], these metals are able to form stable compounds with various organic ligands. This is also confirmed by the value of the positive correlation coefficients between the content of these metals and the content of the organic matter in bottom sediments, calculated in this work (Table 1).

*Zinc*. The content of zinc in sea water and bottom sediments very often exceeds the maximum allowable concentration (MAC). The element maximum concentrations are often determined on the shelf of the Crimean Peninsula and in the waters of the Kerch Strait. The sources of this element are mainly anthropogenic in nature [4].

*Nickel*. For the water area of the Crimean Peninsula shelf zone, the main source of Ni is the river runoff. Increased nickel concentrations are often found in water areas with active shipping lanes. In our work, it is the water area of

[5)] Mitropolskiy, A.Yu., Bezborodov, A.A. and Ovsyany, E.I., 1982. [*Geochemistry of the Black Sea*]. Kiev: Naukova Dumka, 144 p. (in Russian).

the Kerch Strait. Due to active adsorption processes and insignificant geochemical mobility, Ni accumulates in bottom sediments in the immediate vicinity of the main sources [4].

*Chromium*. High content of chromium in the bottom sediments of the Black Sea shelf zone is determined by the proximity of the sources of this element. In [2–4], it is said that Cr can also enter the water area with river waters. Increased chromium concentrations in bottom sediments are often associated with anthropogenic sources [2–4].

Table 2 shows the content of organic carbon in the bottom sediments of the studied water areas.

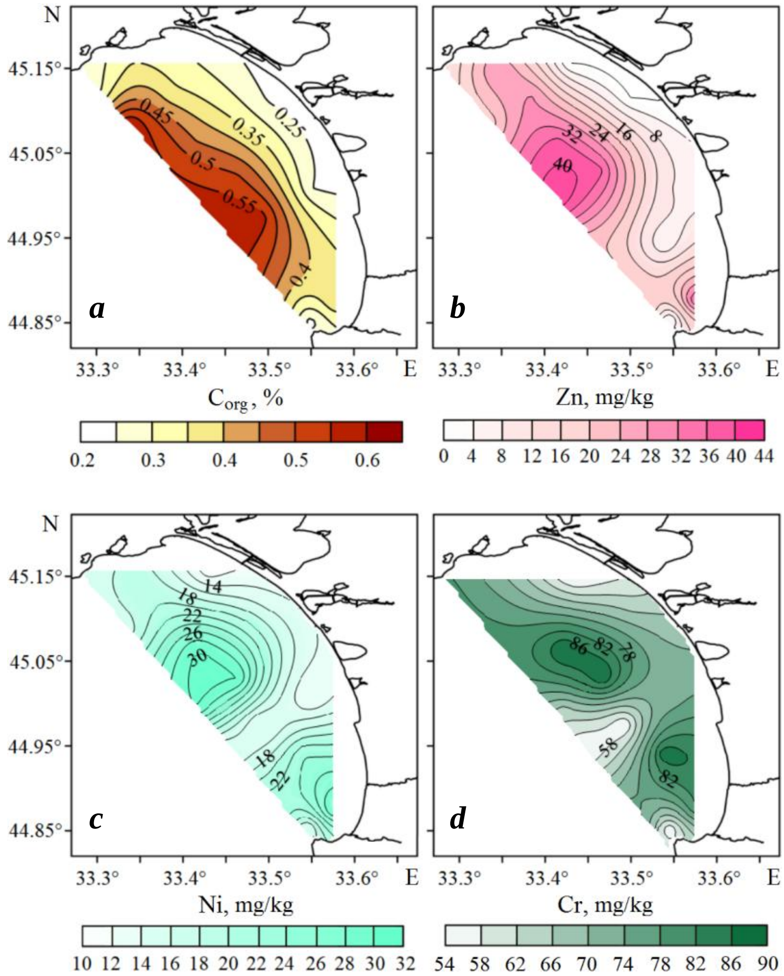
As a result of studies carried out in the water area of Kalamita Bay, data were obtained on the peculiarities of the spatial distribution of heavy metals, which repeated the distribution of organic carbon in the bottom sediments of the bay. Figure 2 shows the distribution of $C_{org}$, Zn, Ni, and Cr. Significant concentrations of the elements were observed in the seaward part of the bay water area, while their minimum concentrations were observed in the coastal part, which coincided with the distribution of the organic matter in the sediments of the bay (Table 3).

