**RESEARCH IN THE BAIKAL WATERSHED**

# **Assessing the Water Quality in the Tributary Streams of Lake Baikal From Chemical Parameters**

**L. M. Sorokovikova, V. N. Sinyukovich, I. V. Tomberg, I. I. Marinaite, and T. V. Khodzher**

*Limnological Institute, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia*

*e-mail: lara@lin.irk.ru e-mail: sin@lin.irk.ru e-mail: kaktus@lin.irk.ru e-mail: marin@lin.irk.ru e-mail: khodher@lin.irk.ru* Received July 25, 2014

**Abstract—**On the basis of hydrochemical investigations from 2010−2012 and with due regard for earlier data, we assess the present status of water quality for the main tributary streams of Lake Baikal. An analysis is made of the observed changes in the chemical composition of water induced by natural and anthropogenic factors. It is shown that the deterioration of the water quality in the Selenga river and in the small tributaries of South Baikal, respectively, is caused by wastewater discharges and by pollution of atmospheric precipitation, respectively.

**DOI:** 10.1134/S1875372815010059

*Keywords:* chemical composition, water quality, streamflow, petroleum products, biogenic elements, PAHs.

# INTRODUCTION

Changes in natural conditions and enhancements in anthropogenic pressure are accompanied by a transformation of various intra-water body processes (the water, thermal and hydrochemical regimes, transport of sediments, etc.) in water bodies and have largely a negative influence on the quality of surface waters. At the end of the  $20<sup>th</sup>$  century the input of pollutants to the tributary streams of Lake Baikal decreased due to a setback in industrial production [1]. Such a decrease in the input of separate components to the lake was also favored by a decline in general moistening over most of the lake's drainage area [2]. The sole exception is provided by the northern areas of the Baikal drainage basin where, as a result of a degradation of permafrost, an increase in water and chemical flow of the rivers is observed.

The objective of this paper is to analyze the contemporary chemical composition of the rivers within the Lake Baikal Drainage basin, and to assess their quality for chemical parameters.

# MATERIALS AND METHODS

During 2010–2012 we carried out the most comprehensive (since the end of the  $20<sup>th</sup>$  century) hydrochemical investigations of the main tributary streams of Lake Baikal. The Selenga was investigated from the Mongolian border to its inflow into Baikal, including the main tributaries and branches of the delta; the Upper Angara and Barguzin from the mouth

and 100–120 km upstream. Water samples were also collected in the mouths of the main tributary streams of South Baikal rising in the Khamar-Daban Range (Snezhnaya, Utulik, Khara-Murin, Pereemnaya, and Solzan), and of the main tributary streams of North Baikal (Kichera, Rel', and Tyya). The schematic map of the aforementioned streams, on which 294 water samples were collected for analyses, is provided in Fig. 1.

The hydraulicity of the rivers under investigation was assessed using data from Rosgidromet (Federal Service for Hydrometeorology and Environmental Monitoring of Russia). For assessing the ongoing streamflow fluctuations the parameters of its variability were adjusted to a single calculated period represented by the time interval from 1959 to 2010 which included two cycles of hydraulicity.

The determination of cations was carried out by the atomic absorption and plasma emission methods; anions were determined by the method of high performance liquid chromatography (HPLQ) [3, 4]. The reliability of the findings was monitored from the value of the error of ionic balance and through a comparison of the calculated and measured conductivity [5]. The determination of biogenic elements was performed by calorimetric methods [4]. The concentration of polycyclic aromatic hydrocarbons (PAH) was determined by the method of chromatemass-spectrometry [6]. The quantification of separate PAH (phenathrene d10, chrysene d12 and perylene d12) was carried out by using Supelco (USA) standards.



**Fig. 1.** General location map of the tributary streams of Lake Baikal under consideration. The inset map shows the tributary streams of South Baikal.

The data obtained have been correlated with results of hydrochemical investigations of the tributary streams of Lake Baikal that were made in the mid- $20<sup>th</sup>$  century [7] and in subsequent years [1, 8, 9]. The constant location of the observation sites at different times improves the reliability of the estimates obtained for the chemical composition of river waters as well as of predictions of its changes.

# RESULTS AND DISCUSSION

## *Hydrological Conditions*

Climate change on Baikal, associated with an intensification of global warming since the beginning of the 1970s, influenced the dynamics of the hydrological processes within its drainage basin [2, 10]. Comparison of some characteristics of the flow of the main rivers and the total inflow of water to the lake shows that during the period under study there was taking place a general decrease in inflow at a rate of about 1 km<sup>3</sup> for 10 years, and since the beginning of warming up to 12  $km<sup>3</sup>$  for 10 years.

