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THE POSSIBILITY OF IMPLEMENTATION OF THE SUSTAINABLE DEVELOPMENT CONCEPT FOR THE RECREATIONAL COASTLINE OF YALTA CITY REGARDING BIOGENIC ELEMENTS, RADIONUCLIDES, HEAVY METALS, AND ORGANOCHLORINE COMPOUNDS (CRIMEA, BLACK SEA)

© 2023 **V. N. Egorov, N. Yu. Mirzoyeva, Yu. G. Artemov, V. Yu. Proskurnin, A. P. Stetsiuk, Yu. G. Marchenko, D. B. Evtushenko, I. N. Moseichenko, and O. D. Chuzhikova-Proskurnina**

A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russian Federation
E-mail: *egorov.ibss@yandex.ru*

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In the Yalta city water area (Crimea, Black Sea), hydroacoustic sounding was carried out, and area and volume of waters of the Vodopadnaya River estuarine zone were determined down to a depth of 40 m. Concentration of biogenic elements (NO_2, NO_3, NH_4, and PO_4) and heavy metals (Cu, Zn, Fe, Co, Ni, Mo, Cd, Pb, and Hg) in freshwater of the river estuary exceeds their content in coastal seawater by 3–64 times. The effect of the river discharge on seawater eutrophication was assessed. Using post-Chernobyl radioisotopes ^{90}Sr and ^{137}Cs, bottom sediments dating was carried out, and the sedimentation rate in the studied water area was determined. Fluxes of pollutants with the Vodopadnaya River runoff and the periods of their turnover in the Yalta city recreational coastline were calculated. The obtained results were used to substantiate the sustainable development concept for the Yalta city recreational zone in terms of the factors of pollution of its marine environment.

Keywords: Black Sea, Crimea, water, biogenic elements, strontium-90, cesium-137, heavy metals, organochlorine compounds, bottom sediments dating

The water area of Yalta city (Crimea) is one of the critical zones of the Black Sea [Zaitsev, Polikarpov, 2002], where pollutant content in the marine environment can exceed natural levels or reach maximum permissible concentrations (hereinafter MPC) for the population and biotic components of ecosystems. The main coastal recreational area of the city, located in the southwestern Yalta Bay, is affected by the seaport, by recreational, touristic, municipal, and agricultural activities on the coast, and by the Vodopadnaya River (Uchan-su), with its flood flow regime. The river originates at the foot of Ai-Petri peak. The river length is 7.0 km; the catchment area is 28.9 km^2; and the slope is 94.3 $m \cdot km^{-1}$. There are certain environmental problems in this area, and the most significant ones are hypereutrophication caused by nutrients [Egorov et al., 2021] and water contamination with heavy metals and organochlorine compounds [Egorov et al., 2018]. The need for minimizing negative consequences of anthropogenic load on the Yalta city recreational coastline requires the development and application of measures aimed at implementation of sustainable development.

The aim of these studies was to standardize maximum permissible fluxes of pollutants into the Yalta city recreational area (Crimea, Black Sea) in terms of biogeochemical criteria and to substantiate the sustainable development concept based on contamination factors for the marine environment of the area analyzed. Accordingly, the following tasks were solved:

- determination of biogenic element concentrations in water and assessment of the limitation of phytoplankton primary production in the Vodopadnaya River estuarine zone;
- bottom sediments dating in terms of the peaks of ^{90}Sr and ^{137}Cs radioactive fallout maximums on the sea surface and determination of sediment fluxes of pollutants into the thickness of the bottom sediments in the Yalta city recreational zone;
- assessment of contamination for freshwater of the river estuary and seawater of the city area with radionuclides and heavy metals, as well as determination, based on the results of our own observations, of biogeochemical characteristics of self-purification of the Yalta city recreational zone from ∑6PCB and ∑DDT according to data given in [Malakhova, Lobko, 2022] and from radionuclides and heavy metals.

MATERIAL AND METHODS

The Yalta city recreational zone is located on the southwestern coast of the Yalta Bay (Crimea, Black Sea) (Fig. 1). To the north, there are marina, berths for coasters serving tourist routes, and the seaport. From the east and the west, the recreational zone borders the open Black Sea area.

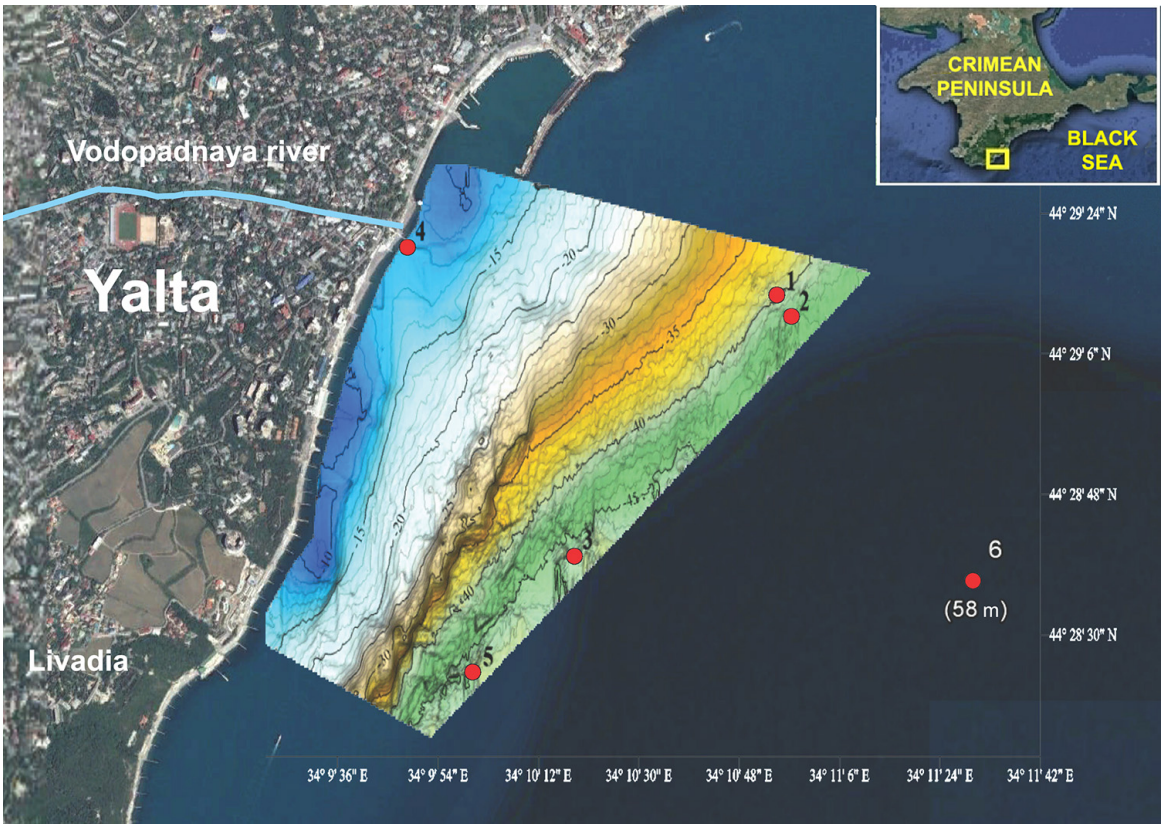

Fig. 1. Bathymetric map of the Yalta city water area and the Vodopadnaya River estuarine zone. Red circles denote the sampling stations. The coastline from the Vodopadnaya River estuary to Livadia settlement is occupied by a city beach, which is included in the Yalta city recreational zone

Methodology of oceanographic works. For hydroacoustic observations, we used boats equipped with Lowrance Elite-7 Ti chartplotter with a built-in GPS receiver. Water was sampled with a 10-L bathometer; sediments were sampled with a manual gravity corer. For geochronological analysis, sediment cores were sampled at stations 5 and 6. Sta. 6 was located outside the polygon, and its research material was used for comparative purposes. A bathymetric map of the Yalta city water area and the Vodopadnaya River estuarine zone is shown in Fig. 1. Sampling metadata are presented in Table 1.

Table 1. Dates, coordinates, and depths of water and sediment sampling stations in the Yalta Bay

Number of the sampling station	Date	Coordinates		Depth, m
		N	E	
1	19.07.2019	44°29.2234′	34°10.9130′	35
2	19.07.2019	44°29.1806′	34°10.9530′	37
3	19.07.2019	44°28.6701′	34°10.3051′	40
4	19.04.2017 28.06.2017 19.07.2019 22.06.2020	44°29.3294′	34°09.8040′	1
5	19.07.2019	44°28.4208′	34°10.0072′	41
6	15.10.2020	44°28.565′	34°11.512′	58

Concentrations of nitrites, nitrates, and ammonium in freshwater of the Vodopadnaya River estuary and in seawater of its estuarine zone were determined by the standard method [Rukovodstvo, 1977]. The absorption of biogenic elements during biosynthesis was established from the ratio [Hutchinson, 1969; Redfield, 1958]:

$$1P : 7N : 40C\,, \tag{1}$$

from which it followed that the absorption coefficient of phosphorus in relation to carbon is 0.025, and the absorption coefficient of nitrogen is 0.175. The degree of limitation of phytoplankton production by biogenic elements was assessed from the stoichiometric ratio N : P = 16 : 1 by molar concentration or 7 : 1 by weight concentration. To determine the biogenic factor limiting production processes, the Redfield stoichiometry (PR_{at}) was used. This ratio, with the dimensions of its parameters expressed in $\mu g \cdot L^{-1}$, had the form as follows [Redfield, 1958]:

$$PR_{at}(N/P) = 1.53(1.35NO_2 + NO_3 + 3.44NH_4)/PO_4\,. \tag{2}$$

At $PR_{at} > 16$, phosphorus is a limiting nutrient; at $PR_{at} < 16$, nitrogen.

