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Current State of the Selenga River Waters in the Russian Territory Concerning Major Components and Trace Elements

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Abstract

Studies were performed concerning the seasonal dynamics of major ions (Na^+, Mg^{2+}, K^+, Ca^{2+}, SO_4^{2-}, Cl^-, HCO_3^-), Si, 52 trace elements, organic carbon, pH, O_2 in the Selenga River, the main tributary of Lake Baikal and the rivers flowing into the Selenga in the Russian territory, the flow paths and lakes of the delta within the barrier area of Lake Baikal (up to 7 km from the mouth of the Selenga River).

Using the factor analysis we revealed four main groups, those differ from each other in the spatial and temporal distribution of the components in the Selenga River.

The first group comprises the water salinity, the major ions and trace elements, some conservative trace elements (B, Br, Sr, Mo, Ba, Re, U). The concentration values for these components are maximal within the ice period (March) and minimal within the flood period (May), exhibit an increase on the frontier with Mongolia reducing towards the mouth as being diluted by less saline water of the tributaries of the Selenga River.

The elements of the second group are connected with the content of dissolved organic matter capable of mobilizing difficultly soluble and almost insoluble elements (Be, Al, Ti, Fe, Ni, Cu, Ga, Y, Zr, Nb, Hf, REE, Pb, Th) to produce fine-dispersed organomineral complexes. The concentration values for these elements demonstrate increasing in the spring, in the course of the snowmelt and of an active removal of organic matter from the catchment area.

The third group of the elements (Si, Li, Cr, Mn, Co, Zn, Ge, Rb, Ag, Cd, Sn, Cs, Bi) reflects the processes of water acidifying against the background of seasonal dynamics inherent in the dissolved oxygen. Concentration values for these elements increase towards the mouth (except for Co within the period of spring and autumn, as well as Ge in winter), being to a significant extent increased in the winter.

The fourth group of the elements (V, As, Sb, I, W, Cu) represents a marker of a weak cross-border transfer in summer. Increased concentration values of these elements are observed in July, especially on the upper section of the river (0–120 km from the frontier with Mongolia).

The maximum and average weighted concentrations of the most of trace elements in the Selenga River are lower than those inherent in the global natural river background. Exceeding the maximum background concentration values is observed for Mo (10 %), Mn (10 %) and Ge (60 %). Average weighted background concentration values exhibit a 2- to 5-fold exceeding in Zr (2.1), Nb (2.1), Sr (2.5), Ti (2.9), U (3.5), Y (3.5), Zn (3.7), Mo (3.8) and Sn (4.9), which could be caused by the geological structure of the basin and the naturally occurring processes of mobilizing the elements.

The concentration of Mo, Mn, Cu, Al, Fe, V in the general river station of the Selenga River and the tributaries thereof in some seasons are slightly higher than Russian standards established for fish-industry water basins (in 80 % of cases less than 2 MPC). Within the barrier zone of Lake Baikal there is an excess over the fish industry water standards in Mo registered to be constant (1.2–2.1 MPC): for Cu in winter (up to 1.8 MPC), in summer (up to 1.9 MPC), in autumn (up to 1.3 MPC); for V in summer (up to 1.6 MPC); for Mn in winter (up to 2.2 MPC).

Key words: Selenga River, major ions, trace elements, ICP-MS analysis

1. INTRODUCTION

The environmental changing of water objects is connected with a violation of the aquatic, chemical and thermal regimes thereof, as well as the conditions of the inflow and deposition of suspended matter. The factors influencing upon these processes can have both naturally occurring and man-caused origin. Under the combination of adverse environmental factors and the growth of anthropogenic load, the hazard of disrupting the normal functioning of aquatic ecosystems increases dramatically. Since the end of the twentieth century, there is information appearing [1] concerning the fact that the water quality is worsened in the main tributary of Lake Baikal, the Selenga River within the Mongolian territory, which, according to the authors [1] could be caused by increasing the anthropogenic load on the catchment area thereof. Within the last two decades, over the frontier regions of Mongolia there is an intensive development of agriculture, a growing number of livestock farms, increasing the population are observed as well as an extensive program of irrigated agriculture is realized. There are actively functioning enterprises for the processing of leather and wool [2]. Gold mining in Mongolia for the past 10 years demonstrated a 17-fold increase. A number of deposits, where gold is extracted hydraulically, there are cyanides and mercury used, which in the absence of the reclamation of waste areas may could cause increasing the content thereof in river waters and aquatic organisms [3, 4].

In the future, the Government of Mongolia provides a number of major projects, including the development of the Khubsugul phosphorites, the construction of another hydroelectric power station at one of the tributaries of the Selenga River, the transfer of the runoff to the Gobi desert, *etc*.

The activation of economic activity observed in northern Mongolia occurs against the background of the climate change, accompanied by a decrease in rainfall in the Selenga River basin, and, as a consequence, by decreasing the water content therein [5]. According to data obtained by the Geological Institute of Mongolia, among 5655 rivers and rivulets registered in the country, as many as 683 waterways have dried. In this situation, the growth of water consumption and water together with violations of the underlying surface, including land degradation and desertification [6], exacerbate negative impacts on water resources of the area and can help to reduce the water content of the Selenga and the quality of its waters.

The purpose of this work consisted in to exploring the seasonal variability of the main ions, trace elements and other characteristics in the water of the Selenga River in the territory of Russia, in order to reveal the main factors influencing the dynamics thereof, to give a modern environmental assessment of water with respect to the components under investigation.

2. PHYSIOGRAPHIC, CLIMATIC AND GEOLOGICAL CHARACTERISTICS OF THE SELENGA RIVER BASIN

The Selenga River basin (447 thousand km^2) is located almost in the centre of the Asian continent between latitude 41 and 53° N and between longitude 98 and 113 E in the territory of the two countries, Mongolia and Russia (Fig. 1). It is a part of the basin of Lake Baikal (570 km^2, [7]) to amount to the main part thereof (78 %). The most part of the basin of the Selenga River (299 km^2) is located in the territory of Mongolia (67 %) in the semi-arid zone with the average level of rainfall of about 300 mm/year [8]. The Russian part of the basin of the Selenga River (148 km^2) is located in a more humid area, with the average level of atmospheric precipitations equal to 460 mm/year [9].

The basin of the Selenga River has a well developed river network. Average river network density ranges quite widely from 0.2 to 1.0 km/km^2, in the Russian territory amounting to 0.47 km/km^2 on the average [10].

The Selenga River connects the two reservoirs such as the Lake Khubsugul and Lake Baikal being the main tributary of the latter. Its length is 1024 km, whereof 409 km are located in the Russian territory. The Selenga supplies about 50 % of water and more than a half of the chemical runoff into Lake Baikal [11]. The mean perennial runoff of the river is equal to about 29 km^3 [12]. Within the last decade a decrease of the river water content is registered to amount to 22 % below long-term average value [5]. Reducing the water flow rate has resulted in a decrease in the river carry-over of dissolved matter to be manifested most clearly within the periods of low water content. Owing to the low water content of the river within the range of 1996–2005, the Selenga ionic runoff was on the average 20 %

