RESEARCH PAPER

LEVELS, D,S-PATTERNS AND SOURCE IDENTIFICATION OF METALS AND METALLOIDS IN RIVER WATERS OF THE GAS-PRODUCING REGION IN THE NORTH OF WESTERN SIBERIA (PUR RIVER BASIN)

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ABSTRACT. The study aimed to determine the levels, spatial and temporal variability of the concentrations, and forms of migration of metals and metalloids in the Pur River basin, which is one of the most important oil and gas producing areas in the north of Western Siberia. The study is based on the results of hydrological and geochemical studies conducted in 2021-2023 during the summer low water and spring flood periods. We found generally low content of dissolved metals and metalloids in water of the Pur River and its tributaries, not exceeding the world average values, except for Fe and Zn. Levels of metals and metalloids in the suspended matter were also lower than the global averages, except for Fe and Mn. Changes in the content of dissolved and suspended forms of metals caused by hydroclimatic factors and anthropogenic impact were determined. Near cities, the maximum concentrations of Zn, Cd, Cu and other metals in suspended matter are 3-5 and more times higher than the baseline values. Analysis of EF values for median contents allowed to identify the association of elements with considerable and high enrichment in suspended matter: Fe, Mn, Sb, As, Cd and Zn. The maximum EF values ranged from 25 to 45, which corresponds to very high degree of enrichment. Three groups of chemical elements were identified on the basis of D,S-analysis.

KEYWORDS: Arctic, hydrological and geochemical research, surface water, dissolved, suspended, pollution, enrichment, sources, natural, anthropogenic

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INTRODUCTION

Over recent years, attention to the ecological state of rivers in the Arctic basin has been growing due to climate change and increasing human impact. Climatic changes contribute to a significant increase in river runoff, which in turn leads to an increase in chemical fluxes into the seas of the Arctic Ocean (Chalov et al., 2023; Chupakov et al., 2020; Demina et al., 2010; Gebhardt et al., 2004; Gordeev et al., 2024; Hartwell et al., 2020). Industrial mining, urban development, the construction of roads and other infrastructures often has a negative impact on the state of river basins. Arctic river ecosystems are particularly vulnerable to anthropogenic impacts in comparison to temperate rivers (Barker et al., 2014; Garnier et al., 1996; Krickov et al., 2019).

Metals and metalloids (MMs) can enter the environment from natural sources such as the weathering of soil and bedrock, as well as through human activities such as mining, industry and agriculture. Generally, metals enter aquatic systems through washout from surface soils, diffuse inflow from groundwater, polluted sediments, leaching from agricultural areas and waste ponds, failure of waste ponds, and discharge of industrial and mining effluents (Hudson-Edwards, 2003; Inam et al., 2011; Macklin et al., 2006; Mighanetara et al., 2009). Natural factors, including the mobilization of sediment material through bank and channel erosion can dominate over pollutant transport in certain conditions (Chalov et al., 2015). Due to their inability to biodegrade, metals in the aquatic environment can threaten ecosystems long after their initial input.

An increasing number of studies confirm that the migration patterns of metals largely determine their mobility, bioavailability and toxicity in the aquatic environment (Ali et al., 2019; de Paiva Magalhães et al., 2015; Fytianos, 2001; Landner and Reuther, 2005; Miranda et al., 2021; Violante et al., 2010; Wu et al., 2016). Understanding the processes that control the migration patterns and transport of metals in a river basin is key to managing this ecosystem. For example, aquatic migration of metals adsorbed on suspended sediments can be significantly slower than metals in dissolved form (S. Chalov et al., 2020; Thorslund et al., 2012).

In recent decades, the number of publications on the content of metals and metalloids in dissolved and suspended forms in river waters has increased dramatically, which is largely due to the development of analytical methods, especially the use of ICP-MS method, which allows the high accuracy determination of a wide range of chemical elements in microquantities. The average content of dissolved (Gaillardet et al., 2014) and suspended forms of elements in the world's rivers has been assessed (V. Savenko, 2006; Viers et al., 2009). There is increasing attention being paid to the ratio of dissolved to suspended forms of metals and metalloids. At the basin level, using the example of the Selenga River, the largest tributary of Lake Baikal, it has been shown that the ratio of element migration forms is determined mainly by the properties of the elements themselves, hydroclimatic conditions and anthropogenic load (Kasimov et al., 2020).

Over the last few decades, an extensive database on the major ions composition and ionic runoff of the world's rivers (Meybeck, 2003) and the Arctic Ocean basin (McClelland et al., 2023) has been collected. However relatively few data on the content and forms of trace elements in Arctic rivers are still available. The paper (Gordeev et al., 2024) summarizes the results of the studies carried out on the largest rivers of the Russian Arctic (Ob, Yenisei, Lena, Kolyma) in 2004-2006. It was concluded that the content of most elements in Arctic rivers is significantly lower than the global average. The assessment of the fluxes of dissolved substances based on the average content of elements and the average annual water flow showed that the Lena River is characterized by the largest flow into the Arctic Ocean, followed by the Yenisei, Ob and Kolyma.

A review on the dissolved forms of chemical elements in the rivers of the Russian Arctic is presented in the paper of (Savenko and Savenko, 2024), who summarized the results of river water analysis obtained by ICP-MS over the last 30 years. The study, which covered rivers in both the Asian and European parts of the Russian Federation, confirmed that the content of most elements in Arctic rivers is close to or significantly below the global average. In the northern part of Western Siberia there is still a lack of data on dissolved forms of elements in most rivers except for the Ob River (Kolesnichenko et al., 2021; Pokrovsky et al., 2015, 2016). The content of metals and metalloids in suspended form in the rivers of this region has been still poorly studied. In one of the few works (Soromotin et al., 2022) it was noted that the content of metals and metalloids in the river sediments of the Ob River estuary is low due to their low content in peat horizons of soils in the catchment areas.

The key factors determining the features of spatial and temporal variability of metal contents and fluxes at the river basin level have been still poorly understood. The lack of detailed information at the basin level makes it impossible to assess the anthropogenic impact on the natural environment and to predict the response of the water system to future climatic changes and the industrial development in the Arctic region. It is difficult to solve these problems at the basin level of the largest Arctic rivers, so in this study the Pur River basin, located between the Ob River in the west and the Yenisei River in the east, was chosen as a model object.

The Pur River basin is one of the most important oil and gas producing areas in the north of Western Siberia with the Urengoy field located on its territory. This field is the world's third largest in terms of explored natural gas reserves, as well as more than 10 other large oil and gas fields. The rivers in the Pur River basin have been experiencing significant anthropogenic impacts over the past few decades due to the influence of the fields themselves, as well as the settlements that are centers of water pollution, oil and gas infrastructure and refining industry, and diffuse pollution during snowmelt and rainfall. The impact of the oil and gas complex on river systems is complex and includes transformation of the catchment area, erosion, input of pollutants from atmospheric deposition, etc. (Moskovchenko, 1998).

The first task of the study was to determine the levels, spatial and temporal variability of dissolved and suspended forms of metals and metalloids in the Pur River and its tributaries. A particular attention was given to the studying of the Evoyakha River, a left tributary of the Pur River, which flows through Novy Urengoy, the largest center of anthropogenic impact in the basin. The second task was to identify the predominant forms of metal and metalloid migration and their variability on the basis of D,S – analysis. The third task was to assess human-induced changes in content of metals and metalloids in river waters and identify their main natural and anthropogenic sources. The study is based on the results of 5 field campaigns conducted in 2021-2023 during the summer low water and spring flood periods (Fig. 1).

STUDY AREA

The Pur River basin is a lowland plain with altitude less than 50 meters a.s.l. The river channels are weakly incised and highly sinuous, flow among low banks, meander in wide valleys, forming branches and channels (Fig. 2). The lithology is formed by siltstones, clays and marls of the Permian system overlain by Quaternary alluvial-marine, lake-alluvial and alluvial Quaternary sediments of different grain size. The weak erosional dissection of the watershed combined with the close occurrence of permafrost results in waterlogging of soils (Kolesnichenko et al., 2021).

The climate of the Pur River basin is continental subarctic, with long winters (up to 8 months), short summers, strong winds, and shallow snow cover. The average annual air temperature is about -5°C. The annual amplitude of temperatures is 35-40°C. The natural features of the territory are largely determined by permafrost, which is mainly discontinuous, but in the north of the basin becomes continuous (Pokrovsky et al., 2015). The topography is extremely flat, and lithology is fairly homogeneous (peat, sand and silt). Soils are presented mainly by Histosols and Histic Gleysols, in the southern areas Gleyic Albic Podzols are predominant. Northern taiga landscapes prevail in the southern part of the basin, while forest-tundra landscapes prevail in the northern part. The most common trees are dwarf birches, polar willows, spruce, fir and larch. Mosses and lichens are common, as well as small shrubs.

The Pur River is 389 km long and has a basin area of 112,000 km^2. The Pur is formed at the confluence of the Pyakupur and Aivasedapur rivers, which flow from the northern slope of the Siberian Uvals. In its lower reaches, the river forms a 21 km wide delta and flows into the Taz Bay of the Kara Sea. The Pur has a large number of tributaries, among which the Evoyakha River, which flows through the Urengoyskoye field and the urban area of Novy Urengoy, is the most affected by anthropogenic pressure.

