

WATER QUALITY AND PROTECTION:  
ENVIRONMENTAL ASPECTS

## Water Isotopic-Geochemical Composition in the Trekhtsvetnoe Meromictic Lake on the White Sea Coast

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**Abstract**—The isotopic features of Lake Trekhtsvetnoe in the White Sea coast area were studied in 2012–2015 in both winter and summer. Lake Trekhtsvetnoe is a water body, separating from the sea, with constant vertical stratification throughout the observation period. Its isotopic, hydrophysical, and biological characteristics have been studied. By the isotopic profile of lake water body, three zones can be identified in the lake: (1) 0–1 m: mixolimnion zone with  $\delta^{18}\text{O}$  varying from  $-12$  to  $-11.1\text{‰}$ ; (2) 1.0–3.0 m: zone with transitional properties with  $\delta^{18}\text{O}$  varying from  $-11.1$  to  $-5.5\text{‰}$ ; (3) 3.0–7.6 m: monimolimnion zone with highest values of  $\delta^{18}\text{O}$ —from  $-5.5$  to  $-4.7\text{‰}$ .

**Keywords:** meromictic water body, isotopic composition, hydrochemical composition

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### INTRODUCTION

The study is focused on the features of water isotopic composition in a meromictic water body—Lake Trekhtsvetnoe on the coast of Kandalaksha Bay, the White Sea.

A meromictic water body (Greek *meros* means *part*, and *mixis* means *mixing*) is a lake in which there is no water circulation involving layers with different mineralization. The bottom-layer water is more mineralized and dense than the top-layer water. The lake under study is referred to as Trekhtsvetnoe (Three-color) because of the three different colors of its three layers: the surface layer is brown, the middle one is emerald-green, and the bottom one is lemon.

### LAKE LOCATION

Lake Trekhtsvetnoe is located in Pekkelinskaya Bay, the White Sea (Fig. 1). Its coordinates are  $66^{\circ}35.53'$  N,  $32^{\circ}59.97'$  E. Lake dimensions are  $340 \times 150$  m at the largest depth of 7.5 m.

The absolute elevation of ice in February 2014 was 1.25 m, and that of water surface was 0.85 m. The lake's drainage area is  $643809$  m<sup>2</sup>, its water area is  $32407$  m<sup>2</sup>, the ratio of the basin to lake water area is 19.9. The lake shows no tidal variations. The top lake water layer is a fresh layer of yellow, sometimes brown color because of the humic substances it receives with flow from a bog; this layer is underlain by a salt-water

layer with a brilliant green water with phototrophic bacteria always present in the zone of chemocline at the boundary between the aerobic and anaerobic zones [15]; further downward is a hydrogen-sulfide, salt-water mass of lemon-yellow color, slightly turbid because of sulfur crystals. When rising to the surface, the bottom water is rapidly releasing gas bubbles. Light penetration into the lake is limited to the top layer 1.5–2 m in thickness, as the green layer, lying in the chemocline, entirely absorbs light because of its higher turbidity due to a huge amount of bacteria [24]. Therefore, the major portion of water mass lies in the aphotic zone.

Among all known water bodies separating from the sea, Lake Trekhtsvetnoe best corresponds to the concept of meromictic. The vertical stratification persists all year round, remaining unchanged throughout the six years of observations [10, 24].

In addition to Lake Trekhtsvetnoe, the field studies covered four other lakes at different stages of separation from the sea: a lagoon on Zelenyi Cape and lakes Kislo-Sladkoe (semifresh lagoon), Nizhnee Ershovskoe, and Verkhnee Ershovskoe (Fig. 1). By the degree of their separation from the sea, the examined water bodies can be arranged in the following order [7, 10, 23, 24]: (1) the lagoon on the Zelenyi Cape is at the initial stage of separation and still keeps to exchange water with the sea through tides; (2) Kislo-Sladkoe Lake has no permanent water exchange, sea water penetrates into it during spring tides; however, the

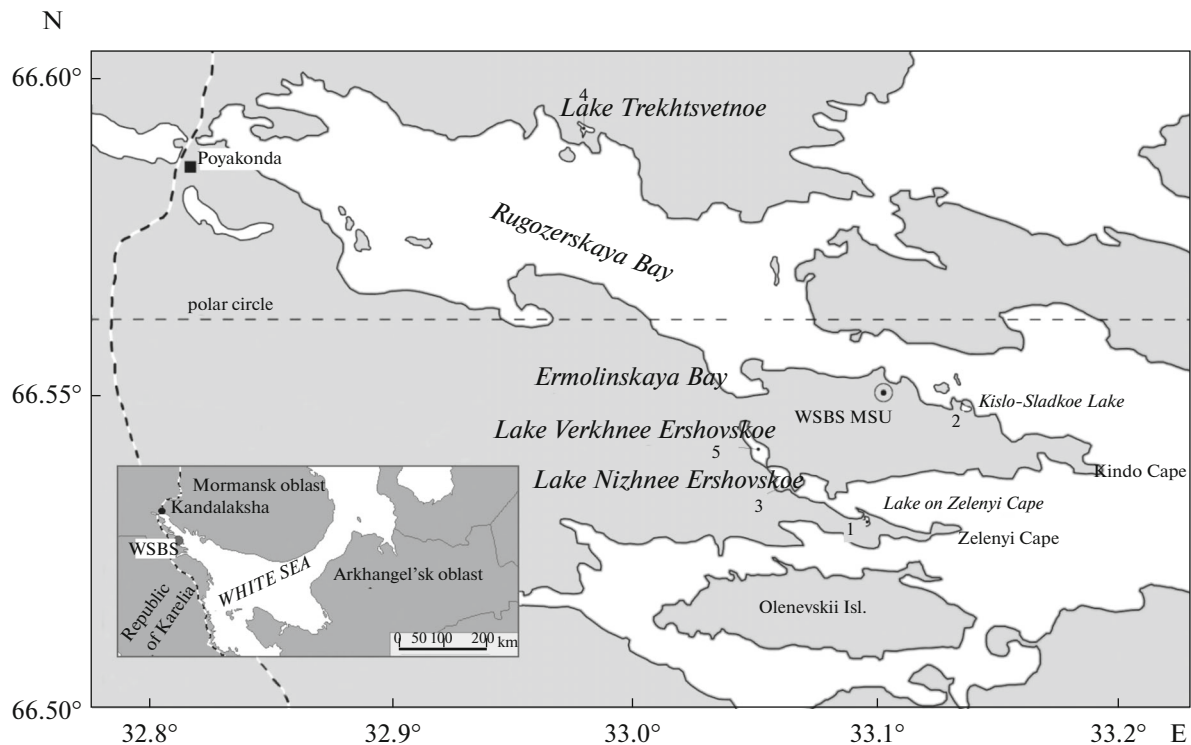


Fig. 1. Schematic map of the location of Lake Trekhtsvetnoe and other examined lakes on Kandalaksha Bay shore, the White Sea.