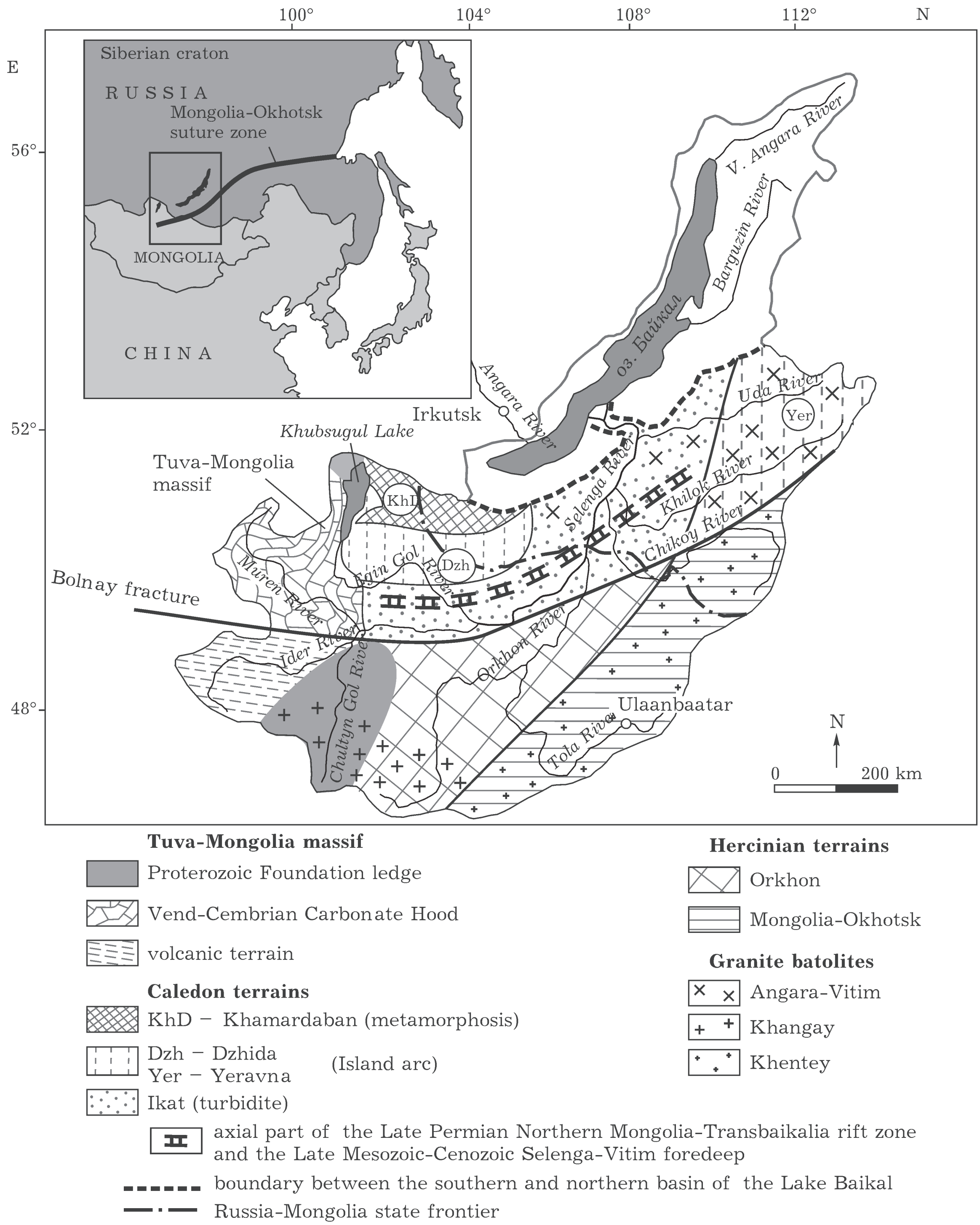

Fig. 1. Schematic map of tectonic and stratigraphic terrains inherent in the Selenga River basin.

below the normal value (4.1 million t/year), whereas within the most arid year 2002 it was 32 % lower than the norm [5].

A sufficient remoteness of the territory under consideration from coastlines, closure by mountains as well as the predominance of mountain relief are causing a severely pronounced continental climate therein. The main features of the climate consist in a large amplitude of the fluctuations of average daily and seasonal air temperature values, substantial air aridity, abrupt changing the seasons, cold long

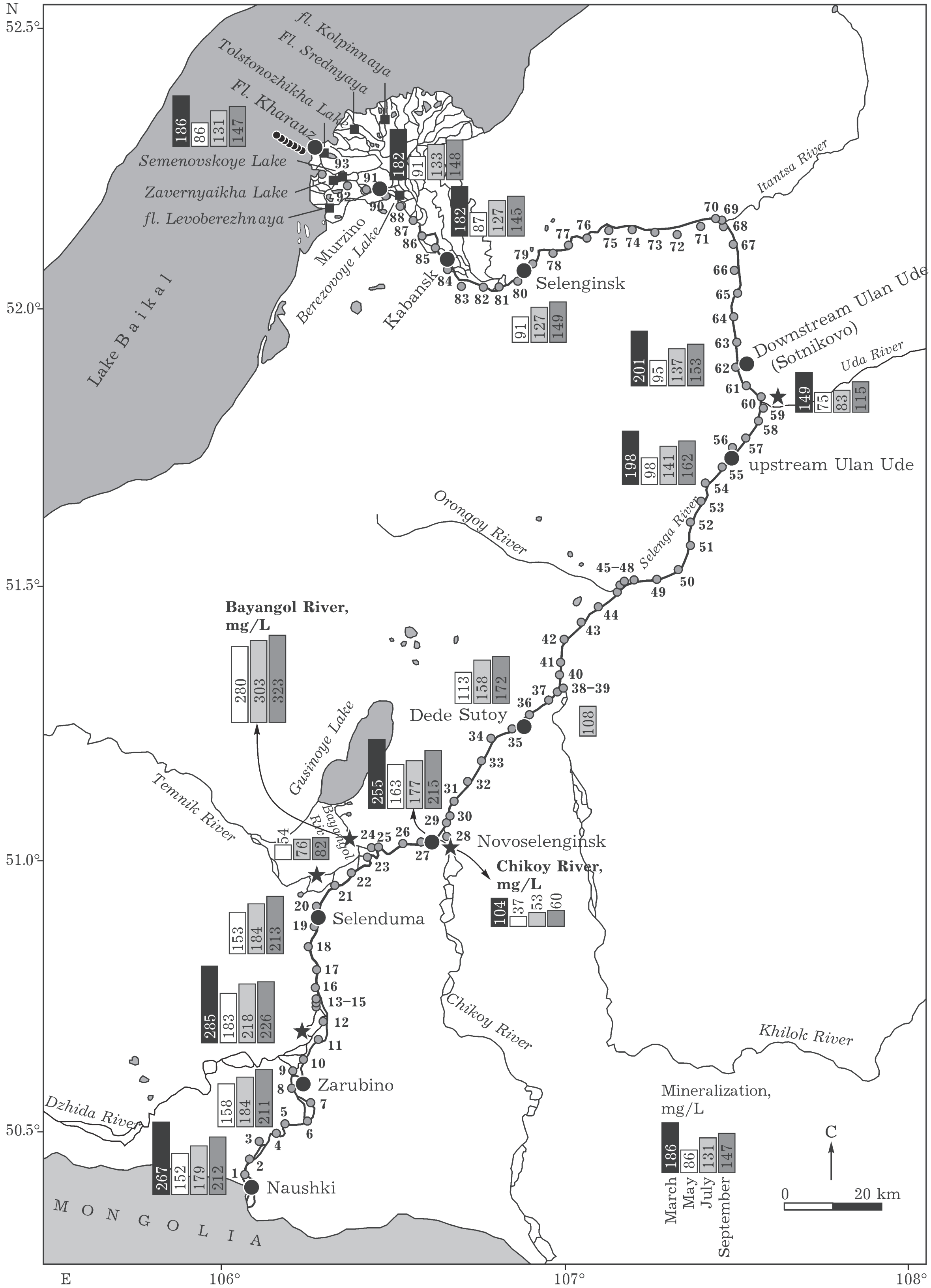

Fig. 2. Schematic map of water sampling from the Selenga River in 2010. Black symbols show sampling points in the course of seasonal road expeditions (large circles – the main riverbed, asterisks – tributaries; the mineralization level is presented in the form of histograms); sampling locations in the delta (lakes, flow paths) are presented as black squares, at the half-section, of the fl. Kharauz – Lake Baikal they are presented b small black circles; sampling in July from a catamaran is shown by gray circles.

winter, and the predominance of blue sky especially in the cold season. The average annual air temperature is everywhere negative to range from −5 °C in the northern and central parts of the basin to −0.1 °C in the southern part thereof.

The geological structure of the river basin of the Selenga River had formed resulting from the closure of the Mongolia-Okhotsk Paleopacific Bay in the late Jurassic period [13] (see Fig. 1).

The tectonic and stratigraphic terrains in the northern and southern flanks of the Mongolia-Okhotsk suture zone differ from each other in composition and age to a significant extent. At the northern flank, there are Caledonides formed along the Neoproterozoic massifs accreted to the Siberian craton in the early Paleozoic. Located At the southern flank there are volcanogenic sedimentary complexes of Hercynides broken through by granite batholiths [14]. The difference in the composition of the rocks of the terrains separated by the suture zone could be reflected in the variations of dissolved components inherent in the waters of the Selenga River and its tributaries, whereas the general picture could be complicated to a considerable extent by local substantial anomalies associated with the concentrations of ore deposits, such as the deposits of rare metals in granitic batholiths [15, 16].

3. EXPERIMENTAL

3.1. Sampling and sample preparation

Water sampling at the Selenga River and its tributaries was performed in 2010 at the control points (Fig. 2) all over the Russian section of the Selenga River from the frontier with Mongolia (the Naushki settlement) before flowing into the Lake Baikal and in the barrier zone of the lake at a distance of 7 km from the mouth of the Selenga River. Water samples were taken from the main riverbed of the Selenga River (see Fig. 2), from the estuarine areas of some of the tributaries thereof (the Dzhida, Temnik, Bayangol, Chikoy, Uda rivers), from some lakes and flows in the delta and from the surface and bottom layers of the barrier zone of Lake Baikal. Sampling was carried out during the ice period (March 10−17), during the spring flood (18?24 May), in summer (July 20−28) and in autumn (September 27−October 2) in the course of land road expeditions. In July, in conjunction with the planned sampling carried out at the control points we undertook a catamaran expedition for detailed testing the river (with a 5 km increment) and tributaries, whereto the road access is difficult (the Khilok, Orongoy, Itantsa rivers). The rafting was carried out for three days using a specially adapted catamaran "Tourist-2".

In order to perform a multi-element ICP-MS analysis, the samples were taken six-meter polymeric pole into preliminary washed 0.5 L polyethylene terephthalate (PET) bottles to store within a day in an EVERCOOL EC-985 portable thermoelectric cooler (at a temperature of ~10 °C). The samples chosen were filtered through a 0.45 μm disposable membrane filters (GyroDisc Syr. CA-PC 30 mm cellulose acetate, Orange Scientific, Belgium). For the elemental analysis, a sample was fixed using a double-distilled 70 % HNO_3 solution (Special Purity grade 18-4, Russian standard GOST 11125−84, a duoPUR subboiling distillation unit, Milestone); the solution contained 350 μg/L of indium (as an internal standard) on the basis of 206 μL of the acid per 10 mL sample (HNO_3 concentration in the samples was 2 %, the concentration of In being equal to10 μg/L). The prepared solutions prior to measurement were stoed in a refrigerator.

