

## Hydrological and Hydrochemical Regime of Hypersaline Koyashskoye Lake (Kerch Peninsula)

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### Abstract

A landscape feature of Crimea and the Kerch Peninsula is the presence of a large number of hypersaline lakes and bays, many of which are valuable reserves of therapeutic muds. The article summarizes the results of the hydrological and hydrochemical field studies conducted by the Sevastopol Branch of State Oceanographic Institute in 2015–2022 in the area of hypersaline Koyashskoye Lake located within Natural Reserve Opuksky. Hydrological studies of the lake included the determination of its morphometric characteristics and calculation of the main components of the water balance. Hydrochemical studies included the analysis of samples of brine and bottom sediments. The mineralization of the lake water was measured using different methods. Besides, the following indicators were identified in the samples: dissolved oxygen content and biochemical oxygen demand for five days, pH and total alkalinity, nutrient and pollutant (anionactive surfactants, petroleum, heavy metals) contents. The microelement composition of brine and pollution of bottom sediments were assessed. It was determined that the lake water balance input is formed mainly from atmospheric precipitation and filtration of the Black Sea water through the bay-bar. The major water balance output is evaporation. During an *in situ* experiment using a ground evaporator GGI-3000 and automatic weather station, evaporation for hypersaline waters was estimated and a formula for its calculation was determined. It was found that high concentrations of inorganic forms of phosphorus and nitrogen characterize the waters of Koyashskoye Lake. In summertime, oxygen concentrations can fall to hypoxic values. The bottom sediments of the lake were polluted with zinc, the concentration of which exceeded the maximum permissible concentration.

**Keywords:** Koyashskoye Lake, natural reserve Opuksky, water balance, thermohaline structure, hydrochemical regime, pollution

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## **Гидролого-гидрохимический режим гиперсоленого озера Кояшского (Керченский полуостров)**

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### **Аннотация**

Ландшафтной особенностью Крыма и Керченского полуострова является наличие большого числа гиперсоленых озер и заливов, многие из которых представляют собой ценные резерваты лечебных грязей. Цель статьи – обобщить результаты гидролого-гидрохимических экспедиционных исследований Севастопольского отделения ФГБУ «ГОИН» за 2015–2022 гг. в районе гиперсоленого озера Кояшского, расположенного в пределах природного заповедника «Опукский». Гидрологические исследования озера включали определение его морфометрических характеристик и расчеты основных компонент водного баланса. Гидрохимические исследования состояли из анализа проб рапы и донных отложений. Минерализацию вод озера измеряли различными методами. Кроме того, в отобранных пробах определяли следующие показатели: содержание растворенного кислорода и биохимическое потребление кислорода за пять суток, водородный показатель и общую щелочность, содержание биогенных элементов и загрязняющих веществ (анионных поверхностно-активных веществ, нефтепродуктов, тяжелых металлов). Оценивали микроэлементный состав рапы и загрязнение донных отложений. Определено, что приходящая часть водного баланса озера формируется преимущественно за счет атмосферных осадков и фильтрации вод Черного моря через пересыпь. Основной расходной частью водного баланса является испарение. В ходе натурного эксперимента с помощью наземного испарителя ГГИ-3000 и автоматической метеостанции получены оценки испарения для гиперсоленых вод и определена формула для его расчета. Выявлено, что воды озера Кояшского характеризуются высокими значениями концентраций неорганических форм фосфора и азота. В летний период возможно понижение концентрации кислорода вплоть до гипоксических значений. Донные отложения озера были загрязнены цинком, концентрация которого превышала предельно допустимую концентрацию.

**Ключевые слова:** озеро Кояшское, природный заповедник Опукский, водный баланс, термохалинная структура, гидрохимический режим, Крымский полуостров, соленые озера

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## Introduction

A landscape feature of Crimea is the presence of a large number of saline waterbodies with a specific composition of water and bottom sediments [1]. In accordance with work<sup>1)</sup>, salt (saline, hypersaline) lakes are commonly referred to as the lakes in which water salt content exceeds the salinity of ocean waters, i.e., more than 35 ‰. There are about 300 saline lakes on the territory of Crimea<sup>2)</sup>, of which 48 are large ones, 26 of which with an area of more than 1 km<sup>2</sup>.

According to the origin of the basins and shallows, feeding conditions and hydrological regime, the saline lakes of Crimea can be divided into two types – waterbodies in the basins of marine and continental origin.

By geographical location and presence of balneological resources, the hypersaline lakes of Crimea are usually divided into four main groups: Perekop, Yevpatoria, Kerch, and Tarkhankut [1]. Some authors<sup>2)</sup> identify additionally the Chersonesus and Sivash Area groups of lakes [2].

The hypersaline lakes of the Kerch group are most numerous, diverse in their origin, and promising for economic use (Fig. 1).

On the Kerch Peninsula, some small shallow lakes of continental origin – Marfovskoye, Kirkoyashskoye, Maryevskoye (Shimakhanskoye, Borisovo, Solenoye), Achi, Karach-Kol, Parpach-Kol, etc. – are located. The hypersaline lakes of marine (estuary) origin of the Kerch group include lakes separated by bay-bars in the coastal zone of the Black Sea – Adzhigol, Kachik, Uzunlarskoye and Koyashskoye; two more lakes (Aktashskoye and Chokraskoye) are located near the coast of the Sea of Azov; and four saline waterbodies (Yanyshskoe, Balchi-Kol, Tobechikskoye and Churubashskoye) border with the Kerch Strait.

Koyashskoye (Opukskoye, Elkinskoye, Elenskoye) Lake, which is a part of the *Opuksky Nature Reserve* (ONR) State Budgetary Institution, is located at the foot of the Parpach Ridge on the eastern outskirts of the southwestern plain of the Kerch Peninsula and forms a closed lagoon [3]. The complete separation of the lake from the Black Sea by a narrow sandy spit took place relatively recently, less than 2 thousand years ago. Earlier, in ancient times, the seaport of the settlement of Kimmerikon was located on the shore of the lake [4]. The lake is the mouth of a flooded gully, which is separated from the Black Sea by a narrow embankment about 30–80 m wide [1]. In accordance with [5, 6], the dimensions of entire Koyashskoye

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<sup>1)</sup> Grokhovsky, L.M., 1972. [*Lake Salt Deposits, their Studies and Commercial Evaluation*]. Moscow: Nedra, 168 p. (in Russian).

<sup>2)</sup> Aizenberg, M.M., ed., 1964. [*Surface Water Resources of the USSR. Main Hydrological Characteristics. Vol. 6. Ukraine and Moldavia. Iss. 4. Crimea*]. Leningrad: Gidrometeoizdat, 243 p. (in Russian).

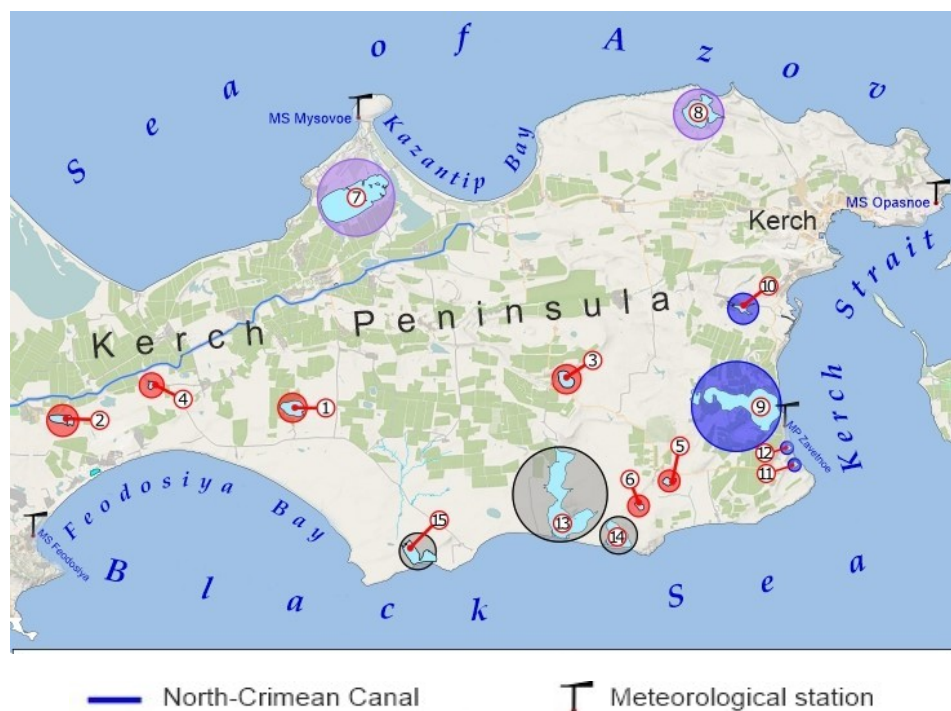


Fig. 1. Major hypersaline lakes of the Kerch group: lakes of continental origin (“kols”) (red colour); lakes of marine (liman) origin of the Sea of Azov basin (violet colour); of the Kerch Strait basin (blue colour); and of the Black Sea basin (grey colour). 1 – Karach-Kol, 2 – Achi, 3 – Marfovskoye, 4 – Parpach-Kol, 6 – Kirkoyashskoye, 7 – Aktashskoe, 8 – Chokraskoye, 9 – Tobechikskoye, 10 – Churubashskoye, 11 – BalchiKol, 12 – Yanyshskoye, 13 – Uzunlarskoye, 14 – Koyashskoye, 15 – Kachik