During 1996–2012 the inflow to the lake was, on the average, 8% below normal (Table 1). Specifically, the Selenga flow, the main tributary stream of the lake, decreased by 23%, and only because of an increase in the streamflow of the other Baikalian rivers (primarily the Upper Angara) was the decrease in the total inflow of the river waters from the lake's drainage basin not as critical.

An assessment of the interannual fluctuations in

discharge of the other rivers shows that statistically significant long-term tendencies for a decrease or an increase in their hydraulicity are absent (the reliability of the corresponding trends below the 5% significance level).

In addition to inter-annual variability in the inflow of water to Lake Baikal and hydraulicity of separate rivers, a warming also influenced the intra-annual runoff distribution. A rise of temperature and the melting-out of ice in degrading permafrost leads to an increase in groundwater storage and in streamflow, especially in the wintertime. For the warming period the mean lowwater (November–March) flow of the Upper Angara and Selenga increased by about 6.3  $\text{m}^3\text{/s}$  (8.1%) and 20 m3 /s (13%), respectively. In recent years, however, the Selenga showed its marked decrease caused by a decrease in moisture saturation of the active layer and in groundwater storage due to a general decline in moistening within its basin. In Kabansk, for example, a reduction in annual precipitation amounts, starting in the latter half of the  $20<sup>th</sup>$  century, was 49 mm [2].

As regards the tributary streams of South Baikal, the tendencies for an increase in winter streamflow are also sufficiently unstable and are interrupted by years with a decreased winter flow. For instance, the winter water flow rate of the Snezhnaya river was particularly increased during 1993–2001, while in the time interval 2002–2005 its discharge was, on the contrary, lowest for the entire period of observations. Only for the Khara-Murin river the discharge of the first quarter (January– March) is characterized by a constant increase, with a significance level above 1%, which was also observed previously [11]. Along with an increase in hydraulicity of the winter months, some decrease in the discharge of the rivers during a warm season deserves mention.

The aforementioned changes in the discharge of the rivers within the Lake Baikal basin are all accompanied by a transformation of the other characteristics of river waters, including contents of dissolved and suspended solids arriving at the lake. Using the Selenga river as an example, it becomes apparent [2] that a decrease in dissolved solids carried by the river is more pronounced at periods of exceptionally low hydraulicity, in spite of a general growth in mineralization of its waters. A decrease in chemical flow to Baikal with the waters of the tributary streams can cause a deficit of separate elements in its ecosystem. With a shortage of biogenic

**Table 1.** Streamflow of the main rivers of the Lake Baikal drainage basin and its inflow for different periods, km<sup>3</sup>/year

Streamflow		Total		
	Selenga	Upper Angara   Barguzin		inflow
Average long-term	28.0	8.66	4.00	63.5
$1971 - 2012$	26.5	8.82	4.05	62.8
1996-2012	21.7	944	4.06	58.5

elements lasting a long time, the production processes will be decreasing at least in the intensity of the production processes the coastal zone where the waters of the tributaries have the lead.

# *Mineralization and Main Ions*

Almost no exceedances of the standards [12] of the mineralization values of river waters and content levels of main ions within the Lake Baikal drainage basin are recorded (Tables 2 and 3); however, these parameters undergo rather impressive spatiotemporal fluctuations and call for detailed examination.

Research results for the time interval 2010–2012 show that the chemical composition of the Selenga waters, when compared with 1950–1960 [7], underwent marked changes along the entire length of the river. The sum of ions  $(\Sigma i)$  in the river downstream of the Russian-Mongolian border (settlement of Naushki) varied with hydraulicity from 142 to 262 mg/dm<sup>3</sup> (Fig.

River Na<sup>+</sup> K<sup>+</sup> Ca2+ Mg2+ Clˉ SO<sup>4</sup>  $SO_4^2$  HCO<sub>3</sub>  $\Sigma$ i Upper Angara, upstream of the Yanchui mouth\* 0.9 | 0.14 | 4.0 | 0.4 | 0.05 | 1.4 | 5.9 | 10.7 Upper Angara, upstream of the Kichera mouth 0.7–5.4 0.43–0.87 5.9–17.6 0.91–3.3 0.13–0.43 4.2–10.2 23.5–74.1 35.9–111.8 Upper Angara, mouth (Kicherskaya Prorva) 1.2–3.7 0.37–0.91 9.6–16.9 1.6–2.9 0.07–0.32 5.5–8.0 32.94–69.54 51.3–102.3 Kholodnaya 0.5–1.1 0.26–0.59 6.4–14.4 1.12–2.6 0.01–0.16 4.5–10.1 10.3–47.5 23.0–76.4 Kichera 0.8–1.9 0.36–0.70 3.2–6.7 0.51–0.9 0.04–0.20 5.0–5.5 16.5–25.2 28.5–40.5

