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Current chemical composition of Lake Baikal water

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ABSTRACT
Habitats of organisms in Lake Baikal have been comprehensively monitored for many years. In 2010–2015, we conducted 8 research expeditions to study ionic composition of the water and measure concentrations of dissolved oxygen, nutrients, organic carbon, and persistent organic pollutants in the entire pelagic area of Lake Baikal. Our data showed that the ionic composition was stable at all depths in the pelagic zone of the lake. We also recorded seasonal variability, vertical stratification, and spatial variations in the content of nutrients, organic matter, and gas components. The concentrations of major ions, nutrients, and dissolved oxygen were favourable for the growth of hydrobionts in the offshore pelagic zone. Concentrations of pollutants in Lake Baikal, such as persistent organic pollutants and heavy metals, were low and did not directly affect the biota. The water in specific areas of the littoral zone of Lake Baikal, however, was polluted near large settlements (Listvyanka, Severobaikalsk, Baikalsk, and Slyudyanka) and in bays because of unsatisfactory operations of sewage treatment plants, growing tourist activity, and intense ship traffic. Continuing investigations are needed to elucidate causes of eutrophication in the littoral zone of Lake Baikal.

KEYWORDS
Lake Baikal; littoral and pelagic areas; major ions; nitrogen; phosphorus; tributaries

Introduction

Lake Baikal, the world's largest freshwater lake (23 000 km^3), has unique flora and fauna, 60% of which is endemic (Timoshkin 1995). The lake is a UNESCO World Heritage Site, and the Federal Law of the Russian Federation "On Conservation of Lake Baikal" prescribes its significance. Lake Baikal is conventionally divided into 3 basins: southern, central, and northern with depths of 1400, 1600, and 800 m, respectively. These 3 basins differ in temperature conditions, water exchange, and water volume (Shimaraev et al. 1996). Lake Baikal has a long water residence time, requiring ~400 years for replacing its water with water from inflowing tributaries. Certain exchange mechanisms cause annual partial renewal of deep waters of Lake Baikal. The age of the water at depths >250 m is 7.2–11.1 years, varying from year to year in different parts of the lake (Hohmann et al. 1997, Peeters et al. 1997, Kodenev et al. 1998). The littoral and pelagic zones of the lake comprise about 7% and 93% of the lake area, respectively.

Hydrochemical investigations of Lake Baikal and habitats of the Baikal flora and fauna were initiated in 1925 by the Baikal Limnological Station (Vereshchagin 1927) and continued by other researchers (Votintsev 1961, Votintsev, Glazunov 1963, Votintsev et al. 1975). In the early 1990s, the Limnological Institute of the Siberian Branch of the Russian Academy of Sciences (Irkutsk, Russia) developed a system for comprehensive monitoring, including hydrophysical, chemical, and biological investigations for current assessments of the aquatic ecosystem of Lake Baikal.

We analysed hydrochemical composition of Baikal water within multiple areas of Lake Baikal, including deep pelagic and littoral zones, and compared the data from 2010 to 2015 with the data obtained earlier.

Materials and methods

We sampled water for analysis in the southern, central, and northern basins of Lake Baikal at 20 deep sites as well as in the littoral zone and in the mouths of the lake's large tributaries (Fig. 1). During each expedition, we collected ~350 samples and performed >7000 analyses. Some components were analysed directly at the sampling sites; other samples were fixed according to the analysis technique and transported in a refrigerated box to the Limnological Institute's laboratory.

In the pelagic zone, we sampled water from surface to bottom (0–1400 m depths) with a Rosette water sampler consisting of 24 water bottles. The water was filtered through a 0.45 µm polycarbonate filter on board the ship, and the filtrates were refrigerated. Dissolved oxygen

