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*Article*

## Nickel in the waters of Lake Teletskoye tributaries (the results of long-term studies)

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**Abstract.** Ecological and biogeochemical studies carried out in the Lake Teletskoye basin in 2016–2021 showed that the total nickel content in the waters of the lake's tributaries ranged from 0.12 to 4.6  $\mu\text{g}/\text{dm}^3$ , an average of  $1.8 \pm 0.1 \mu\text{g}/\text{dm}^3$ . The content of dissolved forms of nickel in rivers of the basin varied as 0.1–4.4  $\mu\text{g}/\text{dm}^3$ . It was within the maximum permissible concentration (MPC), being consistent with the published data for natural waters of Siberia. However, this indicator significantly exceeded the global average. It was established that in the waters of western tributaries of the meridional part of Lake Teletskoye the concentrations of dissolved Ni were significantly higher than in the waters of eastern tributaries. This may be explained by higher soil maturity of the western coast and iron presence, as well as greater sedimentary deposits and stronger anthropogenic impacts. In June 2022, the excess of MPC for nickel in the waters of western tributaries was recorded for the first time in several years of observations that may be explained, among other things, by increasing anthropogenic loads on the ecosystem of the catchments. The waters of the Chulyshman River bring up to 3.5 tons of nickel into Lake Teletskoye during spring-summer floods and 0.8 tons in the autumn low water periods, while the contribution of other tributaries to Ni input to the lake is at least 1–2 orders less. In the summer high-water period, the value of the module of nickel runoff from the catchment areas of different-size tributaries of Lake Teletskoye practically does not differ (0.19–0.21 kg/month from  $\text{km}^2$ ). During autumn low water, the nickel removal is more determined by intra-soil processes occurred in the catchment.

**Keywords:** Lake Teletskoye, water, Ni, catchment area, runoff

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### Научная статья

## Никель в водах притоков Телецкого озера по результатам многолетних исследований

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**Аннотация.** В период с 2026 по 2021 г. изучено содержание никеля в водах притоков озера Телецкого. Согласно результатам исследования, общее содержание никеля в водах притоков озера колебалось от 0.12 до 4.6 мкг/дм<sup>3</sup>, в среднем составляя  $1.8 \pm 0.1$  мкг/дм<sup>3</sup>. Содержание растворенных форм никеля в водах рек бассейна варьировало от 0.1 до 4.4 мкг/дм, не превышало ПДК, согласовывалось с литературными данными для природных вод Сибири, однако заметно превосходило среднемировые значения. Установлено, что в водах западных притоков меридиональной части оз. Телецкого концентрации растворенного Ni заметно выше, чем в водах восточных притоков, что объясняется большей зрелостью почв западных берегов и более существенным присутствием в них железа, препятствующего комплексообразованию, а также наличием большого количества осадочных отложений и более высоким антропогенным воздействием на левобережные ландшафты. В июне 2022 г. впервые за несколько лет наблюдений зафиксировано превышение ПДК<sub>рх</sub> никеля в водах западных притоков озера, что предположительно объясняется, в том числе, усиливающейся антропогенной нагрузкой на экосистему водосборов. Установлено, что максимальное количество никеля в оз. Телецкое привносится водами р. Чулышман: до 3.5 т никеля в период весенне-летнего половодья и 0.8 т – в период осенней межени, в то время как вклад других притоков в поступление Ni в озеро как минимум на 1–2 порядка ниже. Величина модуля стока никеля в летний полноводный период с водосборных площадей разных по величине притоков оз. Телецкого практически не различается (0.19–0.21 кг/мес. с км<sup>2</sup>), в период осенней межени вынос никеля существенно определяется внуртпочвенными процессами на водосборе.

**Ключевые слова:** малые реки, ICP-MS, Ni, водосбор, модуль стока

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## Introduction

Water migration of microelements is the most important stage of the substances movement on the Earth. The content of microelements and their forms in natural waters largely depend on their migration conditions in the soil-water system within the catchment area. The chemical composition of surface waters reflects the natural and climatic properties of the basin, its geology, relief, water balance and regimes, the presence of agricultural landscapes, residential areas, industrial zones and their impact on the catchment environment.

The lack of clean fresh water is a contributory factor for the world scientific community who have to pay attention to natural lake and river water resources, not been adequately investigated. The study of the chemical composition of natural waters of special protected areas of the Altai Mountains is currently central. In connection with the rapid development of tourism in Altai, the annual increase in the number of tourists and new tourist facilities near Lake Teletskoye, it is necessary to monitor the ecological state of its catchment area.

Ni compounds are often present in natural waters, although the element itself is not widespread in the Earth crust – its clarke equals 58 mg/kg, and the average content in the world's soils – 40 mg/kg (Saet et al., 1990). In soils, nickel is mainly found in the form of sulfides and arsenides; it is capable of replacing iron in ferromagnesian deposits. Nickel can be associated with Mn and Fe oxides, phosphates, carbonates, and silicates. The level of Ni content in natural waters depends on its concentration in drained rocks and soils, the hydrochemical regime of a reservoir or a watercourse, the biogeochemical characteristics of the catchment area, and climatic features in the basin. Nickel forms hydroxides and basic salts in an alkaline environment, and easily migrates in acidic and neutral waters (Dobrovolsky, 1998). In addition to pH and Eh, the amount and forms of nickel in natural waters are affected by the presence of humic and fulvic acids that form complexes with Ni (Korshunova and Charykova, 2018; Moiseenko et al., 2013), as well as the content of dissolved oxygen, H<sub>2</sub>S, CO<sub>2</sub>, and the presence of microorganisms (Kashin and Ivanov, 1997). The average water migration coefficient of nickel is low (0.81) that indicates a weak intensity of Ni involvement in this process along with Pb, Mn, Cr, V, Si ( $C_{wm} = 0.1 n$ ) (Dobrovolsky, 1998).