Tyya 0.5–1.4 0.47–1.25 5.6–17.8 1.5–5.5 0.05–0.88 4.3–9.2 21.4–75. 9 34–111.9 Rel' 0.5–4.4 0.25–1.92 1.8–8.7 0.1–0.4 0.16–0.30 1.3–4.6 3.2–36.6 7.3–12.6 Yanchui\* 1.9 | 0.8 | 0.24 | 3.96 | 0.45 | 0.11 | 1.9 | 13.8 | 21.3 Gonkuli\* 1.2 0.52 27.9 8.9 0.04 12.4 113.5 164.4 Katera\* 10.7 | 0.44 | 15.1 | 1.6 | 0.03 | 10.4 | 4.7 | 70.0 MPC [12]\*\* 200 – – – 350 500 – 1000



\* Samples collected in July.

\*\* For noncentralized water supply.

**Table 3.** Limits of concentrations of main ions in the water of the rivers within the Barguzin basin and the tributary streams of South Baikal (2011), mg/dm<sup>3</sup>

River	$Na+$	$K^+$	$Ca^{2+}$	$Mg^{2+}$	Cl <sup>2</sup>	$SO_4^2$	HCO <sub>3</sub>	$\sum i$
Barguzin, upstream of the Argada mouth	$1.1 - 5.0$	$0.66 - 1.39$	$25.0 - 36.7$	$1.2 - 3.1$	$0.11 - 0.49$	$10.0 - 15.1$	73.2-124.41	$115.0 - 181.7$
Barguzin, mouth	$2.3 - 5.2$	$0.73 - 1.2$	$16.7 - 28.4$	$1.8 - 2.8$	$0.48 - 1.46$	$7.5 - 11.6$	$60 - 98.8$	$92.8 - 148.0$
$Ulyun*$	0.93	1.44	30.3	1.4	0.11	20.2	76.9	131.2
Alla*	0.53	1.19	23.9	0.9	0.13	15.5	59.8	102.0
Argada	$1.9 - 4.9$	$0.84 - 2.22$	$10.6 - 57.2$	$2.1 - 10.4$	$0.14 - 0.51$	$4.0 - 7.6$	$43.3 - 268.4$	62.9-347.7
Ina	$0.8 - 2.9$	$0.45 - 0.95$	$6.45 - 21.4$	$1.6 - 5.8$	$0.13 - 0.46$	$4.6 - 22.4$	$32.6 - 76.9$	$49.4 - 130.5$
Utulik	$1.1 - 2.8$	$1.30 - 2.70$	$8.2 - 20.2$	$1.8 - 5.7$	$0.08 - 0.31$	$9.7 - 37.1$	$25.7 - 59.4$	$47.9 - 127.5$
Solzan	$0.7 - 1.2$	$1.53 - 2.14$	$5.3 - 20.2$	$1.1 - 2.1$	$0.09 - 0.31$	$4.8 - 37.1$	$18.2 - 34.4$	$32.0 - 61.4$
Khara-Murin	$0.9 - 2.3$	$0.77 - 0.96$	$3.3 - 8.0$	$0.8 - 1.8$	$0.11 - 0.29$	$4.8 - 12.6$	$10.4 - 24.4$	$21.1 - 48.8$
Snezhnaya	$0.8 - 1.3$	$0.68 - 0.83$	$6.4 - 15.3$	$0.9 - 1.8$	$0.09 - 0.27$	$5.5 - 11.6$	$19.0 - 46.7$	33.4 - 77.7
Pereemnaya	$0.8 - 1.3$	$0.53 - 0.75$	$2.9 - 6.1$	$0.5 - 0.9$	$0.04 - 0.33$	$6.3 - 14.5$	$6.1 - 10.1$	$17.4 - 33.1$
<b>MPC</b> [12]	200				350	500		1000

\*Samples collected in July.



**Fig. 2.** Variation in the sum of ions in the water of the tributary streams of Lake Baikal under investigation, for 2010–2012. (а) Selenga, (b) Barguzin, (c) Upper Angara. (1) March, (2) June, (3) July, (4) September.