Increased Cr content (Fig. 2, *d*) was noted in the bottom sediments of the central and northern parts of the bay. The average content of chromium was 64 mg/kg, and the maximum one was 90 mg/kg. The maximum zinc content was 36 mg/kg, which did not exceed its concentration in the bottom sediments of the shelf [7] and corresponded to its content in the earth's crust according to A.P. Vinogradov [6]. The maximum nickel content was 31 mg/kg, which did not exceed the background values typical for this water area [8]. The excess of the geochemical background was noted only for chromium.

T a b l e 2 . Organic carbon content (%) in the bottom sediments of the studied water areas

| Water area | $C_{org}$ | | | |
|---|---|---|---|---|
| | Content range | Average content | Coastal part | Seaward part |
| Kalamita Bay | 0.07–0.6 | 0.07–0.11 | 0.23–0.4 | 0.24–0.6 |
| Feodosiya Bay | 0.2–3.3 | 1.2 | 1.8–3.2 | 0.8–1.1 |
| Kerch Strait [9] | 0.12–3.35 | 1.25 | 2.0–3.0 | 0.12–1.0 |

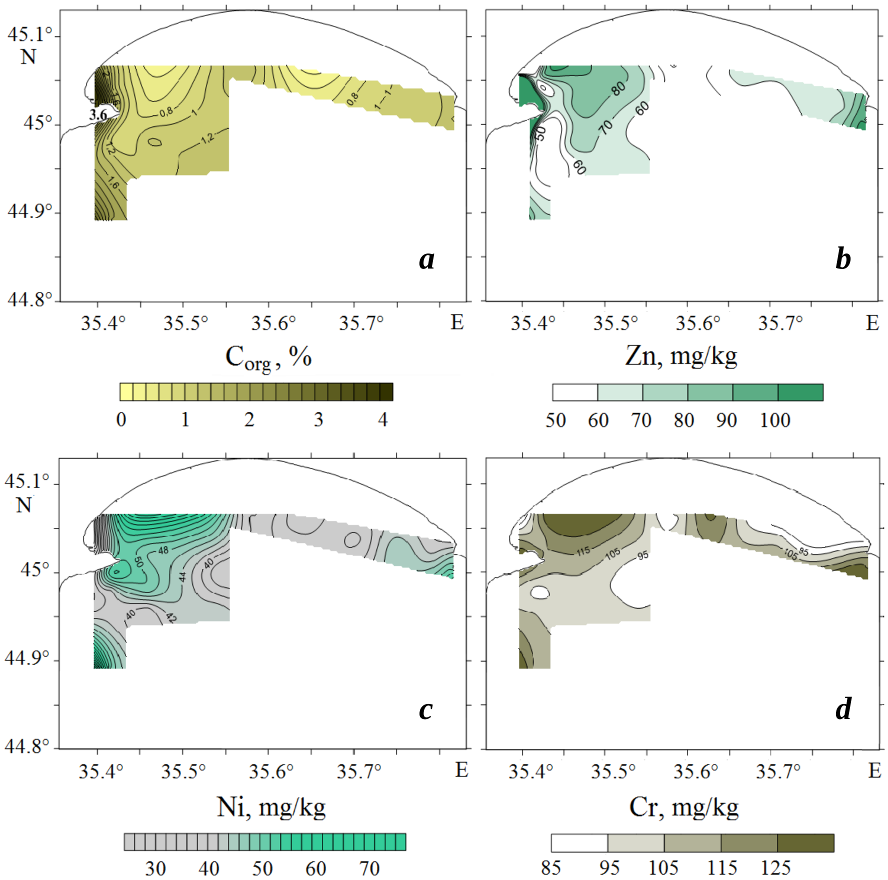
[6] Vinogradov, A.P., 1962. [Average Content of Chemical Elements in Rocks]. *Geokhimiya*, (7), pp. 555–571 (in Russian).




F i g . 2 . Spatial distribution of organic carbon (*a*), zinc (*b*), nickel (*c*), and chrome (*d*) in the bottom sediments of Kalamita Bay

The content of organic carbon in the bottom sediments of the bay varies within 0.07–0.11 %. The $C_{org}$ concentration in the coastal part of the bay is 0.23–0.40 %, and in the seaward part it is 0.24–0.60 %. The maximum positive values of the correlation between the content of the element and the content of organic carbon were recorded for Zn ($r = 0.8$), Ni ($r = 0.8$), and Cr ($r = 0.7$) (Table 2).