Acidic rocks (granites) contain only 5–15 mgNi/kg, while ultrabasic rocks are distinguished by its highest concentrations (1400–2000 mg/kg) (Dobrovolsky, 1998; Voitkevich et al., 1990). Therefore, the nickel content is often elevated in waters draining carbonate deposits. For example, in the surface waters of the Kugdinsky ultrabasic alkaline massif (Krasnoyarsk Krai, Anabar Plateau), the nickel con-

tent reaches  $12.8 \mu\text{g}/\text{dm}^3$ . This allowed the authors (Soldatova et al., 2022) to classify the geochemical specialization of the territory as copper-nickel.

In microdoses, nickel is a biologically important microelement, but in high concentrations, many of its compounds are toxic to living organisms. When in water, Ni has an inhibitory effect on aquatic organisms even in trace amounts (Savorelli et al., 2017). It is believed that dissolved forms of nickel can be more toxic than suspended or sedimentary ones (Shotyk et al., 2017). Untreated industrial and domestic discharges contribute to an increase in the content of nickel soluble forms (Chirila et al., 2014; Zuzolo et al., 2017). In the global environmental monitoring system program adopted by the UN in 1980, nickel, along with Hg, Cr, Cd, Pb, Cu, Zn, As, is listed as one of the main pollutants (Kashin and Ivanov, 1997).

In 2008, the US Environmental Protection Agency<sup>1</sup> declared the nickel average global level in land waters to be  $0.3 \mu\text{g}/\text{dm}^3$ . However, nickel concentrations in natural waters are often significantly higher. For example, according to the research of T.A. Kremleva et al. (2012), among small lakes in Western Siberia, not subject to direct anthropogenic impacts, the highest nickel content (determined by the ICP-MS method) was found in filtered water samples from lakes of the northern taiga zone:  $< 0.2$ – $16.3 \mu\text{g}/\text{dm}^3$ , an average of  $0.73 \mu\text{g}/\text{dm}^3$ . In the southern taiga zone, lake waters contained from  $< 0.2$  to  $4.54 \mu\text{g}/\text{dm}^3$  of nickel, with an average of  $0.46 \mu\text{g}/\text{dm}^3$ , and in the forest-steppe zone – from  $0.2$  to  $0.84 \mu\text{g}/\text{dm}^3$ , with an average of  $0.59 \mu\text{g}/\text{dm}^3$ . In the waters of the rivers of Western Transbaikalia in 1986–1993, the total Ni content determined by the AAS method varied from  $1.8$  to  $12.5 \mu\text{g}/\text{dm}^3$ , and the weighted average amount was  $6.5 \mu\text{g}/\text{dm}^3$  (Kashin and Ivanov, 1997). These scientists noted higher nickel concentrations in large rivers than in mountain streams, which are less mineralized and less polluted. In freshwater lakes of Western Transbaikalia, the nickel content varied within  $5$ – $9.8 \mu\text{g}/\text{dm}^3$  (Kashin and Ivanov, 1997).

In the mountainous rivers of other regions of Russia, the nickel content can vary significantly. In the waters of the North Caucasus rivers, nickel concentrations (determined by the AAS method with electrothermal atomization on the MGA-915 device) make up  $3 \mu\text{g}/\text{dm}^3$  in the middle reaches and decrease to  $0.01$ – $0.06 \mu\text{g}/\text{dm}^3$  towards the closing river sections (Zhinzhakova and Cherednik, 2020). Some authors believe that the Ni content in the Katekhchay River estuary with its slightly mineralized waters may reach  $8.9 \mu\text{g}/\text{dm}^3$  (Salimova, 2012).

According to Serbian researchers, the nickel content in the Danube River waters (determined by inductively coupled plasma optical spectrometry (ICP-OES)) reached  $25.8 \mu\text{g}/\text{dm}^3$  in the spring of 2010 and was considered as very high. However, in the Danube tributaries – the rivers Tisza and Velika Morava – it was found only  $1 \mu\text{g}/\text{dm}^3$  and  $2 \mu\text{g}/\text{dm}^3$ , respectively (Despotovic et al., 2019).

The northeastern part of the Altai Mountains is promising in terms of the discovery and extraction of bauxite, gold, and nickel. Earlier (Puzanov et al., 2015), we noted that the content of nickel, an element of hazard class II, in the surface waters of the Lake Teletskoye basin is higher (from  $1$  to  $6 \mu\text{g}/\text{dm}^3$ ) than the global average in the inland waters ( $2.5 \mu\text{g}/\text{dm}^3$ ) calculated by V.V. Dobrovolsky (1998). According to Gaillardet et al., (2003), the global average of nickel content in river waters makes up only  $0.8 \mu\text{g}/\text{dm}^3$ . The issue of the natural level of nickel concentrations in waters of the Lake Teletskoye basin remains open.

The aim of this work is to study the level of dissolved and suspended nickel forms in waters of Lake Teletskoye tributaries in the context of specific biogeochemical situation in the catchment area.

## Materials and methods

### *Description of the study area*

Lake Teletskoye (Fig. 1) is the largest freshwater reservoir in Altai and one of the deepest lakes in Russia. Since 1998, the buffer zone of the lake has been a UNESCO World Heritage Site<sup>2</sup> The lake is located in the North-Eastern Altai Mountain Province among high mountain ranges at an altitude of

<sup>1</sup> EPA 822-F-18-001. 2012 Edition of the drinking water standards and health advisories.

<sup>2</sup> Golden Mountains of Altai. Documents, Nomination 768rev (inscribed). Web page. URL: <https://whc.unesco.org/en/list/768/documents/> (accessed: 12.02.2023).