2, а). In the lower reach, as a result of the input of the less mineralized waters of the tributaries, except for the Dzhida waters  $(181-273 \text{ mg/dm}^3)$ ,  $\Sigma$ i decreased to 91–189 mg/dm<sup>3</sup> . Within the inter-annual context, the concentrations of the main ions and their sum in 2012 were lower than during 2001–2005 [1] because of the higher hydraulicity. The Selenga waters showed a considerable increase in sulfate concentrations which was largely determined by the level of anthropogenic pressure. In the lower reach of the river, their maximum values were recorded during 1970–1980, followed by a further decrease (during the 1990s) because

of a decline in industrial production in the Baikal region [1]. A recent increase in sulfate concentration, especially during a winter season, is due to an increase in the contribution from groundwater alimentation of the river in conditions of decreased hydraulicity as well as to an intensification of the economic activities, mainly in Mongolia. In the waters arriving from the territory of Mongolia, the concentration of sulfates and chlorides increased by a factor of two [13]. Compared to the mid-20<sup>th</sup> century, the range of present-day  $SO_4^{2-}$ concentrations in the Selenga waters has increased from 6.2–8.6 [7] to 7.6–18.7 mg/dm<sup>3</sup>.

According to relative content of the main ions, the waters of the Selenga and its tributaries along the entire length refer to a hydrocarbonate class, the calcium group. Within the long-term context, the relative content of ions in the river waters remains rather stable [1, 7, 8]. Mineralization of water and concentration of main ions in the water of the Selenga and its tributaries do not exceed MPC standards [12] for watercourses used for recreational purposes and for uncentralized water supply.

Analysis of the concentration of ions and their sum in the water of the Upper Angara, ranking second in hydraulicity among the tributary streams of Lake Baikal, as well as in its tributaries, gives evidence of a considerably smaller variability in absolute concentrations of the main ions within a long-term context. The sum of ions over the course of the year 2012 varied from 10.7 to 111.8 mg/dm<sup>3</sup> (see Fig. 2, c), with a maximum at the winter period and a minimum at the flood period. Along the length of the river, the lowest concentration of the ions and their lowest sum were observed in its upper reach (see Table 2). Thus, in July in the Upper Angara water, along the stretch upstream of the inflow of the Yanchui river, Σi was 10.7 mg/dm<sup>3</sup> , increasing along the stretch upstream of the inflow of the Kichera due to the more mineralized waters of the tributaries to  $64.4 \text{ mg/dm}^3$ , whereas nearer to the mouth, under the influence of the Kichera waters, decreasing again to 51.3 mg/dm<sup>3</sup>.

The Rel' and Tyya rivers, like the Upper Angara, flowing into North Baikal, are distinguished for low concentrations of the main ions. In accordance with changes in streamflow, their minimum values are characteristic for a high-water season, or for high summer flood. According to relative content of main ions, the waters of the Upper Angara, its tributaries as well as of the Rel' and Tyya refer to a hydrocarbonate class, the calcium group.

In the water of the Barguzin river and its tributaries, the concentration of the main ions and their total content within a long-term context has also changed little, except for the concentration of sulfate, with its increase observed since the mid-20<sup>th</sup> century [1, 7]. Seasonally, the highest ion concentration was observed at the period of winter runoff low (see Fig. 2, b). Along the length of the river, the highest values are recorded in the upriver, decreasing downstream as a result of dilution by the waters of the tributaries. This pattern also applies for the Argada river, in the water of which the sum of ions in winter increases to  $347 \text{ mg/dm}^3$ , but the water flow is very low at that period. The range of variation in ion concentration in the Barguzin water and its tributaries (see Table 3) reflects the character of formation of the chemical composition of the waters, the intra-annual variations of which, as is the case with the other rivers, are determined by the seasonal dynamics of streamflow. According to the composition of the main ions, the Barguzin waters refer to a hydrocarbonate class, the calcium group.

The rivers of South Baikal (Snezhnaya, Utulik, Khara-Murin, Solzan, and Pereemnaya), because of considerable elevations of their basins and increased humidity, are distinguished, as is the case with the tributary streams of North Baikal, for low mineralization (see Table 3). The lowest ion concentration was recorded in the water of the Pereemnaya river.