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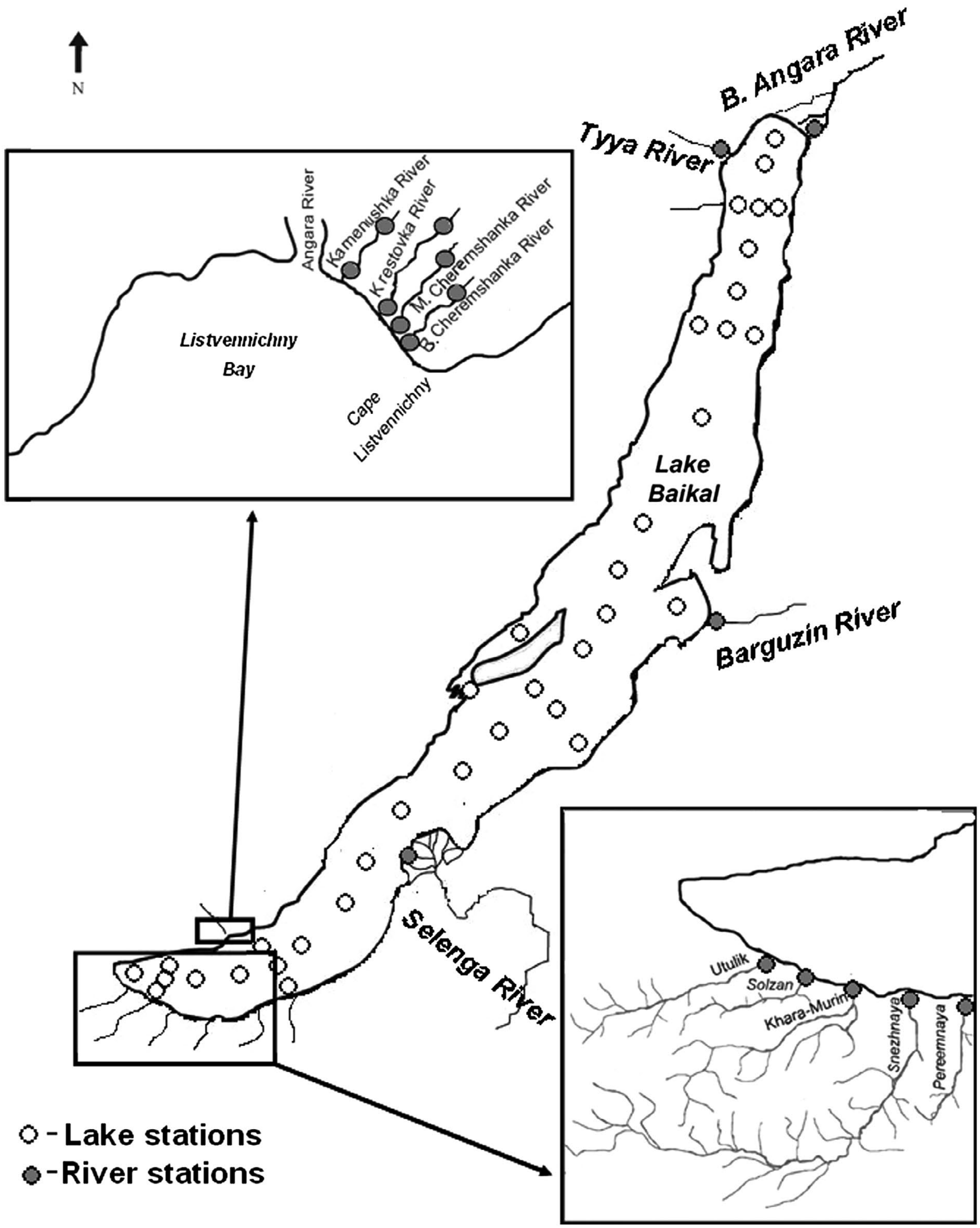

Figure 1. Sampling sites in Lake Baikal and its tributaries.

(DO), bicarbonate ions, and nutrients were measured on board the ship; other components were analysed at the laboratory.

We used classical methods to study chemical composition of water (Wetzel and Likens 1991). Cations were determined by atomic absorption spectroscopy (calcium [Ca^{2+}] and magnesium [Mg^{2+}]) and flame emission method (sodium [Na^{+}] and potassium [K^{+}]) on an AAS-30 spectrophotometer (Germany) with 5–7% error. Anion concentrations (chlorine [Cl^{-}], sulphate [NO_3^{-}][SO_4^{2-}], and nitrate [NO_3^{-}]) were measured by high-performance liquid chromatography on a chromatograph

Milichrom A-02 (EcoNova, Russia) with 5–7% error (Baram et al. 1999). Bicarbonate concentrations were assessed by the potentiometric method, DO content was measured by the Winkler test with 0.3% error, and phosphorus, nitrite, and ammonia were analysed on a photocolorimeter with 2–5% error.