**Feodosiya Bay.** According to [2], the content of $C_{org}$ in the bottom sediments of Feodosiya Bay did not exceed 1.2% of the dry weight. According to the results of studies carried out in the waters of Feodosiya Bay, areas of increased zinc and chromium content were identified. It is shown that the average values of the total concentration of the studied metals in the bottom sediments of Feodosiya Bay do not exceed the value of the geochemical background (Table 3).




F i g . 3 . Spatial distribution of organic carbon (*a*), zinc (*b*), nickel (*c*), and chrome (*d*) in the bottom sediments of Feodosiya Bay

According to the calculations, the maximum correlation coefficient was noted for zinc ($r = 0.9$) (Table 1).

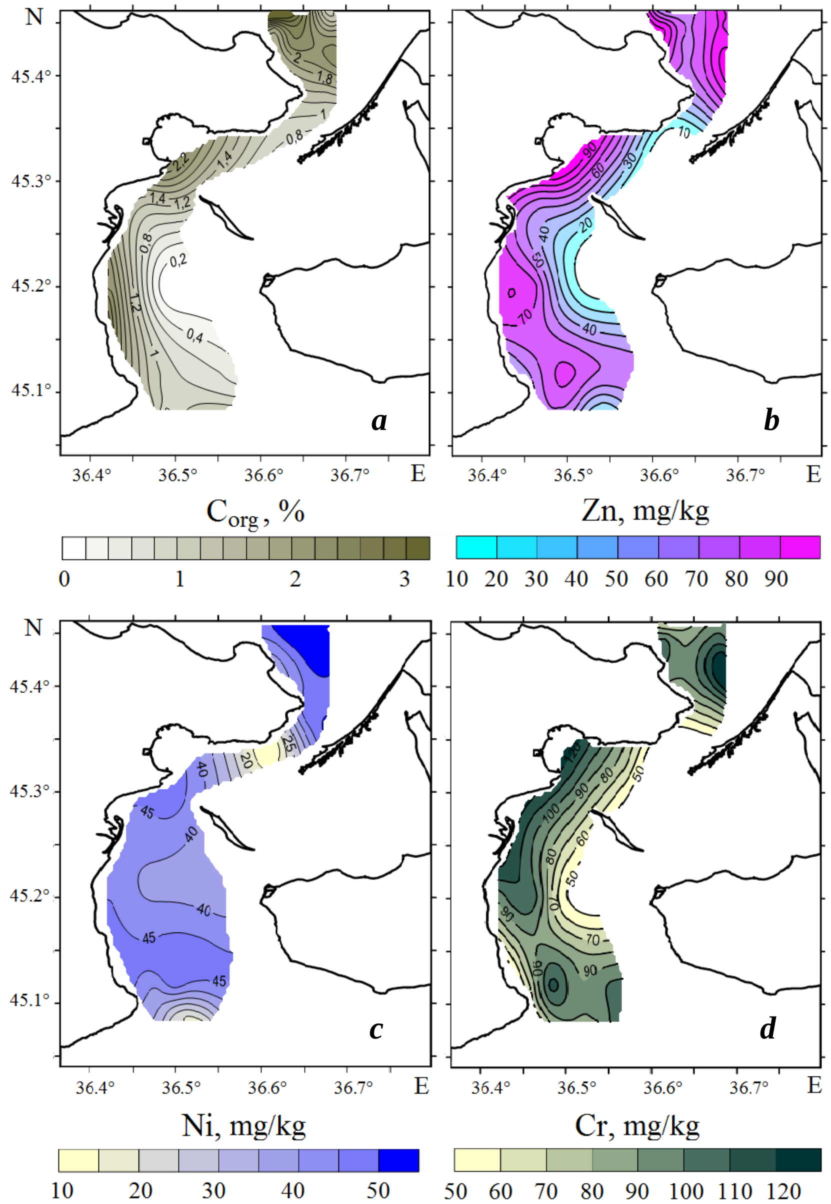
Figure 3 shows that the areas of increased content of zinc, chromium and nickel, as well as $C_{org}$, are observed in the water area of the city and port of Feodosiya located in the bay. In the seaward part of the bay, lower content of the studied metals is observed.