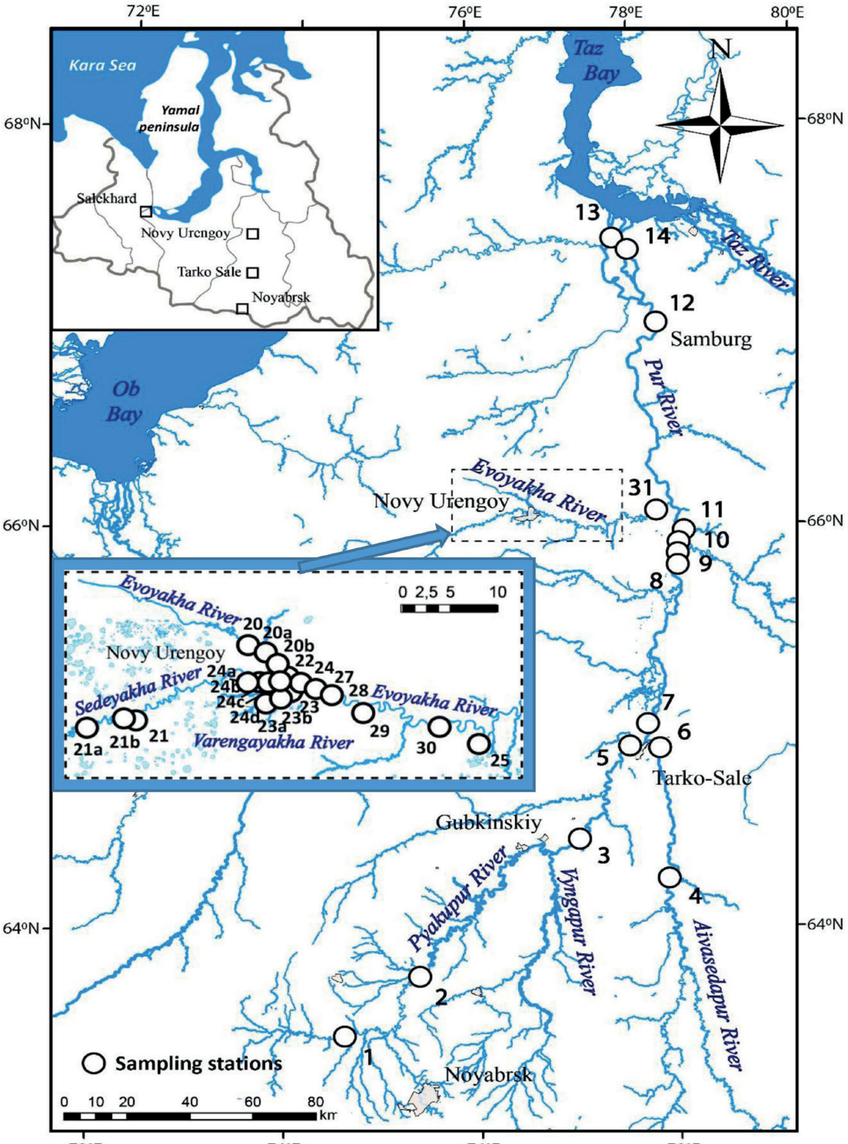


Fig. 1. Study area

Fig. 2. Pur River during snowmelt flood, June 2022

There are a large number of rivers and lakes in the Pur River basin. The density of the river network is 0.38 km/km^2. The total number of lakes exceeds 85,000. Many lakes are directly connected with the river network. The rivers of the Pur basin have mixed feeding with the predominance of ground and marsh feeding, with runoff mainly in the warm season. The rivers of the Pur basin are covered with ice for most of the year. The period of open water even in the warmest years does not exceed 5 months in the upper reaches and 4.5 months in the lower reaches. The appearance of stable ice cover occurs at the end of the first or beginning of the second part of October. The ice cover on the Pur River breaks up in late May to early June. After the ice drift, the water temperature rises rapidly and with the end of the spring level rise, is higher than the air temperature; this remains until the following spring (Popov, 2013).

The rivers of the area feature consistent annual runoff. The flow is formed with sufficient (more than 600 mm) annual precipitation and low evaporation. High wet-land (50%) and lacustrine (10%) areas have an important impact on the runoff and its variability both within a year and in the multi-year dynamics. The average annual flow rate of the rivers into the basin is 9-10 l/sec·km^2. The coefficient of variation of annual runoff decreases from south to north from 0.15 to 0.10 (Agbalyan et al., 2016).

The main flow (57-63% of the annual runoff) occurs in spring and summer, 21-25% in autumn, and 18-20% in winter, depending on the year's water availability. Highest flow occurs during the spring flood, which starts in May-June and lasts for 40-50 days in small rivers. The highest discharge is observed during this period, and lasts for between 1-5 days. Floods sharply intensify all channel processes, ice drift, an increase in river turbidity, and an increase in sediment runoff, and the flushing of pollutants from catchments, while stagnant and heavily polluted old lakes, on the contrary, are washed out, only flowing for a short period. Rain floods are observed almost every year. The volume of total runoff of the largest rain floods is 5-40%, in some years - up to a volume of 73% during the spring runoff. Maximum discharges reach 10-50% of the magnitude of spring maxima. Periods of low flow are common for both summer-autumn and winter seasons. The period of low flow from the end of the flood to the beginning of ice events is recognized as the summer-autumn low-water period. The winter low-water period is stable and continuous, much lower than the summer period.

The Pur River waters have low turbidity, ranging from 9 to 28 mg/l. The sediment flux is 6.5 tons/year from 1 km^2 of the catchment area. The runoff of dissolved substances in water is almost 2.5 times greater than the particulate runoff (Uvarova, 2011).

The main sources of river water pollution in the Pur basin are oil and gas production facilities and cities, including Novy Urengoy, which is the center of a large gas-producing region. The area of the city is surrounded by developed oil and gas fields, the nearest one - Urengoyskoye - is located about 10 km away from the city. The Novourengoy Gas Chemical Complex is located 30 km south-east of the city. Its production infrastructure includes a liquefied gas storage facility, flare units, reagent warehouses, and a waste utilization complex. The city also has 15 heating plants, various food industry facilities, public utilities and transportation facilities.

Field sampling and laboratory processing

The study is based on the results of 5 field campaigns conducted in 2021 - 2023 during different phases of the water regime: in August 2021 during the summer low flow, in 2022 and 2023 during the spring flood (May-June) and summer-autumn low flow period (August-September). Samples were taken along the entire length of the Pur River from its head at the confluence of the Pyakupur River and the Ayvasedapur River to its mouth. Sampling stations were located upstream and downstream the urban areas of Tarko-Sale, Korotchaevo settlement, Samburg, Urengoy, as well as upstream and downstream of major tributaries (Fig. 1). A special attention was given to the Evoyakha River impacted by the of Novy Urengoy. In total, the measurements covered more than 30 sites, and 140 water and river sediment samples were collected (Supplementary 1).

Water discharge and velocities were measured using a SonTek M9 acoustic Doppler current profiler mounted on a PVC raft, from motorized PVC boat, or wading if the depth was less than 0.8 m. Water samples were taken from the surface layer into pre-prepared 1.5-liter bottles. Measurement of the vertical distribution of physicochemical parameters of the water column at several stations showed the absence of significant gradients resulting from turbulent mixing, thus allowing the surface samples to be considered representative. Electrical conductivity, pH and dissolved oxygen content were also measured in situ. River water samples were filtered on a vacuum system using "Millipore" membrane filters with a pore diameter of 0.45 μm. After filtration, all filters were dried and reweighed for further determination of the amount of suspended material.

The particle size distribution of the suspended matter was determined in the laboratory of the Department of Landscape Geochemistry and Soil Geography, Faculty of Geography, Moscow State University using a laser particle analyzer "Fritsch Analysette 22 MicroTec Plus". The concentration of major ions Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_{3}^{-}, Cl^{-}, SO_{4}^{2-} in river water was determined by capillary electrophoresis using the KAPEL®-105M system (Lumex Group of Companies).

The concentration of chemical elements in river water and suspended matter was determined on an Elan-6100 inductively coupled plasma mass spectrometer and an OPTIMA 4300 inductively coupled plasma optical emission spectrometer (Perkin Elmer) at the All-Russian Research Institute of Mineral Raw Materials named after N.M. Fedorovsky (Moscow). In this work we used the results of analysis of Al, Fe, Mn, Ni, Co, V, Cr, Cu, Zn, Pb, Cd, As, Sb, Sn, Bi, U, Sr, Ba, and Rb.

Data analysis

Statistical analysis of the obtained dataset included calculation of median values, standard deviations and coefficients of variation. Due to the high variability of the contents for a number of elements, the regional geochemical features of the river basins were studied on the basis of mean and median values. Calculations were carried out separately for the Pur River and its main tributary Evoyakha River, which is caused by the specific natural conditions and significant anthropogenic load in its basin. The results of replicate river water sampling were used to calculate mean and median values in each hydrological season for both rivers.

The features of MMs accumulation in dissolved forms were identified on the basis of concentration factors Cf - ratios of element contents in the studied sites to average contents in rivers of the world (Gaillardet et al., 2014) and rivers of the Kara Sea basin (Savenko et al., 2020). For suspended matter, Cf values were calculated relative to global average values according to (Viers et al., 2009).

The Enrichment factor (EF) was calculated to assess the contamination of river sediment. EF calculation allows to compensate for differences in the content of rare elements in rocks, soils and sediments caused by differences in their mineralogical composition and grain size (Horowitz, 1986) and to assess the anthropogenic contribution to pollution of solid phase components of the environment - soils, road dust, bottom sediments and suspended matter (Barbiery, 2016; Ediagbonya et al., 2015; Ryan and Windom, 1988; Vlasov et al., 2020). EF is calculated as the ratio of the metal content in the studied sample to a certain metal (reference) in the same sample, to a similar ratio in the Earth's crust:

$$EF = (Ci/Cref)_{Sample} / (Ci/Cref)_{UCC}$$

where *Ci* and *Cref* are the contents of the studied and reference elements, respectively, *UCC* – upper continental crust (Rudnick and Gao, 2013).