Trace elements, oil products, and persistent organic pollutants (POPs) were analysed every 3–5 years. Chemical composition of the lake and river waters was monitored at standard sampling sites (Fig. 1). Reliability of the methods and quality of analyses underwent annual control according to international and Russian programmes on inter-laboratory calibration (Khodzher et al. 2004). Deviations of the results from the reference standard samples did not exceed 10%, attesting to the reliability of our data on chemical composition of the Baikal waters.

Results

One of the most important abiotic factors affecting chemical composition of water in Lake Baikal is the river runoff. According to the content of major ions, water of the lake's tributaries belongs to the bicarbonate class of the calcium group and affects the composition of the lake water. For the last 60 years, an increase in major ion concentrations has been recorded in the water of the Selenga River, the main tributary of Lake Baikal, because of increasing anthropogenic impact and decreasing water runoff (Sorokovikova et al. 2008). We also observed changes in the water composition and acidification in the tributaries of Southern Baikal, especially in rivers with extremely low water mineralisation (Pereemnaya and Khara-Murin rivers), because of the emission of pollutants from enterprises in the Baikal region onto their catchment areas (Sorokovikova et al. 2015). The content of major ions in other tributaries of the lake, including the Upper Angara and Barguzin rivers, varied insignificantly. The changes in chemical composition in the rivers did not affect the concentrations of major ions and their relative composition in Baikal water (Domysheva 2009).

The increase of nutrient input to the lake, in particular nitrogen (N) and phosphorus (P), could affect the lake's biological productivity (Sorokovikova et al. 2009). Seasonal and annual concentration variations of these elements depended on the river water runoff and intensity of phytoplankton development. The concentrations of total phosphorus (TP) and total mineral nitrogen (TMN), respectively, in the water of the main tributaries of the lake varied as follows: 27–158 and 0.01–0.71 μg L^{-1} in the Selenga River; 23–38 and 0.17–0.63 μg L^{-1} in the Upper Angara River; and 24–143 and 0.04–0.32 μg L^{-1} in the Barguzin River. We registered the lowest concentrations of nutrients in summer and fall in all rivers during intense development of phytoplankton. The TP concentrations in the Selenga River during March, June, August, and October were typical of eutrophic waterbodies. In 1983–1984, TP concentrations in this river were 90 μg L^{-1} (Tarasova and Meshcheryakova 1992), whereas currently they are 1.7–3.8 times higher.

All tributaries of the lake bring ~8000 t yr^{-1} N and 1100 t yr^{-1} mineral P (MP), 50% of which comes with the waters of the Selenga River (i.e., half of the lake's total water runoff; Sorokovikova et al. 2000). In recent years, the water level in the Selenga River has dropped (Sinyukovich et al. 2010), thus decreasing current velocity, raising water temperature in spring and summer, intensifying development of phytoplankton, reducing concentrations of mineral nitrogen (MN) and MP in river waters, and decreasing their input into the lake. The input of MP and TP from the Selenga River into the lake varied from 145 to 314 t yr^{-1} and from 1570 to 2940 t yr^{-1}, respectively. The main changes in nutrient concentrations were recorded in the lake 3–4 km from the river mouths. Nutrients affected phytoplankton development in the near-mouth areas of the rivers (Tomberg et al. 2010).

Changes in the chemical composition of the river waters did not influence chemical composition of the lake water. The composition of the water was stable in the lake's pelagic area because of the comparatively huge volume of water relative to the annual river runoff (60 km^3) as well as the intense water exchange in the lake (Falkner et al. 1991, Grachev 2002, Grachev et al. 2004, Domysheva 2009, Khodzher and Domysheva 2012).

Water in the lake has low mineralisation (total ions are ~96 mg L^{-1}) and, like in its tributaries, belongs to the bicarbonate class of the calcium group (Table 1). We observed that the content of major ions was constant within the entire water column in the pelagic area of the lake. Changes in major ion concentrations, however, were registered locally; ion concentrations were higher near the large tributaries of the lake (Selenga and Barguzin rivers and others; Tomberg et al. 2010).