lake at the maximum filling are as follows<sup>3)</sup>: length – 3.9 km, average width – 1.4 km, maximum width – 3 km, area ~5.4 km<sup>2</sup>, depth – from 0.3 to 0.8 m (Table 1). The waterbody is elongated from northwest to southeast and has an oval shape (Fig. 2). Koyashskoye Lake consists of a number of bays ( lagoons) separated by sand spits (arrows). There are some passages in the spits through which water is exchanged among waterbodies. In the southwestern part of Koyashskoye Lake, the system of spits (sand spits) separates two bays (lakes). The largest of the lakes, called Maloye Elkinskoye, has an area of 0.83 km<sup>2</sup>, the greatest length of 1.53 km, and an average width of 0.54 km. From the northeast, Maloye Elkinskoye Lake is separated from Koyashskoye Lake by a nameless spit, which we propose to call

<sup>3)</sup> Lisovsky, A.A., ed.,2011. [Surface Water Bodies of Crimea. Management and Use of Water Resources: Reference Book]. Simferopol: KRP “Izd. Krymchpedgiz”, 242 p. (in Russian).

the Klyukina Spit in honor of A.A. Klyukin, a famous researcher of the Crimea and one of the creators of the ONR. The Klyukina Spit has a length of 1.1 km (Table 2).

The width of the Klyukina Spit under conditions of maximum lake filling (without any extinct areas) is 40–70 m, in the root parts it increases to 100–160 m. In the body of the spit, a ravine has been located for a long time with an average width of 400–480 m, through which water is exchanged between Maloye Elkinskoye Lake and Koyashskoye Lake proper (Fig. 3, *b*). From one to three small islands can periodically appear in the ravine. The width of the ravine

Table 1. Morphometric characteristics of Koyashskoye Lake

Waterbody	Maximum length, km	Width, km		Area, km <sup>2</sup>	Depth, m	
		mean	maximum		mean	maximum
Koyashskoye Lake (without bays)	3.70	1.20	2.00	4.45	0.5	0.8
Maloye Elkinskoye Lake	1.53	0.54	0.78	0.83	0.2	0.3
South-western bay	0.73	0.19	0.39	0.14	0.1	0.2
South-eastern bay	0.15	0.07	0.12	0.01	0.1	0.2
Koyashskoye Lake	3.90	1.40	3.00	5.43	0.3	0.8

Table 2. Morphometric characteristics of spits and bay-bars of Koyashskoye Lake

Accumulation form	Maximum length, km	Width, km		Area, km <sup>2</sup>
		mean	maximum	
Klyukina Spit	1.10	0.060	0.16	0.070
Zapadnaya Spit	0.72	0.010	0.02	0.010
Vostochnaya Spit	0.10	0.006	0.01	0.001
Bay-bar at the sea boundary	3.30	0.110	0.15	0.350



Fig. 2. Schematic map of hypersaline Koyashskoye Lake: red dots are for brine sampling points; diamonds are for mud sampling points; blue cross-hatched area is for the sea water filtration zone (Urochishche – isolated terrain feature)

and the number of islands in it depend on the interannual and seasonal variations of the components of the water balance of Koyashskoye Lake. Over the past 40 years, the spit ravine has increased, and, as a rule, two islands have been observed. The intensity of water exchange through the ravine in the body of the Klyukina Spit is determined by the levels of brine in Koyashskoye Lake and Maloye Elkinskoye Bay (Lake), as well as the speed and direction of the wind.

Based on lithological data [7], the bottom soils of Maloye Elkinskoye Bay (Lake) are composed of silts (muds) about 70 cm deep, below which there is a layer of shell detritus with silty joining material. The Klyukina Spit is composed mainly of shell detritus with shell valves, but at depths of 8–17 cm and below 49 cm there is a layer of silt. The thickness of the accumulated shell material in the body of the Klyukina Spit is small  $\sim 0.308 \cdot 10^{-3} \text{ km}^3$  [7]. Maloye Elkinskoye Lake rarely dries up even during the dry period due to the filtration of sea water through the bay-bar. Thus, water is always present in it.

To the west of Maloye Elkinskoye Lake, the Zapadnaya Spit, 720 m long and 10–20 m wide, separates one more small south-western waterbody (bay), dry for most of the year (Fig. 3, c). Water exchange between the south-western waterbody and Maloye Elkinskoye Lake is possible through a narrow ravine (1–3 m) in the northern root part of the Zapadnaya Spit. The south-western waterbody (bay) is filled with water mainly owing to the filtration of the Black Sea water

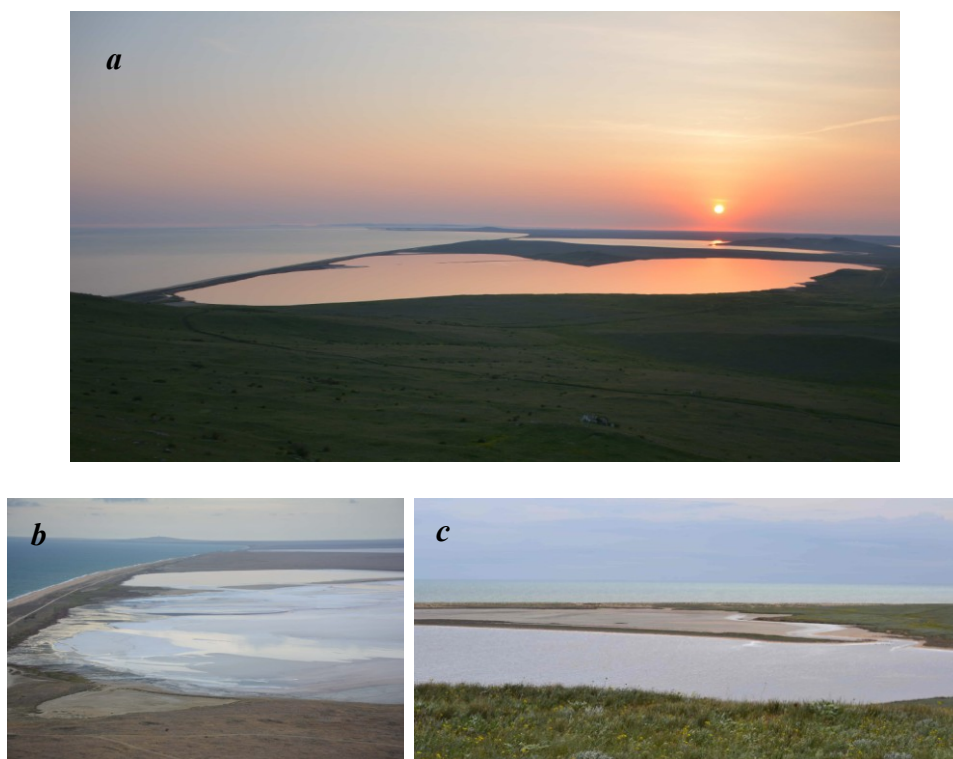


Fig. 3. Koyashskoy Lake (a view from the Mount Opuk) on 25 April 2019 (*a*); in the foreground: south-eastern waterbody and Vostochnaya Spit, in the middle: Koyashskoye Lake, in the background: Klyukina Spit and Maloye Elkinskoye Lake on 17 September 2019 (*b*); Zapadnaya Spit and south-western waterbody on 27 April 2014, through a passage in the spit, water comes on a small scale from Maloye Elkinskoye Lake (*c*)

through the bay-bar, as well as the inflow of water (brine) in a limited volume through a narrow passage from Maloye Elkinskoye Lake. In the west, in the rear part of the bay-bar, the south-western waterbody is sided by a small low (ditch), in which sea water accumulates due to storm overwash and filtration of the Black Sea waters and then enters the waterbody.