height of the threshold does not hamper the free flow of surface waters; (3) Nizhnee Ershovskoe Lake has a salty bottom layer because of water penetrates into deeper parts because of occasional uprushes; (4) Lake Trekhtsvetnoe is fully separated from the sea as can be seen from the two-meter freshwater layer and a salt bottom layer, whose characteristics have not changed over for more than six recent years (a typical feature of a meromictic water body); the bottom water mass in this water body is of yellowish green color (most likely, because of polysulfides), it has a strong hydrogen-sulfide odor, and contains a gas, which forms many fine bubbles when the sample is raised to the surface; (5) the Verkhnee Ershovskoe Lake is fully fresh.

#### SAMPLING AND ANALYSES PROCEDURES

Water and ice samples were taken in Lake Trekhtsvetnoe on March 21, 2012; March 18, 2013; February 2, 2014; June 16, 2014; and January 31, 2015.

The isotopic, hydrophysical, and biological characteristics were studied at different depths in the examined water bodies. The samples were taken by a Whale Premium Submersible Pump GP1352 (Ireland) into flasks 50 mL in volume.

The temperature and salinity (electric conductance) were measured by a conductometer WTW Cond 315i; pH and oxidation–reduction potential Eh were measured by pH-meter and Eh-meter Water-Liner WMM-73, respectively.

In January and June 2014 and in January 2015, the composition of the major ions was determined in the hydrochemical laboratory, Land Hydrology Chair, Faculty of Geography, Moscow State University [11, 12].

Isotopic studies of Lake Trekhtsvetnoe were carried out three times in winter a week after water sampling. The ratios of stable oxygen and hydrogen isotopes were determined in 2012, 2013, and 2015. Water samples were analyzed in the isotope laboratory, Faculty of Geography, MSU, on Delta-V mass spectrometer with a standard gas bench option. The concentration of stable isotopes is given as a relative value in promille (‰), which corresponds to  $10^{-3}$ , and is denoted by  $\delta$ . The values of  $\delta^{18}\text{O}$  are calculated using the difference between  $^{18}\text{O}/^{16}\text{O}$  values in a standard and the sample to be measured by the formula:

$$\delta^{18}\text{O} = \frac{(^{18}\text{O}/^{16}\text{O}_{\text{sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{standard}})}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} \times 1000\text{‰}.$$

The values of  $\delta\text{D}$  are calculated using the difference between  $\text{D}/^1\text{H}$  in the standard and the sample to be measured by the formula:

$$\delta\text{D} = \frac{(\text{D}/^1\text{H}_{\text{sample}} - \text{D}/^1\text{H}_{\text{standard}})}{\text{D}/^1\text{H}_{\text{standard}}} \times 1000\text{‰}.$$

The measurements were based on the International Standard of Mean Oceanic Water V-SMOW ( $\delta^{18}\text{O} =$

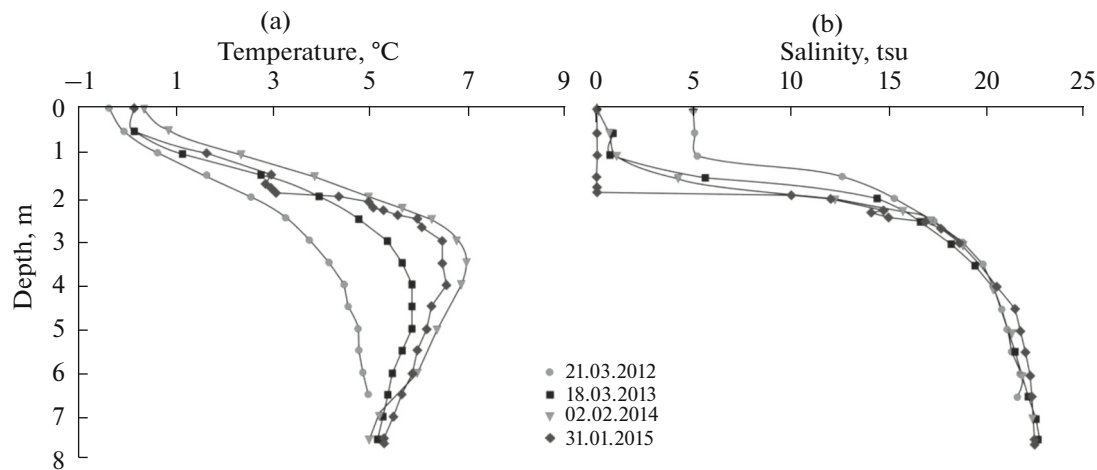


Fig. 2. Profiles of water (a) temperature and (b) salinity in Lake Trekhtsvetnoe.

0‰,  $\delta D = 0‰$ ), international standards GISP ( $\delta^{18}O = -24.76‰$ ,  $\delta D = -189.5‰$ ), SLAP ( $\delta^{18}O = -55.5‰$ ,  $\delta D = -427.5‰$ ), and MSU laboratory standard—snow from Garabashi Glacier ( $\delta^{18}O = -15.60‰$ ,  $\delta D = -110.0‰$ ). The determination accuracy of  $\delta^{18}O$  was 0.1‰, and  $\delta D = 0.6‰$  [1].