434 m above sea level. It has a channel-like shape and is a deep glacial trough filled with 40 km<sup>3</sup> of clean fresh water. The lake is fed by more than 70 rivers, but more than 80% of the water comes from the Chulyshman River – about 5 km<sup>3</sup> per year. The lake's water area is conventionally divided into two parts: the southern, or meridional part (from the mouth of the Chulyshman River to Cape Kuporosny, 50 km), and the northwestern, or latitudinal one (to the source of the Biya River, 2 km) (Maloletko and Shestakova, 1979; Selegey and Selegey, 1978).

The Teletskoye Lake basin is one of the main tourist and recreational areas of Altai. In summer, the basins of the rivers B. Chili, M. Chili, Chulyshman and villages of Artybash, Yailu are subject to increasing anthropogenic loads every year. Deforestation in the river basins of the northern part of the lake (Samysh, Koldor) intensifies erosion processes in the catchments. Currently, a tourist center is being built at the mouth of the Samysh River. The eastern part of the lake's basin is a part of the Altai State Nature Reserve and anthropogenic impact on the environment is minimal here, except for the area near the Korbu waterfall.

The ratio of the water surface area of Lake Teletskoye to the area of its catchment is 1:90; it determines the significance of the lake basin influence on hydrology and hydrochemistry of its waters. For comparison, for Lake Baikal, this ratio is only 1:17 (Selegey and Selegey, 1978). The lake is surrounded by the mountains of 600–2400 m high; its shores are mainly rocky and steep, composed of large boulders and detrital material of granite and shale composition. Sandy and pebble shores are found only at the mouths of the rivers Chulyshman, Kyga, Kokshi, Koldor, and Samysh. There are few bays and gulfs (Kamginsky, Kyginsky). The predominant rocks of the Lake Teletskoye basin are metamorphic and crystalline schists. Much smaller areas are occupied by granite outcrops (Korbu ridge on the eastern shore, the southern part of the lake), granodiorites, diorites, and limestones. The basic rocks are in places covered with glacial deposits in the form of remains of terraces, moraine ridges and hills.

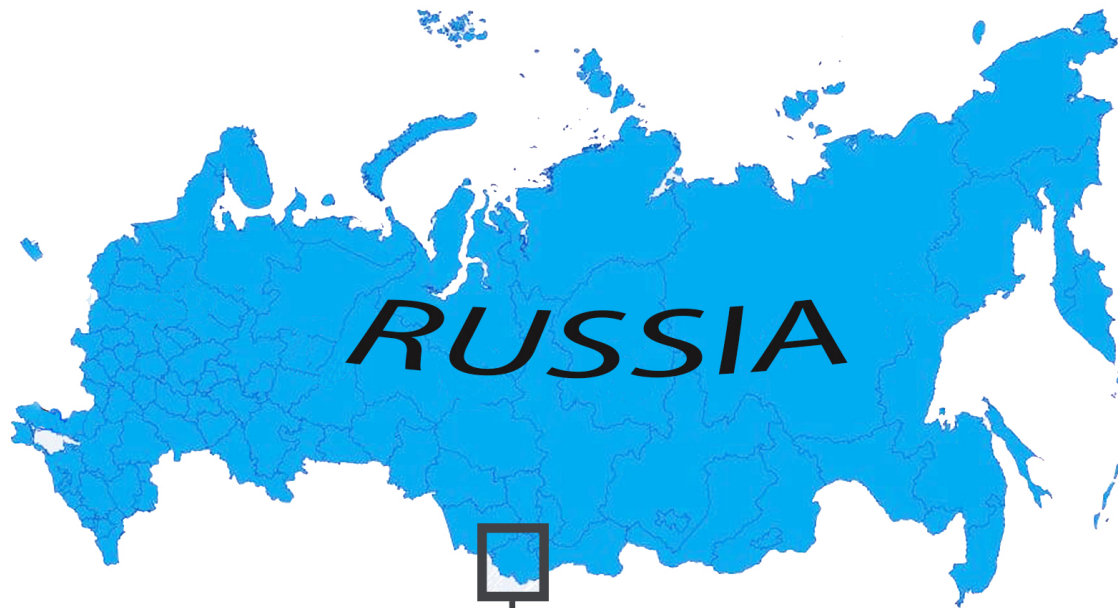
The landscape of the Lake Teletskoye basin by more than 50% is represented by forest communities. The forest cover of the lake basin increases from south to north. In the north, cedar-fir forests with an admixture of pine predominate, and in the south – cedar-larch ones (in Altai, *Pinus sibirica* is called “cedar”). Vast areas of some tributaries of Lake Teletskoye are swampy, which is a driving factor in the formation of the chemical composition of waters. In the landscape structure of the meridional part on the western shore of the reservoir, cedar-taiga forest communities with mountain-forest brown typical and podzolized, less often sod-podzolic and gray forest soils on thick processed sedimentary rocks are more common. The eastern (right) tributaries of the lake mainly drain the exaration-denudation slope surfaces with rocky primitive mountain-tundra and mountain-meadow soils (Chernykh and Samoilova, 2011).

The objects of our study are various-size tributaries of Lake Teletskoye: the Chulyshman and Kyga rivers (southern end of the lake); the rivers Kamga, Koldor and Samysh (latitudinal part of the lake); the rivers Bolshiye and Malye Chili, the small Chedor River (western shore); the Kokshi River, small rivers Korbu and Chelyush, and Verkhniy Kamelik stream (eastern shore of the meridional part of the lake). Rivers Chulyshman, Kyga, Kamga, Koldor and Samysh form alluvial fans in their mouths and are swampy immediately beyond the coastal strip. Water samples were also taken from the Biya River (the only river flowing out of the lake) and from the lake itself, in its northern (latitudinal) part near the village of Yaylyu.