For geochronological studies, the bottom sediment cores were sampled using a manual gravity corer (inner diameter of 58 mm) with a vacuum seal. The resulting cores were cut into layers 1 cm thick with a screw extruder described in [Papucci, 1997]. Immediately after cutting, the samples were weighed, dried at a temperature of +40…+50 °C, and then weighed again to determine the amount of evaporated water. To estimate the initial moisture content of the bottom sediments, the concentration of salts dissolved in pore water was calculated [Schafer et al., 1980]. Artificial radionuclides ^{90}Sr and ^{137}Cs were used as radioactive tracers for bottom sediments dating [Gulin et al., 1994; Mirzoeva et al., 2005; Radioekologicheskii otklik, 2008]. Concentrations of ^{90}Sr and ^{137}Cs were determined separately for each layer of the bottom sediment cores.

^{90}Sr activity was measured by the Cherenkov radiation of its daughter product ^{90}Y with a low background liquid scintillation counter (LSC) LKB Quantulus 1220 [Harvey et al., 1989; Radioekologicheskii otklik, 2008]. The lower limit of detection (LLD) is 0.01–0.04 Bq·kg^{-1} or Bq·m^{-3} of the sample. The relative error of the obtained results did not exceed 20%. The results were subjected to mathematical processing of radiospectrometric data [Radioekologicheskii otklik, 2008]. The correctness of the methodology used and the reliability of the results obtained were controlled *via* constant participation in international intercalibration under the auspices of the IAEA (Vienna, Austria) and the National Laboratory (Risø, Denmark). The data on the intercalibration of the determination techniques obtained from the measurement results for reference samples and field parallel determinations between IBSS and other institutes indicated as follows. The used methodological base made it possible to assess, with the necessary and sufficient degree of reliability, the contamination of the studied ecosystems with the long-lived radionuclide ^{90}Sr [Radioekologicheskii otklik, 2008]. In dried samples, ^{137}Cs content was determined using a NaI(Tl) scintillation detector. It was calibrated with standard samples of bottom sediments IAEA-306 and IAEA-315 supplied by the IAEA [Radioekologicheskii otklik, 2008]; their shape and dimensions were similar to those of the bottom sediment samples studied by us. The mean relative error in the samples did not exceed 27%.

Heavy metals (hereinafter HM) were isolated from seawater by extraction/preconcentration in accordance with the guidance document 52.10.243-92 [1993]. This technique is based on the extraction of the complexes of the elements to be determined with carbon tetrachloride using sodium diethyldithiocarbamate (NaDDC); it is followed by the destruction of the complexes with concentrated nitric acid and the re-extraction of the elements into an aqueous solution of a smaller volume. In this case, the quantitative extraction is achieved for Fe, Co, Ni, Cu, Zn, Mo, Cd, and Pb [Mirzoeva et al., 2022]. HM extraction from samples of the bottom sediments was carried out in accordance with environmental regulatory document 16.2.2:2.3.71-2011 [2011]. This technique is based on the acid mineralization of sediment dry matter and leaching of the elements to be determined into the solution.

In extracts from seawater and mineralizates of the bottom sediments, HM were determined in IBSS core facility "Spectrometry and Chromatography" by inductively coupled plasma mass spectrometry on a PlasmaQuant MS Elite mass spectrometer (Analytik Jena AG, Germany) according to the international technical standard 56219-2014 [2015] and the operating manual [PlasmaQuant MS, 2014]. For the elements to be determined, the machine was calibrated with a multi-element standard solution IV-28 (Inorganic Ventures, the USA). The error of HM determination in the water samples and the bottom sediments for all elements did not exceed 10% at their concentration in water > 0.01 μg·L^{-1} and in bottom sediments > 0.1 mg·kg^{-1}. At lower content, the error reached 60%.

Water and bottom sediments to determine mercury content were sampled simultaneously. To separate dissolved and particulate mercury, seawater was fixed immediately after sampling with concentrated nitric acid (10 mL HNO_3 *per* 1 L of water). Then, in the laboratory, those were filtered through pre-weighed nuclepore filters with a pore diameter of 0.45 μm. Mercury concentration in suspended matter samples was determined in accordance with the international technical standard 26927-86 [2002]. The measurements were carried out by atomic absorption spectrophotometry using a Hiranuma-1 mercury analyzer. To calibrate it and to control the quality of the analysis, certified mercury standard samples were used. The measurement error did not exceed 2%.

The mean sedimentation rate was calculated using the following formula [Gulin et al., 1994]:

$$S = h/(T_0 - T)\,, \tag{3}$$

where S is the mean sedimentation rate, cm·year^{-1};

T is the absolute age of the layer, years;

T_0 is the year of sampling;

h is the mean layer depth, cm.

The age of bottom sediment layers in the cores was determined by the formula [Gulin et al., 1997]:

$$T = T_0 - h/S\,, \tag{4}$$

where T (the age of the layer) is the year of accumulation of the bottom sediment layer;

T_0 is the year of sampling;

h is the mean depth of the bottom sediment layer, cm;

S is the mean sedimentation rate, cm·year^{-1}.

The method for determining the sedimentation rate in weight units (g·m^{-2}·year^{-1}) is described in [Gulin et al., 1994]. Theoretical analysis of the results of observations was carried out based on modern ideas about the radioisotopic and chemical homeostasis of marine ecosystems [Egorov et al., 2021].

RESULTS

Echo sounding data were processed with WaveLens program [Artemov, 2006]. According to these data, the area (S) of the Yalta water area in the Vodopadnaya River estuarine zone down to a depth of 40 m (Fig. 1) is 2.82 km^2, and water volume (V) is 0.08 km^3. As *per* regular measurements of the Yalta stream gauging station, the mean river flow at its estuary (V_r) is 0.384 m^3·s^{-1}, or 12.11×10^6 m^3·year^{-1}.

Bottom sediments dating. Primary data on bottom sediments dating are presented in Tables 2 and 3.

Table 2. ^{90}Sr and ^{137}Cs activity concentration in different layers of the bottom sediment core at station 5

Bottom sediment layer, cm	Layer weight, g		^{90}Sr concentration, Bq·kg^{-1} dry weight		^{137}Cs concentration, Bq·kg^{-1} dry weight	
	wet	dry	^{90}Sr	±	^{137}Cs	±
0–1	46.0	30.5	b. d.	b. d.	26.6	3.0
1–2	56.5	41.0	b. d.	b. d.	14.6	1.5
2–3	42.5	32.0	b. d.	b. d.	15.6	2.2
3–4	22.0	16.5	b. d.	b. d.	0	0
4–5	62.0	52.5	b. d.	b. d.	0	0
5–6	27.0	18.5	1.91	0.52	0	0
6–7	33.5	23.0	5.99	0.87	26.0	4.0
7–8	36.0	25.0	b. d.	b. d.	0	0
8–9	45.0	31.5	2.19	0.51	0	0
9–10	44.5	31.0	1.97	0.43	0	0
10–11	45.5	31.0	b. d.	b. d.	19.3	3.1

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Bottom sediment layer, cm	Layer weight, g		^{90}Sr concentration, Bq·kg^{-1} dry weight		^{137}Cs concentration, Bq·kg^{-1} dry weight	
	wet	dry	^{90}Sr	±	^{137}Cs	±
11–12	45.5	29.5	5.18	0.64	17.2	1.9
12–13	35.0	22.0	4.6	1.0	0	0
13–14	39.0	23.0	b. d.	b. d.	0	0
14–15	39.0	22.5	3.13	0.87	13.5	3.3
15–16	38.0	22.0	7.86	1.26	31.8	2.5
16–17	41.5	24.5	13.17	1.41	22.7	1.8
17–18	43.0	27.5	10.67	1.48	12.1	0
18–19	42.5	28.5	6.7	0.95	0	0
19–20	55.5	37.5	b. d.	b. d.	17.5	1.7
21–22	44.5	29.0	3.22	0.69	0	0
22–23	41.5	27.0	b. d.	b. d.	0	0

Note: b. d. denotes values below the detection limit.

Table 3. ^{137}Cs activity concentration in different layers of the bottom sediment core at station 6

Bottom sediment layer, cm	Layer weight, g		^{137}Cs concentration, Bq·kg^{-1} dry weight	
	wet	dry	^{137}Cs	±
0–1	64.0	42.3	12.0	1.5
1–2	49.5	31.4	11.0	1.0
2–3	45.5	28.6	0	0
3–4	50.0	34.4	0	0
4–5	36.0	23.2	5.0	0.7
5–6	50.5	31.1	0	0
6–7	42.5	25.9	2.5	0.25
7–8	45.0	28.8	32.5	1.6
8–9	45.5	30.3	12.5	1.0
9–10	44.5	29.6	0	0
10–11	51.0	34.0	0	0
11–12	44.5	29.0	0	0
12–13	47.0	30.7	0	0
13–14	41.5	26.1	0	0
14–15	42.5	25.5	0	0
15–16	44.5	27.0	23.0	1.6
16–17	46.5	28.5	14.0	2.1
17–18	43.0	26.5	0	0
18–19	45.0	28.0	0	0
19–20	45.0	29.0	0	0

A graphic representation of the method for bottom sediments dating is given in Fig. 2.