#### RESULTS OF HYDROPHYSICAL, HYDROCHEMICAL, BIOLOGICAL, AND ISOTOPIC STUDIES OF LAKE WATER

In the study period, Lake Trekhtsvetnoe showed distinct vertical stratification and three characteristic layers of different color. In the beginning of observations in February 2012, the salinity of the surface layer was unusually high (4.9–5.2‰) because of the extremely large seawater input during the high tide, which coincided with a wind surge of the autumn of 2011. By the next winter, the salinity in the surface water layer dropped to 0.8‰; a year later, to 0.6‰; and by the winter of 2015, the salinity in it dropped to zero at the total mineralization of ~400 mg/L (Fig. 2).

The boundary of hydrogen sulfide occurrence with the associated chemocline between aerobic and anaerobic zones, and the green bacterial layer, which marks it, also changed their positions. In 2012, this layer lied at a depth of 1.5 m, while, in the following years, it gradually shifted down to a horizon of 2 m. The salinity below this depth was constant in all years, while water temperature in winter 2012 was somewhat lower than in the following years (it was gradually increasing). At the very bottom, at a depth of 7–7.5 m, winter water temperature was the same in all observation years (4.9–5.1°C with variations within the measurement error; see Fig. 2).

In the warm season, the occurrence of oxygen in Lake Trekhtsvetnoe is limited by the depth of 1.5–1.9 m (Fig. 3). In the chemocline, starting from the

depth of 1.6–2.0 m, oxygen disappears and the oxidation-reduction potential becomes negative.

The values of pH measured in 2014–2015 varied within the range of 6.4–8.04, the least values having been recorded under ice (Fig. 4). In the center of freshwater layer, the values of pH increased to reach a record value of 8.04 in 2014. In 2015, a second rise in pH was recorded in chemocline, at a depth of 2 m, most likely, suggesting active photosynthesis. Below the chemocline, starting from the depth of 2.1 m, pH values dropped abruptly and kept decreasing toward the bed. A local rise in pH was observed at a depth of 5.5 m in the layer with high concentration of hydrogen sulfide in 2015.

The isotope profile of the Lake Trekhtsvetnoe (Fig. 5; Table 1) suggests the stratification of water mass. Three zones can be identified by the isotope profile in the water mass. The first zone, at depths of 0–1 m (0–0.5 m), is the mixolimnion zone, where the values of  $\delta^{18}O$  and  $\delta D$  varied from  $-10.8$  to  $-10.2‰$  and from  $-78.3$  to  $-79.4‰$  in 2012; from  $-11.8$  to  $-11.4‰$  and from  $-90.5$  to  $-91.9‰$  in 2013, respectively. In 2015, the values of  $\delta^{18}O$  in the mixolimnion zone varied from  $-12.1$  to  $-11.1‰$ . The second zone, a zone chemocline, was identified in 2013 and 2015 in a depth interval of 0.5–1 (3) m. In 2013, the values of  $\delta^{18}O$  and  $\delta D$  increased from  $-11.4$  to  $-5.8‰$  and from  $-91.9$  to  $-46.2‰$ , respectively. In 2015, the values of  $\delta^{18}O$  in chemocline zone varied from  $-11.1$  to  $-5.5‰$  (Fig. 5b, 5c). The third zone—at depths of 3.0–7.0 (7.6) m—is a monimolimnion zone, in which highest values of  $\delta^{18}O$  were recorded (they, however, never exceeded such values for seawater) along with a relatively uniform distribution of the values over depth. In 2013, the values of  $\delta^{18}O$  varied within a range from  $-5.8$  to  $-5.1‰$ ; in 2015, from  $-5.5$  to  $-4.7‰$  (Fig. 5b, 5c; Table 1). The obtained data show that in 2013 and 2015, Lake Trekhtsvetnoe showed a distinct meromic-

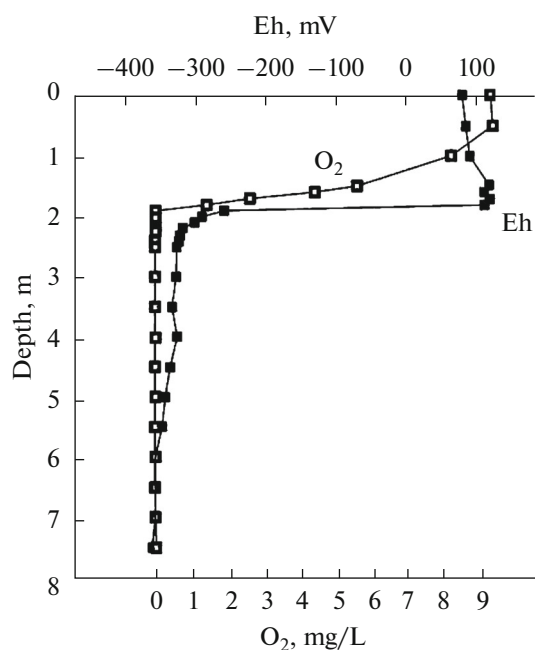


Fig. 3. Dissolved oxygen concentration and Eh in Lake Trekhtsvetnoe in June 2014.

tic structure of the water mass. In 2012, the meromictic structure was disturbed by seawater intrusion. Below the mixolimnion zone, down to the bottom (at depths of 1–6 m), the values of water isotopic composition gradually increased: from  $-10.2$  to  $+2.1$ ‰ for  $\delta^{18}\text{O}$  (Fig. 5a) and from  $-79.4$  to  $-42.4$ ‰ for  $\delta\text{D}$ .

Unusual values of  $\delta\text{D}$  were obtained in the monimolimnion layer: in 2013, anomalously high values of  $\delta\text{D}$  (from 779.1 to 1109.4‰) were recorded at depth from 4 to 6.5 m; and in 2015, the values of  $\delta\text{D}$  from 1638.4 to 2446.7‰ were recorded at depths of 3.5–7.6 m.

Because of its meromictic structure, the input of sufficient amount of organic matter, and the availability of sulfates in the bottom water mass, hydrogen sulfide accumulates in it in large amounts. Sulfate reduction is most active in the chemocline and bottom sediments. Out of the water bodies in which hydrogen sulfide concentration was determined, Lake Trekhtsvetnoe is among the world leaders. While the Black Sea shows hydrogen sulfide concentration reaching 9.6 mg/L, and Framavaren Fjord (Norway), in its bottom water, shows the concentration of up to 6 mM/L [17, 26], corresponding to 204 mg/L (these objects can be taken as demonstrating reference anaerobic conditions), the respective value in the monimolimnion of Lake Trekhtsvetnoe can be two and three times as large as that [24].