D,S-pattern of river waters was determined basing on the DS coefficient, which is a ratio of the volumetric concentration of suspended forms Cvs of an element to the total concentration of suspended and dissolved Cvd forms: *DS =Cvs/(Cvs+Cvd)*, % (Kasimov et al., 2020). The elements were ranking by decreasing DS ratio (%), grouping into quartiles (<25%, 25-50%, 50-75%, >75%) and presented in a matrix form. The prevalence of undissolved forms of the element is characterized by DS > 50 %, dissolved forms < 50 %.

The identification of major factors controlling MMs content in suspended matter and their contribution to the total values was performed using PCA/APCS-MLR. Two data sets for the Pur and Evoyakha rivers were used in the analysis, they included concentrations of 20 metals and metalloids at all sampling points. Z-normalization was applied prior to analysis:

$$Z_{ik} = \left(C_{ik} - \overline{C}_i\right)/\sigma_i$$

where C_{ik} is the concentration of the i-th chemical element in sample *k*, $\overline{C}_i$ is the average concentration of the i-th element for all samples, and σi is the standard deviation of the i-th element.

The Varimax rotation method was used to simplify factor interpretation and reduce the number of items with high factor loadings. Only principal components (PCs) that explain more than 5% of the total variance of the data set with eigenvalues > 1 (Kaiser criterion) were used as factors. We used the PCA method with calculation of absolute principal component scores (APCS) and further application of multiple linear regressions (MLR) to estimate the contribution of sources to elemental concentrations. PCA/ APCS-MLR is a valuable method for identifying independent factors using eigenvector decomposition of the matrix of pairwise correlations between compound concentrations (Thurston et al. 2011). APCS allows the total mass of each element to be distributed among the PCA-derived components, i.e., among the different sources. Detailed methodology can be found in (Liang et al. 2019; Chen et al. 2021). The main steps of the approach are summarized below.

Since the factor scores obtained by PCA are normalized, with the mean equal to zero and the standard deviation equal to one, the true value for each factor score was calculated by introducing an artificial sample with concentrations equal to zero for all variables. For this additional sample, the normalized values of the PTE concentrations would be as follows:

$$\left(Z_o\right)_i = \frac{0 - \overline{C}_i}{\sigma_i} = -\frac{\overline{C}_i}{\sigma_i}$$

The APCs for each component are then estimated by subtracting the coefficients for this artificial sample from the coefficients for each of the true samples. Regression of elemental concentration data to APC provides estimates of coefficients that convert APC to the mass source contribution of contaminants from each source for each sample. Source contributions to Ci can be calculated using MLR:

$$C_i = \varepsilon_{0i} + \sum\left(APCS_p \times \varepsilon_{pi}\right),\ p = 1, 2, \ldots, n$$

where ε_{0i} is the multiple regression crossover point for the i-th element, εpi is the multiple regression coefficient of source *p* for pollutant *i*, and $APCS_p$ is scaled value of the rotated coefficient p for the sample under consideration. $APCSp \times \varepsilon_{pi}$ represents the contribution of source *p* to C_i. Mean value of $APCSp \times \varepsilon_{pi}$ for all samples represents the average contribution of sources (Ma et al., 2021). APCS uncertainty (UNC, %) was calculated as follows:

$$UNC = \left(C_{meas} - C_{model}\right)/C_{meas} \times 100\,\%$$

where C_{meas} is measured concentration, C_{model} is the predicted concentration of the element based on the results PCA / APCS-MLR (Song et al., 2006).

RESULTS AND DISCUSSION

Hydrogeochemical conditions

The first field campaign was conducted in 2021 during the summer low water period from August 16 to August 30. In 2022, the expedition timed to the spring flood phase took place from May 23 to June 16, and to the summer-autumn low water period - from August 2 to 23. During the spring 2023 field campaign we managed to cover the period shortly after spring flood peak (Fig. 3). At the Urengoy station, the flood peak was observed during the first days of the survey, with initial measurements made on the day after its passing at a water level 2 cm below the peak, and final measurements made 8 days later at a water level 39 cm below the peak. The measured water discharges at the beginning and end of this period were 4440 and 3730 m^3/s. The water discharge of the Pur River during the study period decreased in this station by 16% with a 37 cm drop in level.

During the 2023 summer expedition, there was a summer low flow. In mid-August, the water level at all three Roshydromet stations reached the minimum values. The exception is the Pur River - Samburg, where level increases (up to 1 m) were observed due to the steady wind. Discharge of the Pur River naturally increased from 24 m^3/s in the upper reaches of the basin (Pyakupur River near Muravlenko) to 280 m^3 /s in the Purpe district, 414-428 m^3/s in the town of Tarko-Sale, 550-590 m^3/s in the area between Korotchaevo and Urengoy, and 721 m^3/s near the town of Samburg. Flow rates during the period of field campaigns at the flood recession in 2023 were close to those during the same period in 2022. Discharges during the low flow period in 2023 were on average 10-15% lower than in 2022. This is explained by weather conditions of the year and the later period of the expedition.

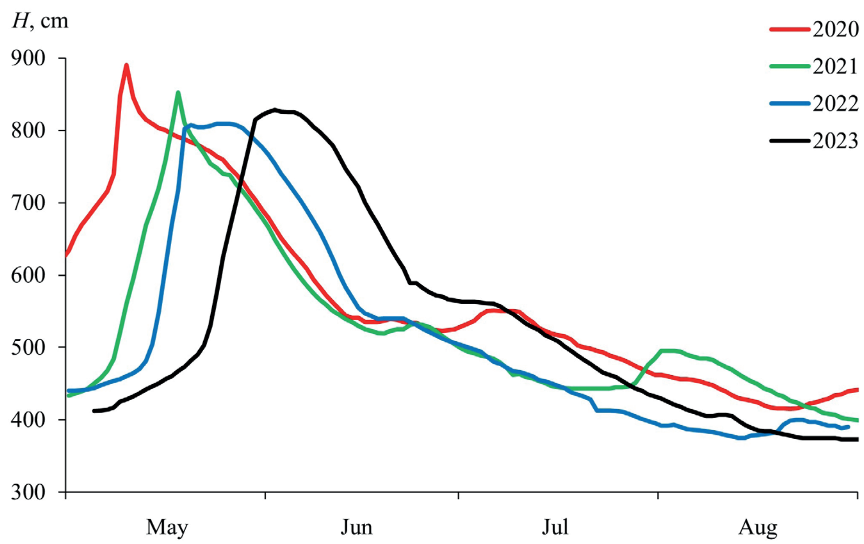


Fig. 3. Water level fluctuations (H, cm) in the station of the Pur River - Urengoy according to the Roshydromet gauging station

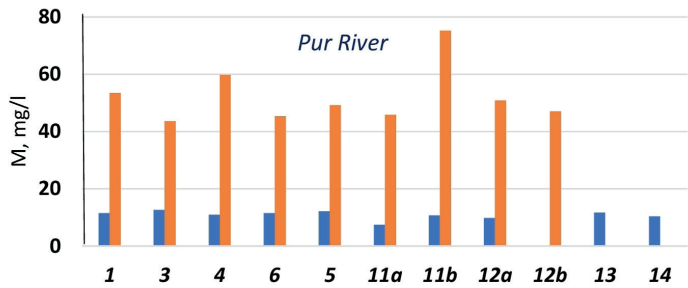
Rivers in the north of Western Siberia in general have low *mineralization*, which is due to the cold humid climate, widespread permafrost and fluvioglacial deposits of sandy and sandy loam composition. According to our data, the average mineralization of the Pur River water in the spring flood was 11 mg/l, during the summer low flow - 49 mg/l, which corresponds to the estimates for other large rivers of the region in the spring flood and summer-autumn low flow: Nadym River - 12 and 49 mg/l, Taz River - 35 and 62 mg/l, respectively.

During the spring flood of 2023, the Pur River mineralization was influenced by melt water inflow from the catchment and varied insignificantly along the river (Fig. 4). During the summer low flow period it increased approximately 4 times due to predominantly groundwater-derived baseflow. The maximum mineralization of 75 mg/l was observed downstream of Urengoy settlement near the right bank of the river (station 11b), where it is one and a half times higher than at the left bank (station 11a). It is caused by the impact of ship repair facilities, fuel and oil storage of the river port Urengoy, which is located on the right bank of the river above this station.

In the Evoyakha River, during the flood period mineralization of water was below 10 mg/l (average – 7.4 mg/l) and varied slightly from source to mouth This river catchment is dominated by permafrost soils, which do not thaw by the beginning of the flood, which defines the predominant role of snowmelt water in the hydrochemical runoff in this period. During low flow, the average mineralization increased to 26 mg/l due to rise of groundwater feeding. The highest mineralization up to 32 mg/l was observed downstream of Novy Urengoy due to the discharge of wastewater from the city sewage treatment plants and storm water from industrial sites.

For Na, K, Ca and Mg, a latitudinal distribution trend was established, consisting in a general decrease of their concentrations to the north (Supplementary 2). The lowest levels of major ions were observed in the Evoyakha River. This latitudinal trend is caused by a decrease in the share of groundwater supply and an increase in the share of snowmelt feeding as the area increases and the depth of permafrost decreases, as previously noted (Pokrovsky et al., 2015). The average pH value of river water during low flow periods is 7.3, while during floods it decreases to 5.5 due to a significant inflow of snowmelt water.