Horizons are identified (Fig. 2), to which layers are linked, related to the period of the prohibition of nuclear weapons tests in open environments (1963) and to the year of the accident at the Chernobyl Nuclear Power Plant (1986). Linking to these dates allows estimating the sedimentation rate and using the “radio-geochemical clock” for bottom sediments dating. The same as in all cases of experimental and natural measurements, the results of observations are always burdened with errors. In this case,

the main errors are determined by inaccuracy in cutting the cores into layers, non-considering the change in sediment density in the core (in terms of depth), and the fact that the dates are linked to certain years, although each identified layer can refer to several years of sedimentation.

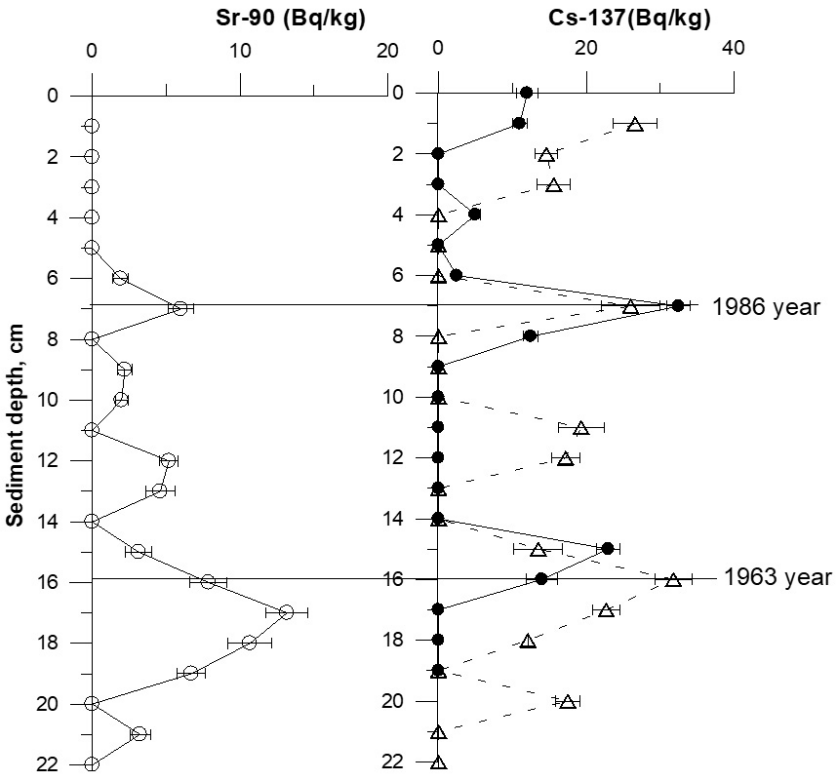

Fig. 2. Bottom sediment vertical distribution profiles of ^{90}Sr (○) at station 5 and ^{137}Cs at stations 5 (Δ) and 6 (●)

In the vertical distribution profiles of ^{90}Sr and ^{137}Cs in the bottom sediments, all three upper peaks almost coincided, and the layer at a 7-cm depth in the core can be dated to 1986 (Fig. 2). At the same time, the sedimentation rate, determined from the upper peak, for 1986–2019 is 70 mm / 33 years = 2.12 mm·year^{-1}. The lower peaks in the vertical distribution profiles of ^{90}Sr and ^{137}Cs in the bottom sediment cores were close to coinciding. If each of them is linked to 1963, then we get that the sedimentation rate, estimated from the vertical distribution profile for ^{137}Cs at sta. 6, will be for 1963–2020 150 mm / 57 years = 2.63 mm·year^{-1}; for ^{137}Cs profile at sta. 5 for 1963–2019, the value will be 160 mm / 56 years = 2.86 mm·year^{-1}; and for ^{90}Sr profile for 1963–2019, the value will be 170 mm / 56 years = 3.036 mm·year^{-1}. The mean sedimentation rate is 10.646 / 4 = 2.66 mm·year^{-1}, with a range from 2.12 to 3.036 mm·year^{-1}. Therefore, it is equally probable that the true value of the sedimentation rate falls within a range of 2.12–3.036 mm·year^{-1}. Specifically, if the mean sedimentation rate is 2.66 mm·year^{-1}, then practically each layer corresponded to four years of sedimentation, and the peak related, for example, to 1986, could fall anywhere within this layer.

It is worth noting that ^{90}Sr and ^{137}Cs occurred in the deeper layers of the cores as well (Fig. 2). Knowing that the Atomic Age began in July 1945, it is possible to verify that the age of these layers corresponds to the dating made. To do this, it is enough to correlate the depth of the layers with the minimum and maximum values of sedimentation rates. ^{90}Sr was found in the core in the 21-cm layer;

^{137}Cs, in the 20-cm layer. This allows assessing the time intervals, to which their localization can be attributed, taking into account the measurement errors. Estimate for ^{90}Sr: at the maximum sedimentation rate Tb(max) = 210 / 3.036 = 69 years, and at the minimum Tb(min) = 210 / 2.12 = 99 years. Thus, in terms of ^{90}Sr, the age of this layer corresponds to Tb interval 1920–1950. Estimate for ^{137}Cs: at the maximum sedimentation rate, Tb(max) = 200 / 3.036 = 66 years, and at the minimum Tb(min) = 200 / 2.12 = 94 years. Thus, in terms of ^{137}Cs, the age of this layer corresponds to Tb interval 1925–1953.

Obviously, all unaccounted errors occur within ranges of intervals of estimates for Tb values. Therefore, as follows from the presented material, these intervals also include the year of the beginning of the Atomic Age (1945). In general, the analysis of vertical distribution profiles for ^{90}Sr and ^{137}Cs in the bottom sediment cores showed that the chosen linking to the peaks of concentration maximums of 1986 and 1963 unambiguously corresponds to the sedimentation rate Vsed, lying in the range of 2.12–3.036 mm·year^{-1} (mean value is 2.66 mm·year^{-1}). Moreover, age estimates for the lowest sediment layers containing non-zero concentrations of measured radionuclides cover the beginning of the Atomic Age.

In general, using radioisotope dating, it was determined that in the Vodopadnaya River estuarine zone at sta. 5 and 6, sedimentation rate is 2.120–3.036 mm·year^{-1}, averaging 2.66 mm·year^{-1}. The specific value MAR_{sp} is 3,072.3 g·m^{-2}·year^{-1}, or 8,663.9 t·year^{-1} for the entire water area down to a depth of 40 m (MAR_{Σ}).

Biogenic elements. The results of determining the concentration of biogenic elements and calculating the parameters of the Redfield equations are given in Table 4 [Egorov et al., 2021].

Table 4. Concentration of nitrogen in form of ammonium (NH_4), nitrites (NO_2), and nitrates (NO_3); concentration of total mineral nitrogen compounds ($\sum N$); concentration of phosphorus (PO_4); and Redfield factor (R_{at}) in 2020 in the Vodopadnaya River estuarine zone [Egorov et al., 2021]

No.	Date	Seawater in the estuarine zone (station 4)						Freshwater in the estuary (44°29′22.0″N, 34°09′46.6″E)				
		NH_4 ± *SD*, μg·L^{-1}	NO_2 ± *SD*, μg·L^{-1}	NO_3 ± *SD*, μg·L^{-1}	$\sum N$, μg·L^{-1}	PO_4 ± *SD*, μg·L^{-1}	R_{at}	NH_4 ± *SD*, μg·L^{-1}	NO_2 ± *SD*, μg·L^{-1}	NO_3 ± *SD*, μg·L^{-1}	$\sum N$, μg·L^{-1}	PO_4 ± *SD*, μg·L^{-1}
1	16.01.2020	11.50 ± 0.60	2.70 ± 0.04	32.00 ± 0.96	46.2	17.00 ± 0.26	6.77	72.50 ± 3.74	19.50 ± 0.29	1,860 ± 56	1,952	44.50 ± 0.67
2	05.03.2020	9.10 ± 0.44	2.90 ± 0.04	20.30 ± 0.61	32.3	12.20 ± 0.18	6.96	23.10 ± 1.20	10.40 ± 0.16	960 ± 29	994	31.30 ± 0.47
3	23.06.2020	24.30 ± 1.17	1.60 ± 0.02	8.30 ± 0.25	34.2	3.40 ± 0.05	42.32	147.20 ± 7.07	43.80 ± 0.66	586 ± 18	777	53.40 ± 0.80
4	14.08.2020	19.10 ± 0.92	4.60 ± 0.07	10.50 ± 0.32	32.2	9.70 ± 0.15	13.00	9.40 ± 0.35	16.50 ± 0.25	690 ± 21	716	86.30 ± 1.50
5	02.10.2020	6.80 ± 0.33	1.90 ± 0.03	10.50 ± 0.32	19.2	10.90 ± 0.16	5.12	23.00 ± 1.0	21.30 ± 0.32	755 ± 22	799	92.80 ± 1.40
6	15.10.2020	11.90 ± 0.36	2.90 ± 0.04	12.80 ± 0.38	27.6	6.10 ± 0.09	14.46	12.70 ± 0.61	10.30 ± 0.15	1,005 ± 30	1,028	70.00 ± 1.05
7	26.11.2020	14.00 ± 1.58	2.30 ± 0.03	11.60 ± 0.35	27.9	6.50 ± 0.10	14.80	24.00 ± 1.1	11.32 ± 0.17	555 ± 17	590	43.90 ± 0.66
8	17.12.2020	10.00 ± 0.48	2.00 ± 0.03	8.00 ± 0.24	20.0	7.50 ± 0.11	9.20	22.00 ± 1.06	16.40 ± 0.25	766 ± 23	792	74.80 ± 1.12
Mean		13.34	2.61	14.25	30.2	9.16	14.08	40.24	18.69	897.12	956	62.12

Heavy metals and trace elements. The results of analytical determinations of HM concentrations in freshwater of the Vodopadnaya River estuary and in seawater of its estuarine zone are presented in Table 5.