Water chemistry of the lake water is chloride-sodium (Table 2). Stable density stratification exists under the chemocline throughout the year; therefore, the concentrations of major ions keep nearly constant.

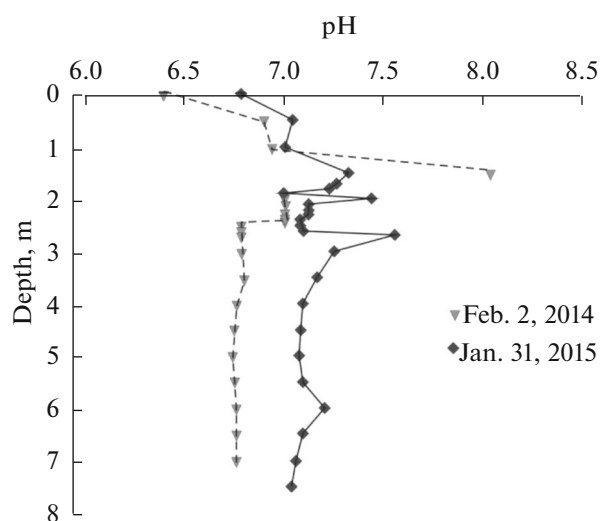


Fig. 4. Water pH distribution over depth in Lake Trekhtsvetnoe.

The sum of ions increases from 13 g/L at a depth of 2 m to 20 g/L at 6 m (Fig. 6). The mineralization values as large as that are typical of the water of Kandalaksha Bay, the White Sea, water mineralization in which under ice in winter reached 26.6 g/L (Table 3). The ice and snow cover of Kandalaksha Bay show much lower mineralization (from 1 to 2.8 g/L) with the predominance of sodium and chloride, as is typical of seawater.

A specific feature of the distribution of sulfate ions over water depth in Lake Trekhtsvetnoe is a pronounced concentration peak within the interval of 2–4 m, after which it decreases; a feature that is not observed in other ions.

At a depth of 2 m,  $\text{SO}_4/\text{Cl} = 0.14$ , and in the bottom layer, it is  $\sim 0.05$ , while in Lake Kislo-Sladkoe and the lake-lagoon with typical seawater, this ratio is  $\sim 0.11$  all over the vertical profile.

The microbiological analysis of water in lakes of Kislo-Sladkoe and Trekhtsvetnoe showed the presence of living anaerobic phototrophic bacteria [6, 13, 25]. Green-color sulfur bacteria dominated in Lake Trekhtsvetnoe.

In August and September 2013 and 2014, the spectra of light absorption and fluorescence were studied in different water layers of five water bodies, separating from the White Sea to obtain the vertical distribution profiles of phototrophic microorganisms.

The obtained values were maximal in chemocline zone, which, in different water bodies, lies at different depths: (a) 1.7–1.9 m in Lake Trekhtsvetnoe; (b) 2.5–2.9 m in Lake Kislo-Sladkoe; (c) 1.9–2 m in Lake Nizhnee Ershovskoe; and (d) 4–5 m in the lagoon on Zelenyi Cape [22, 24].

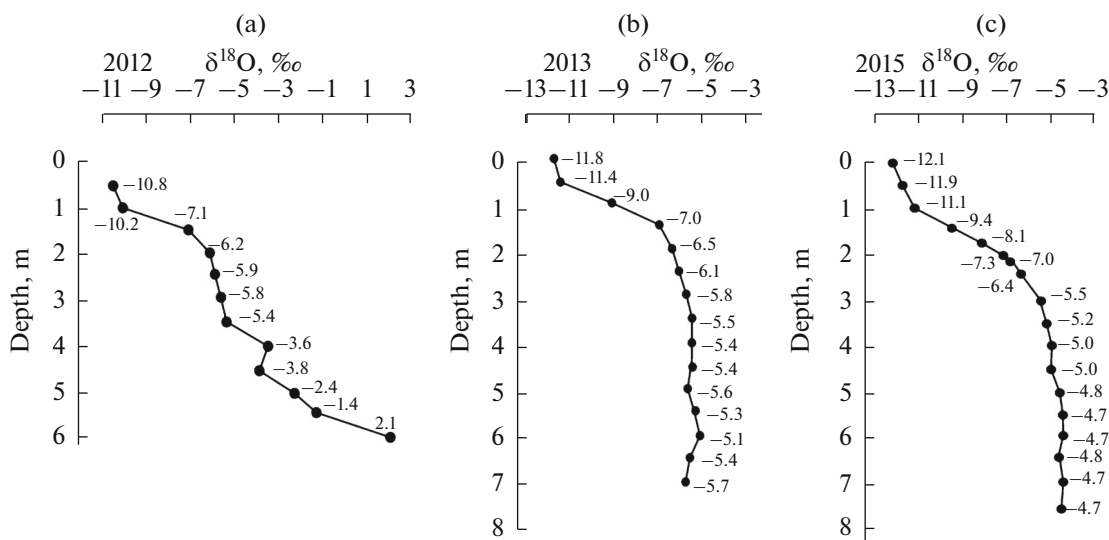


Fig. 5. Distribution of  $\delta^{18}\text{O}$  values over depth in the meromictic Lake Trekhtsvetnoe in 2012 (a), 2013 (b) and in 2015 (c).

Fluorescence emission spectra with peaks in the domain of 745 and 765 nm were used to determine the presence in chemocline of green sulfur bacteria of two types: green-color and brown-color [14]. Estimating the proportions of the concentrations of these two bacterial forms showed that only green-color green sulfur bacteria ( $98.0 \pm 2.0\%$ ) were present in Lake Trekhtsvetnoe at a depth with maximal concentration of green sulfur bacteria. Dominating in the bottom layer are brown-color green sulfur bacteria, because, in virtue of their pigment composition, their photosynthesis requires less light.

#### POSSIBLE CAUSES OF THE ISOTOPIC-GEOCHEMICAL ANOMALIES OF LAKE WATER

Many studies of meromictic continental and separating coastal water bodies have shown that the zone of monimolimnion features a high concentration methane and hydrogen sulfide gases, forming in the process of organic matter decay in anoxic environment.