Unlike major ions, oxygen and nutrient concentrations varied with depth depending on season. Specific features of the Baikal water include high oxygen saturation and low concentrations of nutrients and organic matter. Time variability of concentrations of nutrients and oxygen depends on biological processes and dynamics of water masses of the lake. In contrast to most lakes, the first peak of phytoplankton productivity was recorded in Lake Baikal during the ice-cover period, followed by smaller peaks in summer (Popovskaya 1971, Back et al. 1991, Jewson et al. 2008, Pomazkina et al. 2010). Oxygen concentrations decreased

Table 1. Mean concentrations and standard deviations (SD) of major ions in the water of Lake Baikal (mg L^{-1}, Jun 2010–2015).

Ion	Southern Baikal	Central Baikal	Northern Baikal	Entire lake
HCO_3^-	66.3 (1.8)	66.7 (1.5)	65.7 (1.4)	66.3 (1.6)
SO_4^{2-}	5.4 (0.1)	5.5 (0.2)	5.5 (0.1)	5.5 (0.1)
Cl^-	0.44 (0.02)	0.45 (0.03)	0.43 (0.02)	0.44 (0.03)
Ca^{2+}	16.4 (0.4)	16.5 (0.4)	16.3 (0.3)	16.4 (0.4)
Mg^{2+}	3.0 (0.1)	3.0 (0.1)	3.0 (0.1)	3.0 (0.1)
Na^+	3.3 (0.1)	3.4 (0.14)	3.3 (0.11)	3.3 (0.1)
K^+	1.0 (0.1)	1.0 (0.1)	1.0 (0.1)	1.0 (0.1)

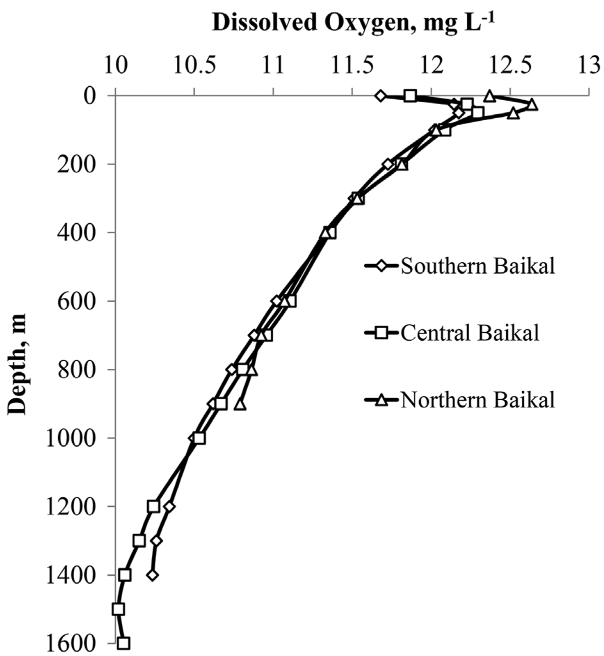

Figure 2. Vertical distribution of oxygen concentrations in each of the 3 basins of Lake Baikal (Jun, Aug, and Oct 2013).

with depth (Fig. 2). In different basins of the lake, oxygen content was similar at the same depths.

We recorded seasonal variation of oxygen concentrations only in the upper (up to 250–300 m) and near-bottom (up to 10–200 m from the bottom) water layers. In spring at low temperature, oxygen concentrations were maximal (13.5–14.5 mg L^{-1}) in the upper water layer. Spatial distribution of oxygen in the upper layer depended on the time of ice breakup; in the southern basin, ice breaks 2–3 weeks earlier than in the north of Lake Baikal (Votintsev 1961).

In summer, oxygen concentrations decreased to 10–11 mg L^{-1} in the upper layer because of water temperature rise. Elevated concentrations of oxygen were recorded at a depth of 25–50 m, associated with accumulation of vegetative phytoplankton at these depths (Votintsev 1961) as well with the increase of oxygen solubility at lower water temperature than that in the surface layer. In fall, the vegetation of the summer phytoplankton communities dies, and oxygen consumption increases because of oxidation of autochthonous organic matter; however, oxygen concentrations remained high (11–12 mg L^{-1}) because of the increase in oxygen solubility and decrease in temperature. Temperature conditions also affected spatial distribution of oxygen concentrations in the upper water layer. The difference in oxygen concentrations between northern and southern basins was 1–1.5 mg L^{-1}, highest in spring.