## **Research methods**

We employed the scientific equipment of the Center for Collective Use of Research Vessels of IWEP SB RAS. Studies of the microelement composition of Lake Teletskoye tributaries were carried out in 2016–2021, as well as in the summer of 2022. Water samples were collected into clean new polyethylene containers in the open water of the flow zone from a depth of 0.5 m. The samples were filtered through membrane filters with a pore size of 0.45 µm; the filtering device was pre-washed with several portions of the sample. The required volume of the filtrate was preserved with a purified nitric acid of the special purity grade (GOST 56219-2014)<sup>3</sup>.

<sup>3</sup> GOST R 56219-2014. Water. Determination of the content of 62 elements by inductively coupled plasma mass spectrometry.

**A****B**

**Fig. 1.** Location of the study area: **A** – Altai on the map of Russia, **B** – Lake Teletskoye on the map of the Republic of Altai.

The nickel content in unfiltered (total content) and filtered (soluble forms) samples was determined by atomic absorption spectrometry at the Analytical Center of the Institute of Geology and Mineralogy SB RAS (Novosibirsk) agreeably to PND F 14.1:2:4.139-98<sup>4</sup>, the NSAM method No. 450 – C<sup>5</sup>, and (along with other trace elements) – at the Chemical-Analytical Center of IWEF SB RAS by inductively coupled plasma mass spectrometry (ICP-MS) on an ICAP-Qc Thermo Scientific device (USA). In accordance with GOST R56219-2014<sup>3</sup>, the relative error did not exceed 10%. The reliability of the obtained data was confirmed by good convergence of the results of determination by different methods.

For statistical data processing, standard methods were used; we calculated the arithmetic mean, the error of the mean, coefficients of variation and correlation coefficients.

The intensity of nickel removal from the various-size rivers' catchments was estimated by the amount of its soluble forms transported from a unit area of the catchment basin (km<sup>2</sup>) per unit time using the following formula:

$$M_{Ni} = (Q/F) \times C_{Ni}$$

where Q is the water flow rate (l/s), F is the catchment area (km<sup>2</sup>), C is the nickel concentration (µg/dm<sup>3</sup>). Data on average daily and average monthly water flow rates (m<sup>3</sup>/s) were also included in the calculations<sup>6</sup>.

## Results and discussion

According to our findings, the total nickel content in the waters of Lake Teletskoye tributaries (2016–2021) varied from 0.12 to 4.6 µg/dm<sup>3</sup>, an average of 1.8 ± 0.3 mg/dm<sup>3</sup> (Cv = 58%), the geometric mean was 1.4 mg/dm<sup>3</sup>, the median – 1.6 mg/dm<sup>3</sup>. The highest average total nickel content was detected in the waters of rivers Samysh and Kyga. The waters of the rivers on the eastern shore, flowing from the top of the granite ridge Korbu, i.e. Kokshi and Korbu, as well as Chelyush and Chiri contain noticeably less Ni: 0.12–2.3 µg/dm<sup>3</sup>. The rivers Koldor, Malye and Bol'shiye Chili, and Chulyshman, which drain mainly sedimentary deposits, contain comparatively higher concentrations of nickel (0.7–4.6 µg/dm<sup>3</sup>).

The total nickel content (2016–2021) in waters of Lake Teletskoye varied from 0.6 (2016) to 2.3 µg/dm<sup>3</sup> (2021); it did not exceed that in the surface waters of Western Transbaikalia (1.8–12.5 µg/dm<sup>3</sup>) (Kashin and Ivanov, 1997), being comparable to this indicator in Lake Seliger, i.e. from 0.27 to 4.0 µg/dm<sup>3</sup> with 1.48 µg/dm<sup>3</sup> on average (Brekhovskikh et al., 1997). According to Yu.V. Robertus et al. (2009), the Ni content in Lake Teletskoye (2009) varied within narrower limits – from 0.34 (in the area of the Artybash village) to 0.43 µg/dm<sup>3</sup> (at the Chelyush River mouth and near the Cape Kyrtsai). The above mentioned authors noted lateral zonality in spatial distribution of microcomponents in the lake due to changes in volumes of river runoff and the characteristics of natural conditions in the river basins.

A.P. Maloletko and T.P. Shestakova (1979) detected 0.58 µg/dm<sup>3</sup> of nickel at a depth of 316 m in the waters of Lake Teletskoye nearby the Korbu waterfall; towards the surface of the reservoir the nickel content decreased to 0.25 µg/dm<sup>3</sup>. Fifty years ago, these authors found 1–1.5 µg/dm<sup>3</sup> of nickel in water samples within the zinc-lead-silver hydrogeochemical region (Kamginsky Bay). In the Koldor River, they recorded a value of 1.02 µg/dm<sup>3</sup>, in the Chedor River – 1.51 µg/dm<sup>3</sup>. The waters of the Kamelik River (13.2 µg Ni/dm<sup>3</sup>) and the Barchik stream in the village of Bele (7.1 µg Ni/dm<sup>3</sup>) were distinguished by a high nickel content (Maloletko and Shestakova, 1979). From our studies it follows that waters of the Kamelik River, on the contrary, are characterized by a very low nickel content: from 0.39 to 1.8 µg/dm<sup>3</sup>, an average of 0.8 µg/dm<sup>3</sup>. In the Koldor River, the total nickel content in 2021 was 4.2 µg/dm<sup>3</sup>, in the Chedor River – 3.5 µg/dm<sup>3</sup>, in the Kamginsky Bay – 4.3 µg/dm<sup>3</sup>.

<sup>4</sup> PND F 14.1:2:4.139-98. Quantitative chemical analysis of water. Methodology for measuring mass concentrations of iron, cobalt, manganese, copper, nickel, silver, chromium and zinc in samples of drinking, natural and waste water using atomic absorption spectrometry.

<sup>5</sup> Method NSAM No. 450-C. Determination of microquantities of beryllium, thallium, lead, bismuth, cadmium, copper, manganese, cobalt, nickel, chromium by the atomic absorption method with electrothermal atomization of the sample in natural objects. Industry method of the III accuracy category.