Water for the determination of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), anions (HCO_3^-, Cl^-, SO_4^{2-}), Si and organic matter were sampled into 1.5-L PET bottles from the control points. Water samples were filtered through membrane filters (0.45 μm polycarbonate) not later than 10 h after sampling. The filtrates were stored in a refrigerator before performing the analyses.

The determination of the water temperature and pH, as well as the fixation of dissolved oxygen was carried out on the spot at the control sampling points. For pH measurement an "Expert-002" potentiometer was used (Econika Expert, Russia) with a combined electrode and temperature compensator. The error of the method was equal to ±0.02 pH.

TABLE 1

Errors in determining the elements in the course of analyzing the solutions with the use of an Agilent 7500ce quadrupole ICP-MS spectrometer

Concentration of elements, μg/L	<0.001	0.001–0.1	0.1–1	>1
RSD, %	>25	25–10	10–5	5

3.2. Determination of major ions, silicon, oxygen and organic carbon

The chemical analyzes of water were performed at the accredited Laboratory of Hydrochemistry and Atmospheric Chemistry of the Limnological Institute (LIN) of the SB RAS according to the procedures and guidance documents accepted in mainland freshwater hydrochemistry [17, 18], as well as those developed and certified in the LIN [19].

3.3. Multi-element ICP-MS analysis

The multi-element ICP-MS analysis was performed at the Laboratory of elemental analysis of the LIN, SB RAS. Prepared samples were analyzed without concentrating with the use of an Agilent 7500ce quadrupole mass spectrometer. For the calibration of mass spectrometer we used multi-element standard solutions ICP-MS68A-A and ICP-MS-68A-B (HIGH-PURITY STANDARDS, Charleston, the USA), and a sample of bottled Baikalian water (Na, Mg, Si, S, Cl, K, Ca [20]). The correction for interfering molecular ions (MeO^+, $MeOH^+$, $MeAr^+$, $MeCl^+$) was carried out with the use of an approach described in [21].

In order to estimate the errors in determining we used an experimentally established relationship between the coefficient of variation (RSD, %) and the intensity of analytical signal (N, pulses/s), which relationship was approximated within the Poisson statistics (quasi-periodic processes) by a power function such as RSD (%) = $125.71N^{-0.33103}$ where N = 20–20 000 pulses/s. The signals over 20 000 pulses/s in value were characterized by the RSD value equal to 5 % or better, the signals lower than 20 pulses/s were characterized by the RSD value greater than 50 %.

Typical detection errors for the elements depending on the measured concentration in the solutions under investigation are presented in Table 1.

4. RESULTS AND DISCUSSION

In order to reveal the main groups of elements those fundamentally differ from each other in the nature of space-time distribution in the Selenga River, a part of the data (in the control points of the main riverbed, (see Fig. 2) was subjected to the factor analysis (principal components method and varimax rotation). We analyzed the distribution of the following components: dissolved oxygen (O_2), acidity (H^+, μg/L), major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}) and the sum thereof (PIS), dissolved organic carbon (DOC), silicon (Si), trace elements (Li, Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, the amount of REE, Hf, W, Re, Tl, Pb, Bi, Th, U).

We have found out four factorial groups comprising almost all of the components (Figs. 3–6). The structure of these groups is not always unambiguous because the space-time distribution of certain elements is influenced by several factors.

4.1. Factorial group 1 "Mineralization"

The first factorial group (see Fig. 3) includes water mineralization (dissolved organic carbon, DOC), major ions and some conservative trace elements (B, Br, Sr, Mo, Ba, Re, U). The concentration of the most of the elements is maximal within the ice period (March) being minimal within the flood period (May); this value exhibits an increase at the frontier with Mongolia to decreases towards the river mouth (see Fig. 3) as dilution occurs with less saline water from the tributaries of the Selenga River (see Fig. 2). The most significant dilution occurs after the confluence of the largest tributary, the Chikoy River, whose fraction in the runoff of the Selenga River at this part is on the average equal to 38.5 % (calculated from average

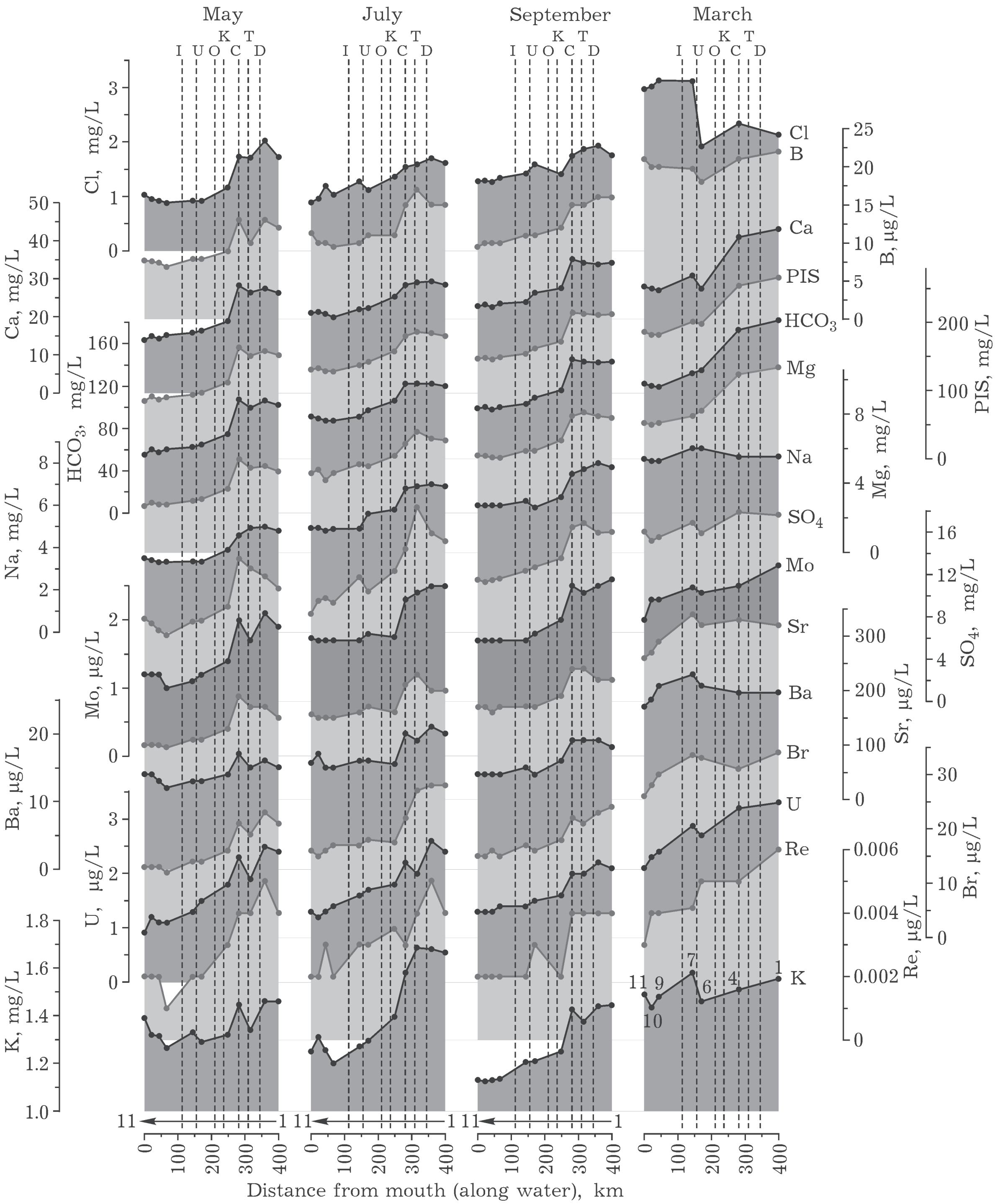

Fig. 3. Space-time distribution of the components in the Selenga River (mainstream) for factorial group 1 "Mineralization". Here, and in Figs. 4, 5: the vertical lines mark the location of tributaries (I – Itantsa River, U – Uda River, O – Orongoy River, K – Khilok River, C – Chikoy River, T – Temnik River, D – Dzhida River); the figures numbers at the bottom stand for the checkpoints of water sampling near the points: 1 – Naushki settlement, 2 – Zarubino settlement, 3 – Selenduma settlement, 4 – Novoselenginsk settlement, 5 – Dede Sutoy settlement, 6 – upstream the Ulan Ude, 7 – downstream Ulan Ude, 8 – Selenginsk settlement, 9 – Kabansk settlement, 10 – Murzino settlement, 11 – Kharauz settlement.