On the opposite section of the bay-bar of Koyashskoye Lake there is another small bay – the south-eastern waterbody with an area of 0.01 km<sup>2</sup>, a length of 150 m and an average width of 70 m (Table 1, Fig. 3, *b*). The waterbody is separated from Koyashskoye Lake by a small spit called “Vostochnaya”, 100 m long and 6–10 m wide. Water exchange of the south-eastern waterbody with Koyashskoye Lake takes place through a 25-meter passage in the spit. As a rule, during the research, the south-eastern waterbody was dried up or filled with a small amount of water (brine).



The bay-bar of Koyashskoye Lake, together with Maloye Elkinskoye Lake and the south-western waterbody, is ~3.3 km long and is composed of sand, shells, and detritus from psephytic to silty sizes [7]. The shell is dominated by modern Black Sea pelecypoda and rapana. The underwater coastal slope of the beach is bold, without a bar. During periods of storms, a strip of beach 20–25 m wide usually undergoes wind and wave action. According to [7, 8], during extreme storms, waves can overflow the bay-bar, reaching the water area of Koyashskoye Lake, and throw shells (*Rapana venosa*, *Cardium edule*) and detritus into the rear part of the bay-bar. During the 2016–2022 field studies, we recorded no facts of the Black Sea water inflow through the lake bay-bar during extreme storm waves. Near the lake, there were no strips of household garbage, plastic, usually carried out by waves, and the shell was represented by single specimens of *Rapana* only, most likely brought there by gulls. According to [8], the bay-bar of Koyashskoye Lake is a typical coastal bar after a two-stage period of formation. Favourable conditions for the formation of bars are created during a slowdown in the sea level rise rate, and the transformation of an underwater bar into an island bar and then into an off-shore one occurs with a subsequent lowering of the sea level.

3 km south of the bay-bar of Koyashskoye Lake, the so-called Ship Rocks (Parus, Elken-Kaya, Elchan-Kaya, Karaviya) protrude from under the water 10.0 to 23.4 m above sea level. Ship Rocks are the remains of eroded layers of Meotian shell and detritus limestone and are inclined in different directions at angles of 30–85 degrees. They top a horseshoe-shaped bank bounded by a 10 m isobath. The depth of the bank near the rocks is 5 m, 500 m from them – 9 m, and at a distance of 1000 m – 12 to 14 m [9].

To the east of the lake, Mount Opuk is located, 183.7 m high, which is one of the highest on the Kerch Peninsula. Near the Black Sea coast, this mount ends the Parabolic Ridge, which is a continuation of the Parpach Ridge [9]. On the northern shore of Koyashskoye Lake, Mount Ostraya is located, with the heights of 80.0–88.9 m. The coast in the northern part of the lake is steep for 500–650 m, with the heights of cliffs up to 5–10 m. On the western shore of Koyashskoye Lake, there is a rounded mountain Priozernaya with the height of 44.9 m and diameter of about 600 m.

Bottom sediments are layered black-gray silts up to 1.5 m thick (with salt interlayers). Almost in all periods of field studies of the Sevastopol Branch of State Oceanographic Institute on Koyashskoye Lake, a pink color of salt was observed, which is associated with high content of beta-carotene and the presence of a large number of cysts *Dunaliella* [3]. Koyashskoye Lake muds have the following granulometric characteristics: coarse silts (median value 6.3  $\mu\text{m}$ , maximum particle size 45  $\mu\text{m}$ ) are located near the sandy coastal bay-bar; thinner silts (median value 5.1  $\mu\text{m}$ , maximum particle size 30  $\mu\text{m}$ ) are found in the areas of the lake, which are remote from the shore. According to their mineral and salt composition, the Koyashskoye Lake muds are comparable to the muds of the Dead Sea [6]. The balance reserves of therapeutic muds are 1720.0 thousand  $\text{m}^3$  in category C1 [1]. Currently, brine and muds are not exploited and can be a reserve for use by the Crimean health resorts.



### Materials and methods

In 2015–2022, in the area of Koyashskoye Lake, the Sevastopol Branch of State Oceanographic Institute totally conducted 30 expeditions, performed 638 hydrochemical determinations in the brine of the lake:

Year	2015	2016	2017	2018	2019	2020	2021	2022
Number of expeditions	1	3	6	3	6	6	3	2
Number of hydrochemical determinations	11	34	94	52	142	150	89	66

At the final stage of studies in 2020–2021, sampling and analysis of bottom sediments (muds) from the bottom of the lake was carried out in order to study their chemical composition and pollution level in order to assess their safety and potential suitability for use in balneological purposes. Fig. 2 shows a map of Koyashskoye Lake with plotted sampling points, including a network of stations for determining the trace element composition described in work <sup>3)</sup>.

The areas of water (brine) and extinct areas were measured, as well as changes in the lake bay-bar. In order to perform morphometric and water balance studies, the information obtained from artificial earth satellites Landsat 4–5 with a resolution of 15–30 m and Sentinel-2 (with a resolution of 10 m per pixel for the visible range) was used from open sources. To interpret the images (distinguishing water bodies within the land and the land-sea boundary), the method of combining space images in different spectral ranges was used in accordance with [10, 11]. When analyzing the state of salt lakes and estuaries, watered soils (silt – mud) in the drained area are displayed in pink, which allows them to be clearly separated from the water surface of the waterbody, which is displayed in shades of blue [10]. Additionally, for greater accuracy of interpretation, UAV surveys made by the specialists of the Sevastopol Branch of State Oceanographic Institute, and photographic documentation of the state of the surface of lakes during regular expeditions were used where possible.

*Water balance studies* included the determination of the formula for the water balance of Koyashskoye Lake and estimates of the main balance components. Calculations were made concerning the amount of atmospheric precipitation falling on the lake surface, for which the specified morphometric data (see Table 1) and the results of measurements of atmospheric precipitation at the nearest marine hydrometeorological station (MS) Feodosiya were used.

Most of the empirical formulas proposed for calculating evaporation from a water surface are based on Dalton's law, i.e., the intensity of evaporation is proportional to the difference in the partial pressure of water vapour over this surface and the wind speed function:

$$E = C (e_0 - e_2) f(V_2),$$

where  $E$  – layer of evaporated water (mm);  $f(V_2)$  – some function of the wind speed at a height of 2 m above the waterbody surface;  $C$  – empirical coefficient;  $e_0$  – saturation air water vapour pressure above the surface of a waterbody

at water temperature (hPa);  $e_2$  – actual air water vapour pressure at a height of 2 m above the waterbody surface (hPa).

The formulas of this type are widely represented by the empirical formulas of V.S. Samoylenko <sup>4)</sup>, Braslavsky – Vikulina [12], State Hydrographical Institute <sup>5)</sup>, Braslavsky – Nurgaliev, and Shulyakovsky <sup>6)</sup>. According to work <sup>5)</sup>, control calculations of evaporation performed with the help of the formulas proposed by various authors for 35 evaporation basins showed that the Braslavsky–Vikulina formula had the smallest standard error (12.5 %), that is why it was recommended as a calculated one in work <sup>5)</sup>:

$$E = 0.14n (e_0 - e_2) (1 + 0.72V_2), \quad (1)$$

where  $n$  – number of days in a month.

In 2020–2022, in the warm period (April – November), we conducted an experiment to calculate the evaporation of water from hypersaline lakes and bays of Crimea (Koyashskoye Lake, Yuzhny Sivash Bay). The actual intensity of evaporation of brines was determined using a ground evaporator GGI-3000; simultaneously with a 15 min discreteness, hydrometeorological parameters were recorded using an automatic weather station and a high-precision electronic thermometer LTA (the water temperature in the surface layer of the evaporator was measured). The performed full-scale experiment made it possible to obtain the relationship equation between the measured and calculated evaporation values. Preliminarily, the best agreement between the calculated and experimental data was obtained by applying formula (1), while the saturation pressure of air water vapour above the water surface in the evaporator was calculated taking into account Raoult's law for dissolved substances, as according to work <sup>2)</sup>, the volume of evaporation from the surface of the brine of a hypersaline lake is 30–40 % less than from the surface of a fresh waterbody. Formula (1) was used to estimate the monthly volumes of evaporation of the brine from Koyashskoye Lake in 2006–2022, taking into account changes in the surface water area of the lake in different months.

