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Original article

Factors Forming the Spatial Distribution of Natural and Man-Made Radionuclides in the Bottom Sediments of the Kamyshovaya Bay, Sevastopol

D. A. Kremenchutskii ✉, Yu. S. Gurova

Marine Hydrophysical Institute of RAS, Sevastopol, Russian Federation
✉ *d.kremenchutskii@mhi-ras.ru*

Abstract

Purpose. The purpose of the article is to reveal the features of spatial distribution of the radionuclide ($^{210}Pb_{ex}$, ^{226}Ra, ^{137}Cs and ^{40}K) contents in the bottom sediments of the Kamyshovaya Bay and to identify the factors determining them.

Methods and Results. The paper presents the results of measurements of the concentrations of $^{210}Pb_{ex}$, ^{226}Ra, ^{137}Cs and ^{40}K in nine samples of the surface (0–5 cm) layer and in two columns of bottom sediments collected in the Kamyshovaya Bay in July 2021. The activity of $^{210}Pb_{ex}$, ^{226}Ra, ^{137}Cs and ^{40}K in the samples was determined using a low-background gamma spectrometer with a well-type *NaI*(*Tl*) scintillation detector. Estimates of the relationship between the activity of the radionuclides under consideration in the bottom sediments with the sediment granulometric composition and the organic carbon content are given. The rate of sedimentation and the flux of matter and radionuclides to the bottom sediments were quantitatively assessed.

Conclusions. Spatial variability of the concentrations of radionuclides under consideration reveals a general tendency towards increase of their values from the northern part of the bay to its southern one. The results of the analysis indicate that the spatial variability of radionuclide content in the surface sediment samples and their vertical distribution in the two columns are explained by the changes in particle size distribution and in sedimentation rates, as well as by presence of the storm water and domestic wastewater sources in the bay southern part. Based on the results of the correlation analysis, the process of water purification in the area under study was assumed to result from the adsorption of radionuclides and organic matter by a fine-grained material that was followed by sedimentation of this material in bottom sediments. The average values of the sedimentation rate and the matter flux to bottom sediments were 0.43 cm/year and 2976 g/(m^2·year), respectively. The flux of radionuclides to the bottom sediments was 53.0 Bq/(m^2·year) for ^{137}Cs, 690.5 Bq/(m^2·year) for ^{40}K, 58.0 Bq/(m^2·year) for ^{226}Ra and 79.5 Bq/ (m^2·year) for $^{210}Pb_{ex}$.

Keywords: Black Sea, Kamyshovaya Bay, bottom sediments, particle size distribution, organic carbon, cesium-137, ^{137}Cs, potassium-40, ^{40}K, radium-226, ^{226}Ra, lead-210, ^{210}Pb, sedimentation rate, radionuclides, sedimentation

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Introduction

Coastal waters are subject to significant anthropogenic pressure, which changes the rate of geochemical processes leading to contamination of bottom sediments. For many years, employees of the Institute of Biology of the Southern Seas of RAS (IBSS, Sevastopol) have been studying the bottom sediments of the Kamyshovaya Bay. Works [1–4] highlight the main physical characteristics of sediment (natural humidity, Eh and pH values), as well as assessments of contamination of the surface layer of bottom sediments with chloroform-extractable substances and petroleum hydrocarbons [2–4]. It was noted that most of the bay's sediments are characterized by oxidizing conditions, giving way to reduced conditions (Eh up to −59 mV [2] and −94 mV [4]) in the silty sediments of the central part. It was noted in [3] that dredging in the bay had previously affected the pollution rate of the bay sediments.

In [5], it was established that the chemistry of pore waters in the bottom sediments of the bay was determined by processes involving dissolved forms of iron (Fe (II, III)) and hydrogen sulfide. It has been shown that the presence of sub-oxygen conditions in the upper layer of sediments indicates the formation of environmental risk zones for the bay ecosystem [5].

Radionuclides are traditionally of interest both as an independent object for research, since in high concentrations they have a negative impact on the ecosystem, and as tracers of processes that determine the entry of substances into the marine environment and their accumulation in bottom sediments [6–21].

Cesium-137 (^{137}Cs) is a radionuclide of a man-made origin with a half-life ($T_{½}$) of 30.05 years. The sources of this radionuclide in the Black Sea region are its flows from the atmosphere and with river runoff [6]. The last large-scale release of this radionuclide into the region was a consequence of the Chernobyl nuclear power plant accident. A large number of works are devoted to the study of this radionuclide content in the Black Sea bottom sediments [6–13]. One of the reasons for such great scientific interest in this radionuclide is that data on its vertical distribution in bottom sediments can be used to estimate the sedimentation rate [12, 14–15].

Potassium-40 (^{40}K), radium-226 (^{226}Ra) and lead-210 (^{210}Pb) are naturally occurring radionuclides ($T_{½}$ is $1.25 \cdot 10^9$, $1.6 \cdot 10^3$ and 22.2 years, respectively). They enter bottom sediments with river runoff, as part of atmospheric precipitation, with aeolian material, due to coastal abrasion and from volcanic sources [1]. ^{40}K and ^{210}Pb can additionally be supplied with settling organic matter. The almost tenfold difference in the ^{40}K content in biogenic and lithogenic matter makes this radionuclide a potentially useful tracer for estimating the biogenic matter proportion in bottom sediments [12, 16, 17]. The radionuclide pair ^{226}Ra and ^{210}Pb is widely used to obtain quantitative estimates of sedimentation rates [18–21]. To carry out such assessments, data on the "excess" activity of $^{210}Pb_{ex}$ in bottom sediments, calculated as the difference between the activity of ^{210}Pb and ^{226}Ra, are used. This "excess" activity occurs due to the adsorption of ^{210}Pb on atmospheric aerosol and sea suspended matter particles along the entire path until these particles become a part of the bottom sediments.