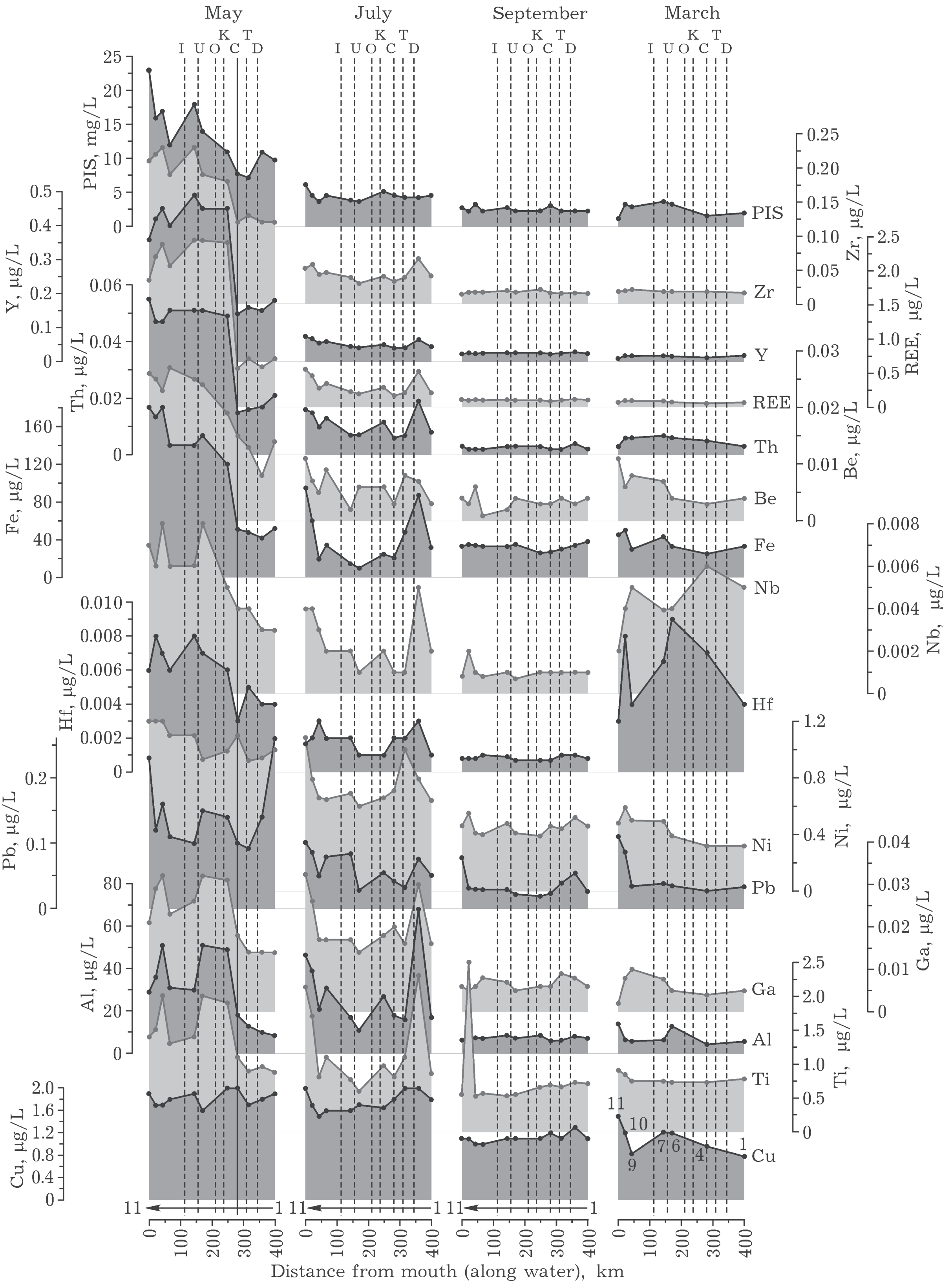

Fig. 4. Space-time distribution of the components in the Selenga River (mainstream) for factorial group 2 "Organic matter" (Cu is also included in the factorial group 4, see Fig. 6). For designations, see Fig. 3.

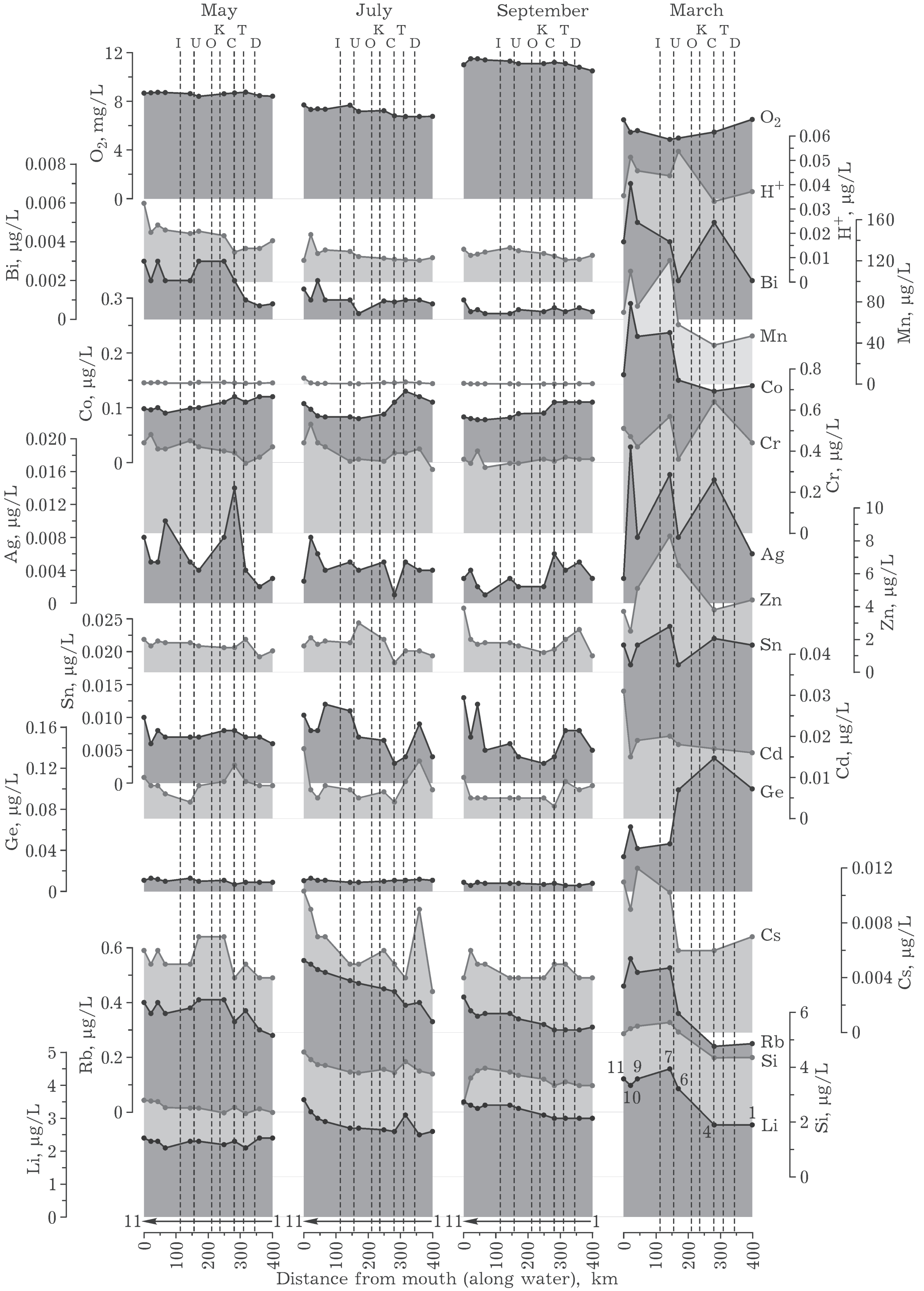

Fig. 5. Space-time distribution of the components in the Selenga River (mainstream) for factorial group 3 "Acidity/oxygen". For designations, see Fig. 3.

