The use of geochemical monitoring to assess the environmental impact on the ecosystem of Lake Baikal (Russia)

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Abstract. Currently, many countries of the world experience drinking water scarcity. In this aspect, Russia has an advantageous position, having on its territory Lake Baikal, the largest storage of fresh water. UNESCO declared Lake Baikal as a World Heritage Site whose state scientists from Russia and other countries monitor and study. An analysis of the literature and the author information about the Baikal aquatic ecosystem has shown 70-year invariability of macroelement water composition of Lake Baikal and its only outflow, the Angara River. The water of Baikal and the Angara River has a constant calcium bicarbonate composition and is saturated with oxygen, 10-14 mg/l or rarely more. The average mineralization of water in Baikal and the Angara source for the study period (1950-2018 and 1997-2018) is 95-97 (87-112) mg/l. The analysis of the 13-year (2006-2018) data on the trace element concentration in the Angara source has revealed a complex pattern of changes in concentrations of some elements. The time trends of the concentrations for the bulk of elements sometimes indicate abnormal (minimum-maximum) concentrations regardless of the season. This can be only due to “one-time or instantaneous” natural or anthropogenic changes in the Baikal environment. The Baikal tributaries indicate different chemical composition, which can be due to not only drainage of rocks with different content but also the anthropogenic impact. A simultaneous testing of water (during a month) has shown that some macro- and trace elements (F\textsuperscript{-}, HCO\textsubscript{3}⁻ and SO\textsubscript{4}\textsuperscript{2⁻}, as well as Li, Mo, B, U, Fe, etc.) have at the same time the similar concentrations in the water from Baikal, the Angara source and most tributaries.

1. Introduction
In the 21st century, many countries of the world (Africa, South Asia, the Middle East, etc.) experience drinking water scarcity. This situation set thinking about preserving existing water supplies. In this aspect, Russia has an advantageous position. Lake Baikal alone contains approximately 23000 km\textsuperscript{3} of pure drinking water, which is 20% of the world’s reserves. For this reason, UNESCO declared Lake Baikal as a World Heritage Site whose state scientists from many countries monitor and study. The Baikal aquatic ecosystem includes Lake Baikal, the Angara River as its only outflow and numerous tributaries (over 360). The water from the Angara source presumably reflects the average chemical composition of Baikal. Much is already known about Lake Baikal: three basins of different depths were distinguished, the maximum depth of 1642 m was determined, the directions of horizontal flows, as well as cyclonic and under-ice currents, were recorded, the presence of upwelling was confirmed,
the temperature and chemical variations of the surface and deep water were identified, and the temperature of the water and air, as well as the water level of Baikal, etc. are being monitored [1-7].

The aim of our studies is to identify the causes of possible changes in the chemical composition of water as well as an integrated assessment of the impact on Lake Baikal of regional natural phenomena, the chemical composition of numerous tributaries, remote industrial ecosystems, locals residing the shore of the lake, and the thriving tourism business.

2. Objects, data and methods

Vinogradov Institute of Geochemistry SB RAS (IGC SB RAS) has been studying the chemical composition of the water in the Angara source for more than 20 years (1997-2019). Lake Baikal, the outflowing Angara River and numerous tributaries are located in the Baikal Rift Zone, where shifts and earthquakes constantly occur [8]. In geological terms, the rocks of different ages (Archean-Cainozoic) and content (from basic to acidic) represent the Baikal environment [9].

In the valleys of the Baikal tributaries, which drain rocks of different content and age, there are various water types depending on their prevailing nutrition. Moreover, precipitation type (rain or snow) influence the nutrition and content of tributaries. The chemical composition of the water divides the Baikal tributaries into various hydromineral provinces [10, 11].

The waters from Baikal, the Angara source and numerous tributaries have different composition even in different seasons. It is also necessary to consider the anthropogenic impact (diverse industries, fires, intensive tourism, etc.) on the Baikal ecosystem. The largest tributaries (the Selenga, the Upper Angara, the Barguzin, the Bolshaya Goloustnaya, the Buguldeika, etc.), when they flow into Baikal, form large deltas of geochemical macrobarriers, where the substances introduced by them are deposited in a significant amount [10].