The particle size distribution of suspended matter in the Pur River basin is mainly dominated by sand particles larger than 50 µm, with an average share of 46%, while for fine particles smaller than 10 µm it is 21% (Fig. 5). The share of sand particles decreases to 40% during low water and increases to 54% during floods. In contrast, the share of PM_{10} particles increases to 23% during low water and decreases to 17% during floods. Changes in the particle size distribution of river suspended



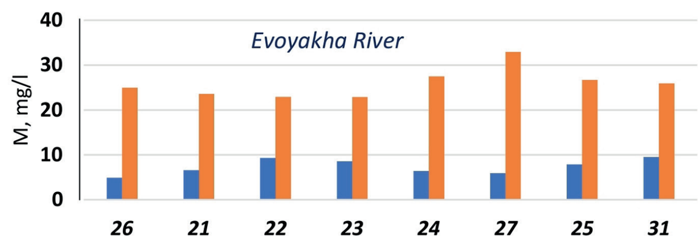


Fig. 4. Changes in water mineralization along the Pur River and Evoyakha River during spring flood (blue) and low flow (orange) periods in 2023; numbers of sampling stations correspond to the numbers in the Fig. 1

sediment naturally reflect changes in flow velocity and suspending capacity of the stream in different hydrological seasons. The average suspended matter diameter in the Pur River basin is about 70 μm, which is slightly less than the average size (83 μm) in rivers of different natural areas (Chalov and Efimov, 2021). This is explained by the lower ability of the Pur River to transport suspended material due to the small amplitude of altitude in its basin.

Dissolved forms of metals and metalloids in river waters

The Pur River and its main tributary, the Evoyakha River, are generally characterized by low levels of dissolved forms of metals and metalloids (Table 1), which is due to their low content in Quaternary sediments of predominantly light texture that comprise the catchments. Compared to global averages (Gaillardet et al., 2014), Fe and Zn contents are elevated in both rivers. The average Fe content in the Pur and Evoyakha rivers (140 μg/l) is 2 times higher than the global average and close to the average Fe content in the rivers of the Kara Sea basin - 180 μg/l (Savenko and Savenko, 2024). Iron accumulation in surface waters is a distinctive feature of Western Siberia (Gordeev et al., 2024; Kolesnichenko et al., 2021; Romanova and Samarin, 2019). The source of iron is peatland waters, feeding small rivers and streams in the study area. The average Zn content in the Pur River (3.1 μg/l) is 5 times higher than the global average (Gaillardet et al., 2014), but generally corresponds to the average for the rivers of the Kara Sea basin - 2.2 μg/l (Savenko and Savenko, 2024) and the lower reaches of the Ob and Taz Rivers - 4-7 μg/l (Pokrovsky et al., 2016; Soromotin et al., 2022). The levels of Ni, Co, Sb, Pb and Cd in the Pur River waters are close to the world average, while V, Cu, As, U, Ba and Rb are several times lower. Statistical analysis of the data revealed the highest variability (v>100%) for the content of Al, Fe, Mn, Co, Cu, Zn, Pb and Cd, caused apparently by the seasonal changes and anthropogenic impact.

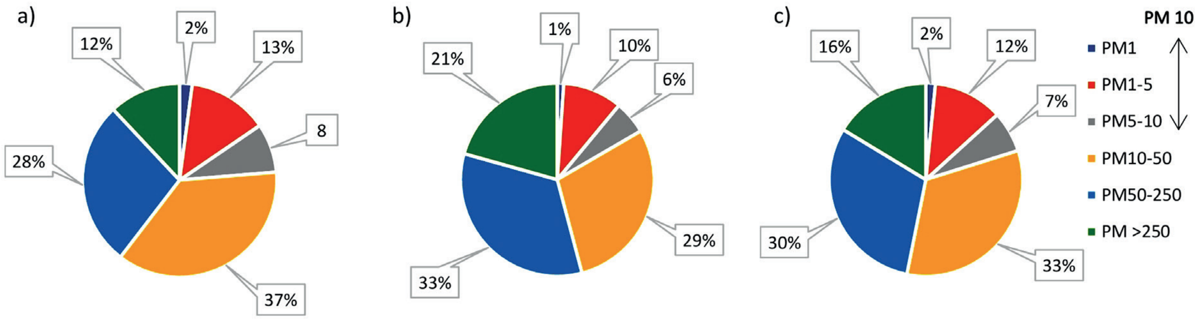


Fig. 5. The grain size distribution of river suspended matter in the Pur River basin: a) low flow; b) flooding; c) annual average

Table 1. Levels of dissolved forms of metals and metalloids in the Pur and Evoyakha rivers compared to the global average and regional background, μg/L

MMs	Pur River, n= 43					Evoyakha River, n=85					World Rivers[1]	Kara Sea Basin[2]	Pur River[3]
	median	mean	min	max	v%	median	mean	min	max	v%			
Al	4,5	25,3	0,35	**82**	118	23,5	27,8	1,6	**157**	85	32	17,7	35,6
Fe	**86***	141	3,0	**510**	110	**117**	**144**	10	**681**	93	66	180	568
Mn	1,4	20,4	0,12	**108**	165	8,0	41,6	0,3	**282**	123	34	22,2	52,4
Ni	0,54	0,65	0,23	**3,60**	79	1,3	1,43	0,06	**14,4**	107	0,8	1,03	1,04
Co	0,04	0,08	0,04	**0,37**	100	0,04	0,36	0,04	**3,74**	148	0,15	0,08	0,10
V	0,13	0,14	0,03	0,28	54	0,15	0,15	0,03	**1,06**	102	0,71	0,93	-
Cu	0,6	1,14	0,10	**11,0**	164	0,93	1,67	0,10	**19,0**	156	1,48	1,54	0,8
Zn	**2,6**	**3,09**	0,20	**21,0**	125	**3,8**	**4,66**	1,19	**19,4**	81	0,6	2,2	-
Pb	0,04	0,11	0,09	**1,20**	186	0,058	0,141	0,01	**2,90**	235	0,08	0,099	0,157
Cd	0,003	0,01	0,002	**0,096**	163	0,003	0,011	0,003	**0,094**	153	0,08	0,007	0,005
As	0,3	0,32	0,20	0,49	22	0,31	0,34	0,09	**0,93**	44	0,62	0,56	0,31
Sb	0,075	0,075	0,036	0,240	43	0,073	0,067	0,011	**0,143**	48	0,07	0,066	-
U	0,003	0,005	0,001	0,013	68	0,007	0,008	0,000	0,026	66	0,37	0,242	-
Sr	27,5	22,6	6,2	42,0	50	7,8	10,8	2,2	**75,0**	92	60	129	17,4
Ba	6,3	6,4	4,3	9,3	20	5,1	9	1,7	**242,7**	293	23	12,1	17,8
Rb	0,54	0,64	0,41	2,6	51	0,79	0,81	0,36	**2,21**	34	1,63	0,61	-

n - number of samples
v% - coefficient of variation

**In bold are values higher than the World average*

[1] Gaillardet et al., 2014;
[2] Savenko, Savenko, 2024
[3] Pokrovsky et al., 2016

According to the seasonal variability in the waters of the Pur River (Table 2), a group of elements with a maximum in the high-water period is distinguished: Al, Fe, Mn, Ni, Co, Cu, Zn, Pb, and Cd. The variability is especially distinct for Al, Fe and Mn, whose contents are tens of times more in the high-water than in the low-water period. The increase in the contents of Al and Fe is associated with their lateral input in the form of organo-mineral colloids from the seasonally thawed soil layer of watersheds (Krickov et al., 2019). In addition, Fe and Mn are mobile in a reducing environment and in the lowest oxidation degree of 2+ may come from water-saturated mineral gley soil horizons. Mn, Ni, Co, Cu, and Zn come to the river water from organic soil horizons mainly in spring in the form of organo-mineral complex compounds (Pokrovsky et al., 2016). For these metals, as well as for Pb and Cd, technogenic supply with atmospheric deposition may be of great importance. The other group is formed by elements, whose contents slightly differ in high and low-water periods, or the maximum occurs in low-water periods. It includes anionic elements such as As, Sb, U, V, and Sr. They are brought into rivers mainly by groundwater in ionic form.

In the waters of the Evoyakha River during floods, the average contents of Al, Fe and Mn are 2-3 times lower than in the Pur River. This is probably explained by more severe climatic conditions of its basin, located in the forest tundra zone. Soil thawing depth in the north of Western Siberia is one of the main factors of dissolved organic matter and associated metals entering river waters (Pokrovsky et al., 2015). It determines a higher Fe content in the Evoyakha River during low-water periods than in the Pur River. According to (Opekunova et al., 2020), in peat-gley soils of northern taiga landscapes occupying the southern part of the Pur River basin, the thickness of the seasonally thawed layer can reach 2 m. This promotes iron deposition on the complex geochemical barrier in the upper soil horizons and a decrease in its input into rivers with the surface runoff. In forest-tundra and tundra landscapes in the northern part of the basin, the thickness of the seasonally thawed layer is less (0.2-0.9 m), which prevents the formation of geochemical barriers and promotes active migration of Fe and other metals. The average contents of Ni, Co, Cu, Zn, Pb, Cd in the Evoyakha River in the high-water period slightly, and in the low-water period significantly higher than in the Pur River, which is obviously associated with the anthropogenic impact of N. Urengoy. The median values of Fe, Mn, Co, Cu, Zn, Pb, Cd contents in the waters of the Pur and Evoyakha rivers are distinctly lower than the mean values. For Fe and Mn this is due to seasonal factor, for other metals - to the anthropogenic one, manifested in local maxima of contents in some river sections.