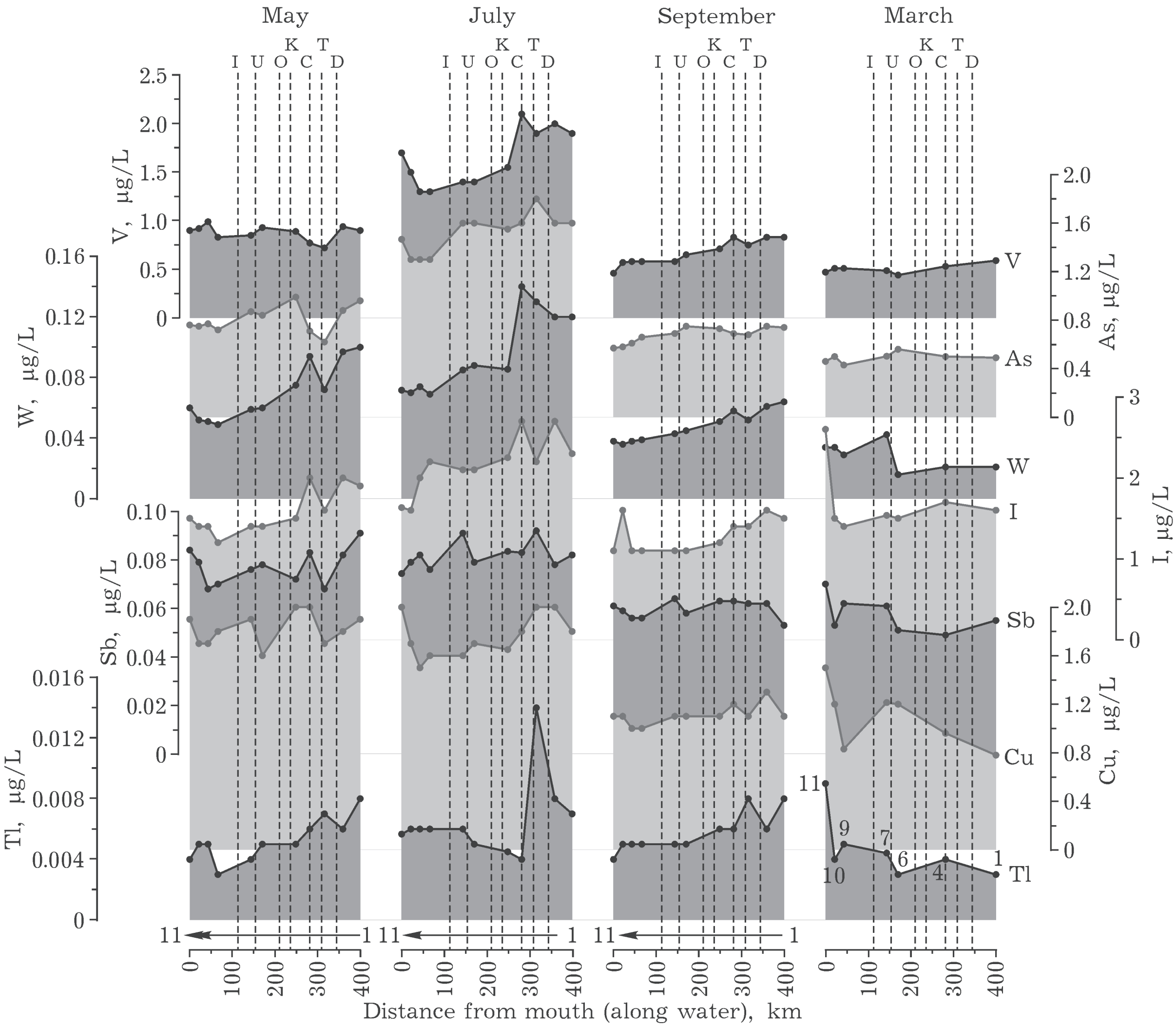

Fig. 6. Space-time distribution of the components in the Selenga River (mainstream) for factorial group 4, and Tl that was not included in any group. For designations see Fig. 3.

annual long-term data for the period of 1987–1997, the data were taken from R-ArcticNET website at http://www.r-arcticnet.sr.unh.edu/v4.0/index.html). The contribution of other rivers in the runoff of the Selenga River at the corresponding parts is to a significant extent lower: the Dzhida River 18.6 %, the Temnik River 5.3 %, the Khilok River 11 %, the Orongoy River 1 %, the Uda River 7 %, and the Itantsa River 1 %. Among the tributaries, only the Dzhida River exhibits the mineralization level higher than the Selenga River (4–20 % higher depending on the season).

The concentration of the elements of the factorial group 1 in the tributaries is lower than that in the Selenga River. Exceptions are presented by the Uda River (Cl in winter and in autumn, B, Na, SO_4^{2-} in winter, Mo in all the seasons) and the Dzhida River (Na, Ba in winter, Br in summer, Ca, Mg, SO_4^{2-}, Sr in all the seasons).

Among the elements under consideration, the general regularity is violated for potassium, whose concentration in July at the site before confluence of the Chikoy River is higher than in winter, which, alongside with the elements of the fourth factorial group (V, As, W, I, Sb, Cu) indicates that there could be a transboundary transport from Mongolia. It is possible that increased potassium concentration values of are associated with the erosion of arable land, whose development has been actively carried out in Mongolia within the frontier areas [2]. The concentration of other elements of the factorial group 1 always exhibits a higher value in winter, within the period of a lowered water runoff [22]. For some elements this pattern is violated: the average concentration values thereof in autumn are almost the same as in summer (B, Mo, Sr), in some cases the autumn values are lower than the values in summer (Br, U, Re), whereas for potassium the concentration is lower than that in spring (see Fig. 3).

In winter, spatial distribution pattern is violated for certain elements: the concentration of B, Na, Ba, K into a significant extent varies along the riverbed, whereas the concentration of Cl downstream the river after Ulan Ude exhibits an abrupt 1.5-fold increase. This could be caused, to all appearance, by an increase in the fraction of groundwater with another chemical composition in feeding the river at this site. Previous studies [23] demonstrated that at the site under consideration there is a layering of several types of aquifers (Quaternary, Pliocene, Miocene and Middle Jurassic ones), whereunder there are waters inherent in crystalline basement rocks. Downstream the Selenginsk settlement there is beginning the zone of the Selenga-Vitim flexure with other conditions of forming the groundwater runoff, where there are the cropouts of thermal waters (within the area of the Il'inka settlement), whereas closer to Ulan Ude there is a small area ob-

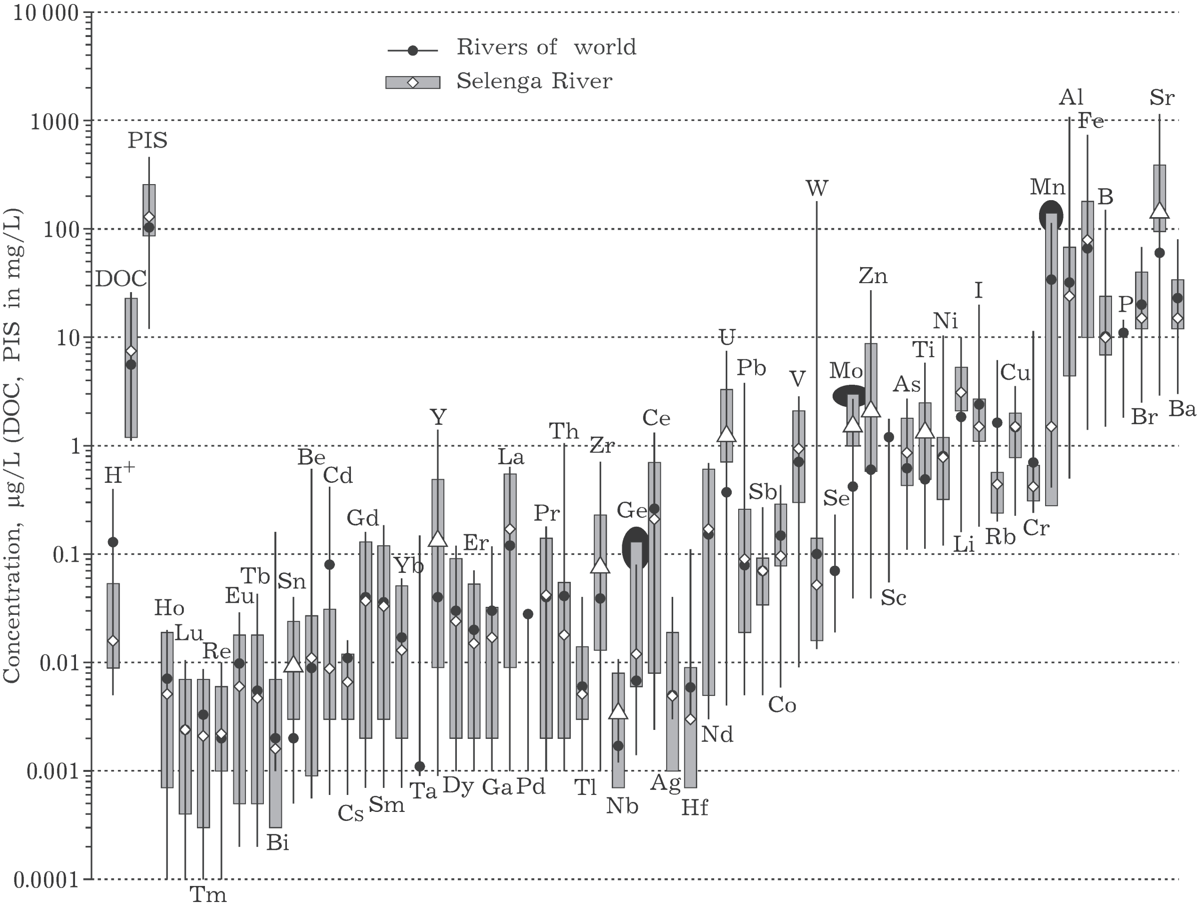

Fig. 7. Concentration of H^+, DOC, PIS and trace elements in the Selenga River (fraction <0.45 μm) in comparison with the GNRB parameters established by the results of studying the largest rivers in the world, located in the areas with a low man-caused load (data from [37], corrected and amended according to: [38] Ag; [25] Mo, Re; [39] Tl; [40] Br; [41] Br, I; [42, 43] I; [33, 35, 44] Sn; [45–48] Bi). The bars show the range of fluctuations of concentration values for the elements, symbols denote average weighted values; triangles mark the average weighted concentration values for the elements in the Selenga River more than 2 times exceeding the parameters of global natural river background (GNRB); exceeding the maximum parameters observed is marked by black ellipses.

served with extremely high modulus of underground feeding (more than 10 L/(s · km^2) [7]. To all appearance, the presence of this region causes high concentration values of some elements in the Selenga River downstream the river after Ulan Ude in winter (see Figs. 3, 5).