The study objects were the waters from Baikal (40 samples – 2011-2018), the Angara source (500 samples – 1997-2018) and the Baikal tributaries (70 samples – May and September 2018) (figure 1).

Figure 1. Scheme-map of water sampling in the Baikal aquatic ecosystem.
Water sampling from the Angara source was carried out every ten days in 1997-2006, and since 2007 – once a month in the monitoring regime. The Baikal water was sampled sporadically (2011-2018). The water from the estuaries of the Baikal tributaries was sampled in the spring and autumn of 2018.

Chemical (macro- and trace element) analysis of the water samples from the Baikal ecosystem was performed using scientific equipment of the accredited Core Facility of Isotope and Geochemical Studies at IGC SB RAS. The analysis of the water macroelement composition was carried out according to generally accepted techniques (titrimetry, potentiometry, turbometry, etc.). The trace element water composition was determined by inductively coupled plasma mass spectrometry (ELEMENT 2, Finnigan MAT, Germany). The analysis of mercury in the water was carried out through atomic absorption technique on an RA-915+ instrument with an RP-91 attachment for computer recording.

3. Results and discussion
Analysis of publications (since 1950) about the ion composition of the water from the Angara source and our long-term monitoring data (1997-2018) allowed us to analyse and compare the available information for the period of 1950-2018. The data on trace element composition of the water is available from 2006 to 2018. In 2018, we obtained chemical data on the composition of 35 water tributaries of Lake Baikal.

A comparison of the literature and the author information about the Baikal aquatic ecosystem has shown 70-year invariability of macroelement water composition of Lake Baikal and its only outflow, the Angara River. The water in Baikal and the Angara source is pure, fresh, low-mineralized, with a constant calcium bicarbonate composition, and oxygen-saturated, 9-14 mg/l or rarely more. For the studied period (1950-2018), the average mineralization in Baikal and the Angara source is 95-97 (87-112) mg/l [3-5, 12-14].

The water in the Angara source never freezes. The monthly monitoring of the chemical composition of the water from the Angara source indicated variational trends in the compositional changes. The obtained data show the three-ten-year cycles in the compositional changes of all macroelements at the Angara source and clear annual seasonal cycles in the ion compositions. We confirm the dependence of the major ion concentrations of the water from the Angara source on the season and, hence, the water temperature. In summer, the concentrations of TDS, HCO$_3^-$, O$_2$ and nitrogen ions decrease due to the rapid development of phyto- and zooplankton. These processes result in peculiar cyclic variations in water compositions throughout the year, which reflect the interannual compositional trends (figure 2).

The mineralization of the water at the Angara source slightly increased from 1950 to 2013. However, in recent years it has been close to mineralization of 1950-1951.

The analysis of the Hg concentrations in the water at the Angara source over the past 20 years confirms the previous assumption [3] about their simultaneous increase in Baikal and the Angara source during natural disasters (earthquakes, hurricanes, storms, etc.). Thus, there were a series of perceptible earthquakes in 1998-1999; then, insignificant shifts were in 2002, 2004, 2008, 2017, and 2018. Almost all of them are recorded in the ice-free Angara source as a three-five-fold increase in mercury in the water. In seismically quiet periods, the mercury concentration in the Baikal ecosystem is very low, 0.0005 μg/l or less. The influx of mercury to the water and the rise of deep water to the surface is most likely to occur some time after the earthquake. Perhaps, in the absence of movements in the deep section of the Baikal water column, mercury concentrations are below the maximum permissible values (0.01 μg/l) for fishery water bodies. After an earthquake, the mercury concentration increases in the bottom part of the lake. This can be recorded at various horizons of the water column as well as in the Angara source. The rate of deep water rise (upwelling) in Baikal depends on hydrometeorological conditions [7]. Physicochemical modelling showed the possible generation of deep waters under the riftogenic geodynamic conditions [15].
Figure 2. The average annual trend of ion concentrations and total mineralization in the water of the source of the Angara River (1950-2018).