In the Pur River waters (Fig. 6), relatively high metal contents were also observed in areas subject to anthropogenic impact. In the low-water period of 2023, in the upper reaches of the river (Pyakupur River) downstream of Muravlenko, Zn content increased to 21, Cu - 4.5, Ni - 3.6, Pb - 1.2 µg/l, which is many times higher than the background levels for this hydrological period. Increased Cu and Zn contents during low water periods were also observed in the waters of the Pur River near Korotchaevo and downstream near Urengoy settlement and Samburg village.

In the basin of the Evoyakha River (Fig. 7) a section polluted with heavy metals was identified in the area of the industrial zone in the eastern part of N.Urengoy, where the content of Cu increases up to 4-8, Zn - 16-19, Pb - 0.4-0.6 µg/l. Maximum concentrations exceed the background values by 5-7 times. The metal contents are similar during both low and high-water periods, which indicates the permanent pollution of river water, probably caused by urban or industrial sewage. In the same area, we found an increase of Ba content up to 10-15 µg/l, and in some samples more than 50 µg/l, which is an order of magnitude higher than background levels. Apparently, drilling operations were previously carried out in the adjacent area. Elevated Ba concentrations in natural waters of oil and gas production areas are usually associated with drilling wells, where barite is used as a weighting agent for drilling fluids.

Table 2. Seasonal differences in the content of dissolved forms of metals and metalloids in the Pur and Evoyakha rivers in 2021-2023, µg/l

River	Pur		Evoyakha	
Season (n)	High water (18)	Low water (25)	High water (44)	Low water (41)
Al	58	1,9	32	11
Fe	268	20	90	138
Mn	54,6	0,6	15,0	4,2
Ni	0,81	0,45	1,10	1,45
Co	0,19	<0,09	0,75	0,64
V	0,17	0,13	0,16	0,18
Cu	0,82	0,45	1,04	0,94
Zn	3,05	0,85	3,50	3,90
Pb	0,11	<0,02	0,23	0,08
Cd	0,011	<0,006	0,023	0,030
As	0,34	0,29	0,28	0,32
Sb	0,085	0,074	0,072	0,080
U	0,007	0,003	0,007	0,005
Sr	11,0	30,0	5,4	18,2
Ba	6,8	6,2	4,7	6,0
Rb	0,59	0,58	0,76	0,81

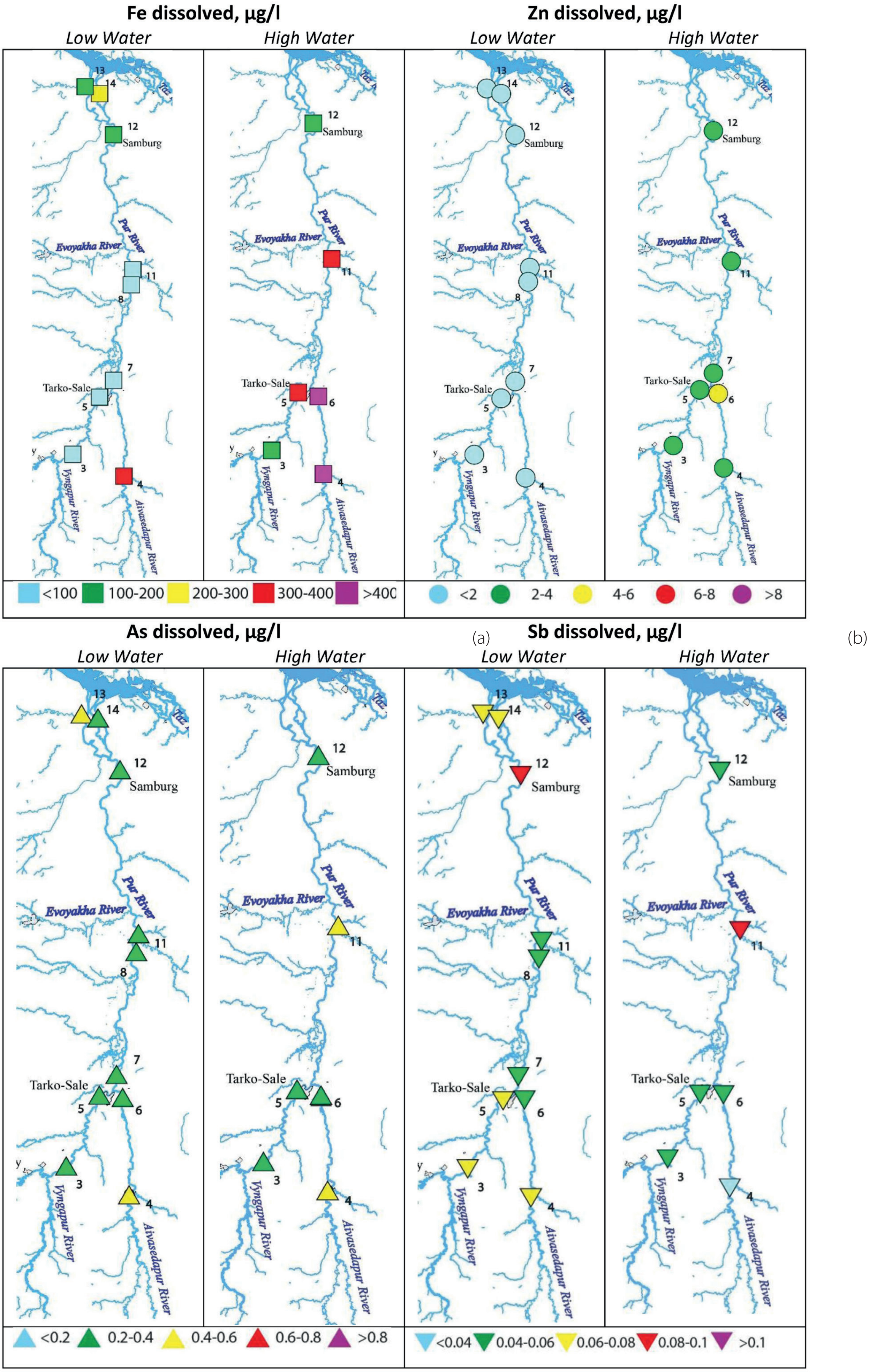


Fig. 6. Dissolved metals and metalloids in the Pur River water

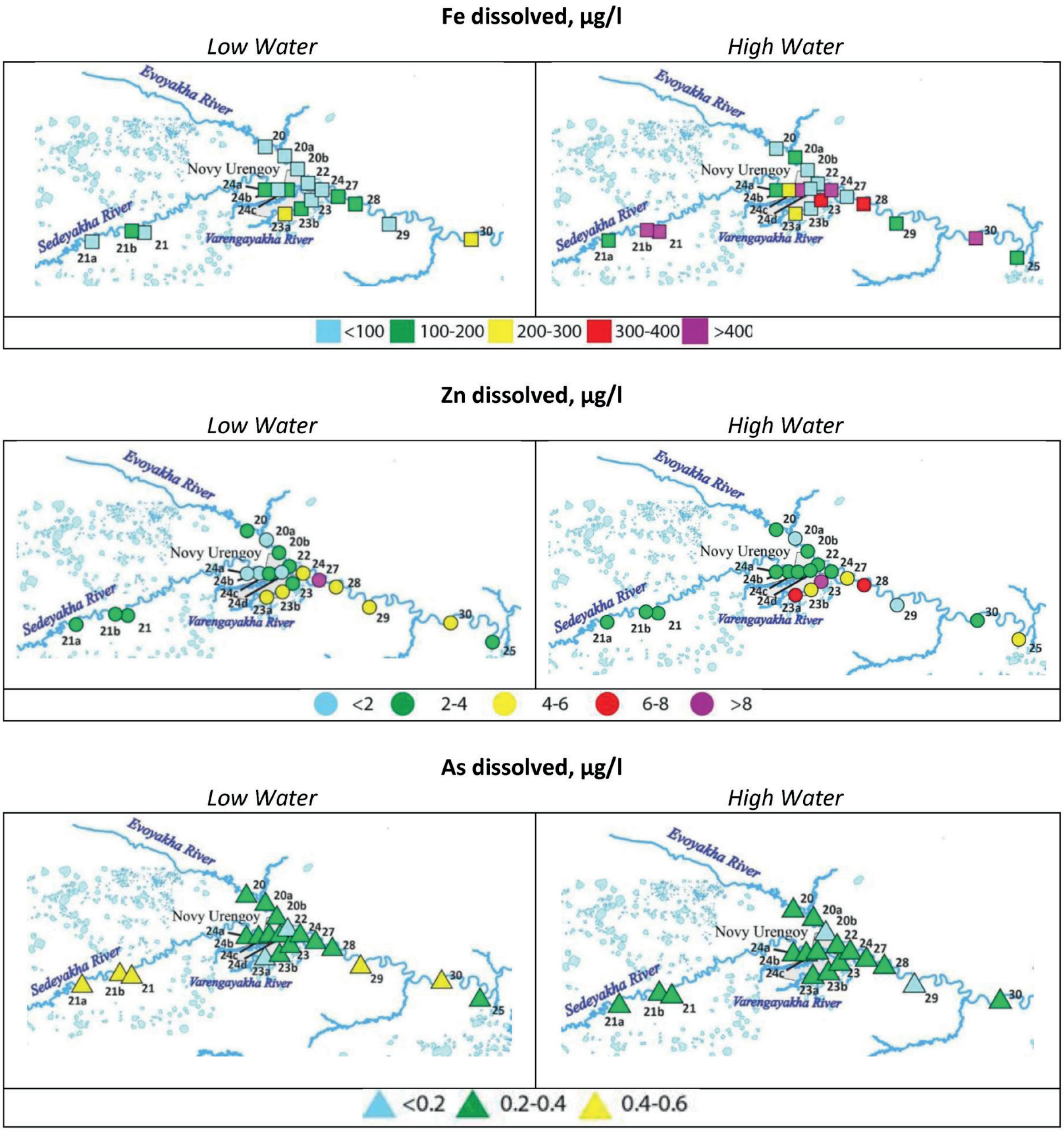


Fig. 7. Dissolved metals and metalloids in the Evoyakha River water

Thus, the river waters in the Pur River basin are characterized by generally low contents of metals and metalloids, not exceeding the world average values, except for Fe and Zn. A high variability of Al, Fe, Mn, Co, Cu, Zn, Pb and Cd contents was observed, caused by seasonal factor and anthropogenic impact. For some metals mean content significantly differs from the median values. It is caused by significant increase in their concentrations at a few river sections. Therefore, it is reasonable to use median values to characterize the regional hydrogeochemical background of the study area.