Over the course of many decades the catchments of the rivers under consideration were situated in the influence area of industrial discharges from the Baikalsk Pulp and Paper Mill and the regional transfer from the Angara-Cheremkhovo industrial complex having a negative influence on the chemical composition of atmospheric precipitation and, as a consequence, of the river waters [9]. Under the effect of acid atmospheric precipitation, the Khara-Murin and Pereemnaya rivers, having a low buffer capacity, showed a decrease in resistance of the waters to acidification [9]. According to the composition of ions, over most of the year the water of these two rivers refers to a sulfate class, the calcium group. The waters of the Solzan, Utulik and Snezhnaya rivers, having a higher buffer capacity and being more resistant to acidification, refer to a hydrocarbonate class, the calcium group. Compared to the period 1950–1960, the relative composition of the main ions in the water of the tributary streams of South Baikal showed an increase in content of sulfates under the effect of anthropogenic factors. The concentration of the standardized components in the water of the tributary streams of South Baikal does not exceed MPC [12] for the water bodies of uncentralized water supply and of recreational purposes.

#### *Biogenic Elements*

The quality of natural waters and the ecological state of water bodies depend to a large measure on contents of biogenic elements and organic matter in them. The most important parameters is represented by the concentration of different forms of nitrogen and phosphorus, promoting an intensification of phytoplankton development, the production of readily hydrolyzed organic matter, and eutrophication of water bodies [14]. In the tributary streams of Baikal, contents of biogenic elements and organic matter depend on the natural conditions of their respective drainage basins, and on the level of anthropogenic pressure; therefore, they differ greatly (Table 4).

The highest concentrations of biogenic elements are observed in the Selenga water, the basin of which is characterized by the most developed industries and agriculture; the lowest concentrations are typical of the water of the Upper Angara and its tributaries because of poor development of the basins of these rivers. The seasonal dynamics of concentrations of biogenic elements is mainly determined by changes in streamflow, and by the intensity of phytoplankton development. Increased concentrations of ammonium nitrogen and organic matter are characteristic for

**Table 4.** Limits of variation in concentrations of biogenic elements in the water of the main tributary streams of Lake Baikal

	River					
Components	Selenga	<b>Upper Angara</b>	Barguzin			
$O_2$ , mg/dm <sup>3</sup>	$4.9 - 12.1$	$7.6 - 12.6$	$5.7 - 12.4$			
$NH4$ , mg N/dm <sup>3</sup>	$0.02 - 0.38$	$0.01 - 029$	$0.03 - 0.32$			
$NO_2$ , mg $N/dm3$	$0 - 0.004$	$0 - 0.005$	$0 - 0.002$			
$NO3$ , mg $N/dm3$	$0.02 - 0.40$	$0.02 - 0.27$	$0.03 - 0.21$			
$PO_{4}^{3}$ , µg $P/dm^{3}$	$2 - 40$	$0 - 9$	$2 - 25$			
$P_{\text{tot}}$ , µg P/dm <sup>3</sup>	18-346	$9 - 23$	$12 - 181$			
BO, mg $O/dm3$	$5.4 - 18.5$	$3.6 - 14.4$	$2.3 - 32.3$			

the high-water and flash-flood seasons; decreased concentrations are typical of the wintertime with no overland runoff from the catchment area. Conversely, the highest and lowest concentrations of nitrate nitrogen and mineral phosphorus are recorded in winters and at the period of summer runoff low, respectively.

According to an ecological classification [15] and SanPiN (Russian abbrev.: Sanitary Regulations and Standards), the Selenga water as regards the content levels of biogenic elements and organic matter largely corresponds to the "quite clean" and "sufficiently clean" categories. The only exception is provided by the border stretch of the Selenga (downstream of the settlement of Naushki), where total phosphorus concentration in 2010 were characteristic for heavily polluted eutrophic watercourses.

An increase in content of biogenic elements throughout a year is also observed downstream of Ulan-Ude, including the branches of the delta, but it does not exceed the MPC standards for water courses of recreational purposes. In conditions of low hydraulicity, however, the development level of the phytoplankton in the lower reach of the Selenga and in the branches of its delta reaches values characteristic for highly eutrophic water bodies [16].

As regards the content levels of biogenic elements  $(NH_4^+$ ,  $NO_3$ , and  $PO_4^3$ ), the waters of the Upper Angara, its tributaries and of the other rivers of North Baikal correspond to the "very clean" and "quite clean" categories. Among the tributaries of the Upper Angara, the "weakly polluted" water quality corresponds to the Katera river where the content level of nitrogen compounds reached 0.54 mg N/dm<sup>3</sup> , with 0.39 mg N/ dm3 was accounted for by NH4. In the Tyya and Rel' rivers, the  $NO_3$  concentration was 0.27 and 0.72 mg N/dm<sup>3</sup> , respectively, while the content of mineral phosphorus in them was at a level of 1  $\mu$ g P/dm<sup>3</sup>. The concentration of biogenic elements as observed in the tributary streams of North Baikal did not exceed the MPC standards for watercourses of recreational purposes [12].