Table 5. Concentration of heavy metals and trace elements in water (C_w) and relative (considering MPC [Ob utverzhdenii, 2016]) contamination of waters

No.	Date	Sampling area	Component	Component concentration, $C_w \pm SD$, $\mu g \cdot L^{-1}$	MPC, $\mu g \cdot L^{-1}$	C_w / MPC, %
1	22.06.2020	Yalta, the Vodopadnaya River, freshwater in the estuary, C_{fw}	Fe	5.220 ± 0.230	100	5.22
			Co	0.015 ± 0.001	5	0.30
			Ni	0.596 ± 0.020	10	5.96
			Cu	1.728 ± 0.044	5	34.56
			Zn	23.408 ± 0.593	50	4.68
			Mo	0.067 ± 0.005	1	6.70
			Cd	< 0.025	10	< 0.25
			Pb	0.157 ± 0.007	10	1.57
2	22.06.2020	Yalta, seawater in the estuarine zone, C_{sw}	Fe	2.453 ± 0.158	100	2.45
			Co	0.001 ± 0.001	5	0.02
			Ni	0.518 ± 0.024	10	5.18
			Cu	0.628 ± 0.028	5	12.56
			Zn	5.818 ± 0.206	50	11.64
			Mo	1.312 ± 0.047	1 (300)	131.20 (0.44)
			Cd	0.123 ± 0.005	10	1.23
			Pb	0.097 ± 0.004	10	0.97

Note: in parentheses, MPC values for seawater are given according to [Warmer, van Dokkum, 2002].

The results of analytical determinations of HM in the bottom sediments are shown in Table 6.

Table 6. Concentrations of heavy metals in the bottom sediments at station 5 (Table 1)

No.	Bottom sediment layer, cm	Layer dating, year	Heavy metal concentration in the bottom sediments, $C_{bs} \pm SD$, $mg \cdot kg^{-1}$ dry weight							
			Cr	Co	Ni	Cu	Zn	Mo	Cd	Pb
1	0.0–0.5	2019	19.39 ± 0.51	7.37 ± 0.09	25.9 ± 0.51	17.28 ± 0.26	63.35 ± 1.22	0.35 ± 0.05	1.35 ± 0.04	12.77 ± 0.36
2	1.5–2.0	2013	23.07 ± 0.90	8.09 ± 0.07	28.88 ± 0.37	17.73 ± 0.15	58.06 ± 1.57	0.30 ± 0.01	0.03 ± 0.02	13.86 ± 0.17
3	4.0–4.5	2003	22.58 ± 0.47	8.06 ± 0.09	32.75 ± 0.23	14.82 ± 0.09	54.46 ± 0.43	0.25 ± 0.02	< 0.01	13.96 ± 0.17
4	8.5–9.0	1989	26.67 ± 0.43	9.41 ± 0.09	33.19 ± 0.29	19.24 ± 0.09	57.94 ± 0.91	0.57 ± 0.01	0.02 ± 0.01	11.68 ± 0.38
5	11.0–11.5	1977	25.94 ± 0.29	8.71 ± 0.08	31.83 ± 0.29	17.76 ± 0.25	56.08 ± 1.03	0.25 ± 0.01	0.02 ± 0.01	11.15 ± 0.29
6	14.5–15.0	1964	19.30 ± 0.44	6.75 ± 0.09	24.67 ± 0.44	13.89 ± 0.19	45.83 ± 0.99	0.35 ± 0.05	< 0.01	7.49 ± 0.19
7	18.5–19.0	1949	23.51 ± 0.23	7.80 ± 0.08	27.47 ± 0.25	13.65 ± 0.07	43.22 ± 0.41	0.24 ± 0.01	< 0.01	7.61 ± 0.20
8	23.5–24.0	1930	25.25 ± 0.27	9.56 ± 0.10	30.36 ± 0.17	16.01 ± 0.14	48.32 ± 0.59	0.12 ± 0.01	< 0.01	9.10 ± 0.22

Mercury. Estimates of the concentrating ability of suspensions in relation to mercury in the Yalta city water area are given in Table 7.

Table 7. Results of mercury concentration measurement in water (C_w) and suspended matter (C_s) and mercury concentration factor (C_f) for suspended matter in the Yalta city water area

No.	Sampling site	Sampling date	Suspended matter concentration, $g \cdot m^{-3}$	C_w, $ng \cdot L^{-1}$			C_{tot} / MPC, %	C_s, $ng \cdot g^{-1}$ dry weight	C_f, $\times 10^5$
				Dissolved	Particulate	Total, C_{tot}			
1	Seawater (surface)	22.06.2020	1.3	40	5	45	45	3,846.15	0.96
2	Seawater (bottom)	15.10.2020	6.9	60	8	68	68	1,159.42	0.19
3	Seawater (surface)	28.04.2021	4	30	24	54	54	6,000.00	2.00
4		09.07.2021	40.7	30	5	35	35	122.85	0.04
5		07.10.2021	31.7	30	120	150	150	3,785.49	1.26
	Mean					60	60		
6	Freshwater in the estuary	22.06.2020	3.1	53	10	63	63	3,225.81	0.61
7		28.04.2021	2.2	20	100	120	120	45,454.55	22.73
8		09.07.2021	546.8	40	230	270	270	420.63	0.11
9		07.10.2021	1.8	35	70	105	105	38,888.89	11.11
	Mean					140	140		

The results of analytical determinations of mercury in the bottom sediments are presented in Table 8.

Table 8. Mercury concentration in bottom sediment layers (C_{bs}) at station 6 (Table 1)

No.	Bottom sediment layer, cm	Layer dating, year	C_{bs}, $\mu g \cdot kg^{-1}$ dry weight	Mercury specific flux into the bottom sediments, $F_{sp} = MAR \cdot C_{bs}$, $\mu g \cdot m^{-2} \cdot year^{-1}$	Mercury flux into the bottom sediments, $F_{Hg} = F_{sp} \cdot S$, $kg \cdot year^{-1}$
1	0–1	2020	62	264.2	0.75
2	1–2	2018	68	289.8	0.82
3	2–3	2014	66	281.2	0.79
4	3–4	2011	53	225.8	0.64
5	4–5	2007	63	268.5	0.76
6	5–6	2003	141	600.8	1.69
7	6–7	1999	63	268.5	0.76
8	7–8	1996	67	285.5	0.81
9	8–9	1992	80	340.9	0.96

The third column in Table 8 shows the age of the layers. The fifth column contains estimates of Hg flux into the bottom sediments of the Yalta city water area at sta. 6.

DISCUSSION

Biogenic elements. Graphic material presented in Fig. 3 reflects the patterns of changes in biogenic element concentration in the Vodopadnaya River estuary and estuarine zone. Freshwater of the estuary is characterized by an increased content of nitrogen in composition of nitrites (by 7.2 times), ammonium (by 3.0 times), nitrates (by 62.9 times), and mineral phosphorus (by 13.2 times) in comparison with their concentrations in seawater of the estuarine zone. These data indicate a statistically significant effect of the river runoff on the shift in concentrations of the total content of nitrogen compounds, as well as mineral phosphorus in seawater of the estuarine zone. The flux of biogenic elements from the river in summer can change the limiting nutrient for primary production from nitrogen to phosphorus.