Suspended forms of metals and metalloids

Median levels of metals and metalloids in the suspended matter of the Pur River (Table 3) are in most cases lower than the global averages (Viers et al., 2009). First of all, this is characteristic of Al, whose content is 3.3 times less than the world average during flood and 6.7 times less than in low-water season. The low content of Al is due to grain-size and mineralogical composition of the suspended matter with the predominance of quartz-rich sandy particles larger than 50 microns, and also active migration of Al in colloidal organo-mineral compounds (see above). The greatest dispersion is characteristic of Cu: in low water it is 75 times less than the world average, in high water - 25 times less. The contents of Ni, Co, V, Cr, Cr, Zn, Cd, Pb, Sn, U, Bi, Rb, Ba, Sr are 2-5 times lower than the world averages. Only Fe and Mn levels exceed the world averages: 1.5 times in the high water and 2 - 4 times in the low water. Enrichment of the Western Siberian rivers with these metals in dissolved and suspended forms was determined earlier by (Agbalyan et al., 2016; Babushkin et al., 2007). Their source is anoxic ground and swamp waters where Mn and Fe have increased mobility. Entering river waters with oxic conditions, they can be precipitated hydroxides and adsorbed on solid suspended particles. The Sb content is slightly higher than the global average. It is anionogenic element that can be deposited together with Fe by adsorption and coprecipitation.

According to seasonal dynamics two groups of elements can be distinguished in suspended matter of the Pur and Evoyakha rivers (Table 4). The first group - iron group elements (Fe, Mn, Ni, Co), as well as As, Sb, Cd, Sr and Ba - is characterized by an increase in concentrations during low-water, the second group - Al, V, Pb, Sn, Bi, U and Rb - during high-water seasons (Fig. 8). The increase of Fe and Mn concentrations in summer period is obviously

Table 3. Levels of metals and metalloids in the Pur and Evoyakha suspended matter compared to global and regional background, µg/g

MMs	Pur River, n=45					Evoyakha River, n=80					World Rivers[1]	UCC[2] (Clarke)
	median	mean	min	max	v%	median	mean	min	max	v%		
Al	16100	19400	8300	43650	49	25300	30800	2665	65962	55	87200	80500
Fe	**105100**	**106400**	52275	**192720**	34	**117700**	**138200**	10462	**287074**	61	58100	46500
Mn	**5988**	**5466**	872	**10000**	51	**3043**	**4660**	206	**32336**	108	1679	1000
Ni	23	25	10	46	36	69	**85**	24	**434**	76	74,5	47
Co	14	13	7	22	27	**36**	**51**	5	**353**	109	22,5	17
V	40	41	17	78	37	104	105	23	**164**	23	129	97
Cr	53	51	25	73	24	108	136	66	**379**	84	130	92
Cu	1,1	4,4	0,4	30,6	162	17	31	0,7	**182**	138	75,9	28
Zn	95	107	19	**393**	61	171	192	59	**582**	62	208	67
Pb	11,2	13,8	5,5	**78,9**	84	14,8	15,4	5	42	31	61	17
Cd	0,38	0,40	0,10	1,04	50	0,49	0,58	0,1	**3,24**	82	1,55	0,09
As	19	19	7	36	41	21	25	6	61	61	36	5
Sb	**2,87**	**2,92**	0,80	**6,02**	40	**2,98**	3,7	0,48	**16,1**	113	2,2	0,4
Sn	1	1,6	0,14	**16,0**	170	2,12	3,41	0,40	**6,48**	273	4,6	2,1
Bi	0,17	0,18	0,09	0,40	44	0,23	0,38	0,09	**2,10**	106	0,85	0,16
U	0,6	0,67	0,30	1,3	37	1,08	1,08	0,25	1,98	31	3,3	2,7
Sr	115	119	84	**225**	23	91	92	24	175	26	187	320
Ba	403	433	281	**1153**	33	319	356	49	**3030**	90	522	624
Rb	20	24	10	50	44	28	34	5	72	57	78,5	84

n*- number of samples
[1] Viers et al., 2009;
[2] Rudnick, Gao, 2003 - Upper Continental Crust
* In bold are values higher than the World average

caused by deposition of their mobile compounds, added with groundwater to river waters with oxidizing conditions. Accumulation of other metals and metalloids during low water may be related to the processes of sorption and coprecipitation with Fe and Mn hydroxides. Al and other metals of the second group enrich suspended solids in rivers during floods due to increased erosion processes.

Iron accumulation in the suspended matter of the Evoyakha River during low-water season is even stronger – up to 21.6% (Cf 3.5). Cf values for Mn, Co and Sb exceed 1.5, for As, Ni, Cr, and Zn they are close to 1.0. Mean contents of metals in suspended matter of the Evoyakha River in summer are close to the global averages, but they are higher than in the Pur River. This is probably due to the significant spread of permafrost in the Evoyakha River catchment, which prevent leaching of elements. During thawing of permafrost, soil solutions interact with mineral soil horizons, thus ensuring active leaching and removal of metals and metalloids. Their highest levels occur in the late summer low-water period, when the maximum thawing of the active layer is reached, and as a consequence, the flow of acidic soil solutions enriched with colloids into the river network increases (Krickov, 2017). Additional confirmation of this hypothesis is the increase in water turbidity in the Evoyakha River during the summer low-water period compared to the spring flood.

Anthropogenic impact can have even more significant effects on the metal contents. Near cities, the maximum concentrations of Zn, Cd, Cu and other metals in suspended matter are 3-5 and more times higher than median (baseline) values. For example, during both seasons baseline content of Zn in the Pur River is about 100 µg/g, however below Tarko-Sale town and Samburg settlement it increases to 200-300 µg/g (Fig. 9). Zn content in the suspended matter of the Evoyakha River and its tributaries upstream of Novy Urengoy is 60-70 µg/g in high water, 90-100 µg/g in low water, and increases to 200-300 and 500-600 µg/g, respectively, downstream of the city (Fig. 10).

A number of indices is used to assess the magnitude of human-induced change in the aquatic environments. G. Birch (2023) examined 11 indices and found the Enrichment Factor (EF) to be most capable to produce high quality enrichment determinations.

EF is calculated as the ratio of the metal content in the studied sample to a certain element (reference) in the same sample, to the same ratio in the Earth's crust:

$$EF = (Ci/Cref)_{Sample} / (Ci/Cref)\, UCC$$

where *Ci* and *Cref* are the contents of the studied and reference elements, respectively, *UCC* – upper continental crust (Rudnick and Gao, 2014).

Table 4. Seasonal differences in metal and metalloid contents in the Pur and Evoyakha suspended matter (2021 – 2023)

River	Pur		Evoyakha	
Season (n)	HW (19)	LW (26)	HW (37)	LW (43)
Al	26110	13000	42460	18640
Fe	91220	111000	58140	216300
Mn	2371	7165	1614	3175
Ni	22	26	39	98
Co	11	15	32	44
V	51	32	105	103
Cr	54	50	83	149
Cu	3,1	1,1	15,4	27,5
Zn	98	93	99	216
Pb	15	9	15	15
Cd	0,3	0,4	0,2	0,8
As	16	20	13	36
Sb	2,6	3,0	2,1	4,0
Sn	1,3	0,9	2,0	2,2
Bi	0,20	0,12	0,23	0,22
U	0,74	0,53	1,21	0,96
Sr	106	121	93	90
Ba	378	425	348	286
Rb	31	18	50	20

