

# Ionic Composition of Water in Lake Baikal, Its Tributaries, and the Angara River Source during the Modern Period

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Received May 28, 2019

Revised June 28, 2019

Accepted June 28, 2019

**Abstract**—The results of long-term routine measurements of the concentration of major ions in the water of the Lake Baikal pelagic zone, the Angara River source, and main tributaries of the lake are analyzed. The average values of ion concentration in the water column of the lake and in the Angara River obtained for the recent decade are presented and compared with the data of previous studies. Long-term trends in the concentration of ions in the main Baikal tributaries are shown. Under low-water conditions, the inflow of ions to Lake Baikal through tributaries decreases despite an increase in their concentration in river water. Changes in the chemical composition of water in the tributaries did not affect the ionic composition of water in the Lake Baikal pelagic zone and in the Angara River source.

**DOI:** 10.3103/S1068373919100078

*Keywords:* Lake Baikal, major ions, concentration, ion sink of rivers, tributaries, Angara River

## INTRODUCTION

The shortage of potable freshwater is a global modern problem. Lake Baikal is the world's largest pure freshwater reservoir, and the preservation of its water quality is important for all mankind.

The lake consists of three basins differing in depth, water exchange, and water mass volume [24, 26]. The external water exchange of Lake Baikal is slowed: about 370 years are needed to replace lake water by water of its tributaries. The deep-water renewal in the lake is provided by the vertical mixing [11, 27, 28]. These factors determine the stability of the chemical composition of Baikal water that was noted by researchers in the 20th century [1, 2].

The development of economic activity in the lake basin in the second half of the 20th century led to changes in its chemical composition and deteriorated water quality in its tributaries and littoral [8, 21] but did not affect the chemical composition of water in the Baikal pelagic zone [5, 7, 25]. The significant deterioration of water quality in the tributaries and littoral of Lake Baikal has been registered in the recent decades under conditions of global warming, a decrease in the total moisture content in the catchment area and in the water inflow to the lake, an increase in anthropogenic load, and an activation of touristic activity [9, 15, 17, 20, 23, 29].

The objective of the present paper is to reveal the features of long-term variations in the ionic composition of water in Lake Baikal, its main tributaries, and the Angara River flowing out of the lake as well as to estimate the inflow and sink of major ions during the modern period.

**Table 1.** Average (weighted in runoff) content of ions (mg/dm<sup>3</sup>) in the River Selenga (Murzino) water in different periods

Period	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total ions
1950–1962 [3]	88.7	6.5	1.23	20.7	4.6	4.1	1.1	127
1971–1974*	113.8	12.4	2.44	27.6	5.2	7.3	2.0	171
1995–1997	97.7	8.4	1.95	20.9	5.8	6.5	1.4	143
2001–2017	98.3	11.4	1.40	23.3	5.1	5.8	1.3	147

Note: \*From data by V.T. Bogdanov (Limnological Institute).

## DATA AND METHODS

Initial data for the analysis are the results of yearly hydrochemical studies of Lake Baikal and its tributaries in 2008–2018 using data from the previous years. Data of analysis of 660 lake water samples taken at one-two deep-water stations in each basin in May–June in 2008–2018 and in August–September in 2011, 2012, 2015, 2017, and 2018 are used. Additionally, water composition in Southern Baikal was analyzed during the under-ice period of 2010, 2016, and 2018. At the deep-water stations, water samples were taken from the depths of 0, 25, 50, 100, 200, and 400 m and further with the step of 200 m to the bottom.