<sup>6</sup> Automated information system for state monitoring of water bodies (AIS SMWB), 2021. Web page. URL: <https://gmvo.skniivh.ru/> (accessed: 21.02.2022).

**Table 1.** Average long-term (2016–2021) concentrations of dissolved nickel forms in tributaries of Lake Teletskoye,  $\mu\text{g}/\text{dm}^3$ .  $X_a \pm x$  is the arithmetic mean and its error; lim – the range of variations, Cv – the coefficient of variation, % DF of TC is the percentage of dissolved nickel forms from the total content of Ni.

River	$X_{cp} \pm x$	lim	Cv, %	% DF of TC	Variability
Western tributaries (from north to south)					
Samysh	$3.1 \pm 0.4$	2.9–4.2	18	$90 \pm 1$	0.4
Chedor	$2.6 \pm 0.2$	1.9–3.1	23	$87 \pm 3$	0.5
M. Chili	$1.1 \pm 0.2$	0.5–2.2	36	$83 \pm 2$	1.2
B. Chili	$2.2 \pm 0.4$	1.1–4.5	50	$83 \pm 3$	1.5
Chulyshman	$1.5 \pm 0.2$	0.7–2.5	40	$81 \pm 2$	1.2
Eastern tributaries (from north to south)					
Kamga	$2.2 \pm 0.4$	1.1–3.8	46	$81 \pm 2$	1.2
Korbu	$0.2 \pm 0.1$	0.1–0.7	84	$72 \pm 2$	2.2
Kokshi	$1.2 \pm 0.4$	0.2–3.4	88	$62 \pm 3$	2.3
Chelyush	$0.8 \pm 0.2$	0.2–2.0	74	$73 \pm 3$	2.2
Kamelik	$0.5 \pm 0.1$	0.3–0.9	45	$72 \pm 5$	1.3
Chiri	$0.8 \pm 0.2$	0.3–1.9	63	$68 \pm 5$	2.1
Kyga	$3.0 \pm 0.2$	2.5–3.5	16	$84 \pm 2$	0.33
The lake water near the village of Yailu (northern part of the lake)					
Lake water	$1.3 \pm 0.2$	0.6 – 2.3	39	$75 \pm 6$	1.0
MPC <sup>7</sup>			10		
MPC <sub>w</sub> <sup>8</sup>			20		
$X_a$ in the waters of the land (according to: Dobrovolsky, 1998)			2.5		

<sup>7</sup> Order of the Ministry of Agriculture of Russia dated December 13, 2016 No. 552 (as amended on August 22, 2023) "On approval of water quality standards for water bodies of fishery importance, including standards for maximum permissible concentrations of harmful substances in the waters of water bodies of fishery importance" (registered with the Ministry of Justice of Russia on January 13, 2017 No. 45203).

<sup>8</sup> GN 2.1.5.1315-03. Maximum permissible concentrations (MAC) of chemical substances in water of water bodies for domestic, drinking and cultural water use.



**Table 2.** Average nickel content in the surface waters of western and eastern shores of Lake Teletskoye in the spring-summer flood of 2021,  $\mu\text{g}/\text{dm}^3$ : arithmetic mean  $\pm$  error of the mean, coefficient of variation (in brackets).

Forms of Ni content	Western tributaries	Eastern tributaries
Total content	3.3 $\pm$ 0.5 (28%)	0.5 $\pm$ 0.2 (78%)
Soluble forms	3.1 $\pm$ 0.4 (43%)	0.4 $\pm$ 0.1 (51%)

The content of nickel dissolved forms in the rivers of the Lake Teletskoye basin in 2016–2021 did not exceed the MPC for waters of fishery and cultural-domestic purposes (SanPiN 1.2.3685-21<sup>9</sup>): it varied from 0.1 to 4.4  $\mu\text{g}/\text{dm}^3$ , averaging to 1.5  $\pm$  0.1  $\mu\text{g}/\text{dm}^3$  (Cv = 77%). For comparison, in the waters of lakes in the southern taiga zone of Western Siberia (Kremleva et al., 2012), the nickel content in filtered samples (determined by the ICP-MS method) fluctuated within the same range : from < 0.2 to 4.5  $\mu\text{g}/\text{dm}^3$ . In small rivers of the Nadym-Purovsky interfluvium (in the north of Western Siberia), originating in swamps, the total nickel content (determined by atomic adsorption and mass spectrometry) in 2017–2018 was lower and varied as < 0.20–1.8  $\mu\text{g}/\text{dm}^3$  (Soromotin et al., 2019). It is worth noting that during our study the lowest nickel content (among the western tributaries of the lake) was found in the waters of the M. Chili River, the valley of which is heavily swamped in the middle reaches (Table 1). In the Ob surface waters (2018), also studied by the ICP-MS method on an ICA-P-Qc device (“Thermo Scientific”) (Eirikh et al., 2018), the content of dissolved forms of nickel varied within 2.2–4.0  $\mu\text{g}/\text{dm}^3$ , being consistent with our results.

The highest content of dissolved nickel was found in the waters of the Samysh River: 2.9–4.2  $\mu\text{g}/\text{dm}^3$ , on average 3.1  $\pm$  0.4  $\mu\text{g}/\text{dm}^3$  (Table 1); these values coincided with the results of our previous studies – 3  $\mu\text{g}/\text{dm}^3$  (Puzanov et al., 2015). We noted a decline in the content of dissolved nickel in the Chulyshman River within 0.7–2.5  $\mu\text{g}/\text{dm}^3$  (2016–2021), compared to 3  $\mu\text{g}/\text{dm}^3$  (2009). Over the past 6 years, the content of dissolved nickel also dropped in rivers B. Chili River (around 4.5  $\mu\text{g}/\text{dm}^3$ ) and Kyga (3.5  $\mu\text{g}/\text{dm}^3$ ) during the autumn low-water period of 2021, as compared to 2009 (5 and 6  $\mu\text{g}/\text{dm}^3$ , respectively). This indicator in the Biya River waters (the only river flowing out of the lake), in the vicinity of Artybash village (1.5–2.5  $\mu\text{g}/\text{dm}^3$ ), turned out to be the same as obtained 10 years ago – 2  $\mu\text{g}/\text{dm}^3$ .