[1] Baturin, G.N., 1975. *Uranium in Recent Marine Sedimentation*. Moscow: Atomizdat, 152 p. (in Russian).

The works [6, 9, 12, 16 and 19] provide information on the content of radionuclides in bottom sediments of bays in the Sevastopol region and focus on the use of radionuclides to estimate sedimentation rates. However, studies of the relationship between the content of radionuclides and geochemical characteristics of sediments have not been carried out. In addition, early studies did not cover the Kamyshovaya Bay water area.

The aim of the present paper is to identify the features of the spatial distribution of radionuclide content ($^{210}Pb_{ex}$, ^{226}Ra, ^{137}Cs and ^{40}K) in the bottom sediments of the Kamyshovaya Bay and to find the factors determining these features.

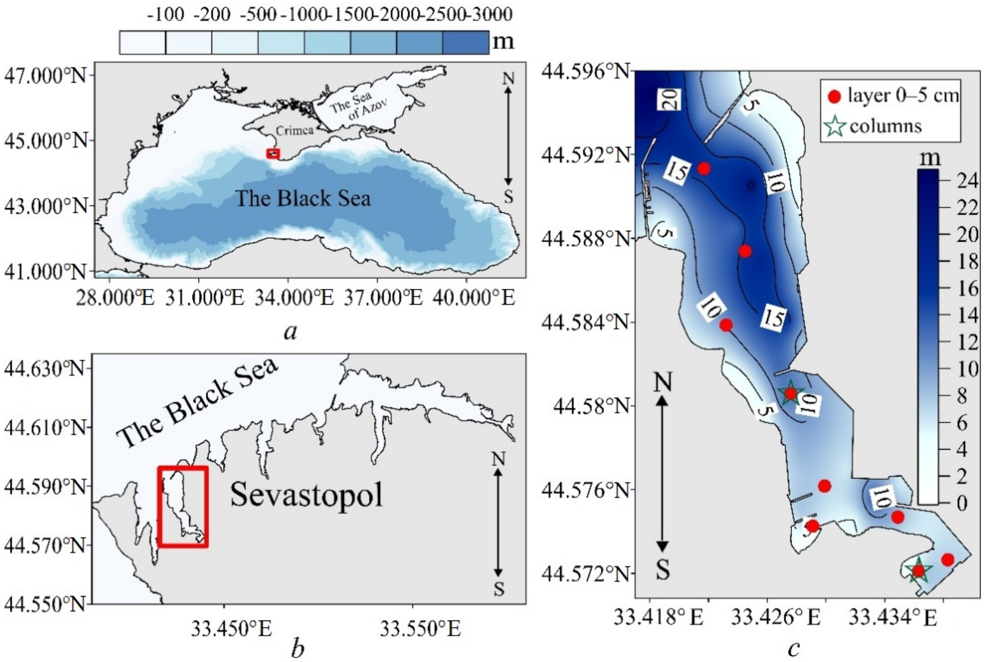
Materials and methods

Research area. The Kamyshovaya Bay is located in the western part of the Herakleian Peninsula and is a typical example of a semi-enclosed water area subject to long-term anthropogenic impact. The main sources of anthropogenic load on the bay ecosystem are as follows: the activities of the Sevastopol sea fishing port, the oil terminal operation, the cement plant, the construction of capital construction projects on the western shore, storm and sewage water runoff [1, 2]. The coastline of the bay is significantly indented and complicated by a large number of piers and ship moorings. In addition, the barrier pier, which prevents water exchange between the bay and the open sea, has a significant impact on the bay condition. All these factors determine the spatial variability of the geochemical characteristics of bottom sediments. Thus, in the upper reaches of the bay, sediments are represented by shell gravel and sand with a low content of organic carbon (0.3%), and in the central and southern parts – aleurite and pelitic silts with a high content of organic carbon (2.2%) [5].

Sampling and processing methods. Selection and preparation of bottom sediment samples were carried out in accordance with regulatory documents (GOST 17.1.5.01-80; ISO 5667-19:2004).

Bottom sediment sampling was carried out in July 2021 (Fig. 1). Samples of the surface layer of bottom sediments (0–5 cm) were taken using a Petersen bottom grab (nine samples). Columns were sampled using a hand sampler and an acrylic primer tube with an internal diameter of 60 mm and a vacuum seal (two samples). On board, the columns were capped at the bottom and transported to the laboratory. In the laboratory, the columns were separated into 2 cm thick layers using a hand extruder and an acrylic ring. Further sample preparation was carried out in accordance with regulatory documents for other analyses.