*Hydrochemical studies* of hypersaline Koyashskoye Lake included analysis of samples of brine and bottom sediments. Samples were studied according to the appropriate analysis methods. Immediately after sampling, the temperature, density, and pH of the water were determined, as well as the fixation of dissolved oxygen, the titrimetric analysis of which was performed in a mobile laboratory. Samples for petroleum were preserved with carbon tetrachloride, samples for anionactive surfactants were preserved with chloroform. Samples for biogenic elements were frozen without preservation, and samples for heavy metals were preserved with nitric acid. Bottom sediments were cooled to 5–6 °C and delivered

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<sup>4)</sup> Samoilenko, V.S., 1952. [Modern Theory of Oceanic Evaporation and its Practical Application]. *Trudy GOIN*, 21, pp. 3–31 (in Russian).

<sup>5)</sup> Kuznetsov V.I., Golubev V.S. and Fedorova T.G., 1969. [Guidelines for Calculation of Evaporation from Water Body Surface]. Leningrad: Gidrometeoizdat, 84 p. (in Russian).

<sup>6)</sup> Vinnikov, S.D. and Proskuryakov, B.V., 1988. [Hydrophysics (Physics of Land Waters)]. Leningrad: Gidrometeoizdat, 248 p. (in Russian).

to the laboratory of the State Autonomous Institution of the Republic of Crimea “Center for Laboratory Analysis and Technical Measurements” within a day to determine their contamination with petroleum and heavy metals (chromium, zinc, cadmium, copper, nickel, lead, cobalt, mercury, arsenic, strontium, and iron). Further, the following indicators were determined in the certified Laboratory of Marine Chemistry of the Sevastopol Branch of State Oceanographic Institute:

- water salinity (mineralization) and chlorine content by various methods;
- total alkalinity;
- content of biogenic elements: nitrates, nitrites, phosphates, silicates, total nitrogen, and total phosphorus;
- content of pollutants: anionactive surfactants, petroleum, heavy metals.

In the study of salinity (mineralization) of lake waters, various physical and chemical methods of determination were used, such as densitometry (measurement of water density), refractometry, argentometric titration, gravimetry and electrical conductivity. The last two methods were used in the work at the final stage of studies in 2019–2022. Different methods of salinity measurements were compared, error estimates were obtained, and the most accurate method for determining salinity of hypersaline Koyashskoye Lake was determined.

## Results and discussion

**Water balance.** Fig. 4 shows the results of calculations of the surface water area of Koyashskoye Lake. It can be seen that the lake surface area water is characterized by significant interannual and seasonal variations – from maximum values in February–April to minimum values in August–October.

The equation of Koyashskoye Lake water balance can be written as follows:

$$\Delta B = V_f + V_u + V_{prec} + V_{sr} - V_{evap},$$

where  $\Delta B$  – changes in the water level (brine) in the lake;  $V_f$  – Black Sea water entering the waterbody by filtration through the bay-bar;  $V_u$  – discharge of underground sources;  $V_{prec}$  – precipitation;  $V_{sr}$  – drainage basin slope runoff;  $V_{evap}$  – evaporation.

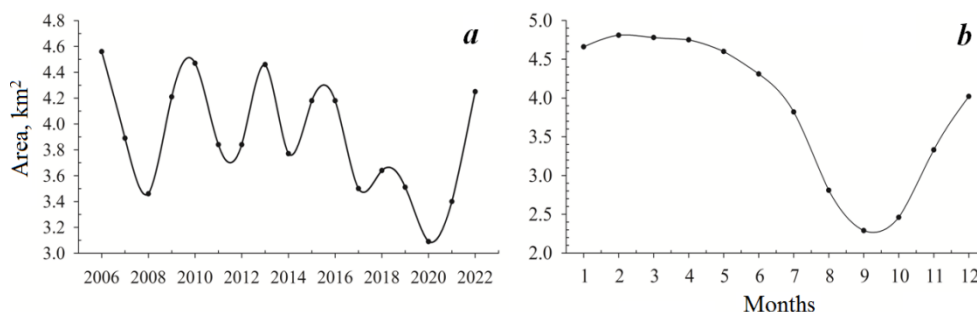


Fig. 4. Interannual (a) and seasonal (b) variations of the surface water area of Koyashskoye Lake

The climate aridity in the area of Koyashskoye Lake determines the poverty of the territory in fresh surface and groundwater [13]. Groundwater outlets into the hypersaline lakes of the Kerch group are rare and small in debit [5], so they can be neglected<sup>2)</sup>.

Most likely, slope runoff in Koyashskoye Lake is also insignificant. The main watercourse runs along an unnamed gully ~2 km long, which flows into Koyashskoye Lake to the north-west of Mount Ostraya. For the entire cycle of our studies, the flow into the lake along this gully was absent or insignificant. On the mountain range, there is one permanent spring, which collects water from the epicarstic horizon in an artificial gallery, and about twenty dry wells. All of them drain into a 50-meter stratum of Meotian limestone with high reservoir properties [13]. Condensation water can act as an additional source of nourishment. According to calculations [14], condensation on the Opuk mountain range can reach 23 % of the annual precipitation norm with a condensation runoff module of  $2.38 \text{ L}\cdot\text{s}^{-1}\cdot\text{km}^2$  per year.

The main inflow of fresh water into Koyashskoye Lake is carried out due to atmospheric precipitation. In the long-term variations of the amount of atmospheric precipitation in the area of the Kerch Peninsula, with their significant inter-annual variability, it is possible to single out periods of increased moisture at the end of the 20<sup>th</sup> century and a decrease in precipitation in the 1950–1980s, as well as in recent years (2006–2020). Over the entire period of measurements at meteorological station Feodosiya, a significant trend towards an increase in annual and seasonal (except summer) precipitation was revealed, but for the WMO last climatic period (1991–2020) and after the regime shift of 1976–1977 (1978–2020) significantly less precipitation fell (Tables 3, 4), especially in spring and autumn seasons, for which significant trends in the decrease in precipitation were revealed in Feodosiya: minus 19.7 mm/10 years and minus 24.0 mm/10 years, respectively.

Climate aridization of the Kerch Peninsula is stipulated by the regional features of global climate change in the Northern Hemisphere. From the 1990s to the present, in the area of Koyashskoye Lake, there have been significant trends in the increase in average annual and average monthly air temperatures. In general, over the long-term period, the average annual values of air temperatures at MS Feodosiya (the station with the longest series of observations in the lake area) have a significant warming trend with a linear trend slope of  $1.1 \text{ }^{\circ}\text{C}/100 \text{ years}$ .

The seasonal distribution of precipitation in the coastal zone of the Kerch Peninsula is typical for territories with a transitional type of climate (from marine to continental) in the temperate zone with a maximum of precipitation in summer and winter and a minimum in spring and autumn. In 2006–2022, the winter maximum amount of precipitation falling on the surface of the lake was 528 thousand  $\text{m}^3$ , or 33 % of the total precipitation per annum (1623 thousand  $\text{m}^3$ ). It is stipulated by the highest frequency of precipitation and is associated with the fact that during this season the Kerch Peninsula is influenced by an area of high pressure in the northeast of the mainland and cyclonic intrusions from the west and southwest leading to an increase in cloudiness and precipitation. The summer,

Table 3. Long-term annual average amount of atmosphere precipitations (AP) and linear trend characteristics (mm/10 years) of annual average precipitation amounts at meteorological station Feodosiya

Period	AP, mm	Trend, mm/10 years	$R^2$	$ t $	$P_0$	$D_0$
<i>Long-term observational series</i>						
1870–2020	415	<b><u>12.0</u></b>	0.421	5.190	< 0.001	1.68
<i>Period after the last regime shift in 1976–1977</i>						
1978–2020	473	–8.1	0.096	1.722	0.100	1.56
<i>Last WMO period</i>						
1991–2020	476	–40.6	0.096	1.722	0.100	1.56

Note: The numbers in bold are trend slope coefficients significant at no less than 95 level; the underlined numbers are trends significant at 99 level;  $D_0$  – Durbin–Watson test.

