

# Seasonal dynamics of mineral forms of nitrogen in the rivers, snow cover and precipitation at the southwest coast of the Southern Baikal

Onischuk N.A.\*, Netsvetaeva O.G., Tomberg I.V., Sakirko M.V., Domysheva V.M., Golobokova L.P., Khodzher T.V.

*Limnological Institute of the Siberian Branch of the Russian Academy of Sciences, Ulan-Batorskaya 3, 664 033 Irkutsk, Russia.*

**ABSTRACT.** In 2015 – 2019, we studied the concentrations of mineral forms of nitrogen ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$ ) in the waters of the Krestovka River and the streams Kamenushka, Bolshaya Cheremshanka and Malaya Cheremshanka as well as in the snow cover of their basins and precipitation of the Listvyanka settlement (southwest coast of Lake Baikal). Towards Lake Baikal the concentrations of the investigated compounds increase as a result of water pollution with domestic wastewater from the Listvyanka settlement. The highest concentrations of nitrates and nitrites are found in the estuary of the Malaya Cheremshanka, and those of ammonium – in the Kamenushka. Nitrate concentrations in the watercourses beyond the Listvyanka settlement have increased compared to the 1950s, which is due to climate change and air pollution. During the study period, the average annual concentrations of nitrates in precipitation and snow cover increased. The maximum concentration of nitrogen compounds in the snow cover is confined to lower parts of these streams. Thus, the snow cover of the Bolshaya Cheremshanka showed the highest nitrate concentrations. We have revealed that nitrate concentration in precipitation increases in the cold season due to air pollution with nitrogen oxides of anthropogenic origin. We indicate that nitrate concentrations in the waters entering Listvennichny Bay are an order of magnitude higher than in Lake Baikal, which can have a negative effect on the Baikal ecosystem

**Keywords:** surface waters, snow cover, precipitation, mineral forms of nitrogen, the Listvyanka settlement, Southern Baikal

## 1. Introduction

Lake Baikal is a unique natural site assigned to the World Heritage Sites, which currently acquires strategic importance as the largest source of drinking water on the Earth. At present, climate change becomes evident for every resident of our planet. Every year its consequences cause ever greater economic damage and often entail irreversible environmental impacts. Climate change at Lake Baikal is more active than throughout the globe; its secular temperature trend is two-four times higher than the temperature trend in the Northern Hemisphere (Shimaraev et al., 2002; Shimaraev and Troitskaya, 2018). Industrial development leads to an increase in pollutant emissions into the atmosphere. Ultimately, an intensive technogenic migration of chemical elements in some cases is comparable to their transfer resulted from natural geological processes. Sustainable development of the region, and especially the tourism sector, increases a local anthropogenic impact on the ecosystem of the lake. In this regard, the study of small rivers and watercourses in the territory of active tourism at Lake Baikal is special relevance.

Our study deals with the area of the Listvyanka settlement. There are a large number of hotel complexes in the settlement, including illegal ones. All hotels have faecal containers, which are often overfilled, and the only sewer is worn out. A large Krestovka River as well as several streams, Bolshaya Cheremshanka, Malaya Cheremshanka and Kamenushka, flow through the area of the settlement. In the 1950s, K.K. Votintsev carried out the first studies of rivers near Listvyanka (Votintsev et al., 1965). Further studies were continued due to the eutrophication threat to the Listvennichny Bay (Naprasnikova et al., 2007; Zagorulko et al., 2014; Alekseeva et al., 2016; Yanchuk, 2016; Vorobyova et al., 2017).

In our study, we took water samples in the monitoring regime from the small rivers of the Listvyanka settlement to determine anthropogenic and natural factors in the formation of the chemical composition of water. Moreover, we investigated the chemical composition of the snow cover on the watersheds of the river and streams as well as atmospheric precipitation in the settlement to identify the impact of air pollution on the composition of surface water.

\*Corresponding author.

E-mail address: [onischuk@lin.irk.ru](mailto:onischuk@lin.irk.ru) (N.A. Onischuk)

## 2. Materials and methods

In 2015-2019, the sampling of water from small rivers located on the west coast of the Southern Baikal near the Listvyanka settlement was carried out every month. The surface water samples were taken from sites not subject to anthropogenic impact (beyond the settlement) as well as from estuarine sites of the Krestovka River and the streams Bolshaya Cheremshanka, Malaya Cheremshanka and Kamenushka, with the nearby highway. At sites of the surface water sampling in late winter (February), the samples of snow cover were taken as an indicator of air pollution of the study area. Precipitation samples were taken at a year-round atmospheric monitoring station in the Listvyanka settlement (51°84' N, 104°89' E) using the US-320 automatic precipitation collector during the warm season and plastic containers during the cold season according to the manual (Technical Document... , 2000). Fig. 1 shows a map of surface water sampling stations near the Listvyanka settlement.

Mineral nitrogen compounds in surface waters, snow cover and precipitation were determined in the Laboratory of Hydrochemistry and Atmosphere Chemistry at Limnological Institute SB RAS according to the methods [GOST 33045–2014, RD 52.24.383–2005, PND F 14.2: 4.209-05, RD 52.24.186-89, RD 52.04.333-93].