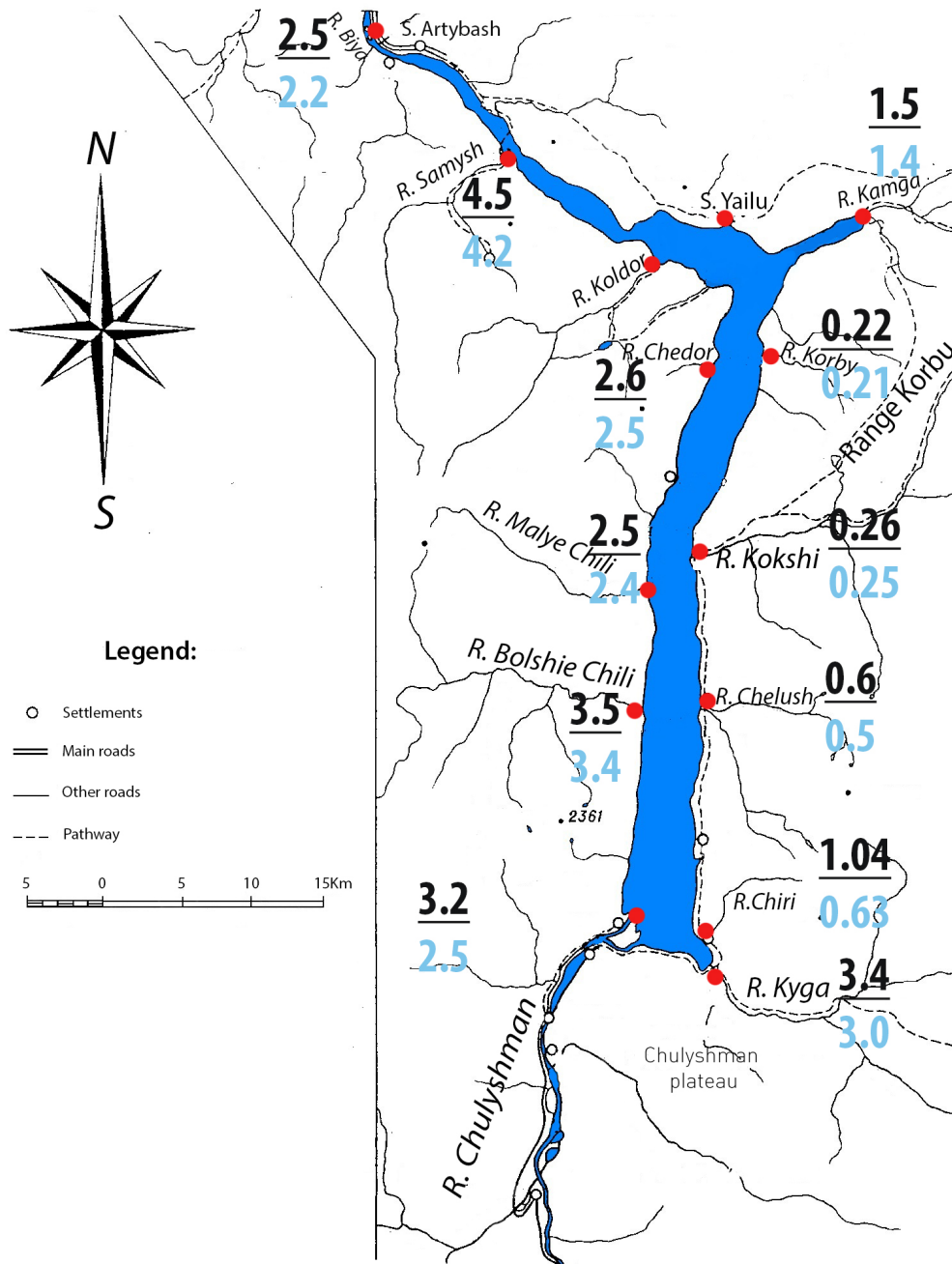
Nickel mostly migrates in dissolved form in the waters of Lake Teletskoye tributaries, accounting for 62–90% of the total Ni content. Eirikh et al. (2018) report that 90% of nickel is present in the Ob River in the form of dissolved compounds. At the same time, from V.V. Dobrovolsky (1998) it follows that 92% of nickel in river waters is transported on suspensions, in the suspended form.

The nickel content in the waters of Lake Teletskoye tributaries is characterized by significant spatial heterogeneity of its distribution (Table 1). The nickel concentrations in the eastern tributaries of the meridional part of the lake (Korbu, Kokshi, Chelyush, Chiri) are more variable (Table 2).

It has been established that in the waters of the western tributaries of the meridional part of the lake (rivers Chedor, Bol'shiye Chili, Samysh), the nickel content (both in dissolved and suspended forms) is significantly higher than in the waters of the eastern tributaries (rivers Korbu, Kokshi, Chelyush, Chiri, Kamga) (Tables 1, 2, Fig. 2). This difference is especially pronounced during the spring-summer flood period when nickel concentrations in the waters of the eastern tributaries do not exceed 1  $\mu\text{g}/\text{dm}^3$ .

The increased nickel content in the rivers draining the western shores of the lake is explained, among other things, by soil maturity of the catchment area, where intensive biogeochemical processes stimulate the formation of nickel migratory-capable soluble forms and, accordingly, its active entry into the river network. An additional reason for higher contents of nickel in dissolved forms in the western shore waters is the predominance of sedimentary carbonate rocks here, where most intensive release of nickel occurs (Soldatova et al., 2022). The proportion of dissolved forms of nickel in the waters of western tributaries (83–90%) is also higher than in those of the eastern ones (62–73%) (Table 1). On

<sup>9</sup> SanPiN 1.2.3685-21. Hygienic standards and requirements for ensuring safety and (or) harmlessness of environmental factors for humans.