High concentrations of oxygen (9.5–14.5 mg L^{-1}) recorded at all depths are attributed to the unique mechanism of deep-water renewal in spring and fall in Lake Baikal, specifically temperature convection and dynamic mixing of water masses up to 200–400 m depth (Shimaraev and Granin 1991). Oxygen input into the deep area, caused by deep forced convection, was generated within the entire water column at 3.1–3.5 °C, close to spring and fall homothermy. This process can occur locally and occasionally around the whole lake water area (Weiss et al. 1991, Shimaraev et al. 2003). Oxygen saturation of the water can be 110–115% in the photic zone and 70% in the near-bottom layer. These high oxygen concentrations create favourable conditions for hydrobiont growth and active transformation of organic matter within the water column and its decrease in bottom sediments.

Lake Baikal is an oligotrophic waterbody. The concentration of nutrients, an indicator of water quality, was not high. Vertical distribution of MP and TP varied insignificantly within the water column of Lake Baikal and their concentrations increased with depth, reaching 14–17 µg L^{-1} in the near-bottom area (Fig. 3); however, we recorded differences only in the upper 200 m, attributed to seasonal dynamics of phytoplankton and dynamics of lake water masses.

During spring water mixing (June), the content of MP, like that of TP and oxygen, was uniform in the upper layer. In summer, concentration of MP decreased to minimal values in the surface layer. In some areas of Lake Baikal during maximal heating of the water and phytoplankton growth, MP concentrations may limit further algal development. Vertical stratification of MP was apparent in the upper 200 m layer (Fig. 4).

The percentage of organic P was maximal in the upper 25 m: 17% in June during reduction of growth of under-ice algal communities; 44% in July at the beginning of growth of summer algal communities; 63% in August during maximal phytoplankton growth; and 35% in October during reduction of algal growth.

Ammonia and N in the form of nitrite were recorded in small amounts, only in the upper layers mainly at the end of algal bloom and the near-bottom layers. Seasonal dynamics and vertical distribution of nitrate were similar to those of MP with minimal values (N: 0.01–0.07 mg L^{-1}) in the surface layer and maximum (N: 0.14–0.15 mg L^{-1}) in the near-bottom layer.

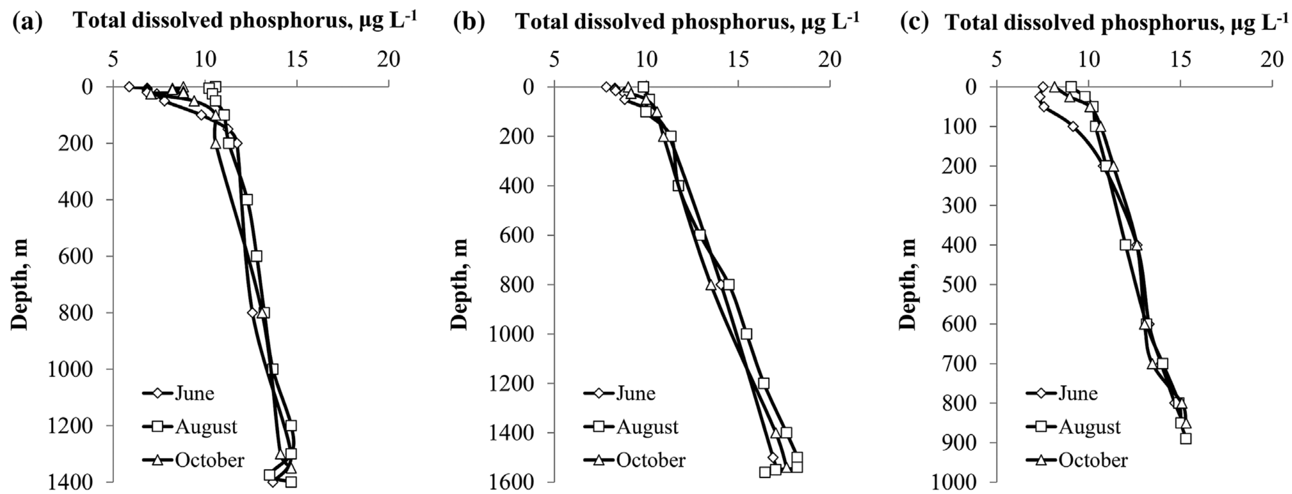

Figure 3. Vertical distribution of mean concentrations of total phosphorus in Lake Baikal offshore waters during Jun through Aug 2013; (a) southern basin; (b) central basin; (c) northern basin.