The water quality of the Barguzin and its tributaries as regards the content levels of biogens varied from the "quite clean" to the "polluted" category, and a deterioration of the water quality is recorded mainly in the lower reaches of the river. Among the tributaries of the Barguzin, the cleanest water was observed in the Ulyun river, and the polluted water in the Argada river, especially in the wintertime, which is due to an extremely low concentration of water diluted oxygen (up to  $0.30 \text{ mg/dm}^3$ ), with a threat of suffocation and death of hydrobionts. At that period, the water in the Argada corresponded to the "extremely dirty" category.

In the water of the tributary streams of South Baikal, concentrations of phosphorus and ammonia nitrogen are mostly recorded at the sensitivity level of the method, whereas the content of nitrate nitrogen varies over the range  $0.22-1.39$  mg N/dm<sup>3</sup>, with the maximum in the Utulik water. In accordance with a classification [15], the waters of the tributaries (except for the Utulik) belong in the «sufficiently clean" category according to nitrate nitrogen content. In spite of the Utulik water quality ranging from "moderately polluted" to "heavily polluted", nitrogen concentration did not exceed the MPC standards [12] for water bodies of recreational purposes.

Content of water dissolved oxygen in all the rivers under investigation is favorable for the life of hydrobionts, except for the Argada in the wintertime.

# *Petroleum Products and Polycyclic Aromatic Hydrocarbons*

The most widespread and hazardous ecotoxicants in water bodies are represented by complex organic compounds: petroleum products, and polycyclic aromatic hydrocarbons (PAH). MPC of petroleum product for water bodies of fisheries and drinking purposes is  $0.05$  and  $0.1$  mg/dm<sup>3</sup>, respectively [17]. The concentration of petroleum products in the water of the Selenga, Upper Angara and Barguzin varied from 0.004 to 0.095, from 0.004 to 0.018 and from  $0.005$  to  $0.026$  mg/dm<sup>3</sup>, respectively, for the period under study. Seasonally, the highest concentration of petroleum products is characteristic for a high-water season, which is due to their input from the drainage basin together with melt waters. Increased contents of petroleum products are most common in the area of settlements. An increase in MPC of petroleum products by a factor of 1.5–2 for water bodies of fisheries purposes was observed at regular intervals in the lower reach of the Selenga, and in the branches of its delta. Nevertheless, the mean annual concentration of petroleum products in the Selenga water in 2010 was below the one for the period 1984–1988. In the area of the settlement of Naushki, upstream of Ulan-Ude, downstream of Ulan-Ude and downstream of Kabansk, at earlier dates it reached 0.10–0.26, 0.04–0.10, 0.06– 0.08 and 0.04–0.17 mg/dm<sup>3</sup>, respectively [18].



**Fig. 3.** PAH content (ng/dm<sup>3</sup>) in the water of the tributary streams of Lake Baikal under investigation, for 2010–2012. For symbols, see Fig. 2.

Standards of natural waters with respect to contents of individual PAH in Russia has been developed for  $benzo(a)$  pyrene only [12], whereas the European Environment Agency monitors total contents of six PAH in drinking waters: (benzo(a)pyrene, benzo(b)<br>fluoranthene, benzo(k)fluoranthene, benzo[g,h,i] fluoranthene,  $\bar{b}$ enzo(k)fluoranthene, perylene, indeno[1,2,3-c,d]pyrene, and fluoranthene) [19, 20]. In the tributary streams of Baikal, we determined the concentration of 12 PAH, the total content of which in the Selenga water varied from 1.0 to 650 ng/dm<sup>3</sup> over a year, with that for the Upper Angara and Barguzin ranging from 10 to 156 and from 7 to 415 ng/dm<sup>3</sup>, respectively (Fig. 3).