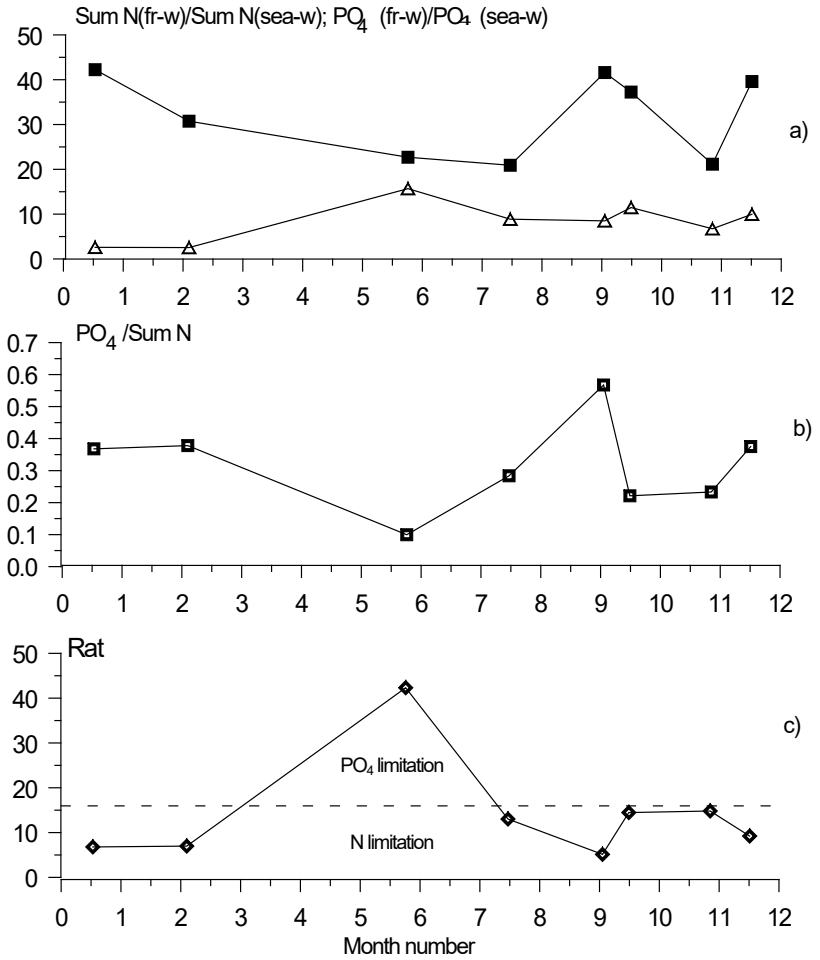

Fig. 3. Ratio of total nitrogen (■) and mineral phosphorus (Δ) concentrations in freshwater of the Vodopadnaya River estuary to the values in seawater of its estuarine zone (a); ratio of mineral phosphorus concentration to the total nitrogen concentration in seawater in the Vodopadnaya River estuarine zone (b); calculated values of the Redfield factor for the sea area of the Vodopadnaya River estuarine zone (c)

In 2019, concentration of biogenic elements in the river estuary at sta. 4 was 14–16 times higher than their content in the estuarine zone in terms of total nitrogen compounds, while the concentration of phosphates could be of the same order of magnitude or up to 25 times higher. This indicated the eutrophic effect of the river runoff on coastal waters of the Yalta city area. That year, with the river runoff,

330.66 kg·day^{-1} of nitrogen compounds and 7.35 kg·day^{-1} of mineral phosphorus entered the city estuarine water area daily. With nitrogen limitation of production processes, the flux of biogenic elements with the river runoff could lead to water hypertrophy on the area of 531,000 m^2, and with phosphorus limitation, on the area of 88,000 m^2 [Egorov, 2021].

In 2020, with a mean annual river flow of 33.18 m^3·day^{-1}, the concentration of total nitrogen compounds ($\sum N_i$) in freshwater was 956 μg·L^{-1}, and mineral phosphorus (PO_4), 62.12 μg·L^{-1} (Table 4). At the same time, the daily flux of $\sum N_i$ into the Yalta city estuarine zone amounted to about 31.717 kg·day^{-1}, and for mineral phosphorus, the value was up to 2.060 kg·day^{-1}. As known, the synthesis of 1,000 g of organic matter in terms of mass requires 80 g of carbon, 2 g of phosphorus, and 14 g of nitrogen [Zilov, 2009]. Accordingly, with nitrogen limitation of production processes, new production can be (31.717 / 14) · 80 = 181.240 kg C_{org}·day^{-1}; with phosphorus limitation, (2.060 / 2) · 80 = 82.400 kg C_{org}·day^{-1}. These data indicate as follows: under water eutrophication by phytoplankton, equal to 100 mg C_{org}·m^{-3}·day^{-1}, and the location of the summer core of primary production in the 0–10-m layer, due to the flux of nitrogen compounds, water hypereutrophication will spread to the area of 181,240 m^2; with phosphorus limitation, the area will be 82,400 m^2. Taking into account the previously published data for 2019 [Egorov, 2021], with prevailing nitrogen limitation of primary production processes, the daily growth rate of water hypereutrophicated by biogenic elements in the Yalta city water area in different years can be 6–18% *per* day of the polygon area.

Water masses of the polygon are exchanged with the open sea through liquid boundaries, especially from the northeast to the southwest [Egorov et al., 2018], along the main coastal recreational zone of Yalta city. This can result in an increase in the primary production of the water area, outbreaks of gelatinous plankton [*Rhizostoma pulmo* (Macri, 1778) and *Aurelia aurita* (Linnaeus, 1758)], and water bloom. Therefore, the flux of biogenic elements with the river runoff is a significant factor in reducing sanitary and hygienic water quality in the city recreational zone.

Heavy metals and mercury. In freshwater of the river estuary, Fe, Co, Ni, Cu, Zn, and Cd concentrations did not exceed MPC. In seawater of the estuarine zone, Mo content in some years could surpass MPC (Tables 5, 7) established for fishery basins [Ob utverzhdenii, 2016]. However, Mo concentration was still two orders of magnitude lower than MPC recommended for marine waters [Chuzhikova-Proskurnina et al., 2022; Warmer, van Dokkum, 2002]. In the Yalta city water area, content of the dissolved form of mercury in freshwater and seawater of the estuarine zone did not exceed MPC (Table 7). At the same time, the concentration of particulate mercury in freshwater and seawater was usually higher and could surpass MPC. High levels of mercury accumulation by suspended matter were established: accumulation coefficients from 0.11×10^5 to 22.73×10^5; this indicated a high significance of suspended matter in Hg migration in the aquatic environment.

HM distribution in the bottom sediments, taking into account the radioactive tracer dating (Fig. 2) of their age from 1930 to 2020 at sta. 5 and 6, is presented in Fig. 4.

Between 1930 and 2020 (Fig. 4), the content of Cr, Fe (after 2000), and Cu (after 1990), under data variability, nevertheless showed a tendency to decrease in the bottom sediments. At the same time, concentrations of Co (since 1990), Mo (since 2000), Cd (after 2010), and Hg (since 2010) in the bottom sediments increased. The trends of rising contamination of the bottom sediments with Zn and Pb from the 1950s to the present time, assessed by the coefficients of determination, had a high degree of statistical significance ($R^2 = 0.715$ and $R^2 = 0.729$, respectively).

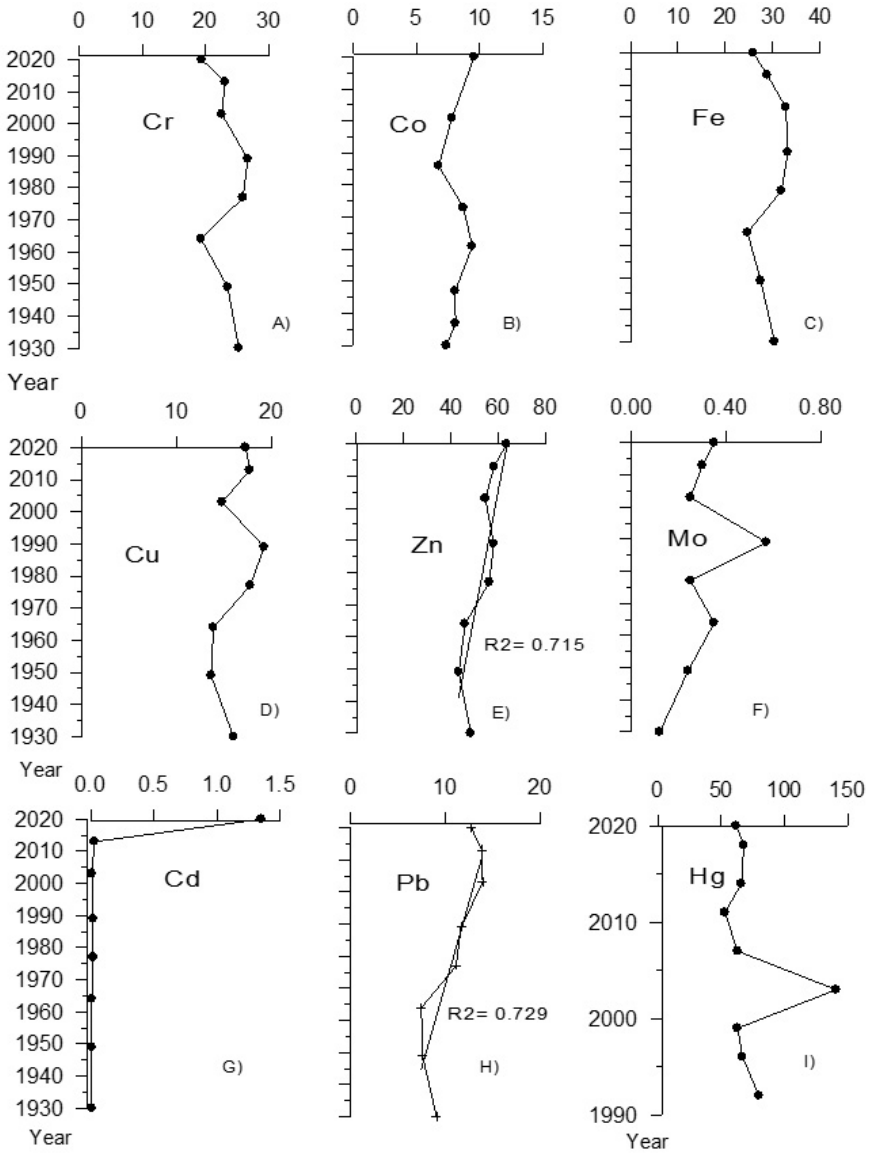

Fig. 4. Vertical distribution profiles for Cr (A), Co (B), Fe (C), Cu (D), Zn (E), Mo (F), Cd (G), Pb (H), and Hg (I), mg·kg^{-1} dry weight, in the thickness of the bottom sediments in the Yalta city water area

Intensity of biogeochemical processes for migration of heavy metals and organochlorine compounds in the Yalta city recreational water area. Indicators of the intensity of biogeochemical processes in the Yalta water area are given in Table 9.