Table 4. Linear trend slope coefficient (mm/10 years) for seasonal amounts of atmosphere precipitations according to the meteorological station Feodosiya's data

Seasons	Long-term observational series (1870–2020)	Period after the last regime shift in 1976–1977	Last WMO period (1991–2020)
Winter	<b><u>2.1</u></b>	–2.5	–0.1
Spring	<b>2.5</b>	–6.4	<b>–19.7</b>
Summer	2.2	1.0	–7.0
Autumn	<b>2.6</b>	–2.0	<b>–24.0</b>

Note: The numbers in bold are trend slope coefficients significant at no less than 95 level; the underlined numbers are trends significant at 99 level.

secondary, maximum of precipitation of 439 thousand  $\text{m}^3$  (27 % of the total precipitation per annum) is usually associated with the development of convective activity. In the summer months, the air masses coming from the sea area are most saturated with water vapour, and this period of the year is marked by the maximum partial pressure. In spring and autumn, when pressure gradients weaken, local circulation develops. The breezes observed during this period, bring no precipitation. In these seasons, the minimum values of precipitation volumes entering Koyashskoye Lake are noted – 239 thousand  $\text{m}^3$  (15 %) in autumn and 417 thousand  $\text{m}^3$  (25 %) in the spring season. Fig. 5 shows long-term seasonal variations of the amount of precipitation (thousand  $\text{m}^3/\text{month}$ ), according to observations at meteorological station Feodosiya in 2006–2022.

*Evaporation* from the lake surface is the main output of its water balance. The long-term average evaporation for the period under study is 3152 thousand  $\text{m}^3$ , i. e., almost twice the amount of precipitation. The largest amount of water evaporates in the warm season (May–September) – 2466 thousand  $\text{m}^3$  (78.2 %) (Fig. 5).

Despite the increase in air temperature in recent decades and the precipitation reduction, studies carried out by the Sevastopol Branch of State Oceanographic Institute, showed that Koyashskoye Lake was one of the few hypersaline lakes of the Kerch Peninsula, which had hardly ever dried up completely. Thus, in the summer seasons of 2017 and 2020, almost all the salt lakes of the Kerch Peninsula dried up, with the exception of Koyashskoye and Aktashskoye Lakes.

In addition to atmospheric precipitation, the lake is fed due to the filtration of the Black Sea waters (as a result, far less salty water is brought by streams through the bay-bar into the lake). Moreover, the employees of the Sevastopol Branch of State Oceanographic Institute discovered for the first time that in cases of intense filtration (on 03.09.2017), the salinity in the areas of the lake close to the bay-bar can decrease to 19.7–20.9‰, i.e., it becomes close to the Black Sea water salinity. It should be noted that the ratio of the length of the bay-bar

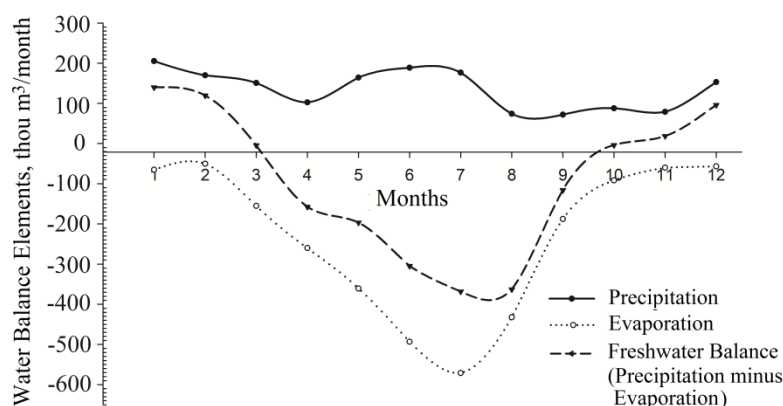


Fig. 5. Seasonal variations of water balance elements of Koyashskoye Lake

to the total length of the coastline of Koyashskoye Lake is the maximum one (0.39) compared with the similar indicator for other large estuary lakes of the Kerch Peninsula – Uzunlarskoye (0.06), Tobechikskoye (0.09), and Chokrakskoye (0.11). In previous studies, it was indicated that in some years (2000, 2001, 2007) salt precipitation occurred over a significant area [10]. At the same time, stripes and spots coloured from pink to reddish-brown often occupied a significant area of the precipitated salt. For the period of work in 2015–2022, the area of salt precipitation (saline land) was 2.8–3.8 km<sup>2</sup>, and that of dried silts (extinct areas) was 0.2–0.5 km<sup>2</sup>. The minimum surface water areas of Koyashskoye Lake, 0.70–0.81 km<sup>2</sup>, were recorded in September 2019 and October 2014; the maximum filling of the lake with water (with the surface water area of 5.0 km<sup>2</sup>) was recorded in January 2017.

In general, the smallest surface water area was observed in late summer and early autumn, which was stipulated by intense evaporation, a decrease in precipitation, and filtration through the bay-bar due to a decrease in wave activity at this time of the year. The measurements performed by us in summertime, showed that the depth of the lake in summer did not exceed 0.1–0.4 m.

**Hydrochemical regime.** Currently, the hydrochemical regime indicators of Koyashskoye Lake are studied insufficiently. The most complete study of the macrocomponent composition of Koyashskoye Lake was carried out in the 1960s<sup>7)</sup>. According to data of work<sup>7)</sup>, when brine density was 1.224 g/cm<sup>3</sup> and total salt content was 26.54 wt. %, the main components were NaCl, MgSO<sub>4</sub>, and MgCl<sub>2</sub> – 20.06, 2.44, and 3.86 wt. %, respectively. The content of other salts was significantly below 0.1 wt. %.

The main feature of the lake is the high value of the metamorphosis coefficient (MC), the value of the ratio of the magnesium sulfate and magnesium chloride concentration, proposed by N.S. Kurnakov<sup>7)</sup> to assess the degree of transformation of the waters of estuary lakes. As a comparison, the MC value of the Black Sea waters is 0.67. Close MC values are observed in the waters of Sivash Bay, as well as in the lakes that have retained a genetic connection with the sea (Chokrakskoye and Tobechikskoye) or are used to evaporate sea water during salt mining (Saks-koye). In other hypersaline lakes of Crimea, which have partially or completely lost their connection with the parent basin, the MC values are much lower. For example, the MC value is 0.25 for the nearby Uzunlarskoye Lake. The high MC value, which is close to that in the sea water, indirectly confirms the significant filtration of the Black Sea waters through the bay-bar and the absence of significant freshwater runoff, which enriches the waterbody with magnesium sulfate.

**Salinity, mineralization.** The conducted studies show that the salinity of waters and their mineralization little depend on the measurement method used in almost the entire range of values. Only when the values of the indicator are close to salt load, there is a decrease in salinity in relation to the value measured by the gravimetric method (dry residue). The results closest to the true value of salinity and

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<sup>7)</sup> Ponizovskii, A.M., 1965. [Salt Resources of the Crimea]. Simferopol: Izd-vo “Krym”, 162 p. (in Russian).



mineralization are obtained by the argentometric titration method, which is quite understandable given the proximity of the MC to the values of the Black Sea water.

In a number of samples, we recorded cases of a decrease in salinity to the sea water values or close to them. At the same time, the mineralization value of the lake waters, as a rule, did not depend on the method of determination used within the error of the densitometric determination of density in highly diluted solutions (Table 5).

In general, the concentration of salts in the waters of Koyashskoye Lake can vary over a very wide range, from 19.7 to 238.0 g/dm<sup>3</sup>. As mentioned above, the cases of detection of extremely low salinity values are associated with the filtration of sea waters. At the same time, diluting waters do not mix immediately due to the high density, but form quasi-stable flows, which, in the absence of wind mixing, can exist for quite a long time. As a rule, abnormally low water salinity was observed in the spring or autumn seasons, when the lake basin was almost completely filled with water, and the freshened areas were invisible during visual inspection. With strong brine evaporation before the salt is loaded, some part of it precipitates, which leads to an apparent conclusion about the MC change. When the water cools and sea water flows in, the salt ratio regains its original value.

Comparison of the results of mineralization measurements performed by various methods with the results obtained by the densitometric method is shown in Fig. 6. It can be seen that the densitometric method gives results comparable with the argentometric method in almost the entire range of measured values. Small deviations are observed only in high salinity values. A similar conclusion can be made with regard to other methods used to measure the indicator, which confirms the above assumption about the genetic proximity of the waters of Koyashskoye Lake and the Black Sea.