## 3. Results and Discussion

### 3.1 Surface water

Nitrogen-containing compounds are important for aquatic ecosystems. Their lack in the water delay growth and development of aquatic vegetation. On the contrary, their excess lead to the development of eutrophication of aquatic ecosystems and the deterioration of water quality. In surface water, there are two main nitrogen groups: inorganic nitrogen compounds (mineral) and organic nitrogen compounds. Mineral nitrogen in aquatic ecosystems is



**Fig. 1.** Schematic map of the study area (Listvennichny Bay, Lake Baikal). Surface water sampling stations: 1 – the Kamenushka stream (beyond the settlement); 2 – the Kamenushka stream (estuary); 3 – the Krestovka River (beyond the settlement); 4 – the Krestovka River (estuary); 5 – the Malaya Cheremshanka stream (beyond the settlement); 6 – the Malaya Cheremshanka stream (estuary); 7 – the Bolshaya Cheremshanka stream (beyond the settlement); 8 – the Bolshaya Cheremshanka (estuary)

mostly dissolved and represented by nitrites, nitrates, ammonia, and ammonium ions (Nikanorov and Ivanik, 2014).

**Nitrates.** In natural water, nitrate ions result from the mineralization of organic nitrogen-containing substances induced by nitrifying bacteria under anaerobic conditions (Nitrates..., 1978; Toxicological profile..., 2017). Nitrate ions as the most stable form of nitrogen prevail in all watercourses during the study period, with an average annual ratio ranging from 82 to 98%.

Table 1 shows the data on the average annual concentration of mineral nitrogen in the watercourses of the Listvyanka settlement for the period of 2015–

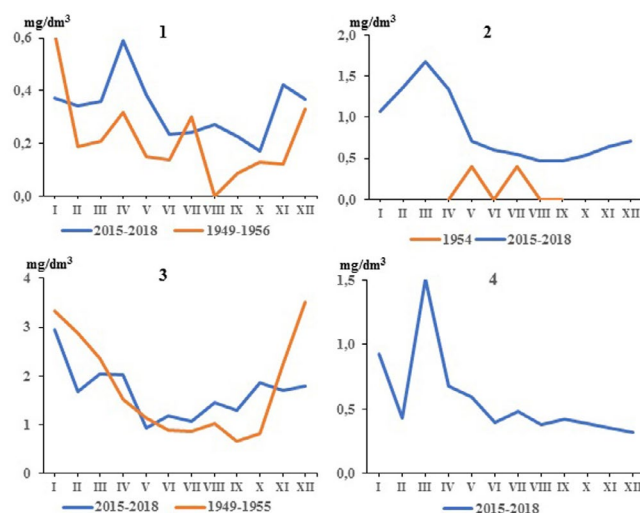
**Table 1.** The average annual concentrations of mineral nitrogen and standard deviation in the watercourses of the Listvyanka settlement in 2015 – 2018 (mg/dm<sup>3</sup>)

Water sampling stations	Indicator		
	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
The Krestovka River (beyond the settlement)	0.31 ± 0.19	0.004 ± 0.003	0.023 ± 0.055
The Krestovka River (estuary)	0.98 ± 1.47	0.005 ± 0.006	0.032 ± 0.075
The Kamenushka stream (beyond the settlement)	0.99 ± 0.64	0.004 ± 0.006	0.012 ± 0.023
The Kamenushka stream (estuary)	4.79 ± 3.79	0.037 ± 0.055	0.323 ± 0.57
The Bolshaya Cheremshanka stream (beyond the settlement)	1.64 ± 0.97	0.003 ± 0.004	0.021 ± 0.030
The Bolshaya Cheremshanka stream (estuary)	9.23 ± 4.68	0.033 ± 0.043	0.111 ± 0.267
The Malaya Cheremshanka stream (beyond the settlement)	0.47 ± 0.38	0.006 ± 0.004	0.022 ± 0.038
The Malaya Cheremshanka stream (estuary)	9.49 ± 12.27	0.044 ± 0.104	0.092 ± 0.138

2018. The nitrate concentration in the surface waters of the studied watercourses varies significantly. The nitrate concentrations in rivers beyond the settlement are minimum and result from the natural biochemical processes in the water bodies. In the estuarine areas of the rivers, there is a significant increase in the nitrate concentrations. Thus, the average annual nitrate concentrations in the Krestovka River and the streams Kamenushka, Bolshaya Cheremshanka and Malaya Cheremshanka are 3, 5, 6, and 20 times higher than the background (beyond the settlement) values. The comparison of the level of nitrate pollution in the estuarine areas of the watercourses indicates that the Krestovka River has the minimum concentration, and the Bolshaya Cheremshanka – the maximum one. In Listvennichny Bay of Lake Baikal, the nitrate concentration varies from 0.08 to 0.90 mg/dm<sup>3</sup> (Kravtsova et al., 2012). Therefore, the nitrate concentrations, inflowing to the lake together with river waters, exceed tenfold the maximum (0.90 mg/dm<sup>3</sup>).