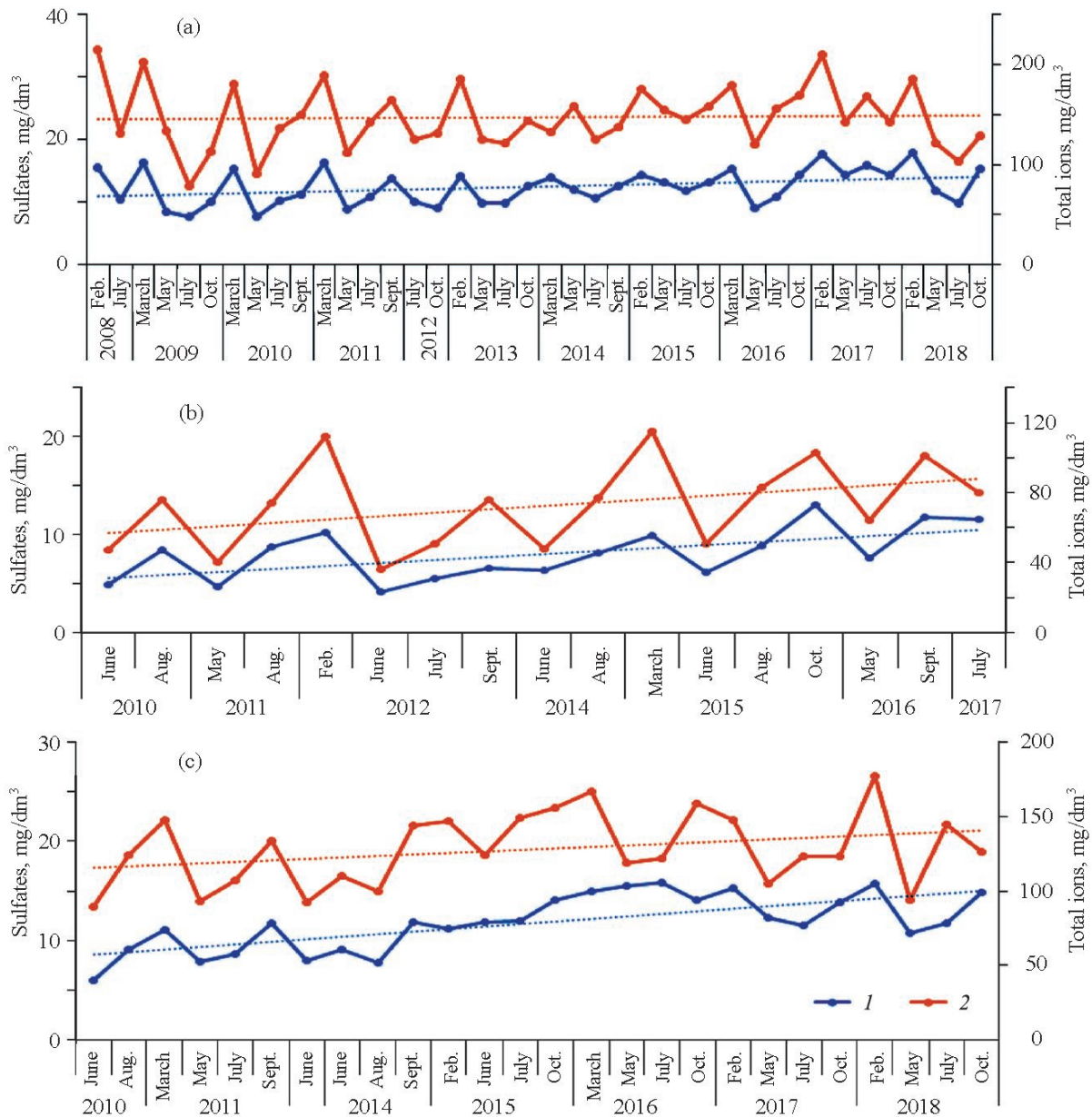
The sampling in the Angara River source was carried out every month in 2014–2018: 55 water samples were analyzed. The studies in monitoring mode were conducted for 22 tributaries. In the main tributaries of the lake (the Selenga, Upper Angara, and Barguzin rivers) as well as in the Southern Baikal tributaries, water samples were taken during the main hydrological phases; for the Central and Northern Baikal tributaries, the samples were taken during the period of open channel.