**Fig. 2.** The map of Ni content in tributaries of Lake Teletskoye and of the Biya River during the spring–summer flood of 2021 (the total content is given in the numerator, soluble forms concentration – in the denominator, µg/l).

the eastern shores, rocky primitive soils are more common, therefore, the processes of formation of mobile forms of nickel, its dissolution and entry into the river network are less significant than on the western side of the lake.

It is known that the greatest contribution to inactivation of metals in natural waters is made by the process of their complexation with humic and fulvic acids. In the aquatic environment, such a complexation of nickel in the waters of forest landscapes depends on the presence of Fe, Al, Cu: in their absence, the degree of Ni binding increases significantly (Moiseenko et al., 2013). The content of humic and fulvic acids in mountain-forest brown soils of the western shore of the lake, due to their greater humification, is obviously significantly higher than in the rocky primitive soils on the eastern side of the lake. The acidic environment of swamps of the landscapes of western shores (in the middle reaches of

rivers Bolshie and Malye Chili) promotes the formation of water-soluble forms of iron. Here, Fe forms complexes with humic and fulvic acids, preventing the complexation of nickel, which can then more intensively enter the watercourse in the form of soluble compounds. It should be noted that in the waters of the Ob River (2018), 90% of nickel was represented by water-soluble compounds, while the bulk of iron was present in the form of suspension (89%) (Eirikh et al., 2018).

The waters of eastern tributaries of the meridional part of the lake (rivers Korbu and Kokshi), which originate from the top of the granite massif and drain mainly rocky primitive soil formations, contain relatively low concentrations of dissolved nickel since granite rocks are distinguished by its lowest content (Dobrovolsky, 1998; Voitkevich et al., 1990). The proportion of soluble forms of Ni in rivers Korbu, Koksha, and Chelyush is lower than in western tributaries (Table 1), only 27–38% of the nickel is in the form of suspended compounds. Perhaps this is due to less competition for nickel in binding and forming insoluble complexes.

In 2016–2020, the iron content in the waters of some tributaries of Lake Teletskoye could reach  $340 \mu\text{g}/\text{dm}^3$  (the Chulyshman River, the small Chiri River and the Kamelik Creek in June 2018), but at such a high concentration most of Ni was in the form of suspended compounds (77–85%). Just the competitive presence of iron was probably the reason that nickel in these rivers was predominantly noted in a water-soluble form (80–89%).

**Table 3.** Hydrological characteristics of various-sized tributaries of Lake Teletskoye and estimated values of nickel runoff for different hydrological periods of 2018. Above the line: data for June, below the line – for September.

Parameter	River		
	Chulyshman	Kokshi	Chiri
Catchment area, $\text{km}^2$	17200	472	37
Average catchment area height, m	2040	1540	1630
River length, m	241	37	11
River slope, %	8.6	18	150
Average annual water flow, $\text{m}^3/\text{s}$	175.8	16.2	0.69
Runoff volume, $\text{km}^3$ per year	5.5	0.51	0.02
Average monthly water flow, $\text{m}^3/\text{s}$	$\frac{728.0}{133.6}$	$\frac{46.5}{22.9}$	$\frac{2.9}{0.59}$
Volume of water flow per month, $\text{km}^3$	$\frac{1.95}{0.36}$	$\frac{0.125}{0.061}$	$\frac{0.0077}{0.0016}$
Total nickel content in water, $\mu\text{g}/\text{dm}^3$ , 2018	$\frac{1.8}{2.2}$	$\frac{0.8}{2.7}$	$\frac{0.9}{0.7}$
Average-monthly module of runoff, $\text{l}/\text{s}$ per $\text{km}^2$	$\frac{42.3}{7.8}$	$\frac{98.6}{48.1}$	$\frac{77.2}{16.2}$
Nickel runoff, $\text{kg}/\text{month}$	$\frac{3510}{787}$	$\frac{99}{164}$	$\frac{6.9}{1.1}$
Nickel runoff module, $\text{kg}/\text{month}$ from $\text{km}^2$ of catchment area	$\frac{0.20}{0.046}$	$\frac{0.21}{0.35}$	$\frac{0.19}{0.03}$

In 2021, one of the highest levels of total and soluble nickel was found in the waters of the Kyga River (Fig. 2). For 2016–2021, the nickel soluble forms content in the Kyga River was also the highest of all the studied tributaries of Lake Teletskoye –  $3.0 \pm 0.2 \mu\text{g}/\text{dm}^3$  (Table 1), accounting for 78–88% of the total content. In our earlier studies, the highest content of dissolved nickel was also recorded in the Kyga River –  $6 \mu\text{g}/\text{dm}^3$  (Puzanov et al., 2015). The waters of the Kyga River are characterized from year to year by one of the highest proportional contents of suspended forms of iron (70–85% of the total content). Maybe that is the reason why Ni, with its reduced ability to complex in the presence of iron, is mainly observed here in the form of water-soluble compounds.

The share of nickel soluble forms in the Samysh River makes up 85–93%. The high degree of Ni solubility in this river is explained by the natural ore occurrence in the catchment area, as well as the presence of iron mainly in the form of suspension (in 2016–2021: 53–85% of the total).