The maximum permissible concentration (MPC) of nitrates in water for drinking, domestic and amenity needs is 45 mg/dm<sup>3</sup> (Hygienic standard GN 2.1.5.1315–03). Only in December 2018, we identified the excess of MPC in the Bolshaya Cheremshanka (68.65 mg/dm<sup>3</sup>). However, L.P. Alekseeva and co-authors (2016) studied the groundwater from 21 boreholes and 18 wells along the Krestovka River. Of them, nine wells and one borehole showed the MPC excess for nitrates and one more borehole – for ammonium ion. The MPC excess for nitrates varied from a small value (1.1 times) to threatening one (5.9 times). In the Krestovaya valley, the nitrate concentration in the surface water is relatively small, but the groundwater is highly polluted, which can also increase the nitrite concentration in surface water. The increase in nitrate concentration is due to the influence of such anthropogenic factors as the operation of improperly equipped septic tanks and the lack of a centralized sewage system in the settlement.

To assess the influence of natural factors on the change in the concentrations of nutrients, in Fig. 2 we show the seasonal variation of nitrate concentrations in river water beyond the settlement in the modern period and the 1950s according to K.K. Votintsev (Votintsev, 1965). During 2015–2019, there were significant seasonal fluctuations in nitrate concentrations in the watercourses of Listvyanka. The Krestovka River in the modern period revealed two peaks. The first spring maximum was during the flood period, and the second – during the winter period, in November. In the 1950s, there were also two peaks. The first one was during the flood period in April, and the second winter peak was in January. In general, the seasonal fluctuations in nitrate concentrations are similar in different years, but in the modern period there is no summer decrease in the concentration. The high nitrate concentrations in winter are likely due to the decomposition of organic substances and transition of nitrogen from organic to mineral forms as well as the lack of nitrogen consumers in the water (aquatic vegetation and phytoplankton). In the spring, the concentration of nitrates normally



**Fig. 2.** Seasonal fluctuations in nitrate concentrations (mg/dm<sup>3</sup>) in the 1950s and modern period: 1 – the Krestovka River; 2 – the Kamenushka stream; 3 – the Bolshaya Cheremshanka stream; 4 – the Malaya Cheremshanka stream

decreases in the water due to their consumption by aquatic vegetation. The summer maximum (July–August) is visible, but it is significantly lower than the winter maximum.

We have identified the maximum for the Kamenushka and Malaya Cheremshanka watercourses during the spring flood in March as well as an increase in nitrate concentrations in January. In comparison with the 1950s, nitrate concentrations have increased in all watercourses, except for the Bolshaya Cheremshanka, where the spring flood is poorly visible, and the maximum nitrate concentration, like in the 1950s, is observed in winter.

The Krestovka River, being the largest in the Listvyanka settlement, is the most studied. Table 2 shows the results obtained in different observation periods. In 2015–2019, there was a fourfold growth in nitrate concentrations compared to the 1950s or twofold growth compared to the beginning of the 21<sup>st</sup> century. According to the 2007–2012 data, nitrate concentrations have tripled. Nitrate concentrations have also tripled in comparison with the data on the beginning of the 21<sup>st</sup> century and are close to the results obtained in 2001–2002. Ammonium ion concentrations have decreased in the modern period. This temporary change in concentrations of nitrogen compounds is likely due to an increase in their inflow not only from the watershed basin but also the atmosphere.

**Nitrites.** Nitrites are unstable compounds that form in surface waters as a result of biochemical ammonium oxidation or during the nitrate reduction. Their increased concentration indicates the contamination of the water body (Khan and Ansari, 2005; Eutrophication..., 2011; Nikanorov and Ivanik, 2014). Seasonal dynamics of nitrites in the investigated watercourses shows their increased concentrations during the spring flood. As a rule, nitrite concentration also increases in water by the end of summer, and in the autumn and winter periods there is a decrease to



**Table 2.** Concentrations of mineral forms of nitrogen in the surface water of the estuary of the Krestovka River (mg/dm<sup>3</sup>) in different observation periods

Indicator			Period
NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	
0-0.62 0.22	N/A	N/A	[Votintsev et al., 1965]
0.01-2.39 0.40	<u>0-0.020</u> 0.002	<u>0.04-0.69</u> 0.27	2001-2002 (our data)
0.11-1.00	<0.001-0.030	0.008- 0.155	2007-2012 [Zagorulko et al., 2014]
0.17	0.011	0.17	2011 [Kravtsova et al., 2012]
<u>(0.24-3.12)</u> 0.98	<u>&lt;0.003-0.019</u> 0.006	<u>&lt;0.020-0.189</u> 0.039	2015-2018 (our data)

Note: the minimum and maximum values are shown above the line, and the average value – below the line.

minimum values.

Nitrite concentrations in water samples taken beyond the settlement are minimal. In the estuarine sections of watercourses, their concentrations are much higher due to the intake of domestic wastewater. In the estuaries of the streams Kamenushka, Bolshaya Cheremshanka and Malaya Cheremshanka, the average annual concentrations of nitrites are 9, 11 and 7 times higher than the background concentrations (see Table 1). Nitrite concentration in the Krestovka River beyond the settlement and its estuary slightly differs. We detected maximum nitrite concentrations in the estuary of the Malaya Cheremshanka. During the study period, the watercourses showed no MPC excess of nitrites (3.3 mg/dm<sup>3</sup>) for water bodies of drinking, domestic and amenity needs (Hygienic standard GN 2.1.5.1315-03).