The concentration of hydrocarbonate in nonfiltered water was determined by potentiometric titration at the sampling point (GOST 31957-2012). The determination of sulfates and chlorides by the high-performance liquid chromatography (FR.1.31.2008.04416) and, since 2015, by the ion chromatography (GOST 31867-2012) was carried out in water samples filtered through the filters with the pore diameter of 0.45 μm in the laboratory of Limnological Institute of the Siberian Branch of Russian Academy of Sciences. The concentration of calcium and magnesium ions was measured by the atomic absorption spectroscopy (PND F 14.1:2:4.137-98), and the concentration of potassium and sodium was measured by the flame emission spectrometry (PND F 14.1:2:4.138-98).

## RESULTS AND DISCUSSION

**Tributaries.** The formation of the chemical composition of water in the Baikal tributaries is determined by the geological structure, soil cover of catchments, amount of precipitation, and groundwater contribution to the recharge of tributaries [3]. The most significant impact of anthropogenic factors on the chemical composition of water in the tributaries is observed for the Selenga River. A change in the chemical composition of the Selenga River water and an increase in the mineralization and concentration of some ions were registered in the 1970s at the peak of development of the Ulan-Ude industrial complex (Table 1). During that period, the concentration of sulfates being an indicator of industrial pollution of water increased twice as compared to the 1950s.

A decline in the industrial production in the 1990s favored the water quality improvement in the Selenga River. Since the beginning of the 2000s, the economic activity in the Selenga River basin on the territory of the Republic of Buryatia and Mongolia intensified again thus causing an increase in the concentration of sulfates and total concentration of ions in the Selenga River water (see Table 1 and Fig. 1). The maximum concentrations of sulfates on the border with Mongolia were equal to 8.5 mg/dm<sup>3</sup> in the 1990s and 16.4 mg/dm<sup>3</sup> in 2010 [17]; in the winter of 2018, sulfates' concentration reached 19.8 mg/dm<sup>3</sup>. In these years, the increase in the mineralization of river water and in the concentration of sulfates was also favored by the river water flow decline by 23% [14]. The high anthropogenic load has been a crucial factor of ion concentration growth in the Selenga River water for many years [13, 18]. In the seasonal dynamics, the highest values of the concentration of sulfates and total concentration of ions in the water of the main tributaries were registered in winter (Fig. 1). An increase in the ion concentration in the Upper Angara water in the recent years can be associated with an increase in the groundwater inflow resulting from the permafrost degradation [15]. In the Barguzin River, an increase in the concentration of ions in water is associated both with water flow reduction and with the increasing anthropogenic load.



**Fig. 1.** The seasonal and interannual dynamics of (1) the concentration of sulfates and (2) total concentration of ions in the water of the main tributaries of Lake Baikal. The dash line is the trend. (a) Selenga River; (b) Upper Angara River; (c) Barguzin River.

The growth of sulfate concentration in the water of the main tributaries of Lake Baikal did not cause significant changes in the relative composition of ions: it remains stable, water corresponds to the hydro-carbonate class, the calcium group.

The rivers of Southern Baikal flowing down the Hamar-Daban Range are characterized by the low mineralization of water (17–133 mg/dm<sup>3</sup>). For many decades the river catchments were situated in the areas affected by industrial emissions from Baikalsk Pulp and Paper Mill (BPPM) and the regional transfer from the Angaro-Cheremkhovskii industrial complex which influence negatively the chemical composition of precipitation and, hence, river water. An increase in the concentration of sulfates in the water of these rivers and a decrease in the concentration of hydrocarbonates and in pH were registered under the influence of acid precipitation. The most significant disturbances of chemical composition were registered for the rivers with low mineralization (the Khara-Murin and Pereemnaya rivers): their water corresponds to the sulfate class, the calcium group during most of the year. An increase in the content of sulfates in the Solzan,