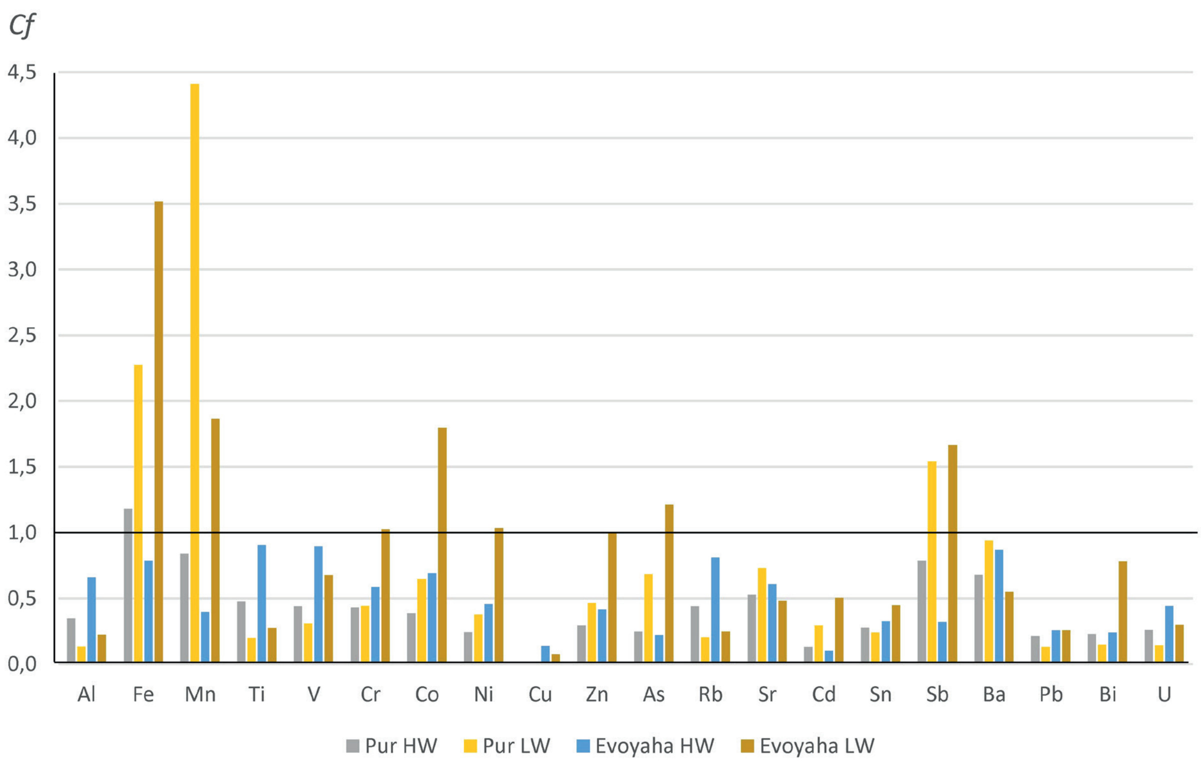


Fig. 8. Concentration factors relative to the world average (according to Viers et al., 2009) in suspended matter of the Pur and Evoyakha rivers during high water (HW) and low water (LW) seasons

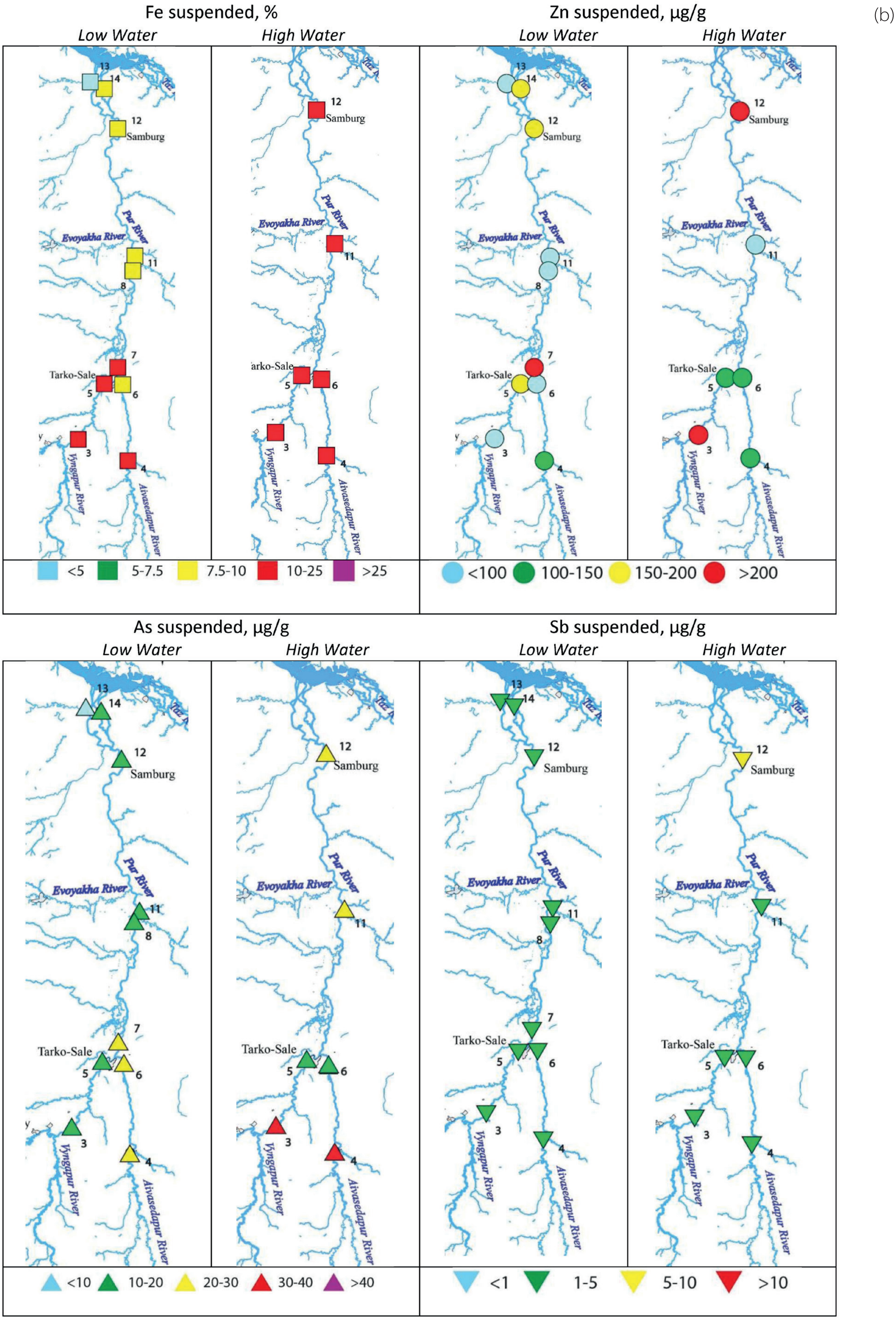


Fig. 9. Metals and metalloids in suspended matter of the Pur River

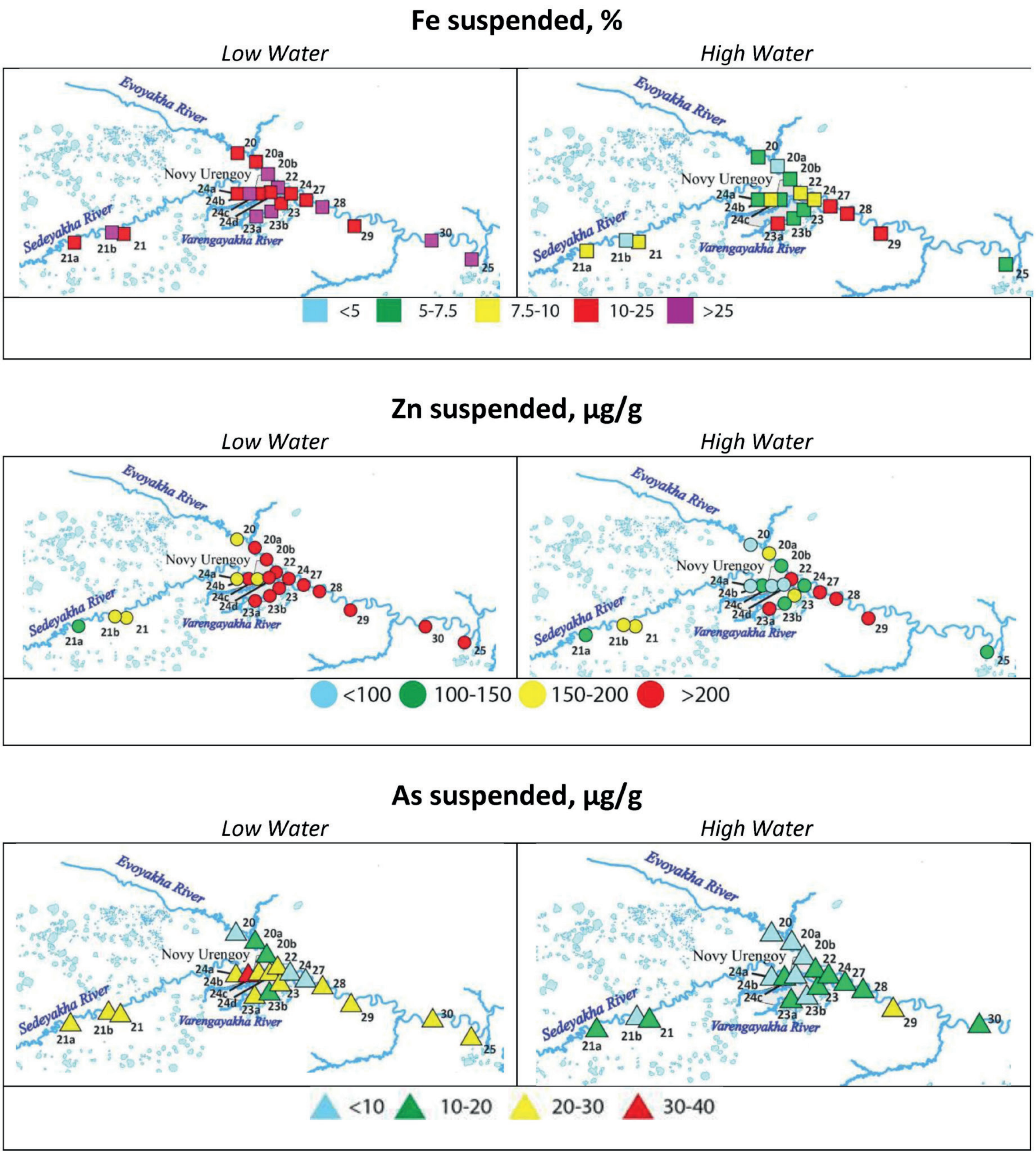


Fig. 10. Metals and metalloids in suspended matter of the Evoyakha River

Al, Fe, Mn, Sc, and La are commonly used as reference elements (Azoulay et al., 2001; Schiff and Weisberg, 1999). In the Pur River basin Al, Fe and Mn show high variability of content and diversity of migration forms, therefore, the EF values obtained on their basis are questionable. That is why we used Sc as a reference element.