The second and fourth columns in Table 9 present data on the concentration of pollutants in seawater and in the upper layer of the bottom sediments in the Yalta water area. The second column contains the results of calculations of pollutant pools in the water area with a volume of $80 \cdot 10^6$ m^3. In the fifth and sixth columns, there are estimates of the total sedimentation flux and periods of pollutant deposition into the thickness of the bottom sediments. The eighth and ninth columns present the results of calculations of pollutant flux into the water area with the river runoff and estimates of the periods of their turnover in the Yalta water area due to the river runoff. In general, those testify to a high significance of contamination factors of the analyzed water area with the river runoff and its sedimentary self-purification due to biogeochemical processes. The data show (Table 9) that the turnover of pollutants in the Yalta

city water area, resulting from the effect of sedimentation processes, occurs on time scales from daily to synoptic, and due to the river runoff, from annual to long-term. At the same time, periods of turnover for these elements due to processes of sedimentary self-purification are 1–2 orders of magnitude lower than due to the river runoff.

Table 9. Biogeochemical characteristics of turnover of pollutants (P) in the Vodopadnaya River estuarine zone and in the Yalta city water area

P	Concentration of P in seawater of the Yalta city water area, C_{sw}, $\mu g \cdot L^{-1}$	Pool of P in the Yalta city water area, $Q_{wa} = C_{sw} \cdot V$, kg	Concentration of P in the upper layer of the bottom sediments, C_{bs}, $mg \cdot kg^{-1}$ dry weight	Sedimentation flux of P into the bottom sediments, $F_{sed} = C_{bs} \cdot MAR \cdot S$, $kg \cdot year^{-1}$	Period of sedimentation turnover of P in the Yalta city water area, $T_{sed} = Q_{wa} / F_{sed}$, days	Concentration of P in freshwater of the Vodopadnaya River, C_{rw}, $\mu g \cdot L^{-1}$	Flux of P with the Vodopadnaya River runoff, $I_r = C_{rw} \cdot V_r$, $kg \cdot year^{-1}$	Period of turnover of P due to the Vodopadnaya River runoff, $T_r = Q_{wa} / I_r$, days
Cu	0.628	50.240	17.280	149.712	122.5	1.728	8.23	$2.2 \cdot 10^3$
Zn	5.818	465.440	63.350	548.857	309.5	23.408	111.47	$1.5 \cdot 10^3$
Fe	2.453	196.240	n. d.	n. d.*	n. d.	5.220	24.86	$2.9 \cdot 10^3$
Co	0.001	0.080	7.370	63.853	0.5	0.015	0.07	408.8
Ni	0.518	41.440	25.900	224.395	67.4	0.596	2.84	$5.3 \cdot 10^3$
Mo	1.312	104.960	0.350	3.032	$1.2 \cdot 10^4$	0.067	0.32	$1.2 \cdot 10^5$
Cd	1.123	9.840	1.350	11.696	307.0	< 0.025	< 0.12	$> 3.0 \cdot 10^4$
Pb	0.097	7.760	12.770	110.638	25.6	0.157	0.75	$3.8 \cdot 10^3$
Hg	0.071	5.700	0.063	0.546	$2.9 \cdot 10^{-2}$	0.14	1.689	$9.2 \cdot 10^{-3}$
^{90}Sr	8.5 $Bq \cdot m^{-3}$	680.0 MBq	1.6 $Bq \cdot kg^{-1}$	13.9 $MBq \cdot year^{-1}$	$1.8 \cdot 10^4$	n. d.	n. d.	n. d.
∑DDT*	$1.42 \cdot 10^{-3}$	0.114	0.036	0.312	132.9	$0.32 \cdot 10^{-3}$	0.002	$2.7 \cdot 10^4$
∑6PCB*	$6.80 \cdot 10^{-3}$	0.544	0.010	0.088	2,244.7	$1.09 \cdot 10^{-3}$	0.005	$3.8 \cdot 10^4$

Note: n. d. denotes no data; * denotes data according to [Malakhova, Lobko, 2022].

In general, consideration of the presented material on HM distribution in the Yalta city water area (Table 5) showed that Fe, Co, Ni, Cu, Zn, Mo, Cd, and Pb concentrations in freshwater of the river estuarine zone ranged from 0.25 to 34.5 % of MPC for respective elements. In seawater of the estuarine zone, Mo content could exceed MPC established for fishery basins [Ob utverzhdenii, 2016], reaching the values of up to 131.2% of MPC, while the concentration of other HM ranged from 0.02 to 12.56% of MPC. However, it should be noted as follows: in the Russian environmental law, there is no MPC for Mo in seawater. At the same time, the values of Mo concentrations measured by us in the Yalta marine area were at the lower limit of values typical for the World Ocean waters [Mirzoeva et al., 2022] and also 2 orders of magnitude lower than MPC recommended for marine waters by the document [Warmer, van Dokkum, 2002]. The data on mercury distribution in the Yalta water area (Table 7) indicated that the content of its dissolved form in freshwater and seawater of the estuarine zone during the observation period did not exceed MPC [Ob utverzhdenii, 2016]. At the same time, the concentration of the particulate form of mercury in freshwater and seawater, as a rule, is higher, and the total content of mercury in water reached 140% of MPC.

It is worth noting that the estimates (Table 9) of maximum permissible fluxes are normalized to the average annual level of the Vodopadnaya River runoff (Fig. 5).

Fig. 5. The Vodopadnaya River estuary at the average annual discharge intensity

However, the Vodopadnaya River has flood flow regime as well. Specifically, on 18.06.2021, 84 mm of precipitation fell at the river source on Ai-Petri peak, and this exceeded the monthly rate of 72 mm. As a result, the water discharge in the river reached 9.9 $m^3 \cdot s^{-1}$, which is almost 28 times higher than the average level. The plume from high water spread far beyond the Yalta city recreational zone, deteriorating water quality on the beaches of the Southern Coast of Crimea (Fig. 6). Apparently, to deflect the plume from the coast, in addition to construction of coastal protection piers (Fig. 1), construction of appropriate hydraulic structures is required.

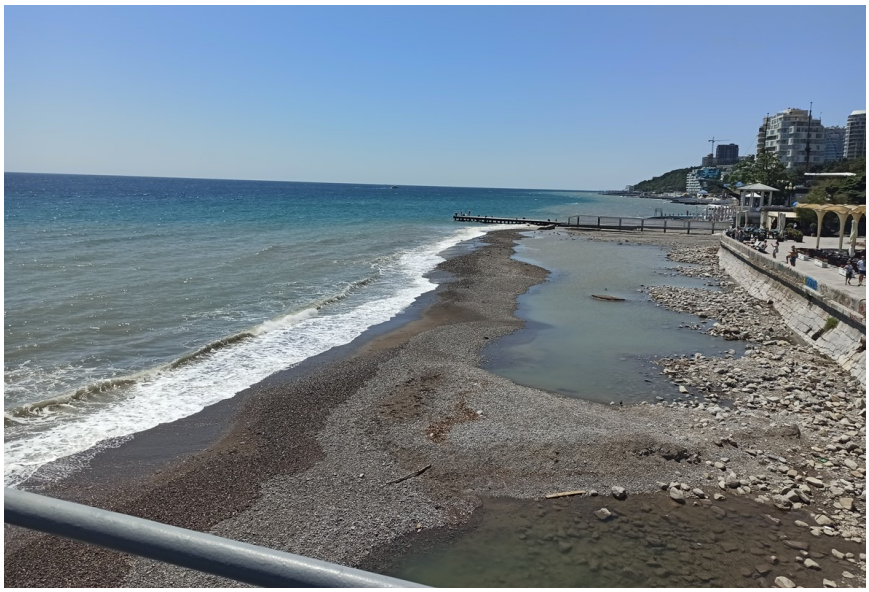

Fig. 6. Estuary and marine estuarine zone in the Yalta city water area during the high water in the Vodopadnaya River

As known, the optimal strategy for nature management is the implementation of the sustainable development concept; its core is to maintain a balance between consumption and reproduction of natural resources of the regions. In the present work, as criteria for consumption and reproduction of water quality resources in relation to pollutants, we used the results of studying the patterns of interaction between living and inert matter with radioactive and chemical components of the marine environment; also, we used modern theoretical ideas about biogeochemical mechanisms of radioisotopic and chemical homeostasis of marine ecosystems [Egorov et al., 2021]. MPC of a pollutant in the aquatic environment is known to serve as an indicator of water quality. In accordance with its dimension, MPC is only a diagnostic assessment. Obviously, the analysis of the ratio C_w / MPC (%) makes it possible to determine the relative environmental hazard from water pollution by various contaminants. On a certain time scale, monitoring of this ratio can characterize trends in changes in sanitary and hygienic water quality, since with a decrease in C_w / MPC value, the ecological situation in the water area in relation to the considered pollutant will improve, while with an increase, it will deteriorate. Obviously, in order to manage the ecological situation of water areas in terms of radioactive and chemical pollution, it is necessary to develop an indicator of consumption and reproduction of water quality, which has the dimension of fluxes.