**Table 2.** Average values of ANC (mg-eq./dm<sup>3</sup>) in the water of the investigated rivers at the southeastern shore of Baikal in different years

Period	Utulik	Solzan	Kara-Murin	Snezhnaya	Pereemnaya
1955–1960 [3]	788	538	382	655	219
1996–2012	702	422	242	487	144
2013–2014	752	472	290	557	131
2015–2018	738	465	232	526	109

**Table 3.** The dynamics of content of main ions in the estuary water of the rivers of the southwestern shore of Baikal, mg/dm<sup>3</sup>

River	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Sum of Na <sup>+</sup> and K <sup>+</sup>
Krestovka	<u>25–74</u> 18–105	<u>3.4–6.5</u> 14–27	<u>0.1–1.9</u> 0.6–9.4	<u>6.3–16</u> 6.8–31	<u>0.8–4.7</u> 1.8–8.5	<u>2.2–5.2</u> 3.0–7.7
Kamenushka	<u>73–137</u> 69–179	<u>5.9–10</u> 14–27	<u>0.1–0.9</u> 2.3–9.6	<u>16–27</u> 19–41	<u>6–14</u> 5–16	<u>4.4–13</u> 2.1–18
Bolshaya	<u>56–109</u>	<u>3.4–8.0</u>	<u>0.1–2.2</u>	<u>14–25</u>	<u>2.4–6.5</u>	<u>2.5–7.4</u>
Cheremshanka	44–182	21–43	2.7–23	21–54	5.3–17	4.0–16
Malaya	<u>112</u>	<u>2.3</u>	<u>0.3</u>	<u>15</u>	<u>0.2</u>	<u>26</u>
Cheremshanka	34–140	21–50	1.1–73	11–57	2.9–16	4.1–39

Note: The numerator contains data from paper [3] (for Malaya Cheremshanka, data for July 1955), the denominator, data by the authors.

Utulik, and Snezhnaya rivers did not induce changes in the relative composition of ions, water in them corresponds to the hydrocarbonate class, the calcium group [16]. An increase in the concentration of acid components reduced the acidification resistance of water, which is indicated by the values of ANC (acid-neutralizing capacity). The rivers with very low buffer capacity (Khara-Murin and Pereemnaya) are the most subjected to acidification (Table 2). Water in the Solzan, Utulik, and Snezhnaya rivers have high buffer capacity and, hence, are more resistant to acidification [19]. As clear from the results, the situation slightly improved after the closure of BPPM (2013–2014); however, the acidification of river water coming from the eastern coast of the lake has recently increased again due to a decrease in pH of precipitation being the main source of recharge for these rivers [22].

The most complicated ecological situation is registered on the tributaries of the southwestern shore of Southern Baikal in the area of the Listvennichnyi Bay (Listvyanka settlement). The intense development of tourism, the construction of hotels, and, hence, the increase in the volume of domestic wastewater led to the increase in the concentration of polluting components in water [23]. The concentration of major ions in river water as compared to the 1950s increased by several times (Table 3), the maximum was registered in winter. The small water runoff of these rivers and the low dilution capacity provoked dramatic increase in the concentration of major ions as a result of wastewater inflow. Despite the ion concentration increase, the water class still remains hydrocarbonate (calcium group).

The rivers flowing into Northern Baikal are characterized by the low concentration of major ions. In accordance to the changes in water runoff, minimum concentrations are typical of the spring flood or high summer floods. In terms of the concentration of major ions, water of the Kichera, Rel', and other tributaries of Northern Baikal belongs to the hydrocarbonate class, the calcium group. Due to the absence of the significant sources of pollution in the catchments, the composition of their water remains stable. The exception is the Tyva River. There the wastewater inflow from the treatment facilities of the town of Severobaikal'sk at the distance of about 2 km upstream of the mouth disturbed the dynamics of the concentration of biogenic elements [29] and a periodic increase in the concentration of sodium, chlorides, and sulfates in the river mouth area.