PAH varied markedly in composition over a year. The highest contents of 12 individual PAH compounds and their sum corresponded to the period of the free flowing channel. In May and September, the main contribution to their sum (up to  $90\%$ ) was made by heavy hydrocarbons with five and six benzene rings  $(benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)$ pyrene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene, and dibenzo[a,h]anthracene). The concentration of Benzo(a)pyrenes in the Selenga water in May and September varied from 0.5 to 50 ng/dm<sup>3</sup>, amounting to as much as 6–15% of the sum of 12 PAH, exceeding MPC by factors of two and 2.5 for water bodies of uncentralized water supply  $(5 \text{ ng/dm}^3)$ . The total content of six PAH in the Selenga water in 2010 was 211 in spring and  $514$  ng/dm<sup>3</sup> in autumn. In accordance with European standards, their sum in the lower reach of the river in autumn exceeded PMC  $(200 \text{ ng/dm}^3)$  by more than a factor of two for natural waters. Along the border stretch of the river (settlement of Naushki), the PAH concentration was even higher, which appears to be due to their input from the territory of Mongolia where the leather industry is being developed, one of the sources of PAH input together with discharges of waste waters [21].

The other rivers of the Baikal drainage basin under investigation showed only occasional exceedances of PAH MPC. No such instances were observed for the Upper Angara in our study, whereas twofold exceedances of the standard rates  $[12]$  for benzo(a) pyrene were recorded in May 2011 along stretches upstream of the inflow of the Argada. In the tributary streams of South Baikal, similar situations can occur in the wake of forest fires (in the water of the Snezhnaya river, for example), where the benzo(a)pyrene content levels exceeded MPC [12] by more than a factor of five [22], while the total content levels of six PAH (500 ng/L) by a factor of 2.5.

## CONCLUSIONS

The analysis of the findings showed that among the tributary streams of Baikal investigated in this study, the lowest water quality for hydrochemical parameters corresponds to the Selenga, the basin of which has concentrated most of settlements and industries. According to the total content levels of the main ions, the Selenga waters meet the standard rates of different water requirements; however, concentrations of petroleum products and PAH exceed MPC at regular intervals thus determining a low water quality and reducing its possible uses for uncentralized water supply, for recreational and fisheries purposes. This can, to a considerably lesser extent, carried over to the waters of the Upper Angara and Barguzin, where pollution is observed mainly in their lower reaches. However, the increased concentration of biogenic elements in the water of the Selenga and Barguzin is favorable for a mass development of algae, and to eutrophication of the water bodies, which also leads to a reduction in the water quality and restricts the possibilities of using them.

The basic challenge concerning the water quality of the tributary streams of South Baikal is one of water acidification with an extremely low mineralization (the Pereemnaya and Khara-Murin), which is caused by pollution of local atmospheric precipitation. At the time of forest fires, the amount of PAH in the water of these

rivers can increase considerably, exceeding MPC for benzo(a)pyrene. The water of small tributary streams of North Baikal largely corresponds to the "quite clean" category and can be used for various purposes.

# ACKNOWLEDGMENTS

This work was done within the VIII.76.1 Program under Priority Direction VIII.76.