**Ammonium.** Ammonium nitrogen is a decay product of nitrogen-containing organic substances of animal origin. In natural water, nitrifying bacteria oxidize ammonium to nitrites and nitrates (Toxicological profile..., 2004). The increased ammonium concentration in the water indicates deterioration in the sanitary state of the water body. MPC of ammonium ions for the sites of drinking, domestic and amenity needs is 1.5 mg/dm<sup>3</sup> (in terms of nitrogen) (Hygienic standard GN 2.1.5.1315-03). Municipal wastewaters containing a significant amount of ammonium compounds, which can penetrate the groundwater or be washed away by surface runoff into the water bodies, are the sources of ammonium in the aquatic ecosystems. Moreover, ammonium enters surface waters with precipitation as a result of dry and wet deposition (Brimblecombe and Dawson, 1984; Asman et al., 1998; Toxicological profile..., 2004; Behera et al., 2013).

Ammonium concentrations in the watercourses beyond the settlement are low, except for the Malaya Cheremshanka and Bolshaya Cheremshanka. The estuarine sections of the watercourses had the maximum concentrations in December, March, April, and July.

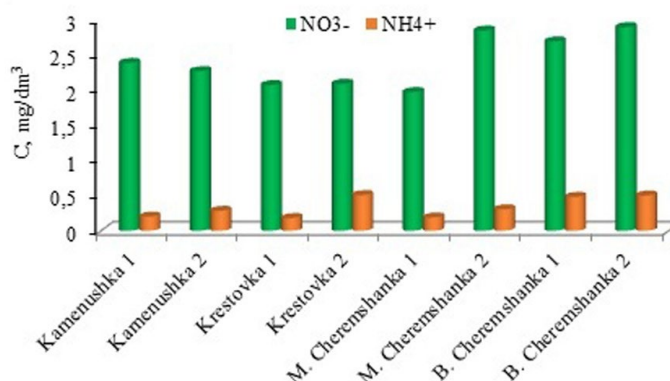
At the estuaries of the Krestovka River as well as the streams Kamenushka, Bolshaya Cheremshanka and Malaya Cheremshanka, the average annual concentrations of ammonium ions are 1,4; 27; 5 and 4

times higher the background values (see Table 1). The minimum ammonium concentration was in the estuary of the Krestovka River. The maximum concentration was in the estuary of the Kamenushka, where background values were exceeded over the entire study period (the average annual value of 0.323 mg/dm<sup>3</sup>) with maximum values in December (0.660 mg/dm<sup>3</sup>). The obtained results indicate the presence of a stable pollution source of this watercourse within the settlement.

### 3.2 Snow cover

Sources of nitrogen compounds in the atmosphere are denitrification processes in the soil; forest fires; fuel combustion; lightning discharges, during which NO monoxide is formed, then oxidized to NO<sub>2</sub> (Brimblecombe, 1986).

**Nitrates.** Investigations of the chemical composition of the snow cover have revealed rather high nitrate concentrations in the basin of the studied tributaries in the Southern Baikal. The average concentrations of this element in 2016-2019 were 2.38 mg/dm<sup>3</sup>, varying from 2.0 to 2.9 mg/dm<sup>3</sup> (Table 3). The highest average nitrate concentrations were in the basin of the Bolshaya Cheremshanka. The maximum was in 2016. The basin of the Krestovka River showed



**Fig 3.** Average (2016-2019) concentrations of nitrates and ammonium in the snow cover beyond the settlement (1) and in the estuarine areas (2) of the studied watercourses.

**Table 3.** Concentrations of mineral forms of nitrogen in the snow cover of the Listvyanka settlement in 2016-2019 (mg/dm<sup>3</sup>)

Snow cover sampling stations	Indicator		
	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
The Kamenushka stream (beyond the settlement)	<u>1.89-3.28</u> 2.39	<u>0.001-0.007</u> 0.004	<u>0.04-0.45</u> 0.020
The Kamenushka stream (estuary)	<u>1.44-2.92</u> 2.27	<u>0.001-0.011</u> 0.005	<u>0.12-0.38</u> 0.029
The Krestovka River (beyond the settlement)	<u>1.50-2.53</u> 2.07	<u>0.001-0.007</u> 0.003	<u>0.03-0.24</u> 0.18
The Krestovka River (estuary)	<u>1.51-2.53</u> 2.09	<u>0.002-0.051</u> 0.017	<u>0.18-0.84</u> 0.51
The Malaya Cheremshanka stream (beyond the settlement)	<u>1.73-2.41</u> 1.97	<u>0.001-0.002</u> 0.002	<u>0.10-0.33</u> 0.19
The Malaya Cheremshanka stream (estuary)	<u>2.50-3.07</u> 2.84	<u>0.001-0.006</u> 0.003	<u>0.26-0.40</u> 0.31
The Bolshaya Cheremshanka stream (beyond the settlement)	<u>1.93-4.08</u> 2.69	<u>0.002-0.007</u> 0.004	<u>0.06-0.87</u> 0.48
The Bolshaya Cheremshanka stream (estuary)	<u>1.73-3.60</u> 2.89	<u>0.002-0.032</u> 0.015	<u>0.28-0.90</u> 0.50

Note: the minimum and maximum values are shown above the line, and the average value – below the line.