Thus, it follows from the above that the formation of the chemical composition of water of Lake Baikal tributaries during the modern period is defined by natural and anthropogenic factors. Under the influence of

**Table 4.** Content and removal of sulfates and total ions with the water of main tributaries

Period	Water runoff, km <sup>3</sup> /year	Sulfates		Total ions	
		C, mg/dm <sup>3</sup>	Removal, t/year	C, mg/dm <sup>3</sup>	Removal, t/year
Selenga River					
1950–1961 [3]	28.3	6.5	176	127	3444
2010–2017	22.0	11.4	241	145	3185
Verkhnyaya Angara River					
1950–1955 [3]	7.84	3.7	30.6	81	672
2010–2017	7.65	8.5	64.7	90	691
Barguzin River					
1950–1960 [3]	3.97	7.9	30.2	131	500
2010–2017	2.85	11.7	33.3	134	384

Note: C is mean concentration.

the latter factors, an increase in the concentration of sulfates, chlorides, sodium, and other components in water is registered; it leads to changes in the relative composition of ions in the rivers with low buffer capacity.

In the recent two decades, the formation of the chemical composition of river water and the inflow of ions to the lake has been affected by water runoff reduction. Table 4 demonstrates changes in the sink of total ions and sulfates with water of the main tributaries of the lake as compared to data for the 1950s–1960s [3]. The calculation of the transport of these components by rivers is based on monthly mean concentrations of ions and monthly mean water flow (the river runoff is taken according to Roshydromet data). In case of data gaps, the corresponding dependences were used between water and chemical runoff of rivers which are characterized by a rather close connection: the coefficients of determination are from 0.74 to 0.85 for sulfates and from 0.82 to 0.98 for total ions. As clear from the results, the ion sink from the Selenga and Barguzin rivers to the lake decreased as the water flow decreased despite the ion concentration increase; at the same time, the increase in the ion sink of the Upper Angara River is caused only by the ion concentration growth. The inflow of sulfates to the lake with water of these main tributaries increased.

The average ion sink to Lake Baikal for 2010–2017 was equal to  $6.5 \cdot 10^6$  t/year and is generally comparable with the estimates presented in [3] ( $6.6 \cdot 10^6$  t). However, such coincidence is mainly explained by the low inflow of river water to the lake during the period of the studies conducted by the authors (Table 4) and by the increase in the concentration of some ions. In the years with high river runoff, for example, in 2012, when the inflow to the lake reached 65.2 km<sup>3</sup>, the ion sink to the lake grew up to  $7.7 \cdot 10^6$  t.

**Lake Baikal and the Angara River.** The tributaries of the lake are the main source of the inflow of dissolved substances to the lake and can affect the chemical composition of its water. Nevertheless, due to the huge volume of Baikal and low water exchange, the ionic composition of its water remains rather stable.

The concentration measured in the water column of the pelagic zone of the lake in different seasons varied from 61.5 to 68.3 mg/dm<sup>3</sup> for hydrocarbonates, from 4.48 to 6.13 mg/dm<sup>3</sup> for sulfates, and from 0.29 to 0.60 mg/dm<sup>3</sup> for chlorides. The concentration of ions varied within 15.04–17.07 mg/dm<sup>3</sup> for calcium, 2.84–3.27 mg/dm<sup>3</sup> for magnesium, 3.11–3.83 mg/dm<sup>3</sup> for sodium, and 0.83–1.09 mg/dm<sup>3</sup> for potassium. The largest relative range of concentration variations is registered for chlorides due to their low content (at the limit of the lower range of determination method). Both maximum and minimum values of ion concentration were registered in different water samples. The discrepancy in the ionic balance calculated from the relationship between the difference and sum of gram-equivalents of anions and cations basically makes up 1–3%. No regularities are observed in the vertical distribution of ion concentration across the lake area.