The granulometric composition of bottom sediments was determined by the mass content of various sized particles, expressed as a percentage, relative to the mass of the dry soil sample taken for analysis. In this case, a combined method of decanting and dispersion was used. The separation of the aleurite-pelitic fraction ($\leq$ 0.05 mm) was carried out by wet sieving, followed by gravimetric determination of the dry mass. Coarse-grained fractions (> 0.05 mm) were separated by a dry sieving method using standard sieves (GOST 12536-2014).



F i g. 1. Location of the area under study (*a*), enlarged image of the Sevastopol region highlighted in Fig. 1, a with a red rectangle (*b*), scheme of the bottom sediment sampling stations in the Kamyshovaya Bay indicated in Fig. 1, *b* with a red rectangle (*c*)

Bottom sediment samples were packed in 50 ml plastic tubes. The volume of a single sample was 30 ml. Each sample was sealed with wax and kept for at least 24 days before measuring the activity of radionuclides in it. During this time, an equilibrium occurs between the ^{226}Ra activity and its daughter decay products ^{214}Pb and ^{214}Bi, which were used to determine the ^{226}Ra activity in the sample. Measurements of the activity of radionuclides (^{210}Pb, ^{226}Ra, ^{137}Cs and ^{40}K) in bottom sediment samples were carried out using a low-background gamma spectrometer with a well-type *NaI(Tl)* scintillation detector. The crystal diameter is 100 mm, its height is 100 mm. The well diameter is 30 mm, its depth is 60 mm. The 7% resolution is for ^{137}Cs line with energy 661 keV. The detector was located in a four-layer protection, the outer layer of which was formed by low-background lead bricks (14 cm), then a layer of cast iron rings (15 cm), a layer of copper (3 mm) and a layer of plexiglass (1 cm). The measurement time for a single sample was determined based on the activity of radionuclides in it and varied from 24 to 48 hours.

Calibration of the gamma quanta registration efficiency with different energies was carried out using certified sources supplied by the IAEA (IAEA-326, IAEA-CU-2006-03) and having a shape and size similar to the studied samples.

Table 1

Quantitative characteristics of the studied parameters

Station No.	Layer	Concentration in bottom sediments, Bq/kg				Content of C_{org}, %	Share of fraction in bottom sediments, %				
		^{137}Cs	^{40}K	^{226}Ra	$^{210}Pb_{ex}$		gravel	sand	clay	aleuritic-pelitic	pelitic-aleuritic
35	0–5	12.1 ± 1.2	188.4 ± 20.6	8.3 ± 0.9	32.1 ± 5.9	12	32.8	11.0	56.2	17.0	39.2
35a	0–5	19.8 ± 1.0	313.8 ± 17.5	13.6 ± 0.8	27.3 ± 4.1	1.33	0.0	1.3	98.7	18.1	80.6
–	0–2	16.5 ± 1.6	343.6 ± 33.1	16.1 ± 1.6	30.7 ± 5.6	1.38	0.9	5.5	93.8	20.3	73.5
–	2–4	15.4 ± 1.4	221.9 ± 22.4	13.4 ± 1.3	9.4 ± 2.0	1.62	17.2	16.0	66.9	17.4	49.5
–	4–6	16.1 ± 1.4	294.1 ± 25.9	13.9 ± 1.3	13.4 ± 2.3	1.13	23.3	11.0	65.7	15.3	50.5
–	6–8	16.5 ± 1.4	272.2 ± 25.3	15.9 ± 1.5	16.0 ± 2.8	1.26	4.4	11.6	84.0	18.4	65.6
–	8–10	10.1 ± 1.0	258.2 ± 24.1	14.4 ± 1.3	6.0 ± 1.2	1.13	24.3	11.4	64.2	16.2	48.1
–	10–12	5.1 ± 0.5	281.7 ± 25.6	14.6 ± 1.3	2.9 ± 0.6	0.75	28.1	15.1	56.9	16.8	40.1
–	12–14	16.1 ± 1.4	295.0 ± 27.3	15.0 ± 1.4	11.6 ± 2.2	1.04	4.8	6.7	88.5	20.4	68.2
–	14–16	22.0 ± 1.9	342.8 ± 32.4	15.7 ± 1.5	25.1 ± 4.5	1.30	0.3	2.1	97.7	22.0	75.7
–	16–18	18.9 ± 1.8	305.2 ± 30.0	18.4 ± 1.7	41.3 ± 6.7	1.49	0.0	2.5	97.5	18.3	79.1
36	0–5	4.1 ± 0.4	303.9 ± 27.0	19.7 ± 1.7	18.1 ± 2.8	1.46	33.0	12.1	55.0	13.0	42.0
37	0–5	21.3 ± 1.9	269.9 ± 27.2	14.5 ± 1.5	29.9 ± 5.3	1.23	0.0	1.1	98.9	33.7	65.2
38	0–5	11.0 ± 1.1	221.3 ± 23.7	17.5 ± 1.7	16.1 ± 3.2	2.21	5.0	5.1	89.9	27.0	63.0
39	0–5	17.8 ± 1.8	232.6 ± 23.7	19.5 ± 1.8	44.1 ± 4.4	1.81	5.1	2.3	92.6	20.7	71.9
–	0–2	21.9 ± 2.0	232.8 ± 25.4	22.0 ± 2.1	44.7 ± 7.3	1.94	5.5	2.5	92.0	25.1	67.0
–	2–4	18.3 ± 1.7	206.8 ± 22.8	20.1 ± 1.9	45.4 ± 7.2	1.75	0.0	1.5	98.5	23.3	75.2
–	4–6	19.5 ± 2.0	203.4 ± 21.3	19.3 ± 1.8	40.4 ± 6.1	1.76	1.5	4.2	94.3	21.1	73.3
–	6–8	17.1 ± 1.5	195.0 ± 19.9	19.6 ± 1.8	30.5 ± 4.7	1.66	3.7	4.5	91.8	24.4	67.4
–	8–10	17.9 ± 1.6	167.7 ± 18.5	15.8 ± 1.5	33.1 ± 5.3	1.82	8.4	12.8	78.8	23.5	55.3
–	10–12	13.3 ± 1.3	210.0 ± 22.0	15.3 ± 1.5	20.8 ± 3.8	12	8.7	10.1	81.3	17.4	63.9
–	12–14	11.2 ± 1.2	183.9 ± 25.5	18.8 ± 2.1	23.2 ± 5.5	1.81	13.9	6.2	79.9	16.2	63.7
40	0–5	1.7 ± 0.3	33.6 ± 6.6	5.3 ± 0.7	6.6 ± 1.7	2.18	75.8	19.3	4.9	3.1	1.8
41	0–5	1.3 ± 0.3	34.8 ± 6.4	4.4 ± 0.6	15.0 ± 3.1	0.38	33.8	63.6	2.7	1.2	1.4
42	0–5	1.2 ± 0.2	30.9 ± 6.6	3.3 ± 0.5	12.6 ± 3.1	0.32	53.4	44.2	2.5	1.3	1.1