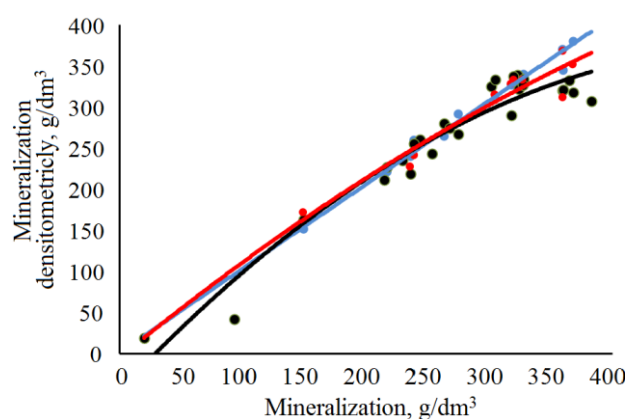


Fig. 6. Comparison of mineralization values obtained by the densitometric method with those obtained by other detection methods: gravimetric method M(Gr) (black line); argentometric method M(Ag) (blue line); electrical conductivity method M(C) (red line) in samples taken by SB SOI for 2015–2022

Table 5. Physical and chemical indicators of Koyashskoye Lake waters according to the data from SB SOI surveys for 2015–2022

Sample number	Date	$T$	Indicators of brine salt composition							
			$\rho$	M(Ds)	$n^{20}$	M(Rf)	Cl	$S$	M(Ag)	M(Gr)
1	09.10.2015	13.0	1.150	215	N/D	N/D	118	184	212	N/D
2	13.04.2016	15.2	1.167	244	N/D	N/D	145	221	261	N/D
3	23.06.2016	37.2	1.209	323	N/D	N/D	189	278	339	N/D
4	14.08.2016	36.0	N/D	N/D	N/D	N/D	12	21	21	N/D
5	09.03.2017	14.8	1.175	254	N/D	N/D	136	208	244	N/D
6	26.04.2017	18.0	1.067	93	N/D	N/D	24	41	43	N/D
7	01.06.2017	26.1	1.201	302	N/D	N/D	181	268	326	N/D
8	17.07.2017	35.4	1.236	365	N/D	N/D	185	273	332	N/D
9	03.09.2017	31.0	1.010	20	N/D	N/D	11	20	20	N/D
10	13.10.2017	22.5	1.188	275	1.378	292	149	226	267	N/D
11	18.04.2018	23.0	1.178	263	1.374	265	156	236	280	N/D
12	01.06.2018	25.6	1.217	328	1.384	340	186	274	335	N/D
13	21.08.2018	25.5	1.252	383	1.392	406	171	255	307	N/D
14	06.02.2019	8.8	1.154	217	1.368	222	126	196	227	N/D
15	23.04.2019	19.0	1.158	230	1.370	235	131	203	236	N/D
16	31.05.2019	29.5	1.178	268	1.376	275	153	233	275	N/D
17	20.06.2019	37.0	1.216	324	1.383	332	179	266	322	N/D
18	17.09.2019	26.8	1.103	149	1.358	152	91	147	163	172
19	17.10.2019	15.0	1.245	368	1.389	380	177	261	318	352
20	15.01.2020	10.2	1.210	305	1.380	310	186	272	334	315
21	09.04.2020	18.5	1.216	320	1.383	330	188	275	338	333

Continued

Sample number	Date	$T$	Indicators of brine salt composition							
			$\rho$	M(Ds)	$n^{20}$	M(Rf)	Cl	$S$	M(Ag)	M(Gr)
22	22.04.2020	17.6	1.215	318	1.382	327	162	242	290	328
23	29.05.2020	17.8	1.221	327	1.383	327	182	268	327	333
24	18.07.2020	36.0	1.235	360	1.388	371	178	265	321	368
25	28.10.2020	16.0	1.241	360	1.384	345	179	264	321	312
26	21.06.2021	31.5	1.160	239	1.374	260	142	219	255	241
27	06.08.2021	32.0	1.158	236	1.371	240	122	189	219	228
28	14.11.2021	13.0	1.222	330	1.382	327	188	275	338	355
29	16.02.2022	12.0	1.142	205	1.366	206	119	186	214	214
30	03.09.2022	27.0	1.169	252	N/D	N/D	179	265	321	341

Note:  $T$  – water temperature ( $^{\circ}\text{C}$ );  $\rho$  – brine density ( $\text{g}/\text{cm}^3$ ); M(Ds) – mineralization ( $\text{g}/\text{cm}^3$ ) by density; M(Rf) – mineralization ( $\text{g}/\text{cm}^3$ ) by refraction; Cl – chlorid ion concentration ( $\text{g}/\text{dm}^3$ ) by argentometry;  $S$  – salinity (‰) by argentometry; M(Ag) – mineralization ( $\text{g}/\text{cm}^3$ ) by argentometry; M(Gr) – mineralization ( $\text{g}/\text{cm}^3$ ) by gravimetry; N/D – determination was not performed.

The results of studies of the hydrochemical regime indicators of the Koyashskoye Lake waters (brine) are presented in Table 6.

*Dissolved oxygen.* The concentration of dissolved oxygen in the lake waters varies from hypoxic values ( $1.1 \text{ mg}/\text{dm}^3$ , 15 % of sat.) to  $8.9 \text{ mg}/\text{dm}^3$  (379 % of sat.), but in general, the concentration of dissolved oxygen was close to saturation at a given temperature and salinity throughout the year.

Normal aeration is maintained due to the absorption of atmospheric oxygen and photosynthesis occurring in the surface layers in colonies of protozoan algae (*Dunaliella*, etc.). Considering that most of the year the surface of the lake is covered with a salt crust, it should be assumed that the penetration of oxygen into the deeper water layers is carried out exclusively due to diffusion, which cannot be recognized as an effective mechanism under conditions of concentrated high-density brines. In the bottom area, the formation of hypoxic zones is possible, in which putrefactive decomposition of dead biomass occurs. As a result, hydrogen sulfide and sulfides can accumulate in the water column.

The periodic development of hypoxia in the lake water column also determines the large range of fluctuations in  $\text{pH}$  values, which is 1.92 pH units (6.92–8.84 pH units). Low pH values correspond to high values of total alkalinity, which in this type

Table 6. Hydrochemical indicators of quality of Koyashskoye Lake waters according to the data of SB SOI in 2015–2022

Sample number	pH	Alk, mmol/dm <sup>3</sup>	BOD <sub>5</sub> , mgO <sub>2</sub> /dm <sup>3</sup>	Content								
				of dissolved oxygen		of nutrients*, µg/dm <sup>3</sup>						
				mg/dm <sup>3</sup>	% sat.	PO <sub>4</sub>	P <sub>tot</sub>	SiO <sub>3</sub> <sup>2-</sup>	NO <sub>2</sub>	NO <sub>3</sub>	NH <sub>4</sub>	N <sub>tot</sub>
1	7.95	5.517	N/D	N/D	N/D	698	N/D	N/D	N/D	N/D	N/D	N/D
2	8.25	3.556	N/D	N/D	N/D	60	302	N/D	N/D	N/D	N/D	N/D
3	7.80	3.960	N/D	N/D	N/D	82	428	N/D	N/D	N/D	N/D	N/D
4	8.60	2.629	N/D	N/D	N/D	64	82	N/D	N/D	N/D	N/D	N/D
5	7.75	4.016	N/D	N/D	N/D	53	716	N/D	N/D	N/D	N/D	N/D
6	8.84	6.014	7.3	2.00	27	312	464	N/D	N/D	N/D	N/D	N/D
7	8.07	2.695	14.4	1.68	90	244	320	N/D	N/D	N/D	N/D	N/D
8	7.19	3.038	92.6	0.74	46	138	626	N/D	N/D	N/D	N/D	N/D