Based on data on the concentration of each component, their mean concentrations and the variation coefficient for the separate basins, for the whole lake, and for the Angara River source are calculated (Table 5). The results demonstrate that the mean concentrations of major ions in the lake basins are

**Table 5.** Average values of concentration  $C$ , variation coefficient ( $C_v$ ), and the accuracy indicator ( ) of measurement methods for main ions' content in Lake Baikal and in the Angara River source

Sampling place	Indicator	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
Southern Baikal	$C$ , mg/dm <sup>3</sup>	65.04	5.36	0.47	16.01	3.03	3.36	0.96
	$C_v$ , %	2.6	6.2	10.6	2.5	3.9	2.3	3.0
	, mg/dm <sup>3</sup>	4.37	0.90	0.10	2.02	0.51	0.48	0.16
Middle Baikal	$C$ , mg/dm <sup>3</sup>	65.26	5.34	0.46	16.01	3.04	3.36	0.96
	$C_v$ , %	2.1	5.4	12.1	1.6	2.3	2.7	2.4
	, mg/dm <sup>3</sup>	4.39	0.90	0.10	2.02	0.51	0.48	0.16
Northern Baikal	$C$ , mg/dm <sup>3</sup>	64.82	5.31	0.46	16.04	3.03	3.35	0.95
	$C_v$ , %	1.9	3.4	11.3	1.7	2.7	3.1	2.3
	, mg/dm <sup>3</sup>	4.36	0.89	0.10	2.02	0.51	0.48	0.16
The whole lake	$C$ , mg/dm <sup>3</sup>	65.05	5.34	0.46	16.02	3.03	3.36	0.96
	$C_v$ , %	2.3	5.4	11.3	2.1	3.2	2.6	2.7
	, mg/dm <sup>3</sup>	4.37	0.90	0.10	2.02	0.51	0.48	0.16
Angara River	$C$ , mg/dm <sup>3</sup>	65.59	5.61	0.45	16.20	3.06	3.41	0.98
	$C_v$ , %	3.4	3.4	10.1	2.6	2.9	2.5	2.9
	, mg/dm <sup>3</sup>	4.41	0.94	0.09	2.04	0.51	0.49	0.16

comparable to each other, and the homogeneity of water masses in the basins is also indicated by the low values of variation coefficient.

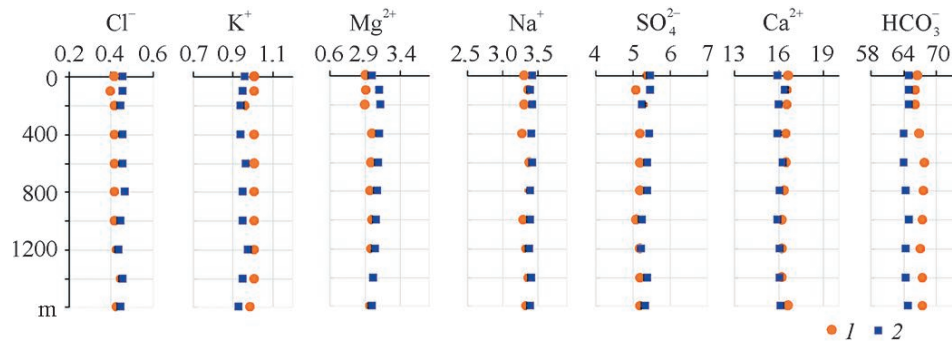
Data obtained in June in 1998 and 2018 are used to assess interannual dynamics. Taking into account that the averaging of data at separate horizons in the lake basins always smooths the inhomogeneity of the vertical distribution of ion concentration, Figure 2 presents the distribution of ions at a separate station in the central basin. It is clear that discrepancies in the ion concentrations have various directions and do not exceed the measurement method accuracy. Differences in the concentration of some ions as compared to the 1950s [1, 2] are caused by the use of different determination methods.