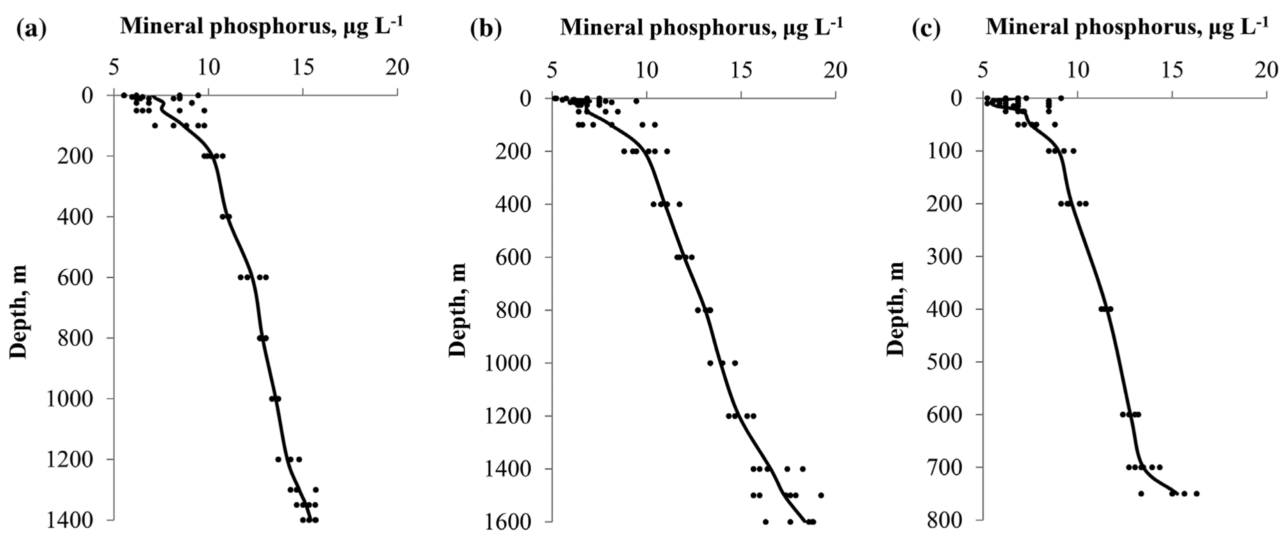

Figure 4. Vertical distribution of mineral phosphorus (MP): (a) southern basin; (b) central basin; (c) northern basin; solid line: mean concentrations in Jun 2010–2015; dots: concentrations in specific years.

Nutrient concentrations showed no apparent differences at the same depths in all basins of the lake (Fig. 5). These differences among depths were associated with nutrient inputs (with the water of tributaries and atmospheric precipitation), water exchange between basins, and the intensity of phytoplankton growth. For example, nutrient inputs per unit of area or volume increased from the southern to the northern basin, whereas the intensity of phytoplankton growth decreased (Popovskaya 1991, Popovskaya et al. 2015).

The latest data (2010–2015) and the data from 1992–2010 (Shimaraev and Domysheva 2013) showed that concentrations of nutrients in the pelagic area of Lake Baikal did not change compared with data obtained in 1950–1980 (Fig. 6).

The concentrations of polychlorinated biphenyls (PCBs) in the waters of Lake Baikal were 130–1900 pg L^{-1} (Nikonova and Gorshkov 2010), comparable with values from Lakes Superior and Huron (Great Lakes of North America) and waterbodies of some countries in Southeast Asia.

Discussion

In previous decades (1950–1990), Lake Baikal studies were conducted mainly in the upper 300 m layer and at some deep sites of the southern and central basins of Lake Baikal (Votintsev 1961, Tarasova and Meshcheryakova 1992). Recent investigations are focused on hydrophysical, hydrochemical, and hydrobiological processes occurring