Sample number	pH	Alk, mmol/dm <sup>3</sup>	BOD <sub>5</sub> , mgO <sub>2</sub> /dm <sup>3</sup>	Content								
				of dissolved oxygen		of nutrients*, µg/dm <sup>3</sup>						
				mg/dm <sup>3</sup>	% sat.	PO <sub>4</sub>	P <sub>tot</sub>	SiO <sub>3</sub> <sup>2-</sup>	NO <sub>2</sub>	NO <sub>3</sub>	NH <sub>4</sub>	N <sub>tot</sub>
9	8.65	1.693	5.9	7.55	113	29	572	N/D	N/D	N/D	N/D	N/D
10	7.66	8.657	9.9	0.95	41	533	1181	N/D	N/D	N/D	N/D	N/D
11	8.11	6.065	26.9	8.91	379	147	423	N/D	N/D	N/D	N/D	N/D
12	8.33	8.715	95.4	1.12	15	202	712	N/D	N/D	N/D	N/D	N/D
13	6.92	22.35	97.6	N/D	N/D	1656	2779	N/D	N/D	N/D	N/D	N/D
14	8.04	9.522	15.1	2.77	83	44	182	N/D	N/D	N/D	N/D	N/D
15	8.09	1.462	8.3	2.68	97	65	232	1823	46	92	890	10450
16	8.08	4.308	34.6	6.38	93	196	386	709	70	87	1577	4951
17	7.80	4.768	53.9	N/D	N/D	55	588	1271	9	57	1333	19282
18	8.01	25.200	13.5	2.85	80	619	828	1914	21	11	1826	10769
19	7.56	29.500	13.9	1.85	91	46	6771	448	53	128	14	565

End of table

Sample number	pH	Alk, mmol/dm <sup>3</sup>	BOD <sub>5</sub> , mgO <sub>2</sub> /dm <sup>3</sup>	Content									
				of dissolved oxygen		of nutrients*, µg/dm <sup>3</sup>							
				mg/dm <sup>3</sup>	% sat.	PO <sub>4</sub>	P <sub>tot</sub>	SiO <sub>3</sub> <sup>2-</sup>	NO <sub>2</sub>	NO <sub>3</sub>	NH <sub>4</sub>	N <sub>tot</sub>	
20	7.93	7.117	62.9	0.42	19	448	965	1058	73	139	1631	3374	
21	7.64	7.407	18.4	1.62	89	215	691	2371	58	66	1681	6981	
22	7.67	7.198	20.6	2.20	111	211	634	654	55	202	1418	8097	
23	7.76	10.747	19.7	6.01	302	109	324	554	80	29	1904	11784	
24	7.07	25.734	21.5	2.58	175	765	2189	1247	107	447	3277	6681	
25	7.48	30.539	23.3	0.26	13	292	865	834	53	201	1657	14610	
26	8.25	2.005	34.5	4.93	226	233	288	662	44	43	883	7320	
27	7.11	5.787	110.3	N/D	N/D	582	356	765	163	18	478	4394	
28	7.73	5.001	119.6	2.46	86	292	869	679	104	7	121	9500	
29	7.80	5.147	2.4	2.38	68	243	475	1511	96	9	498	5598	
30	7.32	8.968	63.9	1.92	107	476	901	972	90	6	275	11700	

\* The concentration is given on element basis.

Note: Alk – alkalinity; N/D – determination was not performed.

of samples is determined not only by bicarbonate alkalinity, but also by hydrosulfide alkalinity. When considering these mechanisms, it is necessary to take into account the fact that, despite the high saturation of water with oxygen, its concentration remains low, which creates favourable conditions for the occurrence of anaerobic processes and the production of hydrogen sulfide, which determines the production of low pH and high total alkalinity values.

The decrease in the concentration of dissolved oxygen is largely determined by the increase in its consumption. In all analyzed samples, an increased value of BOD<sub>5</sub> was observed, which many times exceeded the MPC of natural waters (2.1 mgO<sub>2</sub>/dm<sup>3</sup>). The highest BOD<sub>5</sub> values are observed in summertime and are determined by the excess production of salt-tolerant algae and bacteria. During this period, the lake becomes a eutrophic waterbody, and large reserves of biogenic elements remain in its waters.

The concentration of *biogenic elements* in the waters of Koyashskoye Lake is mainly related to its water content. As can be seen from the data in Table 6, the highest total phosphorus concentrations were observed from July to October. At the same time, the concentrations of mineral forms of phosphorus were minimal. In the rest of the year, the concentrations of total and mineral phosphorus had similar values. This nature of the seasonal distribution of phosphorus forms indicates the activation of the processes of assimilation of phosphorus phosphate in the hot season. Most of it passes into the composition of living matter in the form of organophosphorus compounds and is in suspension. Further, organic forms from dead forms of plankton and their metabolic products are partially removed to bottom sediments and partially mineralized, thus replenishing the loss of the element. The analysis of the obtained data shows that, unlike sea and fresh surface waters, the maximum productivity of which occurs in spring and early summer, the microflora of hypersaline lakes, in particular Koyashskoye Lake, has a maximum level of production in the hottest season.

A similar conclusion can be made concerning other biogenic elements. Thus, a decrease in the concentration of dissolved forms of *silicates* as a rule, was observed in summer, when the consumption of the element necessary for building the protective cover of some organisms and cell membranes reached its maximum.

The concentration of *nitrite nitrogen* in almost all analyzed samples exceeded the MPC and varied within 7–447 µg/dm<sup>3</sup>. Significantly higher concentrations were also observed for *ammonium nitrogen*, but no excess of the MPC (2,900 µg/dm<sup>3</sup>) was recorded in most of the analyzed samples. The one and only sample taken on 18.07.2020, showed that the concentration of ammonium nitrogen was 1.1 of the MPC. High concentrations (565–19,282 µg/dm<sup>3</sup>) in Koyashskoye Lake are also characteristic of *total nitrogen*.

The totality of the listed features of the dynamics of various forms of nitrogen indicates the difference in the mechanisms of nitrogen assimilation and transformation in hypersaline lakes. In slightly saline and fresh waters, part of the nitrogen that enters with surface and underground runoff in the form of nitrates, is released



into the atmosphere in the form of gaseous products during microbiological denitrification. In hypersaline lakes, this mechanism is difficult due to the lack of specific microflora, which creates favorable conditions for the accumulation of nitrites and the production of ammonium salts and amines, which partially pass into bottom sediments, which are a source of secondary pollution. At the same time, depending on the degree of filling of the lake basin, the concentration of nitrogen compounds in the lowest oxidation state can vary by two or more orders of magnitude.

The state of contamination of the waters of Koyashskoye and other lakes with organic xenobiotics was studied in separate samples. The work was not systematic due to methodological difficulties in the analysis of samples with high salinity. Anionactive surfactants and petroleum were determined in the samples. Despite the dilution of the samples, most of them formed a stable emulsion, which did not make it possible to detect organic pollutants. Three determinations of anionactive surfactants were performed, the results of which showed that their concentration varied within  $77\text{--}1200\text{ }\mu\text{g}/\text{dm}^3$  at  $\text{MPC} = 100\text{ }\mu\text{g}/\text{dm}^3$  for fishery waters. The petroleum concentration in a single sample taken on June 1, 2018, was  $0.06\text{ mg}/\text{dm}^3$  (1.2 of the MPC). Given the low man-caused load on the lake located within the specially protected natural area, it can be stated that its waters are slightly polluted. Elevated concentrations of anionactive surfactants can be stipulated by natural surfactants formed as a result of saponification of fatty acids.

Currently, the trace element composition of the Koyashskoye Lake waters and the pollution of its waters with salts of heavy metals are studied insufficiently. In [1], they refer to a survey conducted in the 1970s in order to identify reserves of therapeutic muds<sup>2)</sup>. There was no possibility to find more recent data, so in the future we will rely on the available data. The study mentioned above was carried out on a network of four stations on a section along the axis of the lake (see Fig. 1). Comparative results of this study and our data are presented in Table 7.

The comparison of two series of determination performed in work [1] and those performed by the Sevastopol Branch of State Oceanographic Institute shows that at present, the concentrations of all elements can be higher than the MPC. Particularly high excess of the standard is observed for copper and lead. At the same time, the concentrations of all elements are highly dynamic, and their value often changes by an order of magnitude.

*Pollution of bottom sediments.* On December 11, 2020, we carried out the study of pollution of bottom sediments, which can potentially be used as therapeutic muds. Samples were taken at a point of constant monitoring, analysis was carried out in an accredited laboratory of the State Autonomous Institution of the Republic of Crimea “Center for Laboratory Analysis and Technical Measurements”. In the Russian Federation, MPC values for pollutants in bottom sediments have not officially been established, therefore, the *Neue Niederlandische Liste* was used concerning indicative values for rationing the quality of bottom sediment<sup>8)</sup>.