The single radionuclide (C) concentration in a sample of bottom sediments was calculated using the following formula [22]:

$$C = \frac{N}{t \cdot m \cdot \varepsilon(E) \cdot \gamma(E) \cdot \exp\left(-\lambda \Delta t\right)},$$

where C is radionuclide concentration, Bq/kg; N is radionuclide photopeak area in pulses; t is spectrum acquisition time, s; m is sample weight in kg; $\varepsilon(E)$ is efficiency of gamma quanta registration with energy E; $\gamma(E)$ is yield of gamma quanta with energy E during the corresponding radionuclide decay; where λ is decay constant equal to ^{137}Cs $9.11 \cdot 10^{-5}$ 1/day, for ^{40}K $2.28 \cdot 10^{-12}$ 1/day, for ^{210}Pb $1.23 \cdot 10^{-4}$ 1/day, for ^{226}Ra $1.71 \cdot 10^{-6}$ 1/day; Δt is time interval between sample collection and the beginning of recording its activity, days.

Sedimentation rate estimates were obtained using constant flux and sedimentation rate model [18, 23]

$$A_z = A_0 \cdot \mathrm{e}^{-(\lambda z / SR)},$$

where A_z is excess $^{210}Pb_{ex}$ concentration in z-layer, Bq/kg; z is depth of the bottom sediment layer, cm; A_0 is excess $^{210}Pb_{ex}$ concentration in the surface layer of sediment, Bq/kg; SR is sedimentation rate, cm/year.

The flux of matter into bottom sediments (MAR) was calculated using the following formula:

$$MAR = \frac{m \cdot SR}{V},$$

where m is total mass of dry matter in the bottom sediment column, g; SR is mean sedimentation rate, m/year; V is volume of bottom sediment column, m^3.

The lower detection limit, calculated according to [24], for ^{137}Cs was 0.13 Bq per sample, for ^{40}K – 3.4 Bq per sample, for ^{210}Pb – 1.3 Bq per sample, and for ^{226}Ra – 0.23 Bq per sample. The error in calculating the content of radionuclides in samples (1σ) in most cases did not exceed 20%.