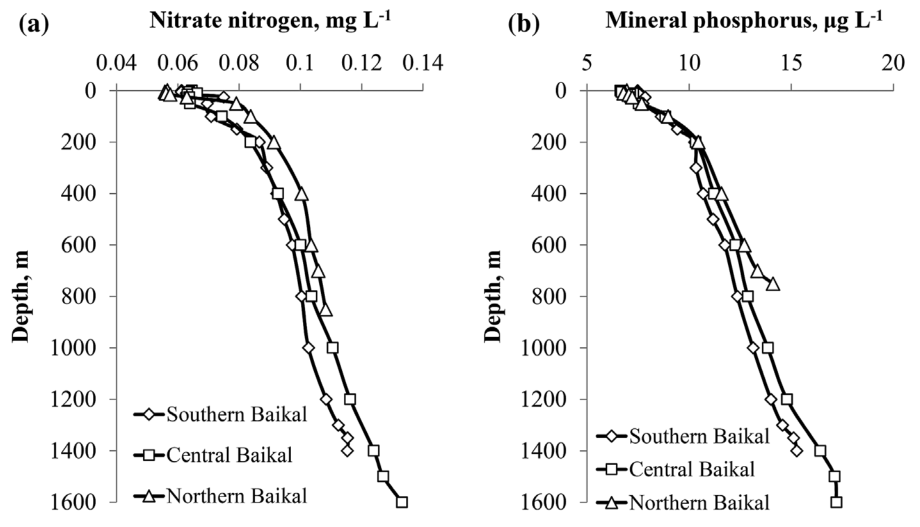

Figure 5. Mean concentrations of (a) nitrate nitrogen and (b) mineral phosphorus in each of the 3 basins of Lake Baikal (Aug 2010–2013).

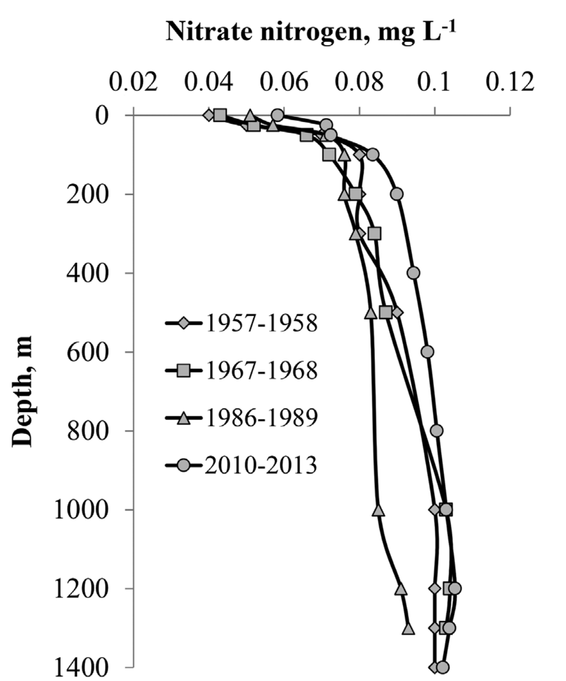

Figure 6. Depth profiles of nitrate-nitrogen concentrations in the southern basin of Lake Baikal for 4 different time periods (Jun 1957–2013).

within the entire water column. Much attention is paid to concentrations of chemical components in the deep part of the lake, which are the main tracers of renewal of deep water and stability of Lake Baikal's chemical composition (Grachev et al. 2004).

Water pollution in the littoral zone of Lake Baikal has recently become topical; undertreated domestic sewage is discharged into the lake, and intense tourist activity and increase of ship traffic also adversely affect the lake ecosystem. Climate change contributes to changes in the temperature regime of the lake. For example, the summer water temperature in the southern basin of Lake Baikal has increased by 2.4 °C over the last 60 years (Shimaraev and Domysheva 2013).

In July–August 2011, high concentrations of nutrients (P up to 420 µg L^{-1} and nitrate as N up to 0.20 mg L^{-1}) were recorded for the first time in the popular tourist area (Listvyanka, Southern Baikal) along the shoreline for 4 km, whereas the background values for P and N are 7 and 0.01 mg L^{-1}, respectively. The increase in nutrients caused abundant growth of benthic filamentous algae of the genus *Spirogyra* as well as the disappearance of *Didymospheniageminate* colonies. In addition, the zonation of phytobenthos was disturbed in the littoral area of the lake (Kravtsova et al. 2012, 2014). One source of nutrient increase is small rivers flowing into the lake near Listvyanka. The N and P content in these rivers increase toward their mouths (Fig. 7).