The final stages of organic matter decomposition are implemented by secondary anaerobes. These include, primarily, hydrogenotrophic organisms, i.e., methanogenes and sulfate reducers. Their metabolism products are methane and hydrogen sulfide. Under the conditions of higher mineralization, sulfate reducers have enough sulfates and organic matter to fully implement their metabolism. Under alkaline conditions, hydrogen sulfide occurs in the form or low-toxicity hydrosulfide and sulfide ions:  $\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$  and  $\text{HS}^- = \text{H}^+ + \text{S}^{2-}$ .

The obtained data on the isotopic composition of oxygen in the water of coastal water bodies may suggest the possible periodic seawater inflow. Thus, the isoto-

pic analysis of water in the salt Nurume Lake in the Antarctica yielded the values of  $\delta^{18}\text{O} = 7.9$  (close to seawater) in monimolimnion zone at a depth of 16 m, while in the zone of mixolimnion at depth of 1.5 m,  $\delta^{18}\text{O} = -16.4\%$  [16].

Table 1. Variations of  $\delta^{18}\text{O}$  values in water in Lake Trekhtsvetnoe in 2012, 2013, and 2015

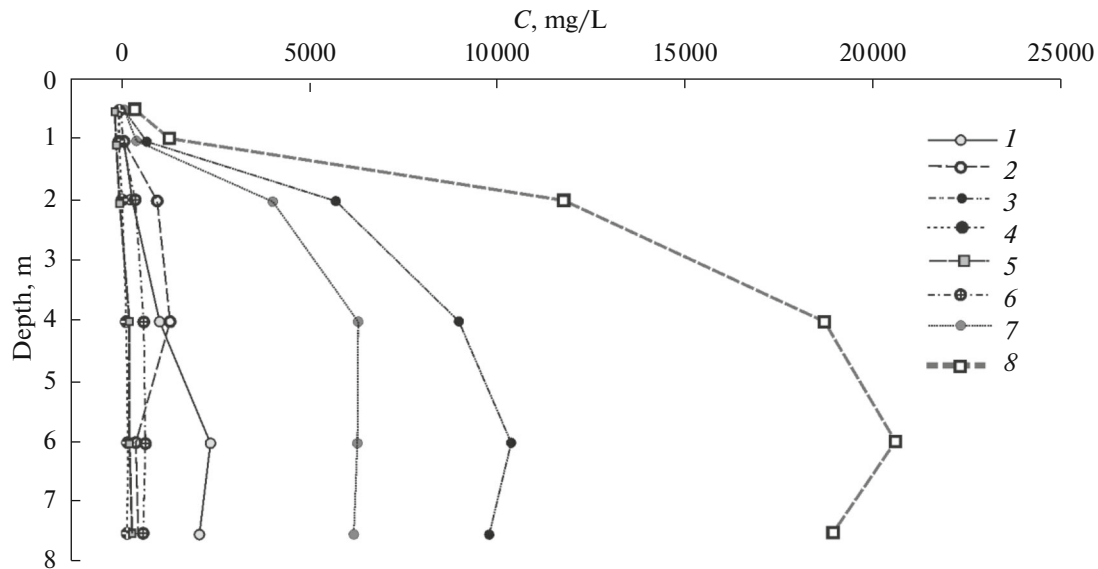
Sampling depth, m	$\delta^{18}\text{O}$ , ‰		
	2012	2013	2015
0	—	-11.8	-12.1
0.5	-10.8	-11.4	-11.9
1	-10.2	-9.0	-11.1
1.5	-7.1	-7	-9.4
1.7	—	—	-8.1
2	-6.2	-6.6	-7.3
2.1	—	—	-7.0
2.5	-5.9	-6.1	-6.4
3	-5.8	-5.8	-5.5
3.5	-5.4	-5.5	-5.2
4	-3.6	-5.4	-5.0
4.5	-3.8	-5.4	-5.0
5	-2.4	-5.6	-4.8
5.5	-1.4	-5.3	-4.7
6	2.1	-5.1	-4.7
6.5	—	-5.4	-4.8
7	—	-5.7	-4.7
7.6	—	—	-4.7

**Table 2.** Water and ice chemistry in Lake Trekhtsvetnoe (January 2014)

Depth, m	pH	Expression form	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Total anions	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total cations	Total ions
Ice	7.04	mg/L	13.4	11.3	58.8	83.5	4.6	7.1	25.5	12.6	49.8	133.3
		%-equiv	5.1	5.4	38.1	48.5	5.3	13.3	25.5	7.4	51.5	
0.5	6.94	mg/L	56.1	39.1	206.9	302.2	10.80	15.6	96.4	3.5	126.3	428.5
		%-equiv	6.8	6.0	42.1	54.9	4.0	9.5	31.0	0.7	45.1	
1	7.04	mg/L	58.6	117.0	704.9	880.5	24.96	49.9	414.0	8.1	497.0	1377.4
		%-equiv	2.1	5.2	42.4	49.7	2.7	8.8	38.5	0.4	50.3	
2	7.11	mg/L	329.5	998.0	5750.0	7077.5	136.5	422.0	4040.0	182.4	4780.8	11858.3
		%-equiv	1.3	5.1	39.5	45.9	1.7	8.5	42.8	1.1	54.1	
4	6.93	mg/L	1055.6	1317.8	9025.8	11399.3	187.8	637.2	6300.0	218.0	7343.0	18742.2
		%-equiv	2.7	4.3	39.7	46.7	1.5	8.2	42.8	0.9	53.3	
6	6.85	mg/L	2410.3	463.6	10392.9	13266.8	213.4	660.5	6300.0	220.0	7394.0	20660.7
		%-equiv	5.8	1.4	42.6	49.8	1.6	7.9	39.9	0.8	50.2	
7.5	6.79	mg/L	2135.7	617.1	9807.0	12559.8	222.4	681.0	6200.0	214.0	7317.4	19877.2
		%-equiv	5.253	1.928	41.464	48.645	1.666	8.405	40.460	0.824	51.4	

The meromictic Lovojarvi Lake (Finland) shows a high concentration of dissolved inorganic carbon (DIC) in the monimolimnion zone (at a depth of 10–17.5 m), i.e., 1750–5020 μmol/L (for comparison, the same characteristic in the mixolimnion zone was 400 μmol/L); also found was an increase in the values of δ<sup>13</sup>C DIC in the bottom part of the water mass—from -18 to -6‰. Methane concentration in the monimolimnion zone also abruptly increases from near-zero values in the top part of the water mass to 200–3100 μmol/L in its bottom part [27].