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<sup>8)</sup> Warmer, H. and van Dokkum, R., 2002. *Water Pollution Control in the Netherlands. Policy and Practice 2001*. Lelystad: RIZA, 77 p.

Table 7. Microelement content ( $\mu\text{g}/\text{dm}^3$ ) of Koyashskoye Lake waters according to the data from work [1] and from monitoring by SB SOI, Clarke values of elements in the ocean [15, 16] and maximum permissible concentration (MPC) <sup>9)</sup>

Parameter	Microelement								
	Zn	Cu	Ni	Pb	Sr	Cr	Co	Fe	Mn
C at point:									
K-1	< 0.05	3.07	< 0.1	< 0.02	<0.50	< 0.02	< 0.02	N/D	N/D
K-3	< 0.05	2.45	< 0.1	< 0.02	24.17	< 0.02	0.53	N/D	N/D
K-4	<b>55.80</b>	1.17	< 0.1	< 0.02	27.57	< 0.02	0.27	N/D	N/D
K-5	2.50	0.76	< 0.1	< 0.02	25.83	< 0.02	< 0.02	N/D	N/D
14	N/D	<b>20.30</b>	N/D	6.00	N/D	0.60	N/D	N/D	1.5
15	N/D	<b>154.80</b>	N/D	<b>212.60</b>	N/D	17.30	N/D	N/D	<b>280.0</b>
17	N/D	<b>96.10</b>	N/D	<b>335.10</b>	N/D	17.00	N/D	N/D	<b>480.9</b>
20	N/D	<b>83.00</b>	N/D	<b>34.00</b>	N/D	5.20	N/D	<b>305.50</b>	<b>277.0</b>
21	N/D	<b>6.00</b>	N/D	<b>22.00</b>	N/D	<b>32.80</b>	N/D	<b>91.30</b>	<b>115.3</b>
22	N/D	<b>32.00</b>	N/D	<b>37.00</b>	N/D	13.50	N/D	47.38	<b>137.0</b>
25	N/D	<b>46.40</b>	N/D	<b>217.00</b>	N/D	6.60	N/D	<b>150.80</b>	<b>200.4</b>
26	N/D	<b>10.50</b>	N/D	<b>131.30</b>	N/D	<b>112.20</b>	N/D	<b>2567.90</b>	<b>129.6</b>
27	N/D	<b>64.60</b>	N/D	<b>49.30</b>	N/D	<b>313.30</b>	N/D	<b>997.10</b>	<b>391.5</b>
28	N/D	<b>53.10</b>	N/D	<b>38.10</b>	N/D	<b>238.30</b>	N/D	<b>1379.20</b>	<b>196.0</b>
29	N/D	<b>49.90</b>	N/D	<b>135.10</b>	N/D	11.90	N/D	<b>57.20</b>	5.9

<sup>9)</sup> Ministry of Agriculture of the Russian Federation, 2016. *On the Approval of Water Quality Standards for Water Bodies of Fishing Importance, Including Standards for the Maximum Permissible Concentrations of Harmful Substances in the Waters of Water-Based Fishing Objects*. Order No. 552 of the Ministry of Agriculture of the Russian Federation of 13.12.2016 (in Russian).

Continued

Parameter	Microelement								
	Zn	Cu	Ni	Pb	Sr	Cr	Co	Fe	Mn
Clarke*	4.90	0.50	1.7	0.03	200.00	0.20	0.05	20.00	0.2
MPC*	50.00	5.00	10.0	10.00	4140.0	20.00	5.00	50.00	50.0

\* Values of MPC of elements and of their Clarkes in the Earth's crust.

Note: N/D – determination was not performed; values exceeding MPC are given in bold.

Indicators of pollution of bottom sediments are presented in Table 8. High level of pollution of bottom sediments with the elements, for which the MPC standard is established according to document <sup>8)</sup>, was observed for zinc only. For other elements, the concentration did not exceed the rated value. The same can be said about petroleum, the concentration of which was below the accepted MPC value. Attention is also drawn to the ratio of the obtained values of the concentration of elements to the accepted values of their Clarkes. Thus, the concentration of zinc and strontium exceeded the accepted Clarke value by two and three times, respectively. On the other hand, for iron, the technophilicity of which is characterized by rather high values, the ratio to Clarke was less than 0.5. Such a low concentration of iron is probably due to specific features of the surrounding landscape, since almost the entire territory of the peninsula is included in the so-called Kerch iron-ore basin. In particular, the Kyz-Aulskoye and Novoselovskoye deposits are known in this area. The depth of formation of ores is 25–100 m,

Table 8. Pollutant concentration (mg/kg) in the surface layer of bottom sediments of Koyashskoye Lake (at K-1 point)

Parameter	OP	Cr	Zn	Cd	Cu	Ni	Pb	Co	Hg	As	Sr	Fe
Concentration	< 50	< 5	<b>174</b>	< 1	< 20	< 50	< 10	< 5	0.005	< 1	1114	19480
MPC	50	–	140	0.80	35	35	85	N/D	0.300	29	N/D	N/D
Clarke	–	83	83	0.13	47	58	16	18	0.08	1.7	340	46500

Note: N/D – determination was not performed; values exceeding MPC are given in bold.

and water process of these areas, which are a part of the drainage basin of lakes, leads to an increase in the iron content in bottom sediments. In particular, the iron content in bottom sediments of the Uzunlarskoye Lake exceeded 50,000 mg/kg during the expeditions of the Sevastopol Branch of State Oceanographic Institute. Such a significant difference in the composition of bottom sediments of closely located lakes can be explained by the small amount of surface slope runoff into Koyashskoye Lake.

### **Conclusion**

Based on the above, the following conclusions can be made:

1. The surface water area of Koyashskoye Lake is characterized by significant interannual and seasonal variations – from maximum values in February–April to minimum values in August–October. The aridity of the climate in the Koyashskoye Lake area determines the poorness of the territory in fresh surface and underground waters. The slope runoff of Koyashskoye Lake is minor.

2. Atmospheric precipitation provides the main inflow of fresh water into Koyashskoye Lake. The seasonal distribution of precipitation in the coastal zone of the Kerch Peninsula is typical for territories with a transitional type of climate (from marine to continental) in the temperate zone with a maximum of precipitation in summer and winter and a minimum in spring and autumn. In 2006–2022, the winter maximum amount of precipitation falling on the surface of the lake was 528 thousand m<sup>3</sup>, or 33 % of the total precipitation per annum (1623 thousand m<sup>3</sup>). The summer, secondary, maximum of precipitation of 439 thousand m<sup>3</sup> (27 % of the total precipitation per annum) is usually associated with the development of convective activity.

3. In addition to atmospheric precipitation, of all other input components, the lake is fed to a greater extent due to the filtration of the Black Sea waters (as a result, far less salty water enters Koyashskoye Lake through the bay-bar separating the lake from the sea). In cases of intense filtration (on September 3, 2017), the salinity in the areas of the lake close to the bay-bar can decrease to 19.7–20.9 ‰, i. e., it becomes close to the Black Sea water salinity.

4. Comparison of changes in the surface water area of the lake, obtained as a result of the analysis of satellite images for 2006–2022, with the calculated main components of the Koyashskoye Lake water balance (evaporation, precipitation, freshwater balance) showed that the main contribution to the formation of the balance in the warm period of the year was made by evaporation. During the cold period of the year, the water balance of the lake is determined mainly by precipitation and filtration of the Black Sea waters through the bay-bar.

5. In most of the analyzed chemical samples, the waters of Koyashskoye Lake were characterized by good oxygen saturation. Nevertheless, in summertime, oxygen concentrations can fall to hypoxic values. The main reason here is the high value of BOD<sub>5</sub>, which in all samples exceeded the maximum permissible concentration established for sea waters.

6. The brine of the lake is characterized by high concentrations of inorganic forms of phosphorus and nitrogen. At the same time, under conditions of hypoxia, a sufficiently large amount of reduced forms of nitrogen (nitrite and ammonium) is formed in the waters, and the concentration of nitrate nitrogen decreases.

7. The bottom sediments of Lake Koyashskoye are polluted with zinc, the concentration of which exceeded the established maximum permissible concentration and Clarke standards. At the same time, the concentration of iron, which exceeded the Clarke in Uzunlarskoye Lake, amounted to only 0.5 of the Clarke value in the waters of Koyashskoye Lake. This indicates a small amount of surface slope water runoff entering the waterbody and good filtration of the Black Sea waters through the bay-bar.

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