The similarity in the space-time distribution of the main ions and trace elements could be most likely caused by common entry sources thereof. The most part of alkaline earth metals (Mg, Ca, Sr, Ba), and U, could be, to all appearance, extracted from carbonate rocks. Uranium under the alkalinity conditions inherent in the Selenga River forms stable readily soluble hydrocarbonate complexes and behaves as a conservative element [24]. Such elements as Mo and Re can enter the river water mainly from sulphides and some accessory minerals: Mo from molybdenite (MoS_2), magnetite, sphene; Re from ReS_2, ReS_3, $CuReS_4$ *et al.* [25]. These elements under oxidizing conditions can migrate, just as sulphur does, in the form of readily soluble oxoanions (MoO_4^{2-}, ReO_4^-). The average weighted concentration ratio for Re and SO_4^{2-} is typical for pollution-free rivers [25], which indicates the absence of man-caused pollution with rhenium.

The maximum (3 μg/L) and average weighted (1.6 μg/L) Mo concentration in the Selenga River are higher than those inherent in the global natural river background (GNRB) by 10 % and 3.8 times, respectively (Fig. 7). In order to reveal the causes of the increased concentration of Mo in the Selenga River we performed a balance estimation of Mo entering Lake Baikal. We revealed the concentration of Mo in Lake Baikal to be constant everywhere (it does not exhibit any change either vertically or horizontally) being at a level of 1.3 μg/L. For the case of supplying the Mo to Lake Baikal through main tributaries (in July the Selenga River 1.7 μg/L, the Barguzin River 1.1 μg/L, the Verkhnyaya Angara River 0.65 μg/L under corresponding monthly perennial water flow rate values amounting to 1884, 246 and 604 m^3/s, the data being taken from website R-ArcticNET) the estimated concentration thereof in the lake is equal to 1.4 μg/L, which is in a good agreement with the values observed (1.3 μg/L). Basing on these estimates and taking into account a low rate of water exchange in the lake (~400 years) [26], one could conclude that the increased concentration of Mo in the Selenga River is of naturally occurring nature, rather than a consequence of a man-caused impact resulting from the Erdenet Mining and Processing Enterprise in Mongolia, where molybdenum concentrate is processed. In any case, the data available are insufficient in order to reveal and properly assess the impact of the plant on the Selenga River. For this purpose, it is necessary to perform a more detailed study in the Mongolian territory (upstream and downstream the Erdenet City along the Orkhon River, the tributary of the Selenga River).

The concentration of Mo in the tributaries is markedly lower than that in the Selenga River, except the Uda River, wherein there is higher Mo concentration values of in all the seasons, especially in winter (5 μg/L); however this does not affect the concentration of Mo in the Selenga River.

In winter, the concentration of some other elements (Cl, B, Sb, Ga, Ge, W, Bi) in the Uda River was also higher to a significant extent (from 3 to 10 times) than that in the Selenga River. It could not be excluded that at this time against the background of low water content one observes an influence of the Ulan Ude, large-scale industrial centre (about 60 industrial enterprises, 400 thousand inhabitants), which is stretched within 15 km along both the banks of the river from the confluence thereof with the Selenga River (see Fig. 2).

The maximum concentration of Sr in the Selenga River is lower of the corresponding GNRB lower than parameter, however the average weighed concentration of Sr (150 μg/L) is 2.5 times higher than the GNRB value (see Fig. 7). Just as it is in the case of Mo, the mass balance of Sr in the Lake Baikal [27, 28] indicates the natural causes of the increased Sr concentration in the Selenga River.

The average weighed concentration of U (1.3 μg/L) in the Selenga River is 3.5 times higher than corresponding GRPF parameter (see Fig. 7), which, to all appearance, could be also determined by natural features inherent in the catchment area.

The concentration values of the elements of this group in the Selenga River and other aquatic objects under investigation (tributaries, flow paths, lakes, deltas, the Baikal barrier zone) do not exceed the Russian standards established for water of potable and residential use [29], for drinking water [30, 31] and fishing industry purpose [32]. The exception is presented by Mo and Sr, whose concentration values exceed those recommended by fishing industry regulations.

The Mo concentration in the Selenga River is 2.8 times higher than the value recommended by the Russian fishing industry regulations (MPC = 1 μg/L) in all the seasons throughout all the river. The concentration of Mo is also higher than the value recommended by the fishing industry regulations in the delta of the Selenga River and in the barrier zone of Lake Baikal in all the seasons (1.1–2.1 MPC).

The Sr concentration exceeds the values recommended by the fishing industry regulations (MPC = 400 μg/L) in winter in the Dzhida River (1.3 MPC) in some flow paths (fl. Kolpinnaya 1.5 MPC, fl. Srednyaya 2.4 MPC) and in the lakes of the delta (the Zavernyaikha Lake and the Berezovoye Lake 2.1 MPC), as well as in spring and in autumn in the Bayangol River (1.1–1.2 MPC) that flows from the Gusinoye Lake to flow into the Temnik River 4.5 km from the mouth thereof (see Fig. 2).

4.2. Factorial group 2 "Organic matter"

The second factorial group involves dissolved organic matter (calculated as carbon equivalent) and a number of poorly soluble and almost insoluble elements: Be, Al, Ti, Fe, Ni, Cu, Ga, Y, Zr, Nb, Hf, REM, Pb, Th (see Fig. 4). Numerous studies demonstrated that these elements migrate mainly in the structure of fine-dispersed Fe–Al colloids (>50 kDa) stabilized by organic matter, whose presence is a crucial factor in the formation and quantification thereof [33, 34]. The genesis of such organic matter is mainly associated with the upper soil horizon litter [33]. In our studies, the highest content of organic matter and mobilized elements was observed in the spring, in the course of the active snowmelt and removal of a part of the upper soil horizons (see Fig. 4). During this period, the concentration of elements markedly increased after the Chikoy River confluence, particularly that of Y, REE, Th, Fe, Ga, Al, Ti. The content of organic matter in the Chikoy River is maximum (DOC 22 mg/L) among the other tributaries being 2–3 times higher than in the Selenga River upstream the Chikoy River confluence. The concentration of dissolved organic matter in the Selenga River increases in the direction from Mongolia to Lake Baikal; in the same direction one can observe increasing the concentration of the related elements. Copper is also included in this group, but it has no pronounced spatial trend (see Fig. 4), which may indicate the influence of other controlling factors those represent, to all appearance, sorption and ion exchange processes under interaction with suspended matter absorbed by biota.

In the seasonal dynamics there is a decrease in DOC concentration observed from spring to autumn, with a slight increase in winter (see Fig. 4). Likewise, also changing the concentration of the most elements in the group occurs. Exceptions are presented by Nb and Hf, whose concentration values in winter are comparable with the values thereof in the spring, whereas the spatial distribution is rather of inverse character (the concentration of the elements decreases from Mongolia to Lake Baikal). Copper concentration in the Selenga River in summer, as well as in spring, is increased (1.5–2 μg/L) being slightly varied along the river.

In spring, in summer and in winter the spatial trend of increasing the concentration of the most of elements in the Selenga River is directed from Mongolia to Lake Baikal. In autumn, this trend is almost absent, whereas that inherent in Ti and Cu changes to be reversed (see Fig. 4).

Average weighted concentration values for some elements of the factorial group 2 (Be, La, Pr, Nd, Fe) in the Selenga River are slightly higher (1.1–1.4 times) than similar GNRB parameters (see Fig. 7). Exceeding the average parameters for the other elements is somewhat greater (Zr, Nb 2.1 times, Ti 2.9 times, Y 3.5 times). It is difficult to assume that there is the presence of anthropogenic sources for some specific elements (Be, Zr, Nb, Y, REE). We believe that the increased concentrations of poorly soluble elements in Selenga River represent a result of the action of geological and climatic factors.

The concentration of the elements belonging to this group in the Selenga River and other aquatic objects studied does not exceed the Russian standards. An exception is presented by Cu, Al and Fe, whose concentration exceeds the values recommended by fishing industry regulations.

In spring and in summer the concentration of Cu in the Selenga River is constant, but it is to a minor extent (1.5–2 times) higher than the values recommended by rather rigid Russian fishing industry regulations (MPC = 1 μg/L). In autumn and in winter the concentration of copper in the river decreases (0.8–1.5 μg/L), but in most cases the value is also higher than the MPC. The copper concentration value in the tributaries is lower than that in the Selenga River, or comparable with. Exceeding the maximum permissible concentration in the tributaries is registered in spring and in summer in the Chikoy River (2.2 and 1.1 MPC) and in the Dzhida River (1.7 and 1.3 MPC). Within the barrier zone of the Lake Baikal, the copper concentration decreases with distance from the coast to be less than 2 MPC. One could not say unambiguously whether these "disorders" are caused by human impact, since both maximum and average weighted copper concentration values in the Selenga River are comparable with the parameters of the global naturally-occurring river background (see Fig. 7). Moreover, the copper content in the rivers depends on the specific geological and climatic characteristics of their basins being able to reach very high values (*e. g.*, 5 μg/L) in the rivers belonging to the basin of the Nizhnyaya Tunguska River and the Kochechuma River (involved in the Yenisey River basin) those, certainly are located within ecologically clean regions [33, 35].