The high concentrations of DIC and methane, as well as the high values of δ<sup>13</sup>C in DIC in the monimolimnion zone are due to the anaerobic oxidation of organic matter. The preferential consumption of <sup>12</sup>C of DIC in the course of methanogenesis accounts for the enrichment in δ<sup>13</sup>C. The value of methane δ<sup>13</sup>C gradually become heavier from bottom to top—from -74‰ at a depth of 15 m to -50‰ at a depth of 1 m, thereby suggesting the aerobic and anaerobic oxidation of methane. Water in Lake Lovojarvi is very poor in oxygen; therefore, all types of methane oxidation



**Fig. 6.** Vertical distribution of ion composition components in Lake Trekhtsvetnoe in winter 2014. (1) Hydrocarbonates, (2) sulfates, (3) chlorides, (4) calcium, (5) potassium, (6) magnesium, (7) sodium, (8) mineralization.

**Table 3.** Hydrochemical composition, mineralization (M) and total dissolved solids (TDS) in snow and ice on the coast of Kandalaksha Bay, the White Sea

pH	M, mg/L (TDS, $\mu$ S)	HCO <sub>3</sub> <sup>-</sup> , %-equiv	Cl <sup>-</sup> , %-equiv	SO <sub>4</sub> <sup>2-</sup> , %-equiv	NO <sub>3</sub> <sup>-</sup> , %-equiv	Ca <sup>2+</sup> , %-equiv	Mg <sup>2+</sup> , %-equiv	Na <sup>+</sup> %-equiv	K <sup>+</sup> %-equiv
fresh snow									
6.56	992.4 (1944)	0.00	88.08	11.92	0.00	7.26	17.98	70.22	4.54
ice, depth 0–5 cm									
6.69	2750.6 (5420)	0.00	87.22	12.78	0.00	7.92	16.53	73.81	1.74
ice, depth 15–20 cm									
6.79	2647.7(5410)	0.00	88.24	11.76	0.00	8.13	17.11	72.81	1.95
ice, depth 20–27 cm									
6.58	2388.7 (4200)	0.00	87.89	12.11	0.00	7.25	17.44	72.85	2.46
water under ice									
7.31	26599.3(40000)	0.00	86.62	13.38	0.00	3.88	16.39	78.00	1.73

proceed under anaerobic conditions. The isotopically depleted carbon in methane is better consumed by zooplankton, as can be seen from the lighter isotopic composition of <sup>13</sup>C of zooplankton as compared with the isotopic composition of <sup>13</sup>C of disperse organic material [27].

However, the determination of the oxygen-isotope and deuterium composition of water lake has not revealed in the monimolimnion zone an enriched isotope composition, similar to that found in the lakes on the White Sea coast. The highest values of  $\delta^{18}\text{O}$  ( $-9.5$ ,  $-11.5\text{‰}$ ) and  $\delta\text{D}$  ( $-75$ ,  $-85\text{‰}$ ) were recorded there in the surface water horizon. The isotopic composition was found to become lighter with the depth, reaching  $-12.3\text{‰}$  for  $\delta^{18}\text{O}$  and  $88\text{‰}$  for  $\delta\text{D}$ , except for the water layer at depth of 7–8 m, where water is slightly enriched with heavy isotopes because of a groundwater intrusion at this depth [27].

Studies of water isotopic composition and chemistry in meromictic lakes of Canadian Arctic show constant water stratification [21, 29]. The isotopic composition of two typical meromictic lakes was studied: (1) Lake Garrow ( $97^\circ\text{W}$ ,  $76^\circ\text{N}$ ), a small coastal lake on Little Cornwall Isl.; its depth is 47 m, its water surface lies 12 m above sea level; (2) Sofia Lake on the eastern margin of Cornwall Isl. ( $94^\circ\text{W}$ ,  $74^\circ\text{N}$ ), its depth is 50 m; water surface lies 7 m above sea level.

The mixolimnion of these lakes contains waters with  $\delta^{18}\text{O}$  values between  $-13.16$  and  $-21.98\text{‰}$  (Fig. 7), which is close to the isotopic composition of local precipitation. In the chemocline zone, the values of  $\delta^{18}\text{O}$  increase to  $-10\text{‰}$  parallel to an increase in chloride concentration to 42 g/L, suggesting the mixing of surface and deep waters. In the monimolimnion zone, hypersaline waters show  $\delta^{18}\text{O}$  values around  $-8\text{‰}$ .

The radiocarbon dating of carbon dissolved in water in the monimolimnion zone of Lake Garrow