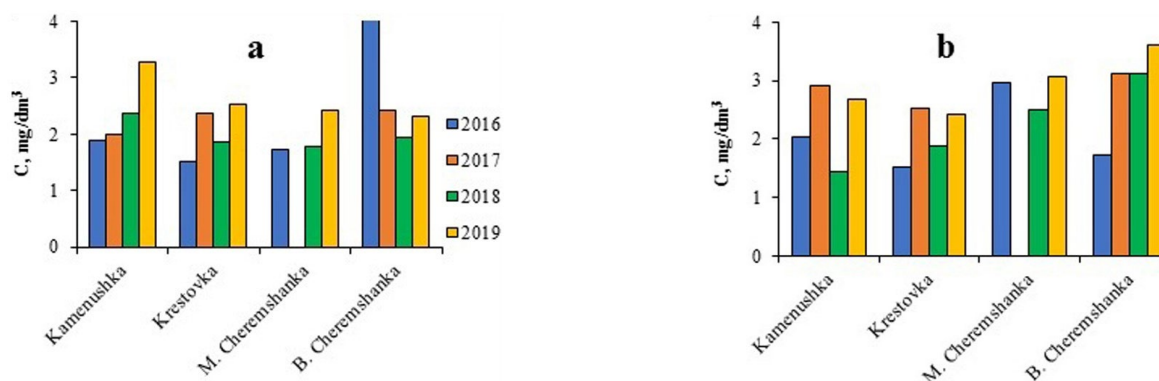
the minimum nitrate concentrations (Fig. 3).

**Ammonium.** The long-term average concentration of ammonium ions in the snow water is 0.34 mg/dm<sup>3</sup>. The highest average concentration of this compound was in the snow cover from the estuarine area of the Krestovka River. The maximum was in 2019 at the estuary of the Bolshaya Cheremshanka. The minimum was in the snow cover from the upper reaches the Krestovka River (beyond the settlement).

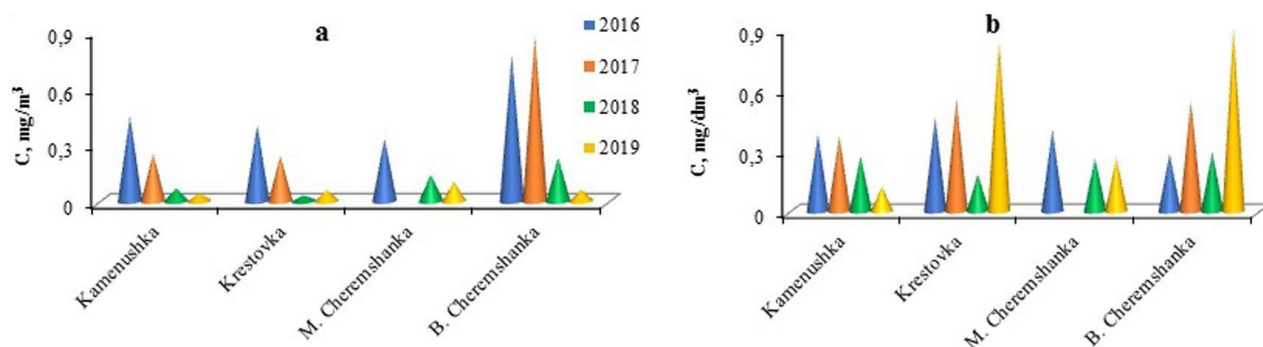
A comparison of the concentrations of nitrates and ammonium in the snow cover beyond the settlement and the estuarine sections of the watercourses reveals higher values mainly in the estuarine areas, where the anthropogenic impact is more obvious. The exception is the Kamenushka stream, where nitrate concentrations near the ski lodge (beyond the settlement) in the past two years are higher than near the Baikal Museum (at the estuary). The difference in concentrations of this compound in different parts of the Krestovka River basin is also small. The Malaya Cheremshanka basin shows the greatest differences in nitrate concentrations, and the Krestovka River– in ammonium ions (Fig. 4-5).

In the inter-annual dynamics from 2016 to 2019, there was an increase in nitrate concentrations in the basins of all studied watercourses, except for the upper reach of the Bolshaya Cheremshanka (Fig. 4). The concentrations mostly increased (twice) in the snow cover at the estuary of this stream. Concerning ammonium ions, over the study period their concentration significantly reduced (6–13 times) in the snow beyond the settlement. In the estuarine area of the Kamenushka and the Malaya Cheremshanka, a decrease in the concentrations was less significant (1.5–3 times). The concentrations of this element increased only in the basins of the estuarine area of the Krestovka and the Bolshaya Cheremshanka (2–3 times). (Fig. 5).