The analysis of 13-year (2006-2018) data on other trace elements in the water of the Angara source revealed low concentrations and more complex irregular pattern of compositional changes in some trace elements. Time trends of most trace elements sometimes show extremums that are not associated with seasons, which can be only due to “one-time or instantaneous” natural or anthropogenic changes in the environment of Lake Baikal and its source (figure 3). Single abnormal concentrations are then levelled thanks to the climate and self-cleaning processes in Lake Baikal as well as the “aggressiveness” of the Baikal water.

The use of ultraviolet protection at the water intake of the Angara source in 2011 led to temporal two-year increases and then decreases in the concentrations of elements of the iron group, Ni, Co, Mn, Zn, Cu, and Pb. Despite variations in the chemical composition of the Baikal water, it should be noted that over the past 20 years there was actually no excess of the maximum permissible concentrations of macro- and trace elements for drinking water and fishery water bodies.

A single (May-June 2018) macro- and trace-element analysis of the surface (in the pelagic zone) and deep (central basin, 1642 m) water from Baikal and, at the same time, the Angara source has shown their proximity and identity.

Interestingly, despite the wide variety in the chemical compositions of the water from rivers inflowing to Baikal, its average chemical composition for most elements in the central part of the lake (length ~ 700 km) and the composition of the Angara source are practically the same and remain stable. This is due to the formation of geochemical barriers in deltas of the large and small Baikal tributaries and the deposition in them of the bulk of the suspended matters introduced by rivers [6, 10].

In 2018, the deep water in the central part of Baikal had high Si, P and Ca concentrations at deep horizons and insignificant oxygen reduction, which was previously shown and confirmed in recent years [12-14]. Our preliminary data indicate unusual (season-free) distribution to a depth for concentrations of certain trace elements (increased, decreased or chaotic) in the spring and autumn, Zn, S, B, U, etc. (figure 5).
A comparison of chemical data on the surface Baikal water with the water from tributaries has shown both the similarity of the element concentrations in the water from tributaries to the Baikal water and their differences. Most elements in the tributaries are significantly higher (exceed the maximum permissible concentrations for drinking water) than in the surface Baikal water, its pelagic zone and the Angara source. This is due to the different content of rocks drained by tributaries and different anthropogenic impact in their basins. Moreover, it is necessary to consider the influence of diverse industries adjacent to the banks of rivers.

However, there are also elements whose concentrations in the waters of tributaries and Lake Baikal are rather close. This concerns, for example, the concentrations of F, HCO₃⁻ and SO₄²⁻, as well as Li, Mo, B, U, Fe, etc. (figure 4).

A sanitary-microbiological assessment of the water quality of the Baikal ecosystem in 2018 showed [16] that the Baikal water in the pelagic zone complies with the recommended standards for drinking water. In the littoral zone of Baikal, the water from some bays cannot be used by residents and tourists for recreational purposes. Such Baikal tributaries as the Barguzin, the Turka, the Snezhnaya, the Solzan, and the Goloustnaya show the most likely epidemiological danger.
Figure 5. Distribution of trace element concentrations in the deep section of the Baikal water (green trend – May 2018, orange trend – September 2018).
4. Conclusion
The analysis of the available data on the chemical composition of the Baikal aquatic ecosystem indicates an additional inflow of deep (juvenile) water to Baikal and its renewal, which can be due to the numerous earthquakes in the Baikal Rift Zone and shifts in the deep part of Lake Baikal. A possible generation of deep fluids in these zones was previously assumed. The self-cleaning ability and deposition of the bulk of the pollutants in the deltas of large tributaries at geochemical barriers can also explain the purity of the Baikal water.

At present, the main threat for Lake Baikal and its outflow is local pollution of the littoral zone by the sewage from settlements, a great number of touristic bases, which often do not follow the regulations, and increasing shipping at Lake Baikal. The water of some coastal areas of Lake Baikal contains an elevated amount of microplastics, which becomes hazardous for both the water and biota and for humans.

In recent years, scientific organizations and public authorities of the Baikal region have been constantly monitoring the central ecological zone of Lake Baikal.

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