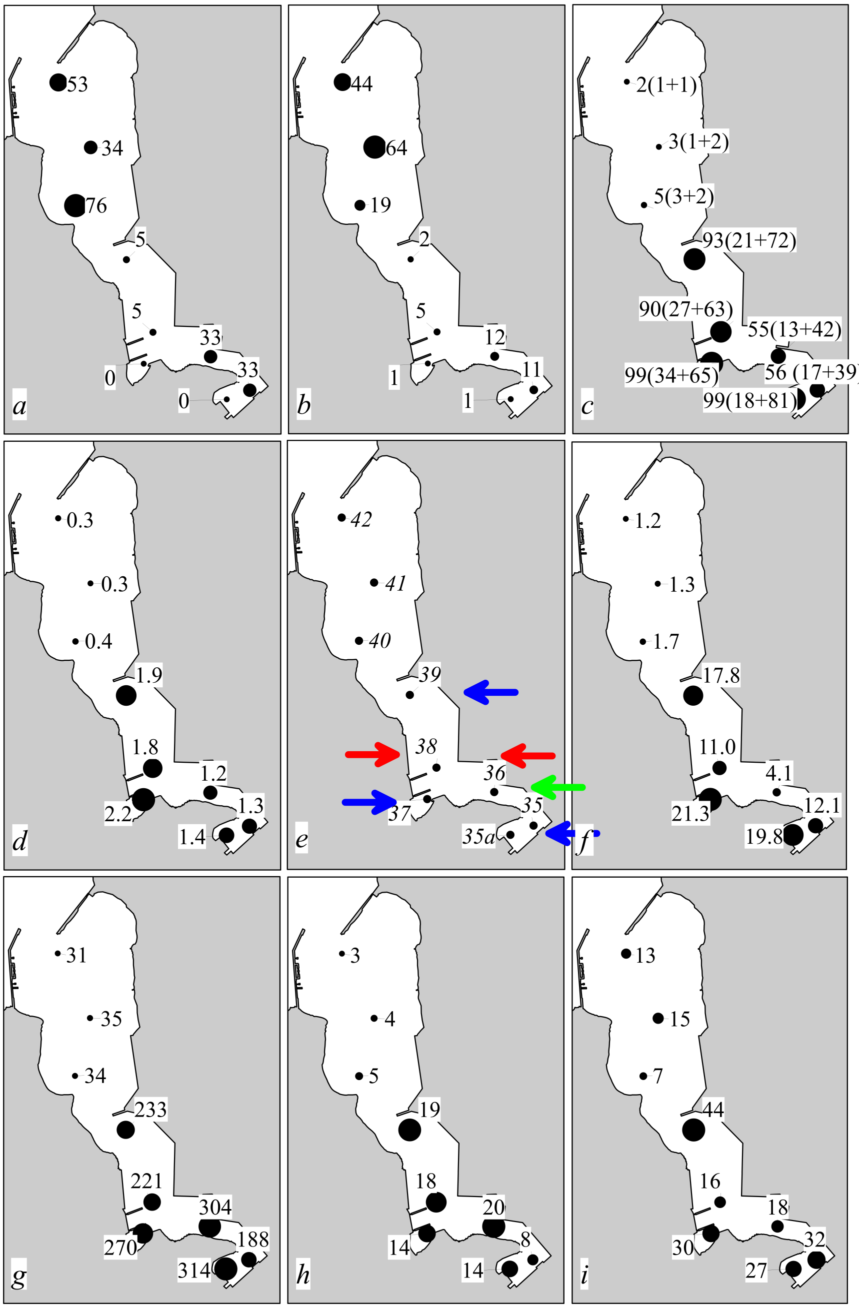
The values of organic carbon content in bottom sediment samples were taken from [5].

The data used in this study is presented in Table 1.

Results and discussion

Variability of the characteristics of the surface layer of bottom sediments

The ^{137}Cs concentration in bottom sediments varied from 1.2 to 21.3 Bq/kg, the mean value was 10.0 ± 0.9 Bq/kg (n = 9). The ^{40}K concentration ranged from 30.9 to 313.8 Bq/kg with a mean value of 181 ± 17.7 Bq/kg (n = 9). The ^{226}Ra concentrations ranged from 3.3 to 19.7 Bq/kg around a mean of 11.8 ± 1.1 Bq/kg (n = 9). The $^{210}Pb_{ex}$ concentrations ranged from 6.6 to 32.1 Bq/kg with a mean value of 20.5 ± 3.7 Bq/kg (n = 9). In the spatial variability of the concentrations of the radionuclides under consideration, there is a general tendency towards increasing values from the northern part of the bay to the southern one (Fig. 2, *f* – *i*).



F i g. 2. Spatial variability of the gravel (*a*), sand (*b*) and clay (aleurite-pelitic and pelite-aleuritic) (*c*) shares of a fraction, %, C_{org} content, %, (*d*), wastewater sources (*e*) and the ^{137}Cs (*f*), ^{40}K(*g*), ^{226}Ra (*h*) and ^{210}Pb$_{ex}$ contents, Bq/kg, (*i*) in the 0–5 cm layer of bottom sediments. Position of the storm (blue arrows), emergency (green arrow) and domestic waste water (red arrows) drains according to [25]

The obtained values of radionuclide concentrations in bottom sediment samples are consistent with literature data. Thus, according to works [19, 22], the ^{137}Cs, ^{40}K, ^{226}Ra and ^{210}Pb$_{ex}$ concentrations in the Balaklava Bay bottom sediments varied in the ranges of 11–62 Bq/kg, 155–562 Bq/kg, 8–42 Bq/kg and 41–48 Bq/kg, respectively. According to works [17, 26], the ^{137}Cs and ^{40}K concentrations in the Sevastopol Bay bottom sediments varied in the ranges of 68–142 Bq/kg and 276–687 Bq/kg, respectively.

The correlation analysis results (Table 2) indicate a strong, statistically significant relationship at the 95% confidence level between the activity of the radionuclides in bottom sediments and the geochemical characteristics of the latter: the position of areas with increased activity of radionuclides coincides with areas characterized by an increased proportion of the clay fraction, its pelite-aleuritic part, particularly (Fig. 2, *c*).

In the central part of the bay (stations *37–39*), due to its isolation, the large number of incoming sources of municipal and storm water runoff (Fig. 2, *e*), as well as the dense location of ship moorings, the proportion of the clay fraction is maximum. The sediments here consist on average of 94% fine-grained material. The minimum content of fine-grained material is observed in the upper reaches of the bay near the western shore (stations *40–42*) and in the southern part of the bay (stations *35*, *36*), which is due to the presence of open coastal cliffs and the supply of gravel-sandy material as a result of coastal abrasion [5].