In June 2022, for the first time in several years of observations, we detected elevated (up to  $1.1 \text{ MPC}_t$ ) concentrations of Ni in the rivers of the Lake Teletskoye basin. In the waters of the western tributaries, the catchments of which were most exposed to anthropogenic loads, the content of dissolved forms of Ni was significantly higher ( $9.1\text{--}11.0 \mu\text{g}/\text{dm}^3$ ) than in the waters of the eastern tributaries ( $1.0\text{--}1.2 \mu\text{g}/\text{dm}^3$ ) flowing through the territory of the Altai Nature Reserve. The highest total nickel content in the summer of 2022 was found in rivers Samysh, Koldor, Chedor of the northern part of the lake's western coast. High Ni content in the Samysh River waters (Table 1) is explained by the basin complicated geology – the presence of a gold-bearing deposit in the river valley (the Kalychak mine, that operated until the mid-20th century). It is known that nickel is an element accompanying gold mineralization (Korshunova and Charykova, 2018; Saet et al., 1990). In addition, in 2022, a tourist base was actively built here.

Based on the available data (AIS SMWB, 2021<sup>10</sup>; Selegey and Selegey, 1978) on water flow rates and river basin areas (where hydrological stations currently operate), we calculated nickel runoff and its removal per unit of the catchment area in 2018 (Table 3).

It has been established that nickel runoff by the Lake Teletskoye tributaries directly depends on a water flow in rivers. The largest amount of Ni is brought into the lake by the Chulyshman River: during the spring-summer flood – up to 3.5 tons, in the autumn low water period and a 5-fold drop in water flow – 0.8 tons (Table 3). At the same time, the Biya River (the only river flowing out of Lake Teletskoye) with a Ni concentration of  $2.5 \mu\text{g}/\text{dm}^3$  in its water and water flow of  $452 \text{ m}^3/\text{s}$  in September transports 2.9 tons of nickel. Only 6.7 kg of Ni during the spring-summer flood and 1.1 kg in the autumn low water period enter Lake Teletskoye with waters of the Chiri River. The Koksha River brings more nickel (164 kg) in autumn (when soils play the greater role in water migration of elements) than in summer (99 kg), which is explained by the greater influence of soil cover in the basin on the formation of chemical water composition of this river.

The removal of nickel from a unit of the catchment area is less determined by hydrological parameters of the river – its size, water flow and runoff volumes. During the summer high-flow period, the intensity of nickel transport from the catchment areas of various-size tributaries is practically the same, amounting to  $0.19\text{--}0.21 \text{ kg}/\text{km}^2$  per month. During the autumn low-water period, the removal of microelements largely depends on intra-soil processes in the catchment area due to water content and flow decline in rivers. The lowest nickel runoff modulus is noted for the basin of the small river with the greatest slope (Chiri River) that is a consequence of the short-term contact of water with rocks and soils.

The total content of dissolved and suspended forms of Ni has been calculated (about 68 tons) based on the average annual concentration of nickel in the lake ( $1.7 \pm 0.1$ ,  $C_v = 26\%$ ) and its volume ( $40 \text{ km}^3$ ). From the average annual flow of the Biya River ( $472 \text{ m}^3/\text{s}$ ) and the nickel content in its waters ( $1.5\text{--}2.5 \mu\text{g}/\text{dm}^3$ ) it follows that nickel removal here reaches 22–37 tons per year, that is 2–3 times higher than the annual input of Ni by the Chulyshman River (about 10 tons per year at the average annual flow of the Chulyshman River of  $158 \text{ m}^3/\text{s}$  and the average long-term concentration of nickel in its waters –  $2 \mu\text{g}/\text{dm}^3$ ). Thus, in contrast to the volume of water flow into Lake Teletskoye, which is more than 2/3 represented by waters of the Chulyshman River, the nickel content in the lake is only half determined by its inflow with the waters of the largest waterway.

<sup>10</sup> Automated information system for state monitoring of water bodies (AIS SMWB), 2021. Web page. URL: <https://gmvo.skniivh.ru/> (accessed: 21.02.2022).

## Conclusion

The nickel content in tributaries of Lake Teletskoye (2016–2021) varies from 0.12 to 4.6  $\mu\text{g}/\text{dm}^3$ ; it does not exceed the  $\text{MPC}_w$ ,  $\text{MPC}_i$  and is consistent with Ni concentrations in other rivers of Western Siberia, being higher than the world average. Nickel concentrations in the lake are also within MPC, however, they are higher than 50 years ago that can be explained both by differences in analytical determination methods and increasing anthropogenic impacts on the environment.

The concentrations and proportions of dissolved forms of Ni are higher in the waters of the western tributaries of the meridional part of Lake Teletskoye than in those of the eastern ones. This is due to biogeochemical and geological features of their catchment areas: the processes of formation of water-soluble forms of nickel and its entry into the river network are more intensive in well-formed and mature mountain-forest brown soils of the western shores of the lake than in the primitive rocky soils of the eastern ones. Another factor is the predominance of sedimentary carbonate rocks on the western shores and granites on the eastern ones.

The increased nickel solubility in waters of western tributaries can also be explained by more noticeable presence of iron in mountain-forest brown, in places, swampy soils. Fe competes with nickel for binding with humic and fulvic acids thereby reducing the ability of Ni to form complexes.

In June 2022, for the first time in several years of observations, elevated nickel concentrations were detected in waters of western tributaries of the lake – up to 11  $\mu\text{g}/\text{dm}^3$  (1.1  $\text{MPC}_r$ ). High concentrations of nickel in western tributaries may be attributed to both the greater exposure of western shores to anthropogenic loads (construction of tourist centers, deforestation, increasing erosion processes in the catchment area) and the specifics of the geochemical situation (the presence of a gold-bearing deposit in the Samysh River basin, the erosion of wastes from the previously functioning gold mining industry).

The mass transfer of Ni from the catchment areas of Lake Teletskoye tributaries has been calculated. During spring-summer floods, the Chulyshman River brings up to 3.5 tons of nickel into the lake, and in the autumn low water period – 0.8 tons. The contribution of other tributaries to the nickel influx is one to two orders of magnitude less. The largest tributary of Lake Teletskoye provides not more than 50% of nickel content to its waters.

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