In spring and in summer, small (up to 1.7-fold) exceeding the fish-industry requirements concerning Al (MPC = 40 μg/L) is observed in some parts of the Selenga River. In the springtime, this is associated with a high content of organic matter, whereas in summer, this could be, to all appearance, caused by an abnormally high turbidity of water (see sect. 4.4). As the tributaries are concerned, exceeding the standards is registered in three cases: in the spring in the Chikoy River (2.5 MPC) and the Temnik River (1.3 MPC), and in the summer in the Uda River (1.1 MPC).

Small (less than 1.8-fold) exceeding the fishing industry standards with respect to Fe (MPC = 100 μg/L) is observed in the Selenga River in spring downstream of the confluence with the Chikoy River, as well as in the Chikoy River (2.1 MPC) and in the Uda River (1.8 MPC). In the flow paths and the delta lakes the Fe concentration in the springtime also exceeds the standards (1.4–2.6 MPC). In some cases, the violation of the standards in the delta lakes is registered also in other seasons: in summer for the Semenovskoye Lake (1.2 MPC) and for the Berezovoye Lake (1.9 MPC), in autumn for the Semenovskoye Lake (2 MPC), in winter for the Zavernyaikha Lake (1.2 MPC) and for the Berezovoye Lake (49 MPC). The main causes of the increased concentration of Fe in the water could be associated with naturally occurring processes those consist in an intensive removal of organomineral complexes from the upper soil horizons in the course of flood and Fe mobilization from bottom sediments (see sect. 4.3).

The concentration of Fe in the Selenga River is comparable with the GNRB parameters: the maximum concentration of Fe is 4 times lower than the maximum value, whereas the average weighted value slightly (20 %) higher than the mentioned parameter (see Fig. 7).

4.3. Factorial Group 3 "Acidity/oxygen"

The third factorial group involves Si, Li, Cr, Mn, Co, Zn, Ge, Rb, Ag, Cd, Sn, Cs, Bi, acidity (H^+) and dissolved oxygen (O_2). The concentrations thereof in the Selenga River, as well as those for the factorial group 2, demonstrate an increase from Mongolia to the Baikal Lake, but the highest values are observed within the ice period (March), except for O_2. The concentration of O_2 is, on the contrary, minimal this time being maximal in the autumn (see Fig. 5).

The main controlling factor for these elements is presented, to all appearance, by the acidity level of the medium against the background of the seasonal dynamics of dissolved oxygen, as well as by the influence of other factors those cause increasing to a great extent the concentration of the most of the elements in the winter (see Fig. 5). Such factors could be presented by groundwater and/or the processes of mobilizing the elements from sludgy sediments, whose role in winter period should increase, because within this period there is changing the physicochemical conditions (T, pH, O_2) to a significant extent and reducing the water content of the rivers observed.

All the tributaries, except for the Dzhida River, those are more acidic than the waters of the Selenga River in the course of the year, contain usually a little greater amount of dissolved oxygen. Therefore it is quite natural that as the dilution by tributaries occurs the acidity and the oxygen content in the Selenga River demonstrate an increase. The concentration of Rb in the tributaries is also higher than in the Selenga River, except the Uda River in September and the Dzhida River in March. The concentration of other elements belonging to the factorial group 3 in the tributaries is in general comparable with that in the Selenga River, but in some cases there are significant deviations in both directions.

Taking into account a complex nature of the influence of different factors, there are more exceptions inherent in this group of elements. In the winter period, the part of Selenga River downstream the Ulan Ude exhibit a noticeable increase in the concentration of Bi, Mn, Co, Cs, Rb, (as well as Cl and some other elements of the factorial group 1, see sect. 4.1), whereas the concentration of Ge, on the contrary, decreases to a significant extent (see Fig. 5). The concentration of elements such as Si and Li, begin to increase noticeably much upstream after the confluence with the Chikoy River, whereas the concentration of other elements does not change (Sn, Cd) or fluctuate to a great extent (Cr, Ag). To all appearance, this indicates the presence of several types of groundwater or other sources of elements. Another exception is presented by Co, whose the concentration in the springtime, in summer and in autumn demonstrates a decrease towards the Lake Baikal, and the spatial distribution thereof is similar to the factorial group 1 (see sect. 4.1 and Fig. 3).

In the spring, summer, autumn seasonal dynamics one cannot see any equal picture of the distribution for all the elements: the type of the spatial distribution is retained (except for Co), but the gradient and the average concentration values of the elements in the Selenga River vary in different ways (see Fig. 5). Average concentration values for Bi, Mn, Cr and Ag decrease from spring to autumn, the values for Zn, Sn and Cd do not change, Ge being at the same level in spring and in summer, but slightly less than in autumn, the concentration of Cs, Rb are higher in summer, Si is almost at the same level in summer and in autumn, but 1.5 times lower than in spring, the concentration of Li exhibits an increase from spring to autumn.

The concentration of the elements of this group in the Selenga River and other aquatic objects studied do not exceed the requirements of the Russian standards, except for Mn in winter.

The Mn concentration in the rivers in winter increases to a significant extent (38–120 μg/L, except the Dzhida River 4.4 μg/L) as to compare with other seasons (0.28–6 μg/L) consistently exceeding the values recommended by fish-industry regulations (MPC = 10 μg/L), and in some cases (downstream the Ulan Ude 120 μg/L, downstream the Murzino settlement 110 μg/L) is higher than the values recommended by the Russian standards for drinking water, domestic water, water for cultural and domestic use (MPC = 100 μg/L), but it does not exceed the standards for drinking water recommended by WHO (400 μg/L). The Mn concentration in winter in some flow paths and lakes of the delta is much greater than that in the Selenga River, 4.6–88 times exceeding the values recommended by the Russian standards for drinking water.

A significant change in the concentration of Mn (almost 70 times) in the seasonal cycle results in a significant difference when compared with the parameters of global river background: the average weighted concentration of Mn in the Selenga River is to a significant extent lower (23 times), whereas the maximum Mn concentration is slightly higher (10 %) than the respective characteristics of GNRB.

Significant increasing the concentration of Mn in winter, both in the Selenga River and in the tributaries thereof indicates some naturally occurring processes of the mobilization of this element. To all appearance, Mn is either supplied together with the groundwater or mobilized from sludgy sediments [36]. The Mn mobilization processes are also promoted by a swampy landscape and decreasing the flow velocity [36]. It is known that Mn is sensitive with respect to Red/Ox potential value to migrate mostly (~90 %) under moderate oxidizing conditions as suspended species [33, 35]. No measuring the E_h of water was performed, so it is difficult to evaluate thermodynamic conditions inherent in the existence of soluble manganese species. However, a more acidic environment (pH 6.95–7.48) and a reduced concentration of dissolved oxygen in water (4.2–6.5 mg/L) in the winter as compared to the other seasons are much more favourable both for Mn mobilization from sludgy sediments and suspensions and for revealing thereof as true soluble species (Mn^{2+}). To all appearance, a very low Mn concentration in the Dzhida River in winter (4.4 μg/L) could be a consequence of less favourable physicochemical conditions (O_2 7.23 mg/L, pH 7.65) as to compare with other rivers.

The processes of Mn mobilization from the river sediments are most pronounced in the delta of the Selenga River. The Mn concentration in winter in the flow paths is much greater than in the main river station (fl. Srednyaya 460 μg/L, fl. Kolpinnaya 3300 μg/L), and even greater in some delta lakes (the Berezovoye Lake 6000 μg/L, the Zavernyaikha Lake 8800 μg/L), to a significant extent exceeding the values required by any regulations. The Berezovoye Lake, alongside with a high content of Mn, exhibit also the maximum concentration of Fe (4900 μg/L) and As (20 μg/L) observed. This is an isolated suffocation lake in the delta of the Selenga River (see Fig. 2) with a high content of organic matter. In winter, in the absence of oxygen, there are reducing conditions occur those promote the mobilization of Fe, Mn and As diagenetically associated therewith from the sediments into the water bulk of the lake.

Within the barrier zone of the Lake Baikal, the Mn concentration decreases to a significant extent, passing through a geochemical barrier, to decrease with the distance from the shore. However, in the bottom layer, as it is in the case of Cd, there are an order of magnitude higher concentration values (5.9–22 μg/L) observed as to compare with the superficial layer (0.68–4.6 μg/L).

4.4. Factorial group 4

The fourth factorial group involves V, As, Sb, I, W and Cu, whose concentration values are increased in the summer, especially in the upstream water (0–120 km) of the river (see Fig. 6). At this site there were also noted maximum values of potassium (see sect. 4.1 and Fig. 3) and thallium content (see Fig. 6). Within the period of spring-autumn the concentration of the most of elements demonstrate a decrease from Mongolia to the mouth, whereas in winter (except for V, As, I), on the contrary, the values are increased (see Fig. 6). The concentration of V and Cu unlike the other elements, almost do not exhibit in spring any changing along the riverbed. Average concentration values for the elements of the factorial group 4 in the Selenga River increase from spring to summer (except for Cu), decreasing to a significant extent in autumn almost down to the level of the concentration inherent in the winter period (see Fig. 6).