Thus, for the surface layer of bottom sediments, an increase in the proportion of pelite-aleuritic fraction from 1 to 81% (i.e., 81 times) is accompanied by an increase in the ^{137}Cs, ^{40}K, ^{226}Ra and ^{210}Pb$_{ex}$ activity by approximately 16, 10, 4 and 2 times, respectively. This result is consistent with the conclusions made in early studies [27–29]: smaller suspended particles are characterized by a large specific surface area and remove various substances from the marine environment into bottom sediments more effectively.

Table 2

Pearson correlation coefficients among the studied parameters in the upper layer of bottom sediments

Radio-nuclide	Share of fraction in bottom sediments, %					Content of C$_{org}$, %
	gravel	sand	sand	aleurite-pelitic	pelite-aleuritic	
^{137}Cs	–0.85‡	–0.77†	0.92‡	0.86‡	0.91‡	0.87‡
^{40}K	–0.78†	–0.81‡	0.90‡	0.78†	0.91‡	0.82‡
^{226}Ra	–0.70†	–0.75†	0.82‡	0.72†	0.83‡	0.82‡
^{210}Pb$_{ex}$	–0.72†	–0.55	0.74†	0.69†	0.73†	0.73†

‡ Correlation coefficient is statistically significant at the 99% confidence level ($p < 0.01$).
† Correlation coefficient is statistically significant at the 95% confidence level ($p < 0.05$).

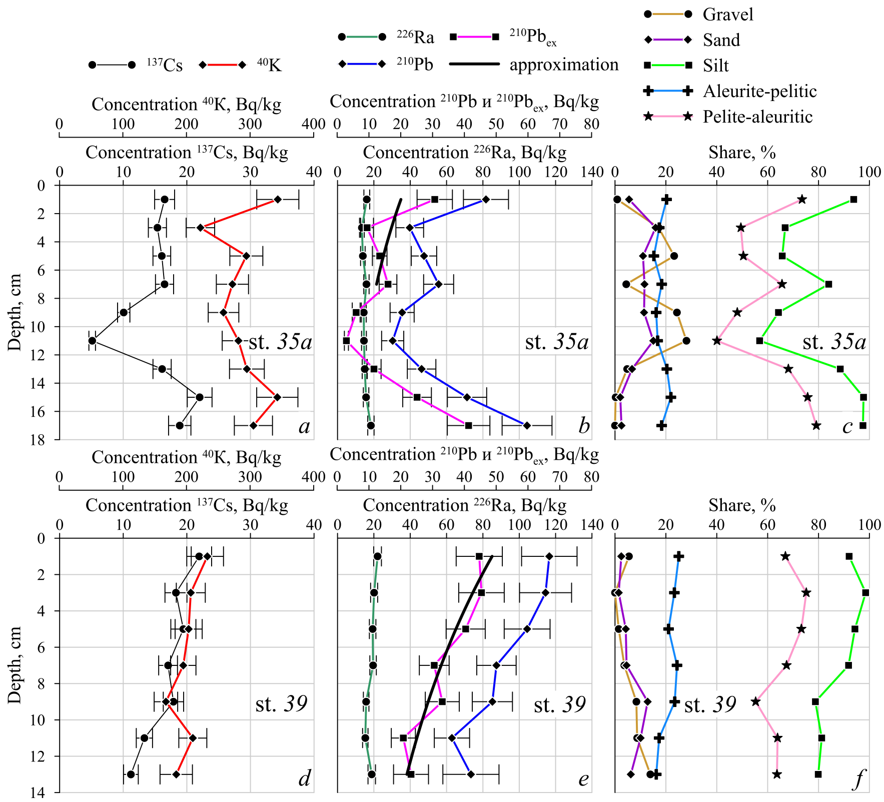
There is a strong direct relationship between the activity of radionuclides and the organic carbon content. The organic carbon content in the surface layer of bottom sediments of the Kamyshovaya Bay varied from 0.3% dry wt. in gravel-sand deposits of the upper reaches of the bay up to 1.8–2.2% dry wt. in pelite-aleuritic sediments of the apex parts of the bay (Fig. 2, *d*). The high content of C_{org} in the southern part of the bay is explained by numerous sources of material (municipal wastewater), as well as weak water exchange [5].

As noted in the introduction, the ^{40}K content in inorganic matter is approximately an order of magnitude higher than in organic matter [17]. Therefore, high positive values of the correlation coefficient (Table 2) among the ^{40}K activity in bottom sediments and the content of the clay fraction, as well as the proportion of organic carbon, indicate the inorganic nature of the clay. Most likely, in the study area, there is a water purification process as a result of the adsorption of radionuclides and organic matter by fine-grained material with the subsequent burial of this material in bottom sediments.

Local features in the distribution of individual radionuclide concentrations are noted. Thus, relatively lower values of ^{137}Cs activity were observed at stations *35*, 36 and 38. This is probably due to the close location of sources of storm water and domestic wastewater (Fig. 2, *e*), the expected ^{137}Cs content in which is close to zero. In turn, the increased values of $^{210}Pb_{ex}$ activity noted at stations *35*, *35a*, *37* and *39* can be associated with the additional supply of this radionuclide with storm water, being a result of precipitation. High activity ^{40}K and ^{226}Ra values noted at stations *35a*, *36*, *37* and *38* are apparently due to the supply of terrigenous material as a result of coastal abrasion, since the content of these radionuclides in terrigenous suspension is higher than in biogenic one.