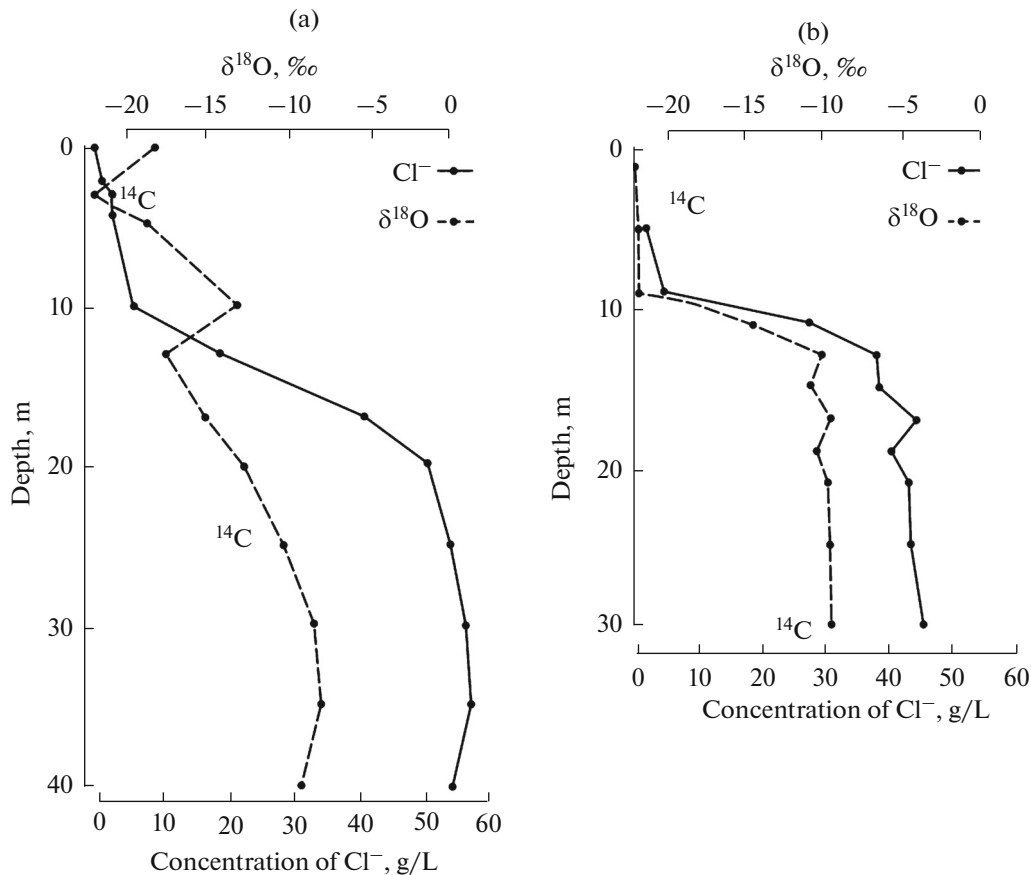
yielded the age of  $2580 \pm 260$  years; current activity of <sup>14</sup>C was recorded in Lake Sofia (i.e., 121.4% of the present-day carbon), thereby suggesting current infiltration of seawater into the lake [29].

The oxygen-isotope profile of the water mass in Lake Garrow shows high values of  $\delta^{18}\text{O}$  in the bottom part (Fig. 7a), allowing 3 zones to be identified in the water mass: 0–12 m, mixolimnion zone, where water varies between fresh and brackish; 12–20 m, chemocline zone with transitory properties; 20–47 m, monimolimnion zone with extremely high salinity (2.5 times higher than that in seawater).

In the surface water of Lake Garrow, the values of  $\delta^{18}\text{O}$  vary from  $-18.16$  to  $-21.98\text{‰}$ ; and the concentration of chlorides, from 0.08 to 5.96 g/L. This isotopic sign is in agreement with the composition of precipitation in the high-latitude isotopic minimum. The very small amount of marine aerosols and dissolved cyclic salts, washed out from the atmosphere in the coastal regions, reflects the weak effect of seawater on the precipitation. The sea pack ice from the western coast of Little Cornwall Isl. shows  $\delta^{18}\text{O} = -1.48\text{‰}$  and chloride concentration of 18.08 g/L [29]. The topmost part of the surface water features  $\delta^{18}\text{O} = -18.16\text{‰}$ , maybe reflecting the recent precipitation events with seasonally enriched isotopic composition. The decrease in  $\delta^{18}\text{O}$  in the underlying water layer ( $-21.98\text{‰}$ ) can reflect some inflow of early spring precipitation or even snowmelt water.

In the chemocline zone, the values of  $\delta^{18}\text{O}$  for water vary from  $-17.56$  to  $-13.04\text{‰}$ , parallel to changes in chloride concentration. Such composition corresponds to moderate mixing of two different components (surface or near-surface and bottom waters).

Water salinity at large depth is higher than that for undiluted seawater with homogeneous composition, isotopically depleted relative to SMOW. For comparison, S. Epstein and T. Mayeda [19] give a mean value



**Fig. 7.** Distribution of the isotopic composition and chloride concentration over depth in the meromictic lakes (a) Garrow, Little Cornwall Isl. and (b) Sofia, Cornwall Isl., Canadian Arctic Archipelago (according to [29]).

of salinity of 34.7‰ and  $\delta^{18}\text{O} = -0.04\text{‰}$  for 31 water samples taken in the Atlantic and Pacific at depths between 500 and 2000 m. The surface water in polar seas has  $\delta^{18}\text{O}$  between  $-2$  and  $0\text{‰}$ . In the monimolimnion zone, the values of  $\delta^{18}\text{O}$  are still negative, varying between  $-10.56$  and  $-8.21\text{‰}$  [29]. Such isotopic depletion and chemical concentration can be a result of freezing, which is accompanied by the isotopic enrichment of ice by 3‰ in terms of  $^{18}\text{O}$  at the expense of the retained water in which the solution concentrates. If water crystallization proceeds according to Rayleigh process, in which the ice is all the time isolated from residual water after equilibrium fractionation, the isotopic composition of the residual water should suffer exponential depleting. P. Page with coauthors [29] observed such trend in the distribution of chloride content and  $\delta^{18}\text{O}$  over depth (Fig. 7b): a layer of diluted water in the top 10-m stratum passes into chemocline down to 13 m, which, in its turn, passes into monimolimnion with a maximal thickness of 37 m. By its isotopic composition, Lake Sofia is similar to Lake Garrow: the surface water shows very low values of  $\delta^{18}\text{O}$  (up to  $-21\text{‰}$ ) and relatively low chloride concentration (0.86 g/L).

The meromixis in Lake Sofia has formed recently because of infiltration of brines as the result of freezing. There seems to exist a permanent seawater inflow, caused by the coastal transgression, through the non-frozen zone into the permafrost domain. The permanent infiltration of fresh water into deeper horizons of the lake leads to a more homogeneous sign in the monimolimnion layer and a thinner chemocline layer [29].

The values of  $\delta^{18}\text{O}$  for both lakes clearly show isotopic fluctuations of meteoric waters in the mixolimnion, characterized by a short water residence time.

Hypersaline waters with their especially heavy isotope composition can also occur in the monimolimnion in both lakes without freezing. This most likely takes place because of the so-called crenogene salinization immediately after the rise of the area after the retreat of an ice dam more than 4 thousand years ago, when the lake became isolated from the sea [28].