The summer period of 2010 was anomalous for the Selenga River: the water temperature in July was 26 °C (typically 22 °C); the water was turbid, containing a great amount of pathogenic organisms (O. Kravchenko, personal communication).

It is difficult to determine what caused increasing the concentration of these elements in the Selenga River in July, however, there is no doubt that the mobilization thereof occurred mainly in Mongolia, since the concentration of elements in the tributaries over the territory of Russia was to a significant extent lower (except for W, As, Sb in the Chikoy River, W, Sb in the Dzhida River).

The concentration of V in summer in the Uda River, the Selenga River and in the river branches of the delta, as well as in the surface water of the Lake Baikal at a distance up to 2 km from the coast is into a significant extent higher than the fishing industry standards for MPC (MPC = 1 μg/L). Maximum exceeding the MPC (2.4 times) was registered in the Selenga River upstream from confluence with the Chikoy River (see Fig. 6).

One could not say that July a weak transboundary transport of V, As, Sb, I, W, Cu registered in has a significant load on the Russian part of the Selenga River, since the maximum concentration of these elements is below the corresponding levels of GNRB, whereas the average weighted concentration values thereof are comparable (V and As level only is slightly (~30 %) higher than the GNRB level, see Fig. 7). A human impact with respect to these elements is also not obvious.

4.5. Comparing the Selenga River with the global natural background concerning trace elements

The concentrations of trace elements (<1 mg/L) in the Selenga River (the fluctuation range and average weighted values) were compared with roughly determined GNRB parameters (see Fig. 7). The main set of the GNRB parameters was taken from review [37] which summarized the results of studies carried out using modern methods (mostly ICP-MS) during previous decade in the basins of three dozen world's largest rivers flowing within environmentally clean areas or the areas with a low anthropogenic load. We have supplemented and verified the database of review [37] concerning a number of elements in the course the analysis of date available from the literature: [38] Ag; [25] Mo, Re; [39] Tl; [40] Br; [41] Br, I; [42, 43] I; [33, 35, 44] Sn, [45–48] Bi). These data are presented in Fig. 7.

The average weighted concentration of elements in the Selenga River was calculated from the average concentration values in the lower reaches of the river within the length between the Kabansk settlement and the Kharauz tribute. Data concerning water consumption (the Kabansk settlement) within the corresponding months were taken from the data for 1997 (ArcticNET data) those are closest to the hydrological conditions in 2010. The range of elemental concentration values was determined from all the data totality (all checkpoints being in the main river station, for all the seasons).

As it follows from the comparison, the concentration values for the most of elements in the water of the Selenga River do not exceed the GNRB level (see Fig. 7). Small exceeding the maximum concentration was noted for Mo (10 %) and Mn (10 %), whereas those were observed to be somewhat higher for Ge (60 %). The average weighted parameters were 2 to 5 times exceeded for Zr (2.1), Nb (2.1), Sr (2.5), Ti (2.9), U (3.5), Y (3.5), Zn (3.7), Mo (3.8) and Sn (4.9). Taking into account that the level of GNRB were determined tentatively not taking into account any specific climatic and geological features of river flow formation, one could not state that the observed exceeding level indicates a man-caused impact.

5. CONCLUSIONS

The seasonal dynamics of major ions, Si, trace elements, organic carbon, pH and dissolved oxygen in the waters of the Selenga River in the territory of Russia was studied, as well as that concerning its tributaries, lakes and flows of the delta, within the area of the barrier zone of Lake Baikal at a distance up to 7 km from the river mouth. We have revealed four groups of components in water chemical composition fundamentally different in the character of space-time distribution.

The first group of elements is united by water salinity, the major ions and some conservative trace elements (B, Br, Sr, Mo, Ba, Re, U), which indicates the common sources of supplying thereof. The concentration values for these components are maximal within the ice period (March) and minimal within the flood period (May), they exhibit an increase at the frontier with Mongolia to reduce towards the river mouth as being diluted by less mineralized waters of the tributaries of the river. The most significant dilution occurs after the confluence of the main tributary the Chikoy River (~1/3 of the total runoff of the Selenga River). The spatial pattern is broken for a number of chemical elements in winter: the concentration of B, Na, Ba, K, and especially that of Cl demonstrate an increase with respect to the mineralization (salinity) level in the River part below Ulan Ude, which could be caused to all appearance, by increasing the proportion of groundwater with another chemical composition in the feeding of the river.

The factor in determining the behaviour of the second group of the elements is related to the content of dissolved organic matter, capable of transferring difficultly soluble and almost insoluble elements (Be, Al, Ti, Fe, Ni, Cu, Ga, Y, Zr, Nb, Hf, REE, Pb, Th) into finely dispersed organomineral complexes. The concentration values of these elements demonstrate an increase in the spring, in the course of snowmelt and the carryover of organic matter from the catchment basin. The most significant increase in the concentration values for these elements in Selenga River is observed after the confluence of the Chikoy River, wherein the highest concentration of dissolved organic carbon is noted (DOC = 22 mg/L). The DOC concentration in the Selenga River increases from Mongolia towards Lake Baikal in the same direction there is an increase of the concentration observed concerning the elements connected therewith.

The factors those exert an effect on the third group of elements (Si, Li, Cr, Mn, Co, Zn, Ge, Rb, Ag, Cd, Sn, Cs, Bi), are more complicated. They reflect the processes of water acidification against the background of the seasonal dynamics of dissolved oxygen. The concentration values for the elements of the third group in the Selenga River, as well as those for the second one, demonstrate an increase in the direction from Mongolia towards Baikal (except for Co within the period of spring and autumn, and for Ge in winter), but these values are to a significant extent increased in winter, when the water content in the river decreases and the physicochemical conditions (T, O_2, pH) are changed to a considerable extent. This is facilitated by freeze-up conditions and by growing the role of the processes of organic matter decomposition as to compare with photosynthesis, as well as, to all appearance, by increasing the contribution of groundwater.

Lowering the O_2 concentration and pH in the water in winter promote the mobilization of some elements from the solid phase (river sediment, suspension, colloids). Within this period, as compared to other seasons, Mn concentration in the Selenga River increases to a greatest extent (70 times). In winter, at the river part downstream with respect to Ulan Ude there is a noticeable increase in the concentration of Bi, Mn, Co, Cs, Rb, whereas the concentration of Ge, on the contrary, abruptly and to a significant extent decreases, which indicates an increase in the fraction of groundwaters with another chemical composition in feeding the river, those are marked also by some other components (B, Na, Ba, K, Cl).

The fourth group of the elements (V, As, Sb, I, W, Cu) reflects a weak transboundary transport from Mongolia in the summer. The concentration of these elements are increased in July (particularly at the upstream (0–120 km) section of the river), alongside with an abnormally high turbidity, and a high temperature of water (up to 26 °C). One could not say that the transboundary transfer of the mentioned elements has a significant burden on the Russian part of the Selenga River, because their maximum concentration values are below the corresponding levels of the global naturally-occurring river background, whereas the average weighted values are comparable between each other.

Basing on the analysis of data available from the literature concerning the other rivers of the world, it has been found that the maximum and the average weighted concentration values for the most of trace elements in the Selenga River are lower than those inherent the global naturally occurring river background. Exceeding the maximum concentration is observed for Mo, Mn and Ge. The average weighted parameters demonstrate a 2 to 5-fold exceeding in Zr, Nb, Sr, Ti, U, Y, Zn, Mo and Sn, which is associated with a complicated geological structure of the river basin and with the natural processes of mobilizing the elements.

Within the main station of the Selenga River and its tributaries there is exceeding the MPC observed with respect to Mo, Mn, Cu, Al, Fe, V revealed for fish-industry ponds. In the most of the cases (80 %) the exceeding is small (less than 2 MPC). In winter in the flows and lakes of the river delta there is a significant excess in concentration values with respect to the standards for Mn (within the range of 46–880 MPC) and Fe (49 MPC, the Berezovoye Lake), which could be connected with the naturally occurring processes of mobilizing these elements from bottom sediments: the oxygen deficiency and prevailing the organic matter degradation processes over the photosynthesis in the course of freeze-up promote appearing the reducing conditions under those Mn and Fe could become mobile. Within the barrier zone of the Lake Baikal there was registered exceeding the MPC recommended for fish industry reservoirs: for Mo the value is constant (1.2–2.1 MPC), for Cu in winter (up to 1.8 MPC), summer (up to 1.9 MPC) and autumn (up to 1.3 MPC), for V in summer (up to 1.6 MPC), for Mn in winter (up to 2.2 MPC).

The Russian MPC standards for drinking water are slightly exceeded in the Selenga River in winter concerning Mn (MPC = 100 μg/L, Russia) in two cases: downstream the Ulan Ude (1.2 MPC) and near the settlement of Murzino (1.1 MPC).

Exceeding the standards revealed are to a greater extent associated with the naturally occurring processes of mobilizing the elements; no man-caused influence upon the Selenga River connected with trace elements was found out.

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