Vertical variability of bottom sediment characteristics

The first column was selected at station *35a*, located in the apex of the bay at 6 m depth. The vertical ^{137}Cs distribution in this column is heterogeneous and varies in the range from 5.1 ± 0.5 to 22.0 ± 1.9 Bq/kg (Fig. 3, *a*). A pronounced minimum concentration of this radionuclide is observed in the 8–12 cm layer, indicating the presence of an event that led to additional input of different origin material into bottom sediments. This event is also reflected in the vertical profile of the granulometric composition: the gravel-sand fraction proportion increases from 22% in the 0–8 cm layer to 40% in the layer under consideration. The vertical ^{40}K distribution in the column is heterogeneous with a concentration minimum (221.9 ± 22.4 Bq/kg) in the 2–4 cm layer and maxima (343.6 ± 33.1 and 342.8 ± 32.4 Bq/kg) in layer 0–2 and 14–16 cm, respectively (Fig. 3, *a*). The vertical distribution of ^{226}Ra at station *35a* varies within the error in determining its activity and averages 15.3 ± 1.5 Bq/kg (Fig. 3*b*). The vertical $^{210}Pb_{ex}$ distribution in the 0–14 cm layer shows alternating areas of increase and decrease in its concentration (from 2.9 to 30.7 Bq/kg), ending with an increase to 41.3 ± 6.7 Bq/kg in the 14–18 cm layer. In general, the $^{210}Pb_{ex}$ concentration increase with depth indicates that in the past, there was an additional source of entry of this radionuclide into bottom sediments (Fig. 3, *b*).



F i g. 3. Vertical distribution of the ^{137}Cs, ^{40}K, ^{226}Ra, ^{210}Pb, ^{210}Pb$_{ex}$ concentrations (*a*, *b*, *d*, *e*), and the share of the gravel, silt and sand fractions (*c*, *f*) for stations *35a* and *39*. Black line shows exponential approximation of the ^{210}Pb$_{ex}$ unsupported concentration in the bottom sediments

The second column was selected at station *39*, located in the central part of the water area at 13 m depth. The vertical distribution of the studied radionuclides at this station is more uniform than at station *35a* (Fig. 3, *d*, *e*). There is a gradual decrease in the ^{137}Cs and ^{210}Pb$_{ex}$ concentration with depth from 21.9 and 66.7 Bq/kg in the 0–2 cm layer to 11.2 and 36.1 Bq/kg in the 12–14 cm layer, respectively. The ^{40}K and ^{226}Ra contents varied from 167.7 to 232.8 and from 15.3 to 22.0 Bq/kg, respectively. In general, variability in the vertical profile of ^{40}K and ^{226}Ra concentrations occurs within the error limits for determining the activity of these radionuclides.

Thus, there is spatial variability in the vertical distribution of the analyzed radionuclides: the ^{40}K content in bottom sediments at station *35a* is on average 45% more, and the ^{137}Cs, ^{226}Ra and ^{210}Pb content is on average 11, 18 and 49% less, respectively, than at station *39*. Estimates of sedimentation rates were carried out to analyze the factors determining the features identified.

Features of the ^{137}Cs concentration variability in the bottom sediment column sampled at station *35a* do not allow dating the sediment and determining the sedimentation rate, since there is no pronounced maximum in the vertical distribution of ^{137}Cs concentration. This indicates that the layer in question was formed after 1986. Data on the excess activity of ^{210}Pb$_{ex}$ in the first four horizons were used to estimate the sedimentation rate and matter flux. The choice of horizons was based on data on the vertical distribution of ^{137}Cs – in this interval a "stable" supply of this radionuclide to bottom sediments is observed. The sedimentation rate for this station was 0.39 cm/year, the matter flux was 2841 g/(m^2·year).

In the vertical profile of ^{137}Cs concentration obtained at station *39*, there is also no clearly defined maximum concentration of this radionuclide. The sedimentation rate estimate was carried out for station *39* based on the data concerning the vertical distribution of $^{210}Pb_{ex}$. According to the result obtained (Fig. 3, *f*), the sedimentation rate was 0.47 cm/year. The matter flux into bottom sediments was 3111 g/(m^2·year). As noted earlier, estimates of sedimentation rates in the Kamyshovaya Bay are absent in the literature available to the authors. According to published data, the sedimentation rate and matter flux into sediment varies in the bays of the Sevastopol region in a wide range [12, 22]: 0.35 cm/year and 830 g/(m^2·year) in the Streletskaya Bay, 0.24–0.93 cm/year and 607–7094 g/(m^2·year) in the Sevastopol Bay, 0.50–0.55 cm/year and 2131–3519 g/(m^2·year) in the Balaklava Bay. The work [2] indicates that the number of macrozoobenthos in the Kamyshovaya Bay increased in the 1991–2000 period, and then, according to the 2003 data, there was a sharp decline (about four times). According to the obtained sedimentation rate estimates, the sediment depth made about 10 cm in 2000. Thus, the minimum proportion of the clay fraction observed at station *39* in 8–10 cm layer, can be due precisely to this event, which, in turn, confirms the adequacy of the sedimentation rate estimates obtained in the present study.