Studying of salt soda-chloride and chloride-soda lakes of Southeastern Transbaikalia showed a high activity of microbiologically determined sulfate reduction. Sulfate reduction is active in both bottom sediments and water mass. The chloride-soda Lake



Doroninskoe, in individual periods showed up to 50 mg/L of hydrogen sulfide in its bottom layers. Judging by the strong characteristic odor and the presence of black silty mud deposits, among the lakes under consideration, sulfate reduction is maximal in lakes Ulan-Nor and Zun-Kholvo. Lake Barun-Torei shows a high rate of sulfate reduction, reaching 12 mg S/(dm<sup>3</sup> day) in the cyanobacteria mat [2].

In Lake Solenoe (Buryatia), a high concentration of sulfides was recorded in the bottom horizons of bottom sediments, represented by black tough silt with strong hydrogen-sulfide odor. The determination of sulfide concentration in water and in bottom sediment core showed them to increase with depth. In the water mass on lake surface, sulfide ion concentration was minimal, amounting to 5 mg/L. With an increase in the depth from 0.5 to 1.5 m, HS<sup>-</sup> concentration varied from 14.2 to 15 mg/L. An abrupt increase in sulfide ions to 104.2 mg/L was recorded in the bottom layer at a depth of 2 m. At the same depth, a very low redox potential was recorded. In the samples of lake bottom sediments taken from the depth of 20 cm, the amount of sulfide ions was minimal in the surface and subsurface sediment layers. Thus, in the top horizon of bottom sediments (1–5 cm), HS<sup>-</sup> concentration varied from 25 to 95.8 mg/L. The concentration of HS<sup>-</sup> in bottom sediment column increased appreciably. In the bottom sediments and mat of Lake Solenoe, showing the highest abundance of sulfate-reducing bacteria, the rate of sulfate reduction reaches 0.70–1.80 mg S/(kg day) [3].

The microorganism activity in Lake Shira in winter was found to be relatively high. A.S. Savichev with coauthors [31] showed that hydrogen sulfide concentration in the water mass of Lake Shira did not change in winter. An obvious additional source of hydrogen sulfide in water in winter is bottom sediments, where the rate of sulfate reduction in winter (146 mg S m<sup>2</sup>/day) is even higher than in summer (48 mg S m<sup>2</sup>/day). Data of the isotopic analysis of sulfur in hydrogen sulfide in water column also suggests an increase in the inflow from bottom sediment in winter: the mean value of δ<sup>34</sup>S is –43.1‰ in summer and –40.1‰ in winter. The heavier isotopic composition of sulfur in winter can be explained only by the inflow of isotopically heavier hydrogen sulfide from bottom sediments [31]. It was also found that the rate of methane oxidation in Lake Shira bottom sediments was higher in winter than in summer.

Data on Lake Shira were used to show that light conditions in winter can be more favorable than in summer because of the higher mixolimnion transparency. The result is that the abundance of purple bacteria can be very high in under-ice period, and their maximally possible photosynthetic production in this period in the case of low-snow winter can form a considerable portion (~30%) in its annual value [4].

The anomalously high values of δD established by the authors in the monimolimnion of Lake Trekhtsvetnoe can be caused by the high activity of the microorganisms implementing oxidation–reduction processes with the formation of hydrogen, hydrogen sulfide, and methane.

It is worth noting that the values of δD as high as that have not been found in other lakes examined by the authors, including the coastal White Sea lakes, nor in terrestrial natural objects. In the known soda meromictic lakes, the extreme values of δD in water reach +29.7‰ in the crater lake of El Chichon volcano (Mexico) [32] and +18‰ in Lake Cueva de la Mora (Spain) [30].

The only object that showed equally high δD values is the production water extracted during the development of oil and gas condensate deposits, e.g., the formation waters of the Astrakhan Gas Condensate Field. Studies of the production waters of several more fields, in which gas deposits contain appreciable amounts of acid components, showed a systematic deviation of hydrogen isotopic composition from 10–100 to 200, 500, and 1300‰ (SMOW) in terms of δD. In one case, the enrichment of formation water by heavy hydrogen was in excess of +2200‰ [5].

The isotopic effects in biological systems with deuterated water have been studied for more than 30 years [8, 18]. The ability to adapt to high concentrations of heavy water is known to be associated with the evolution level of the organisms, i.e., the lower the development level, the higher the adaptation ability. Studying the isotopic effect of deuterium in microorganism cells (methylotrophic bacteria, halophilic bacteria, unicellular green algae) at their growth on media with deuterated heavy water (D<sub>2</sub>O) showed that even the cells that have grown on media with low D<sub>2</sub>O concentration can adapt to its high concentration up to 98%. The result is that, on the maximally deuterated medium, adapted cells were obtained with hydrogen replaced by δD in all their biological material [9, 20].

The authors suppose two major causes of this anomalously high deuterium enrichment: (1) the inflow of deuterated fluids from juvenile waters into the lake from below and (2) bacterial fractionation by selective absorption of protium by microorganisms.

## CONCLUSIONS

Four-year dynamics of the isotopic-geochemical composition of water was studied in the meromictic Lake Trekhtsvetnoe on the Kandalaksha Bay coast.

The bottom water mass in the lake is of yellowish green color (most likely, due to polysulfides). The boundary of hydrogen sulfide occurrence, the associated chemocline between the aerobic and anaerobic zones, and the green bacterial layer that marks it, have also changed their position: in 2012, it was at a depth

of 1.5 m, and in the subsequent 3 years, it gradually moved downwards to the horizon 2 m.

In 2012, the isotope profile of lake water mass showed a disturbance of the meromictic stratification, caused by the inflow of a large amount of seawater at a setup in the autumn of 2011. In the years that followed, the isotopic stratification of the water mass showed the presence of three zones: mixolimnion, extending to the depth of 1 m, with most negative isotope values; a zone with transitional properties (the depth of 1–3 m), where  $\delta^{18}\text{O}$  values increase from  $-11$  to  $-5.5\text{‰}$ ; the bottom monimolimnion zone with the highest values of the isotopic composition, which slightly vary over depth.

The anomalously high values of  $\delta\text{D}$  (reaching  $2446\text{‰}$  in the monimolimnion zone), may be caused by deuterated fluids of juvenile formation waters, which enter the water body from below, or bacterial fractionation by selective absorption of protium by microorganisms.

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