As follows from the data presented (Table 9), under conditions of stationarity of the ecosystem state in the Yalta city recreational zone, the flux of pollutants into the water area with the Vodopadnaya River runoff on an annual time scale was an indicator of a deterioration (*i. e.*, consumption) in water quality. With such an interpretation of the mechanisms of ecosystem stationarity formation, the sedimentation flow that compensates for pollution due to biogeochemical processes is obviously a measure of natural reproduction of water quality, and the data on the periods of pollutant turnover in the water area due to sedimentation processes (the sixth column in Table 9) reflect its relative intensity. Naturally, the data given in the eighth and ninth columns, within the accepted assumptions, evidence for relative intensity of the deterioration in water quality of the Yalta city recreational zone because of the river runoff.

CONCLUSION

Water self-purification from conservative pollutants, which results from the effect of biogeochemical processes, is necessarily associated with the depot of their elimination. Adjacent water areas and underlying water layers can act as water depots, while the bottom sediments can act as geological depots. Living, inert, and terrigenous matter can serve as a source of sediments. The coefficients of pollutant accumulation by various components of sediments (K_{sed}) differ and may depend on pollutant concentration in the aquatic environment. For radionuclides, K_{sed} = const in the range of radioactive contamination of water up to $10^{-6}…10^{-3}$ mol·L^{-1} [Polikarpov, 1964]. For other pollutants, K_{sed} values depend on the size spectra of sediment particles, as well as on their sorption, metabolic, and trophic characteristics, which are described by the patterns of Michaelis–Menten, Langmuir, or Freundlich. If K_{sed} = const, then the maximum permissible flux of water self-purification due to entering the depot, equal to the ecological capacity of a water area, can be determined as the result of the product of the maximum permissible concentration of pollutants in the aquatic environment (MPC) by K_{sed} value and the intensity of the sedimentation flux. At the same time, if pollutants enter the thickness of the bottom sediments, then the flux of their elimination, called the assimilation capacity of the marine environment, also depends on the degree of saturation of the adsorption capacity for sediments in relation to the studied pollutant [Egorov, 2021]. Therefore, the sorption properties of bottom sediments should be studied and taken into account when setting maximum permissible anthropogenic load on marine ecosystems.

The presented data indicate a statistically significant effect of the river runoff on the shift in the concentrations of the total content of nitrogen compounds, as well as mineral phosphorus in seawater of the river estuarine zone. The flux of biogenic elements from the river in summer could change the regime of limitation of primary production from nitrogen to phosphorus. As a result of the river runoff, Co and Zn turnover in the Yalta city water area occurs on time scales from hourly to synoptic, and periods of Ni, Cu, ∑6PCB, Pb, Hg, and Mo turnover are estimated at $81.8 \div 17.2 \cdot 10^3$ days. The processes of sedimentation turnover for Co and Hg occur on time scales from daily to monthly, while for Cu, Pb, Cd, ^{90}Sr, and Mo, those are in the range from $1.1 \cdot 10^3$ to $185.2 \cdot 10^3$ days.

An analysis of the distribution profiles for pollutants in the bottom sediments showed as follows: between 1930 and 2020, in the content of Cr, Fe (after 2000), and Cu (after 1990), under data variability, there was a tendency to a decrease in concentrations of these heavy metals in the bottom sediments. At the same time, the content of Co (since 1990), Mo (since 2000), Cd (after 2010), and Hg (since 2010) in the bottom sediments increased. Trends in rising contamination of the bottom sediments with Zn and Pb from 1950s to the present time had a high degree of statistical significance. In total, the results of observations and analytical assessments testified as follows: against the backdrop of generally favorable environmental situation in terms of water contamination with heavy metals, the content of various pollutants in some years could exceed MPC and significantly worsen the quality of the Yalta city recreational water area. In this regard, it is required to develop standards for regulating water quality in recreational areas.

Highlights:

1. The specific sedimentation of the water area of the coastal and marine recreational zone of Yalta city is estimated at 2.120–3.036 mm·year^{-1}, averaging 2.66 mm·year^{-1}. In terms of mass, the value is 3,072.3 g·m^{-2}·year^{-1}, or 8,663.9 t·year^{-1} for the entire water area down to a depth of 40 m.
2. Freshwater of the Vodopadnaya River estuary is characterized by an increased content of nitrogen in composition of nitrites (by 7.2 times), ammonium (by 3.0 times), nitrates (by 62.9 times), and mineral phosphorus (by 13.2 times) compared to their concentrations in seawater of the estuarine zone. In the coastal recreational zone of the Yalta city, nitrogen limitation of phytoplankton primary production prevails. The flux of biogenic elements from the river can change the regime of limitation of phytoplankton primary production from nitrogen to phosphorus. Due to the flux of biogenic elements with the river runoff, new production in the Yalta water area under nitrogen limitation of production processes can amount to 181.240 kg C_{org}·day^{-1}; under phosphorus limitation, 82.400 kg C_{org}·day^{-1}. With nitrogen limitation of production processes, the growth rate of hypereutrophicated water in summer can be 6–18% *per* day of the Yalta city recreational water area.
3. In freshwater of the river estuarine zone, concentrations of Fe, Co, Ni, Cu, Zn, Mo, Cd, and Pb ranged from 0.25 to 34.5% of MPC. In seawater of the estuarine zone, relative content of heavy metals varied from 0.02 to 12.56% of MPC. In freshwater, the total concentration of mercury averaged 60% of MPC, and in seawater, 140%.
4. As a result of the river runoff, Co and Zn turnover in waters of the Yalta city area occurs on time scales from hourly to synoptic; periods of Ni, Cu, Pb, Hg, and Mo turnover are estimated at $81.8 \div 17.2 \cdot 10^3$ days. The processes of sedimentation turnover for Co and Hg occur on time scales from daily to monthly, while for Cu, Pb, Cd, ^{90}Sr, and Mo, those are in the range from $1.1 \cdot 10^3$ to $185.2 \cdot 10^3$ days.

5. Over the period from 1930 to 2020, the content of Cr, Fe (after 2000), and Cu (after 1990) in the bottom sediments had a decreasing trend. Concentrations of Co (since 1990), Mo (since 2000), Cd (after 2010), and Hg (since 2010) in more recent bottom sediments increased.
6. On the example of the Vodopadnaya River estuarine zone, the development of a methodology for implementation of the sustainable development concept is shown for water areas under conditions when the consumption of water quality in relation to pollutants does not exceed their reproduction resulting from biogeochemical processes. To implement the sustainable development of the Yalta water area, in terms of the current level of marine pollution, the permissible flux into its estuarine zone should not exceed: for Cu, 149.7 kg·year^{-1}; Zn, 548.9 kg·year^{-1}; Co, 63.9 kg·year^{-1}; Ni, 224.4 kg·year^{-1}; Mo, 3.0 kg·year^{-1}; Cd, 11.7 kg·year^{-1}; Pb, 110.6 kg·year^{-1}; Hg, 0.546 kg·year^{-1}; ∑DDT, 0.3 kg·year^{-1}; and ∑6PCB, 0.1 kg·year^{-1}.

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REFERENCES

1. Gulin S. B., Polikarpov G. G., Egorov V. N., Stokozov N. A. Ispol'zovanie prirodnykh i iskusstvennykh radiotrasserov dlya izucheniya biogeokhimicheskikh protsessov perenosa i deponirovaniya radioaktivnykh i khimicheskikh zagryaznenii v usloviyakh okislitel'no-vosstanovitel'noi vodnoi tolshchi Chernogo morya. In: *Radioekologiya: uspekhi i perspektivy* : materialy nauchnogo seminara, Sevastopol, 3–7 Oct., 1994. Sevastopol : [s. n.], 1994, pp. 103–104. (in Russ.)
2. GOST R 56219-2014. *Voda. Opredelenie soderzhaniya 62 elementov metodom mass-spektrometrii s induktivno-svyazannoi plazmoi.* Moscow : Standartinform, 2015, 36 p. (in Russ.)
3. GOST 26927-86. *Syr'e i produkty pishchevye. Metody opredeleniya rtuti.* Moscow : IPK Izd-vo standartov, 2002, 12 p. (in Russ.)
4. Egorov V. N., Bobko N. I., Marchenko Yu. G., Sadogurskiy S. Ye. Nutrient content and limitation of the phytoplankton primary production in the estuary area of the Vodopadnaya River (south coast of Crimea). *Ekologicheskaya bezopasnost' pribrezhnoi i shel'fovoi zon morya*, 2021, no. 3, pp. 37–51. (in Russ.). https://doi.org/10.22449/2413-5577-2021-3-37-51
5. Egorov V. N., Plugatar Yu. V., Malakhova L. V., Mirzoeva N. Yu., Gulin S. B., Popovichev V. N., Sadogurskiy S. E., Malakhova T. V., Shchurov S. V., Proskurnin V. Yu., Bobko N. I., Marchenko Yu. G., Stetsyuk A. P. Ekologicheskoe sostoyanie akvatorii osobo okhranyaemoi prirodnoi territorii "Mys Mart'yan" i problema realizatsii ee ustoichivogo razvitiya po faktoram evtrofikatsii, radioaktivnogo i khimicheskogo zagryazneniya vod. In: *Sokhranenie biologicheskogo raznoobraziya i zapovednoe delo v Krymu* : materialy nauch.-prakt. konf. s mezhdunar. uchastiem, Yalta, 23–26 Oct., 2018. Yalta : NBG – NSC, 2018, pp. 36–40. (Nauchnye zapiski prirodnogo zapovednika "Mys Mart'yan" ; iss. 9). (in Russ.). https://doi.org/10.25684/NBG.scnote.009.2018.04
6. Zaitsev Ju. P., Polikarpov G. G. Ecological processes in critical zones of the Black Sea (results synthesis of two research directions, middle of the XX – beginning of the XXI cen-

tury). *Morskoj ekologicheskij zhurnal*, 2002, vol. 1, no. 1, pp. 35–55. (in Russ.). https://repository.marine-research.ru/handle/299011/686