Data of studying the chemical composition of water in the Angara River source [6, 10, 12] indicate that an increase in the concentration of sulfates, chlorides, and magnesium ions occurred by the end of the 20th century. Wastewater from BPPM is considered as the source of sulfates in Lake Baikal and, hence, in the Angara River source. However, paper [4] performing the correlation analysis between the concentration of sulfates and ions of sodium whose significant amount came to the lake with the BPPM wastewater revealed that the BPPM wastewater could not be the source of such significant increase in sulfate concentration.

According to the results of our studies, the mean concentration of major ions in the Angara River source corresponds to that in Baikal (see Table 5). The comparison of the obtained values with the mean values for 2001–2010 presented in [12] demonstrated that the discrepancies do not exceed the measurement method accuracy (except for the concentration of chlorides) and are caused by the use of different measurement methods. The possible mineralization increase in winter in the thin under-ice layer of Baikal water resulting from the ice formation is leveled by dilution, and the ion concentration growth is not registered in the Angara River.

Thus, the seasonal and interannual variations in the concentration of major ions in water of the lake and the Angara River source during the analyzed period do not exceed the accuracy of measurement methods. The results show that the concentrations of major ions in the lake and in the Angara River source are close and remain stable for many years.

**Ion sink with the Angara River water.** In accordance with the above stability of the ionic composition of water in Lake Baikal and in the Angara River, the ion sink from the lake almost fully depends on the river water runoff. Despite the fact that the low-water period accompanied by the decrease in the lake water level and in the Angara River runoff has continued on Lake Baikal since the beginning of the 21st century [14], the concentration of major ions in the Angara River water did not almost change according to the results of studies in 2014–2017. For example, the average weighted (based on runoff) concentrations of hydrocarbonates and the total concentration of ions for different years differed within 0.1–0.2 mg/dm<sup>3</sup>, and the range of their variation did not exceed 9.4 mg/dm<sup>3</sup> for all 55 samples. In view of this, the ion sink from the lake varied in accordance to the Angara River runoff and was equal to  $3.9 \cdot 10^6$  t/year in the lowest-water years 2015–2016 (at the runoff of 40.6–40.7 km<sup>3</sup>/year) and to  $4.9 \cdot 10^6$  t/year in 2014, when the high runoff



**Fig. 2.** The vertical distribution of the concentration of major ions ( $\text{mg}/\text{dm}^3$ ) at Ukhan-Tonkii central station in Central Baikal in June in (1) 1998 and (2) 2018.

( $51.6 \text{ km}^3/\text{year}$ ) was registered. According to [3], the ion sink in the 1950s was equal to  $5.76 \cdot 10^6 \text{ t}/\text{year}$  at the water runoff of  $60.1 \text{ km}^3/\text{year}$ .

## CONCLUSIONS

At present, water in Lake Baikal and in the Angara River source is of the hydrocarbonate class, the calcium group. Low water flow, high anthropogenic load on the tributaries, and permafrost degradation have caused the increase in the concentration of major ions in river water in the recent decade. As compared to the 1950s, the concentration of ions considerably increased in the mouth areas of the small tributaries of the Listvenichnyi Bay due to recreation and touristic activity. Under low-water conditions, there is a decrease in the inflow of ions to Lake Baikal with water of the tributaries, despite the increase in their concentration in river water. The changes in water of the tributaries did not affect the ionic composition of water in the pelagic zone of Lake Baikal and in the Angara River source. The concentration of hydrocarbonates, sulfates, chlorides, calcium, magnesium, sodium, and potassium remains stable both on seasonal and interannual scales; the variations in their content are within the measurement method accuracy. The output of major ions with the Angara River water depends on the value of water runoff alone.

## FUNDING

The studies were performed in the framework of the state task 0345-2019-0008 of Limnological Institute of Siberian Branch of Russian Academy of Sciences.

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