**Nitrites.** The snow cover of the Krestovka estuarine area showed the maximum nitrite concentrations in 2019. In general, the concentration of this element is low; the average value for the study period is 0.006 mg/dm<sup>3</sup>, which is almost by an order of magnitude lower than the maximum value (0.051 mg/dm<sup>3</sup>). The minimum of the concentration was in the snow cover



**Fig. 4.** Interannual dynamics of nitrate concentrations (mg/dm<sup>3</sup>) in the snow cover beyond the settlement (a) and in the estuarine areas (b) of the studied watercourses.



**Fig. 5.** Inter-annual dynamics of ion ammonium concentrations ( $\text{mg}/\text{dm}^3$ ) in the snow cover beyond the settlement (a) and in the estuarine areas (b) of the studied watercourses.

near the Malaya Cheremshanka (beyond the settlement). The distribution of nitrite concentrations in the snow cover along the channel of the watercourses is the same as that of ammonium ions, i.e. nitrite concentration is higher (up to 6 times) in more polluted estuarine area of the watercourse basins.

### 3.3 Precipitation

Sources of nitrogen compounds in the atmosphere are denitrification processes in the soil, forest fires, fuel combustion; lightning discharges result in formation of  $\text{NO}$  monoxide, which is then oxidized to  $\text{NO}_2$  dioxide (Brimblecombe, 1986).

A study of concentration levels of mineral nitrogen compounds and the characteristics of their seasonal distribution in the precipitation of the Listvyanka settlement has revealed the following.

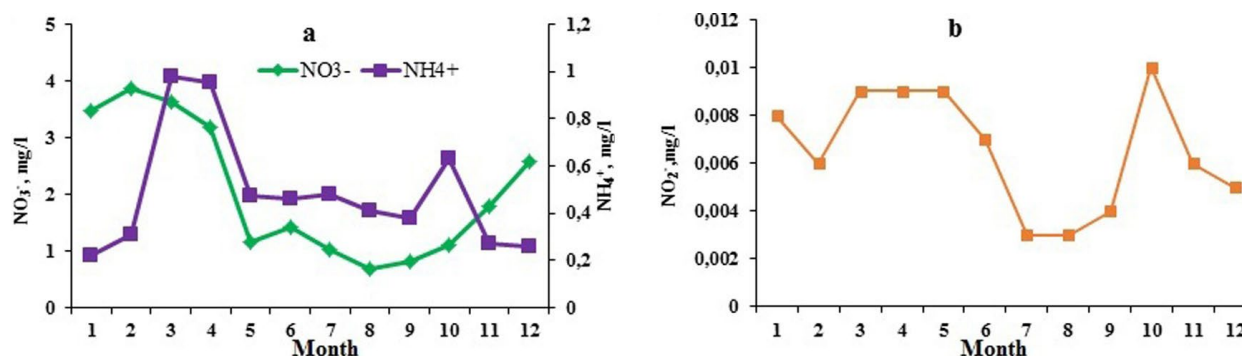
**Nitrates.** The average annual nitrates concentration for 2015-2018 was  $1.95 \text{ mg}/\text{dm}^3$ , varying within  $1.69 - 2.19 \text{ mg}/\text{dm}^3$ , and from 2015 to 2018, like in the snow cover, it gradually increased. For comparison, in Irkutsk, the average annual content of this component was lower ( $1.80 \text{ mg}/\text{dm}^3$ ) and varied within  $1.72 - 2.00 \text{ mg}/\text{dm}^3$ . The proportion of nitrates in ion composition of the snowfall averaged 21%, whereas that of rainfall did not exceed 13%. The maximum was in February and the minimum – in August (Fig. 6a). The average long-term nitrate concentration in snowfall ( $3.36 \text{ mg}/\text{dm}^3$ ) is three times higher than in rainfall and 1.4 times higher than in the snow cover.

High nitrate concentration in snowfall and

snow cover of the Listvyanka settlement is due to air pollution in the Irkutsk Region with nitrogen oxides resulted from an increase in the fuel combustion by thermal power enterprises during the heating season, growth of vehicles both in the Region and on the lake coast as a result of the rapid development of tourism business at Baikal.

According to the data (On the state and environmental protection..., 2018), in the Irkutsk Region, there has been an increase in emissions from the stationary sources by 10.5%;  $\text{NO}_x$  emissions varied in 2014-2017 within 99–103 thousand tons. In 2017, nitrogen dioxide was 1.2 and 1.1 times higher than the permissible concentrations in Irkutsk and Angarsk cities, respectively. In such cities as Usolye-Sibirskoye, Cheremkhovo, Shelekhov, Angarsk, and Irkutsk, one-time maximum concentrations of nitrogen dioxide were 1.8-6.7 times higher than MPC, and those of nitrogen oxide were 1.4-3.1 times higher than MPC (On the state of Lake Baikal..., 2018).

From 2005 to 2014, the number of personal cars per 1000 people increased almost twice in the Region. In 2017, there were 836 thousand cars, which is 1.4% higher than in 2016 (The official website..., 2019). In the same year, there was an increase in air pollution near highways due to vehicle emissions, from 0.6% of samples exceeding MPC in 2015 to 2.2% – in 2017. From 2011 to 2017, the number of tourists in the Region almost doubled. The number of tourists in Listvyanka is increasing every year. Hence, the number of automobile and water transport is also increasing, which affects the state of the atmosphere in the settlement (On the state



**Fig. 6.** Seasonal dynamics of mineral nitrogen concentrations in precipitation of the Listvyanka settlement in 2015 – 2018.

of the sanitary-epidemiological..., 2018; On the state of Lake Baikal..., 2018).