**The Kerch Strait** is subject to a significant influence of both natural and climatic and anthropogenic factors (intense traffic flows, bottom dredging). At the same time, the strait is characterized by along-strait currents, the direction of which changes up to the opposite, depending on the prevailing wind direction and speed. The specific features of the studied water area were reflected in the general nature of the spatial distribution of the studied heavy metals in the strait bottom sediments.

In the modern period, the content of $C_{org}$ in the bottom sediments of the part of the strait adjacent to the Kerch Peninsula varies from 0.12 to 3.35 wt % with the average value of 1.25 wt. % (see Table 2) [9].

Figure 4 shows the spatial distribution of nickel, zinc and chromium depending on the content of organic carbon in the bottom sediments of the Kerch Strait.

It follows from Figure 4 that the spatial distribution of Zn, Ni, Cr in the water area of the strait corresponds to the distribution of the organic matter with the formation of maxima in the pre-strait area of the Sea of Azov and in the coastal part of




F i g . 4 . Spatial distribution of organic carbon (*a*), zinc (*b*), nickel (*c*) and chrome (*d*) in the bottom sediments of the Kerch Strait the strait. At the same time, high values of the coefficients of correlation between the content of metals and the content of the organic matter in bottom sediments suggest that these pollutants accumulate in the bottom sediments of the Kerch Strait.

The accumulation levels of heavy metals Zn, Ni, Cr in the bottom sediments of water areas with intensive water exchange against the geochemical background are shown in Table 3.

T a b l e 3 . Microelement accumulation level (mg/kg) in the bottom sediments of Kalamita Bay, Feodosiya Bay and the Kerch Strait against the geochemical background

| Elements | Content | | | Clarkes according to A.P. Vinogradov 6) | Average content in shelf bottom sediments [8] |
|---|---|---|---|---|---|
| | Kalamita Bay (2011, 2012) | Feodosiya Bay (2006) | Kerch Strait (2007, 2008) | | |
| Zn | 4–48 | 50–412 | 25–78 | 83 | 60 |
| Ni | 10–32 | 34–54 | 10–50 | 58 | 34 |
| Cr | 48–90 | 87–124 | 43–147 | 83 | 45 |

From the data presented in Table 3, it can be seen that Zn and Ni concentrations in the bottom sediments of Kalamita Bay are lower than in the sediments of Feodosiya Bay, the Kerch Strait, and the background areas of the Black Sea shelf [7]. At the same time, in Kalamita Bay, as in a water area with low content of the organic matter in bottom sediments, an excess of the geochemical background is observed only for chromium due to the noticeable correlation between the metal content and the $C_{org}$ content (0.7) (see Table 1).

It is shown that in the bottom sediments of areas with high content of organic carbon (Feodosiya Bay and the Kerch Strait), the excess of the geochemical background of such metals as zinc and chromium is characteristic.

It was noted that the geochemical background for nickel was not exceeded in any of the studied water areas (Table 3). At the same time, despite the excess of the geochemical background for chromium in Feodosiya Bay, the correlation coefficient between the content of this metal and the content of the organic matter is rather low ($r = 0.3$) (Table 1).

It is possible that in addition to the organic matter, other components of bottom sediments, which are not considered in this work, contribute to the accumulation of the studied metals.

## Conclusion

Analysis of the array of field data made it possible to evaluate the spatial heterogeneity of the Zn, Ni, Cr distribution in the bottom sediments of Kalamita Bay, Feodosiya Bay, and the Kerch Strait, taking into account the levels of the organic matter content and the calculated correlation coefficients between metal content and $C_{org}$ content.

The high values of these correlation coefficients for water areas with intensive water exchange are explained by the ability of the studied metals to form stable compounds with organic ligands.

The spatial heterogeneity of the organic matter distribution is determined by the hydrodynamic regime of the considered water areas and its intensity. This distribution heterogeneity also influences the behavior of the metals under study.

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**Elena E. Sovga** – goal statement, critical analysis of the text and its revision

**Ekaterina A. Kotelyanets** – sampling, identification of studied microelements, quantitative and qualitative analysis of the results, preparation of graphic materials, goal statement

*All the authors have read and approved the final manuscript.*