# REFERENCES

- 1. Sorokovikova, L.M., Tomberg, I.V. and Bashenkhaeva, N.V., Chemical Composition of the Waters of the Selenga River and the Outlets of Its Delta, in *The Selenga River Delta: A Natural Biofilter and Indicator of the State of Lake Baikal: Integration Projects*, issue 15, 2008, A.K. Tulokhonov and V.M. Plyusnin, Eds., Novosibirsk: Nauka, 2008, pp. 88–101 [in Russian].
- 2. Sinyukovich, V.N., Sorokovikova, L.M., Tomberg, I.V., and Tulokhonov, A.K., Climate Changes and the Selenga River Chemical Flow, *Doklady Earth Sci.*, vol. 433, issue 2, pp. 1127–1131.
- 3. Baram, G.I., Vereshchagin, A.L. and Golobokova, L.P., Use of Microcolumn Highly Efficient Liquid Chromatography with UV Detection for Determination of Inions in Environmental Objects, *Analiticheskaya Khimiya*, 1999, vol. 54, no. 9, pp. 962–965 [in Russian].
- 4. *Manual for Chemical Analysis of Surface Waters of Land*, Part 1, L.V. Boeva, Ed., Rostov-on-Don: Rosgidromet, 2009 [in Russian].
- 5. *Technical Manual for Wet Deposition Monitoring in East Asia – 2010*, Network Center for EANET, November, 2010.
- 6. Gorshkov, A.G., Marinaite, I.I., Zhamsueva, G.S., and Zayakhanov, A.S., Benzopyrene Isomer Ratio in Organic Reaction of Aerosols Over Water Surface of Lake Baikal, *J. Aerosol Sci.*, 2004, vol. 35, Suppl. 2, pp. 1059–1060.
- 7. Votintsev, K.K., Glazunov, I.V. and Tolmacheva, A.P., *The Hydrochemistry of the Rivers Within the Lake Baikal Drainage Basin*, Moscow: Nauka, 1965 [in Russian].
- 8. Obozhin, V.N., Bogdanov, V.T. and Klikunova, O.F., *The Hydrochemistry of the Rivers and Lakes of Buryatia*, Novosibirsk: Nauka, 1984 [in Russian].
- 9. Sorokovikova, L.M., Netsvetaeva, O.G., Tomberg, I.V., Khodzher, T.V., and Pogodaeva, T.V., Effect of Atmospheric Precipitation on the Chemical Composition of River Waters in the South Baikal, *Atmos. Oceanic.Opt.*, 2004, vol. 17, issues 5–6, pp. 373–377.
- 10. Shimaraev, M.N., Kuimova, L.N., Sinyukovich, V.N., and Tsekhanovskii, V.V., Manifestation of Global Climatic Changes in Lake Baikal During the 20th Century, *Dokl. Earth Sci.*, 2002, vol. 383, issue 3, pp. 288–291.
- 11. Latysheva, I.V., Sinyukovich, V.N. and Chumakova, E.V., Recent Peculiarities of Hydrological and Meteorological Regime of the Lake Baikal Southern Coast, *Izvestiya Irkutskogo Universiteta, Ser. Nauki o Zemle*, 2009, no. 2, pp. 117–133 [in Russian].
- 12. *Water. Hygienic Sanitary Regulations, Standards and Methods of Safe Water Use by the Population. A Collection of Documents*, Moscow: InterSEN, 2004 [in Russian].
- 13. Sorokovikova, L.M., Popovskaya, G.I., Tomberg, I.V., Sinyukovich, V.N., Kravchenko, O.S., Marinaite, I.I., Bashenkhaeva, N.V., and Khodzher, T.V., The Selenga River Water Quality on the Border With Mongolia at the Beginning of the 21st Century, *Russ. Meteorol. Hydrol.*, 2013, vol. 38, issue 2, pp. 126–133.
- 14. Petrova, N.A., *Phytoplankton Successions During Anthropogenic Eutrophication of Large Lakes*, M.A. Rychkova, Ed., Leningrad: Nauka, 1990 [in Russian].
- 15. Zhukinskii, V.N., Oksiyuk, O.P., Oleinik, G.N., and Koshelev, S.I., The Principles and Experience of Constructing an Ecological Classification of the Surface Water Quality on Land, *Gidrobiol. Zhurn.*, 1981, vol. 17, no. 2, pp. 38–49 [in Russian].
- 16. Popovskaya, G.I. and Tashlykova, N.A., Phytoplankton of the Selenga River, in *The Selenga River Delta: A Natural Biofilter and Indicator of the State of Lake Baikal: Integration Projects*, issue 15, 2008, A.K. Tulokhonov and V.M. Plyusnin, Eds., Novosibirsk: Nauka, 2008, pp. 167–182 [in Russian].
- 17. *List of Fishery Standards: Maximum Possible Concentrations (MPC) and Tentative Safe Exposure*

*Levels (TSEL) of Pollutants for Water of Water Bodies Having a Significance for Fisheries*, Moscow: Izd. VNIRO, 2010 [in Russian].

- 18. Shandibaeva, E.F., Odnopalyi, V.V. and Tatarnikov, V.K., Dynamics of the Degree of Water Pollution in the Selenga River (Within the USSR) as Deduced From Hydrochemical and Hydrobiological Parameters, in *Improvement of a Regional Monitoring of the State of Lake Baikal*, Yu.A. Izrael', Ed., Leningrad: Gidrometeoizdat, 1985, pp. 212–219 [in Russian].
- 19. Keith, L.H., Organic Pollutants in Water: Identification and Analysis, *Environ. Sci. Technol.*, 1981, vol.15, no. 2, pp. 156–162.
- 20. Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption. URL: http://eur-lex.europa.eu/LexUriServ/LexUriServ. do?uri=CELEX:31998L0083:en:NOT Accessed 06.25.2014.
- 21. Li, J., Shang, X., Zhao, Zh., Tanguay, R.L., Dong, Q., and Huang, Ch., Polycyclic Aromatic Hydrocarbons in Water, Sediment, Soil, and Plants of the Aojiang River Waterway in Wenzhou, China, *J. Hazard. Mater.*, 2010, vol. 173, issues 1–3, pp. 75–81.
- 22. Marinaite, I.I., Polycyclic Aromatic Hydrocarbons in Waters of Tributaries of South Baikal, *Atmos. Oceanic Opt.*, 2006, vol. 19, no. 06, pp. 448–451.