The stably high (2.50-3.54 mg/dm<sup>3</sup>) and slightly varying (C var.=12%) nitrate concentrations in the snow cover, which we sampled along the Irkutsk-Listvyanka highway in 2019, indicate the effect of automobile transport on the composition of the atmosphere.

**Ammonium.** Ammonium is the predominant form (%) of mineral nitrogen in precipitation. The average annual concentration of ammonium ions ranged from 0.32 to 0.75 mg/dm<sup>3</sup>. From 2015 to 2018, there was a decrease in the concentrations of this nutrient. The highest concentrations (on average 0.47 mg/dm<sup>3</sup>) were in rainfall. This is due to the presence of numerous natural and anthropogenic sources of this compound during the warm season, such as annual wildfires, bacterial decomposition of soil organic matters, the disintegration of animal urine, and the introduction of nitrogen fertilizers into the soil (vizlit.ru). The spring maximum of ammonium ions in March and April is due to their entry to the atmosphere when the snow cover is melting. Despite the maximum in March and April, the average concentrations of ammonium ions in snowfall (0.33 mg/dm<sup>3</sup>) are lower than in rainfall (Fig. 6a). The concentrations of ammonium ions in precipitation of the cold season are close to those in the snow cover.

**Nitrites.** The average annual concentrations of nitrites are 0.006-0.007 mg/dm<sup>3</sup>. The maximum is in October and the minimum – in the summer months with the greatest amount of precipitation, contributing to the cleansing the atmosphere from impurities (Fig. 6b).

#### 4. Conclusion

In all studied watercourses, we have revealed an increase in the concentrations of nitrogen compounds in the waters after their passing through the settlement, which is due to the influx of domestic sewage. In estuarine areas of the watercourses, there is a significant increase in nitrate concentrations. The water of the Malaya Cheremshanka stream has the greatest excess of background values. Waters flowing into Listvennichny Bay have nitrate concentrations that are 10-20 times higher than in the bay. Despite the high nitrate concentrations in the watercourses, there was no MPC excess in the study period. Beyond the Listvyanka settlement, nitrate concentrations in waters of all watercourses have increased compared to the 1950s, which is likely due to climate change and an increase in the intake of nitrogen compounds from the atmosphere. Seasonal dynamics of nitrate concentrations in the river water has not changed in the modern period; however, in recent years, a summer decrease in the concentrations is less obvious.

The average annual concentrations of nitrites at the estuaries of the watercourses exceed the background concentrations by an order of magnitude. The Bolshaya Cheremshanka stream show the highest exceed. At the estuary of the Kamenushka stream, the average annual

concentration of ammonium ions is 30 times higher than the background concentration.

In the study period, there was an increase in the average annual concentration of nitrates in precipitation and snow cover. The maximum nitrate concentrations in precipitation were in the cold season as a result of the intensive operation of thermal power enterprises during the heating season. The maximum nitrate concentration in the snow cover was in the basin of the Bolshaya Cheremshanka stream, the minimum – in the basin of the Krestovka River. In the snow cover, like in surface water, nitrate concentrations increase towards the estuarine areas of the watercourses.

#### Acknowledgments

The study was carried out within the project No. 0345–2019–0008 Assessment and Forecast of Ecological State of Lake Baikal and Adjacent Territories under Conditions of Anthropogenic Impact and Climate Change.

#### References

- Alekseeva L.P., Alekseev S.V., Sholokhov P.A. et al. 2016. Ground and surface water quality in the Krestovaya valley (Listvyanka settlement). *Geografiya i Prirodnyye Resursy [Geography and Natural Resources]* 6: 37–42. DOI: 10.21782/GiPR0206-1619-2016-6(37-42) (in Russian)
- Eutrophication: causes, consequences and control. 2011. In: Ansari A.A., Gill S.S. (Eds.). Dordrecht: Springer.
- Asman W.A. H., Sutton M.A., Schjorring J.K. 1998. Ammonia: Emission, atmospheric transport and deposition. *New Phytologist* 139: 27–48. DOI: 10.1046/j.1469-8137.1998.00180.x
- Behera S.N., Sharma M., Aneja V.P. et al. 2013. Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. *Environmental Science and Pollution Research* 20: 8092–8131. DOI: 10.1007/s11356-013-2051-9
- Brimblecombe P. 1986. Air composition and chemistry. Cambridge: Cambridge University Press.
- Brimblecombe P., Dawson G.A. 1984. Wet removal of highly soluble gases. *Journal of Atmospheric Chemistry* 2: 95–107. DOI: 10.1007/BF00127265
- Environmental federal regulation PND F 14.2: 4.209-05 Quantitative chemical analysis of waters. Method for measuring the mass concentration of ammonium ions in samples of drinking and natural waters by the photometric method in the form of indophenol blue. 2017. (in Russian)
- Guidelines for controlling air pollution. RD 52.04.186–89. 1991. The USSR State Committee for Hydrometeorology and the USSR Ministry of Health. Moscow. (in Russian)
- Guiding document RD 52.04.333-93 Guidelines. Chromatographic method for determining the content of chlorides, nitrates, sulfates, lithium, sodium, ammonium, and potassium in precipitation. 1993. The Federal Service for Hydrometeorology and Environmental Monitoring of Russia. Moscow. (in Russian)
- Guiding document RD 52.24.383–2005 Mass concentration of ammonia and ammonium ions in water. Measurement procedure by the photometric method in the form of indophenol blue. 2004. The Federal Service for Hydrometeorology and Environmental Monitoring of Russia. Hydrochemical institute. Rostov-na-Donu. (in Russian)