In 2013, we recorded an intense algal bloom atypical for Lake Baikal near the town of Severobaikalsk in the north of the lake (Timoshkin et al. 2016) caused by the input of poorly treated sewage from the town into the Tyya River (3 km from its mouth). Concentrations of MP and MN in the sewage were 5–6 and 35–38 mg L^{-1}, respectively, an input of nutrients that caused eutrophication of the littoral area on the western coast of northern Baikal, where massive accumulations of rotting algae of the genus *Spirogyra* accumulated.

Our results show that concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, bicarbonates, and chloride are constant within the entire waterbody. The lake water is enriched with oxygen, ranging from 14.5 mg L^{-1} on the surface to 9.5 mg L^{-1} in the near-bottom water layers. Nutrient concentrations (N and P) are low but increase with depth, differing between and within basins. These differences depend on the renewal of water masses and intensity of phytoplankton development. The comparison of the

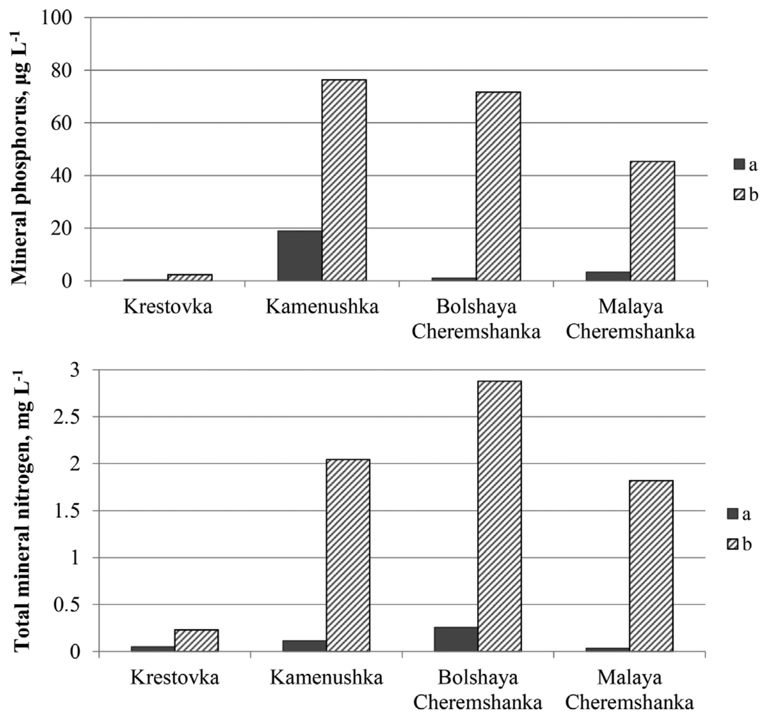

Figure 7. Concentrations of mineral phosphorus (a) and total mineral nitrogen (b) in tributaries of Lake Baikal near Listvyanka along the southwestern coast in the southern basin (Nov 2015). See Fig. 1 for location of tributaries.

2010–2015 data with the data obtained earlier showed insignificant differences in the concentrations of these elements in the deep parts of Lake Baikal. The content of DO and nutrients in the pelagic area of Lake Baikal is favourable for hydrobiont growth.

We note that Lake Baikal has its own natural sources of hydrocarbons. For example, the discharge of biodegraded oil from the lake bottom was 2 t yr^{-1} at Cape Tolsty and 4 t yr^{-1} at Cape Gorevoy Utes (Kontorovich et al. 2007); however, the concentration of oil products decreased abruptly with the distance from oil seepage (Gorshkov et al. 2010). Emissions from ship engines are a main anthropogenic source of oil products in Lake Baikal. Analysis of distribution of oil and oil products in the lake shows that the oil content in the pelagic area did not exceed 10 µg L^{-1}, n-alkanes were 0.15 µg L^{-1}, and polyaromatic hydrocarbons (PAH) were 0.012 µg L^{-1}.

The main threat to the lake is local pollution of littoral waters with nutrients and organic matter. The sources of this pollution are sewage from settlements, tourist camps located on the lake coast, and ships, whose numbers are constantly increasing. Changes in the structure, abundance, and biomass of the littoral communities and accumulation of rotting algae of the genus *Spirogyra* on the lake coast are striking signs of the lake's eutrophication.

Continued monitoring of chemical composition in Lake Baikal and its tributaries using sophisticated analytical equipment and high-precision methods is crucial to developing a Lake Baikal conservation strategy.

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Disclosure statement

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