7. Zilov E. A. *Gidrobiologiya i vodnaya ekologiya (organizatsiya, funktsionirovanie i zagryaznenie vodnykh ekosistem).* Irkutsk : Izd-vo Irkutskogo gos. un-ta, 2009, 147 p. (in Russ.)
8. Malakhova L. V., Lobko V. V. Assessment of pollution of the Yalta Bay ecosystem components with organochlorine xenobiotics. *Ekologicheskaya bezopasnost' pribrezhnoi i shel'fovoi zon morya*, 2022, no. 3, pp. 104–116. (in Russ.)
9. Mirzoeva N. Yu., Egorov V. N., Polikarpov G. G. Soderzhanie ^{90}Sr v donnykh otlozheniyakh Chernogo morya posle avarii na Chernobyl'skoi AES i ego ispol'zovanie v kachestve radiotrassera dlya otsenki skorosti osadkonakopleniya. In: *Sistemy kontrolya okruzhayushchei sredy: sredstva i monitoring*. Sevastopol : EKOSI-Gidrofizika, 2005, iss. 8, pp. 276–282. (in Russ.)
10. *Ob utverzhdenii normativov kachestva vody vodnykh ob"ektov rybokhozyaistvennogo znacheniya, v tom chisle normativov predel'no dopustimykh kontsentratsii vrednykh veshchestv v vodakh vodnykh ob"ektov rybokhozyaistvennogo znacheniya* : prikaz Minsel'khoza Rossii ot 13.12.2016 no. 552 [v red. ot 10.03.2020]. (in Russ.). URL: https://docs.cntd.ru/document/420389120 [accessed: 04.05.2023].
11. PND F 16.2.2:2.3.71-2011. *Metodika izmerenii massovykh dolei metallov v osadkakh stochnykh vod, donnykh otlozheniyakh, obraztsakh rastitel'nogo proiskhozhdeniya spektral'nymi metodami.* Moscow : Federal'naya sluzhba po nadzoru v sfere prirodopol'zovaniya, 2011, 45 p. (in Russ.)
12. Polikarpov G. G. *Radioekologiya morskikh organizmov.* Moscow : Atomizdat, 1964, 295 p. (in Russ.). https://repository.marine-research.ru/handle/299011/12748
13. *Radioekologicheskii otklik Chernogo morya na chernobyl'skuyu avariyu* / G. G. Polikarpov, V. N. Egorov (Eds). Sevastopol : EKOSI-Gidrofizika, 2008, 667 p. (in Russ.). https://repository.marine-research.ru/handle/299011/9280
14. *Rukovodstvo po khimicheskomu analizu morskikh vod* : rukovodyashchii dokument RD 52.10.243-92. Saint Petersburg : Gidrometeoizdat, 1993, 264 p. (in Russ.). URL: https://meganorm.ru/Data2/1/4293815/4293815261.pdf [accessed: 04.05.2023].
15. *Rukovodstvo po metodam khimicheskogo analiza morskikh vod.* Leningrad : Gidrometeoizdat, 1977, 208 p. (in Russ.)
16. Hutchinson D. *Limnologiya: geograficheskie, fizicheskie i khimicheskie kharakteristiki ozer* : transl. from Engl. Moscow : Progress, 1969, 591 p. (in Russ.)
17. Chuzhikova-Proskurnina O. D., Proskurnin V. Yu., Tereshchenko N. N., Kobechinskaya V. G. Heavy metals in the coastal waters of Russian sector of the Black Sea and the Sea of Azov. *Ekosistemy*, 2022, no. 31, pp. 111–122. (in Russ.)
18. Artemov Yu. G. Software support for investigation of natural methane seeps by hydroacoustic method. *Morskoj ekologicheskij zhurnal*, 2006, vol. 5, no. 1, pp. 57–71. https://repository.marine-research.ru/handle/299011/850
19. Egorov V. N. *Theory of Radioisotopic and Chemical Homeostasis of Marine Ecosystems.* Cham, Switzerland : Springer, 2021, 320 p. https://doi.org/10.1007/978-3-030-80579-1
20. Gulin S. B., Aarkrog A., Polikarpov G. G., Nielsen S. P., Egorov V. N. Chronological study of ^{137}Cs input to the Black Sea deep and shelf sediments. In: *Radionuclides*

in the Oceans : RADOS 96–97 : [intern. symp., Octeville – Cherbourg, France, 7–11 Oct., 1996] : proceedings / Eds: P. Germain [et al.]. Les Ulis : Éd. de Physique, 1997, pt 1: Inventories, behaviour and processes, pp. 257–262. (Radioprotection ; vol. 32, spec. iss. C2).

21. Harvey B. K., Ibbett R. D., Lovett M. B., Williams K. J. *Analytical Procedures for the Determination of Strontium Radionuclides in Environmental Materials.* Lowestoft : [s. n.], 1989, 33 p. (Aquatic Environment Protection: Analytical Methods / MAFF, Direct. Fish. Res. ; no. 5).
22. Mirzoeva N., Polyakova T., Samyshev E., Churilova T., Mukhanov V., Melnik A., Proskurnin V., Sakhon E., Skorokhod E., Chuzhikova-Proskurnina O., Chudinovskih E., Minkina N., Moiseeva N., Melnikov V., Paraskiv A., Melnik L., Efimova T. Current assessment of water quality and biota characteristics of the pelagic ecosystem of the Atlantic sector of Antarctica: The multidisciplinary studies by the Institute of Biology of the Southern Seas. *Water*, 2022, vol. 14, iss. 24, art. no. 4103 (20 p.). https://doi.org/10.3390/w14244103
23. Papucci C. Sampling marine sediments for radionuclide monitoring. In: *Strategies and Methodologies for Applied Marine Radioactivity Studies*. Vienna : IAEA, 1997, chap. 13, pp. 279–297. (Training Course Series ; no. 7).
24. *PlasmaQuant MS and PlasmaQuant MS Elite Mass-spectrometers With Inductively Coupled Plasma (ICP-MS).* User's Manual. Analytik Jena AG, 2014, 143 p.
25. Redfield A. C. The biological control of chemical factors in the environment. *American Scientist*, 1958, vol. 46, no. 3, pp. 205–221.
26. Schafer C. T., Smith J. N., Loring D. H. Recent sedimentation events at the head of Saguenay Fjord, Canada. *Environmental Geology*, 1980, vol. 3, iss. 3, pp. 139–150. https://doi.org/10.1007/BF02473489
27. Warmer H., van Dokkum R. *Water Pollution Control in the Netherlands: Policy and Practice 2021* / [Institute for Inland Water Management and Waste Water Treatment. RIZA]. The Netherlands : RIZA, 2002, 76 p. (RIZA report 2002.009).

ВОЗМОЖНОСТЬ РЕАЛИЗАЦИИ КОНЦЕПЦИИ УСТОЙЧИВОГО РАЗВИТИЯ РЕКРЕАЦИОННОГО ПРИБРЕЖЬЯ ГОРОДА ЯЛТА В ОТНОШЕНИИ БИОГЕННЫХ ЭЛЕМЕНТОВ, РАДИОНУКЛИДОВ, ТЯЖЁЛЫХ МЕТАЛЛОВ И ХЛОРОРГАНИЧЕСКИХ СОЕДИНЕНИЙ (КРЫМ, ЧЁРНОЕ МОРЕ)

В. Н. Егоров, Н. Ю. Мирзоева, Ю. Г. Артёмов, В. Ю. Проскурнин, А. П. Стецюк, Ю. Г. Марченко, Д. Б. Евтушенко, И. Н. Мосейченко, О. Д. Чужикова-Проскурнина

ФГБУН ФИЦ «Институт биологии южных морей имени А. О. Ковалевского РАН»,
Севастополь, Российская Федерация
E-mail: *egorov.ibss@yandex.ru*

Проведено гидроакустическое зондирование, определены площадь и объём вод приустьевой зоны реки Водопадная до глубины 40 м в акватории города Ялта (Крым, Чёрное море). Концентрации биогенных элементов (NO_2, NO_3, NH_4 и PO_4) и тяжёлых металлов (Cu, Zn, Fe, Co, Ni, Mo, Cd, Pb и Hg) в пресной воде устья реки превышают их концентрации в прибрежной морской воде

в 3–64 раза. Выявлено влияние стока реки на эвтрофикацию вод изучаемой морской акватории. С использованием постчернобыльских радиоизотопов ^{90}Sr и ^{137}Cs выполнена датировка донных осадков и определена скорость седиментации с исследованной площади акватории региона. Рассчитаны потоки поступления загрязняющих веществ со стоком реки и периоды их оборота в рекреационном прибрежье города Ялта. Полученные результаты использованы для обоснования концепции устойчивого развития рекреационной зоны города Ялта по факторам загрязнения морской среды.

Ключевые слова: Чёрное море, Крым, вода, биогенные элементы, стронций-90, цезий-137, тяжёлые металлы, хлорорганические соединения, датировка донных отложений