Hygienic standard GN 2.1.5.1315–03 Maximum permissible concentrations (MPC) of chemicals in the water of water bodies for drinking, domestic and amenity water use. 2003. Moscow: Ministry of Health of Russian Federation. (in Russian)

Khan F.A., Ansari A.A. 2005. Eutrophication: an ecological vision. *The Botanical Review* 71: 449–482. DOI: 10.1663/0006-8101(2005)071[0449:EAEV]2.0.CO;2

Kravtsova L.S., Izhboldina L.A., Khanaev I.V. et al. 2012. Disturbances of the vertical zoning of green algae in the coastal part of the Listvennichnyi Gulf of Lake Baikal. *Doklady Biological Sciences* 447: 350–352. DOI: 10.1134/S0012496612060026

Naprasnikova E.V., Vorobyova I.B., Vlasova N.V. et al. 2007. Sanitary and environmental assessment of water wells on the coast of Lake Baikal (Listvyanka settlement). *Sibirsky Meditsinsky Zhurnal [Siberian Medical Journal]* 8: 6–8. (in Russian)

Nikanorov A.M., Ivanik V.M. 2014. Vocabulary and reference book on hydrochemistry and land water quality (concepts and definitions). Rostov-na-Donu. (in Russian)

Nitrates, nitrites and N-nitroso compounds. 1978. World Health Organization (WHO). International programme on chemical safety, Environmental Health Criteria 5. Geneva. URL: <http://www.inchem.org/documents/ehc/ehc/ehc005.htm>

On the state and environmental protection of the Russian Federation in 2017. State report. URL: [www.gosdoklad-ecology.ru](http://www.gosdoklad-ecology.ru). (in Russian)

On the state of Lake Baikal and measures for its protection in 2017. State report. 2018. Moscow. URL: [www.mnr.gov.ru](http://www.mnr.gov.ru). (in Russian)

On the state of the sanitary-epidemiological welfare of the population in the Irkutsk Region in 2017. State report. 2018. URL: [www.38.rospotrebnadzor.ru](http://www.38.rospotrebnadzor.ru). (in Russian)

Shimaraev M.N., Kuimova L.N., Sinyukovich V.N. et al. 2002. Manifestation of global climatic changes in Lake Baikal during the twentieth century. *Doklady Earth Sciences* 383:

288–291.

Shimaraev M.N., Troitskaya E.S. 2018. Trends in the temperature of the upper water layer in the coastal areas of Lake Baikal in the modern period. *Geografiya i Prirodnyye Resursy [Geography and Natural Resources]* 4: 95–104. DOI: 10.21782 / GIPR0206-1619-2018-4 (95-104) (in Russian)

State standard GOST 33045-2014 Water. Methods for determining nitrogen-containing substances. 2015. The Interstate Council for Standardization, Metrology and Certification. Moscow: Standartinform. (in Russian)

Technical document for wet deposition monitoring in East Asia. March 2000. URL: <http://www.eanet.asia/product/manual/prev/techwet.pdf>

The official website of the traffic police of the Irkutsk Region. URL: <http://www.gibdd.ru/r/38/news> (in Russian)

Toxicological profile for ammonia. 2004. U.S. Department of Health and Human Services, Public Health Service. Agency for Toxic Substances and Disease Registry (ATSDR). Atlanta, GA. URL: <https://www.atsdr.cdc.gov/toxprofiles/tp126.pdf>

Vorobyova I.B., Vlasova N.V., Naprasnikova E.V. 2017. Assessment of the ecological state of water bodies of the Baikal Natural Territory (south-western coast of Lake Baikal, Listvyanka village). *Voda: Khimiya i Ekologiya [Water: Chemistry and Ecology]* 6: 86–93. (in Russian)

Votintsev K.K., Glazunov I.V., Tolmacheva A.P. 1965. Hydrochemistry of the rivers of the Baikal basin. Moscow: Nauka. (in Russian)

Yanchuk M.S. 2016. Petroleum products in the surface and snow waters of the southwest coast of Lake Baikal. *Izvestiya Irkutskogo Gosudarstvennogo Universiteta. Seriya: Nauki o zemle [The bulletin of Irkutsk State University. Series: Earth Sciences]* 18: 140–149. (in Russian)

Zagorulko N.A., Grebenshchikova V.I., Sklyarova O.A. 2014. Long-term dynamics of the chemical composition of the waters in the Krestovka River (a tributary of Lake Baikal). *Geografiya i Prirodnyye Resursy [Geography and Natural Resources]* 3: 76–82. (in Russian)