Table 3

Pearson correlation coefficients among the studied parameters in the vertical profile of bottom sediments*

Radio-nuclide	Share of fraction in bottom sediments, %					Content of C_{org}, %
	gravel	sand	sand	aleurite-pelitic	pelite-aleuritic	
^{137}Cs	–0.79‡	–0.65‡	0.78‡	0.68‡	0.72‡	0.36
^{40}K	–0.05	–0.13	0.08	–0.23	0.16	–0.47*
^{226}Ra	–0.57†	–0.77‡	0.67‡	0.65‡	0.61‡	0.67‡
$^{210}Pb_{ex}$	–0.76‡	–0.77‡	0.81‡	0.71‡	0.75‡	0.68‡

* Correlation coefficient is statistically significant at the 90% confidence level ($p < 0.1$).
‡ Correlation coefficient is statistically significant at the 99% confidence level ($p < 0.01$).
† Correlation coefficient is statistically significant at the 95% confidence level ($p < 0.05$).

Thus, the sedimentation rates between stations *35a* and *39* differ by approximately 18%. This can explain the differences in the ^{137}Cs and ^{226}Ra activities noted above for these stations (11 and 18%, respectively). At the same time, this does not explain the difference in the ^{40}K and $^{210}Pb_{ex}$ activity (45 and 49%). Such differences can be stipulated by the variability in the geochemical characteristics of sediments. To confirm this, a correlation analysis was carried out. The results obtained (Table 3) indicate that the relationships among the ^{137}Cs, ^{226}Ra and $^{210}Pb_{ex}$ activity in them and their granulometric composition, previously identified for the surface layer of bottom sediments, are preserved. Thus, the spatial variability of $^{210}Pb_{ex}$ concentration is due to the clay fraction content variability.

As for the ^{40}K concentration, the strongest correlation is observed with the proportion of organic carbon, although this relationship is statistically relevant only at the 90% significance level. Thus, an increase in the organic carbon content and, accordingly, an increase in the biogenic component of sediment is accompanied by a decrease in the ^{40}K concentration in it, which is consistent with literature data [12, 16, 17].

After averaging the matter flux data into bottom sediments and the concentration of radionuclides in the 0–5 cm layer, quantitative estimates of the mean values of the entry of these radionuclides into bottom sediments were obtained. According to the results, these values were 53.0 Bq/(m^2·year) for ^{137}Cs, 690.5 Bq/(m^2·year) for ^{40}K, 58.0 Bq/(m^2·year) for ^{226}Ra and 79.5 Bq /(m^2·year) for ^{210}Pb$_{ex}$. To compare: in the Sevastopol Bay, the ^{137}Cs flow values into bottom sediments are in the range of 59.8–667.0 Bq/(m^2·year) [26], in the Streletskaya Bay – 57.7 Bq/(m^2·year) [30]. Thus, the estimates obtained in the present study do not contradict the literature data.

Conclusions

According to the results obtained, the concentration values of ^{210}Pb$_{ex}$, ^{226}Ra, ^{137}Cs and ^{40}K in the surface layer of the Kamyshovaya Bay bottom sediments varied in the range of 7–32, 3–20, 1–21 and 31–314 Bq/kg, respectively.

It has been established that in the spatial variability of the concentrations of the considered radionuclides, there is a general tendency towards increasing values from the northern part of the bay to the southern one. The correlation analysis results indicate a strong direct relationship among the activity of radionuclides and the clay fraction proportion (on average r = 0.85) and organic carbon content (on average r = 0.81). In the case of ^{40}K, the observed positive values of the correlation coefficients indicate that in the study area, there is a process of water purification as a result of the adsorption of radionuclides and organic matter by fine-grained material with subsequent sedimentation of this material into bottom sediments. Local features of spatial variability of radionuclide content can be stipulated by the terrigenous material supply as a result of coastal abrasion and storm runoff and biogenic material from municipal wastewater.

The spatial variability of the vertical distribution of radionuclide concentrations in two columns has been established: the ^{40}K content in bottom sediments at station *35a* is on average 45% higher, and the ^{137}Cs, ^{226}Ra and ^{210}Pb$_{ex}$ content is on average 11, 18 and 49% less, respectively, than at station *39*. It has been shown that such variability is associated with spatial heterogeneity in sedimentation rates and geochemical characteristics of sediments.

Flow of radionuclides into bottom sediments was 53.0 Bq/(m^2·year) for ^{137}Cs, 690.5 Bq/(m^2·year) for ^{40}K, 58.0 Bq/(m^2·year) for ^{226}Ra and 79.5 Bq/ (m^2·year) for ^{210}Pb$_{ex}$.

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About the authors:

Dmitrii A. Kremenchutskii, Senior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya Str., Sevastopol, 299011, Russian Federation), Ph.D. (Geogr.), **ORCID ID: 0000-0002-8747-6612, ResearcherID: AAC-1673-2020,** d.kremenchutskii@mhi-ras.ru

Yuliya S. Gurova, Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya Str., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0002-9826-4789, ResearcherID: AAB-5628-2019**, kurinnaya-jul@yandex.ru

Contribution of the co-authors:

Dmitrii A. Kremenchutskii – conceptualization, formal analysis, investigation, data curation, visualization, writing of the original draft, review and editing

Yuliya S. Gurova – conceptualization, formal analysis, investigation, data curation, visualization, writing of the original draft, review and editing

The authors have read and approved the final manuscript.

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