For sediments the following categories of enrichment are most commonly used: 1-3 – low, 3-5 - moderate, 5-10 – considerable, 10-25 – high, 25-50 - very high, > 50 - extremely high (Birch, 2020).

Analysis of EF values for median contents of MMs allowed to identify the association of elements with considerable and high enrichment of suspended matter: Fe, Mn, Sb, As, Cd and Zn. In low water it is characteristic of both rivers, in high water it is characteristic only of the Pur River (Fig. 11).

The enrichment of suspended particles by Fe and Mn can be explained by the natural process of precipitation of their hydroxides in the oxidizing environment of river waters. However, enrichment by Sb, As, Cd and Zn is most likely of anthropogenic origin. This association of elements is typical for urban soils and road dust and is mainly due to the impact of motor vehicles. Particulate matter enriched with these elements enters rivers with urban stormwater and snowmelt runoff and contributes significantly to the deterioration of surface waters quality (Müller et al., 2020). EF elements of this association strongly increase in suspended particles of the Pur and Evoyakha rivers below the settlements (Tarko-Sale, Urengoy, Novy Urengoy). The maximum values range from 25 to 45, which corresponds to very high degree of enrichment.

Forms of migration of metals and metalloids

The ratio of element migration forms in water flows is determined by the DS coefficient, which characterizes the distribution of chemical elements between suspended (S) and dissolved (D) forms. Until relatively recently, it was considered in geochemistry that suspended forms of element migration prevail distinctly in river runoff (Gordeev et al., 2024; V. Savenko, 2006). The results of our studies in the Selenga, Volga, Don and other rivers showed that for a number of elements the role of dissolved forms was underestimated. On the basis of D,S-analysis (Kasimov et al., 2020a; Kasimov et al., 2020b; Kuryakova, 2011; Lychagin et al., 2017, etc), we identified three groups of chemical elements: D-elements with the predominance

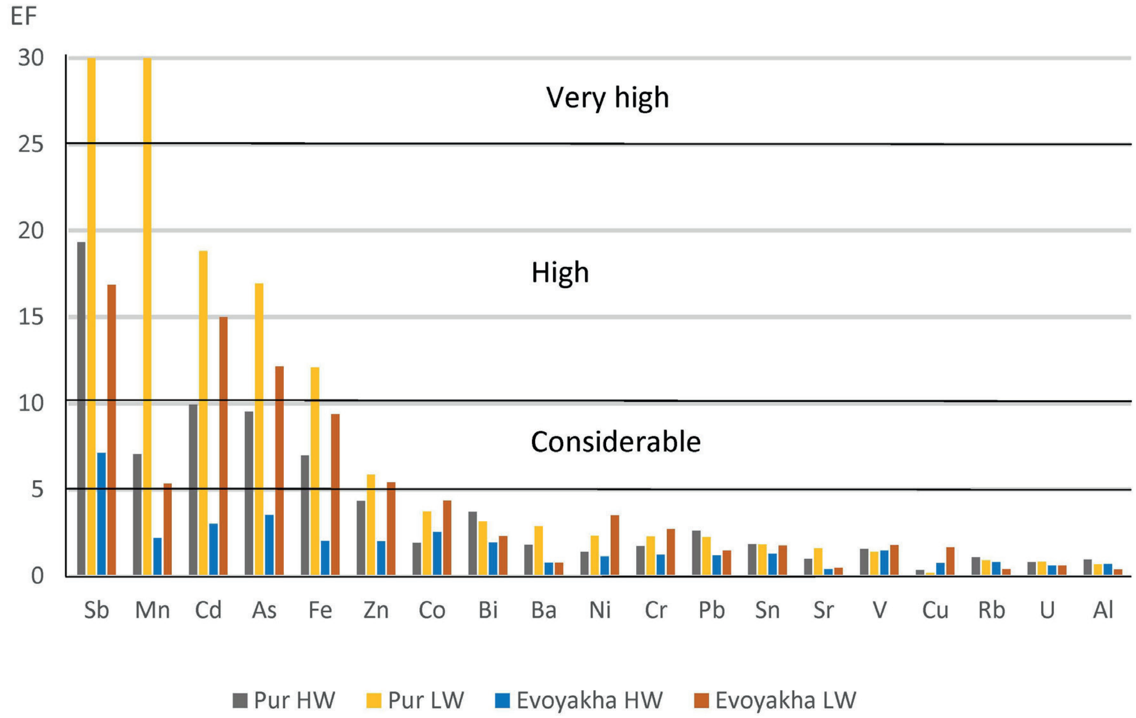


Fig. 11. EF for median values of chemical elements referenced to Sc in suspended matter of the Pur and Evoyakha rivers for high water (HW) and low water (LW) seasons

of dissolved form of migration, S-elements, the main form of migration of which is suspended, and a transitional group of D,S-elements, for which the ratio of suspended and dissolved forms varies widely. The position of chemical elements within a particular group is determined by internal migration factors (properties of the elements themselves), while their behavior within groups (change in DS value) is determined by external factors, mainly hydroclimatic and anthropogenic.

In the Pur and Evoyakha rivers the D-element group includes Ca, Sr, Cu, Mo, Rb (Fig. 12). Ca, as well as Mg, Na and K are among the main cations of natural waters, for which the dissolved form is almost always predominant. Sr is a typical cationic element, many of its compounds are well soluble. In terms of water migration rate, it is close to Ca. Mo migrates in natural waters in the form of anions, it is also characterized by the predominance of dissolved forms of migration, which we have previously reported for other rivers. The appearance of Cu among the D-elements is a specific feature of the Pur River. This is due to the very low Cu content in its suspended matter, where the median value (1.1 μg/g) is 70 times lower than the global average (Table 3). In the Evoyakha River, the median Cu content is 17 μg/g, which is only 4 times lower than the global average, so Cu moves to the group of D,S-elements, which is more usual (Fig. 12b) .

The group of D,S-elements includes Sb, As, Ba, Ni, Cd, Zn, and U. Almost all of them are the priority pollutants of the environment. For these elements, seasonal differences in the proportion of migration forms are most pronounced in the Evoyakha river, where the share of suspended forms increases during floods. This is caused by a significant increase in turbidity during the flood period - up to 20-30, and in some places up to 50-70 mg/l, while during low season it is 8-10 mg/l. Spring flooding on the Evoyakha River is short and high, while on the Pur River it is lower and longer lasting. The turbidity of the Pur River water is 15-20 mg/l and almost does not change seasonally. Therefore, the anthropogenic factor is more important for the ratio of different migration forms in the Pur River. Below cities, the share of suspended forms tends to increase. This is especially noticeable for Urengoy, where at the site downstream of the river port the share of suspended forms of not only DS but also D-elements, Mo and Rb, increases.

The group of S-elements includes lithophilic elements firmly bound to mineral particles – Al, Fe, Mn, Ti, Bi, Co, V, Pb. For them the share of suspended forms may change quantitatively, but always remains predominant.

Source identification of suspended forms of MMs

The PCA/APCS-MLR method was applied for two data sets, the first one included the data on MMs contents in 63 samples collected during 2021-2023 in the Evoyaha River, and the second one comprised the chemical data on 40 samples collected during the same period in the Pur River. In the first step of the analysis, the data were normalized and then principal component analysis was applied.

The Evoyaha River

For the dataset from the Evoyaha River, four factors (F1-F4) were identified. They explained 78% of the total variance (Supplementary 3). The first factor (F1) had the largest contribution (40%) to the total variance. According to APCS-MLR results, this factor explained more than 50% of the mass input of Fe, As, Cr, Ni, Zn, Cd, Sb (Fig. 13), and probably related to the sorption of elements by iron hydroxides. The EF values ranging from 5 to 10, as well as the coefficient of variation (60-70%) suggest a mixed origin of these elements - natural and anthropogenic. The human-induced contribution of As, Cr, Zn and Ni is probably related to oil and gas production ((Xu et al., 2018; Saravanan et al., 2022).

The second factor (F2) explained 23% of the total variance. Large proportions of Sr, V and Pb (more than 80%) and U, Ba, Rb, Al, Ti and Cu (60-80%) inputs were associated with this factor. The contents of these elements varied little along the river course and did not depend on the season (Cv 20-50%), the EF values were also low. So, the F2 factor was interpreted as a lithogenic factor. The third (F3) and the fourth (F4) factors accounted for 8 and 7% of the total variance, respectively. The F3 contributed to 50% of Mn and 45% of Co. Mn is considered to be one of the main markers of oil pollution (Saravanan et al., 2022). The F4 explains the partial input of Bi, Sn, Cu, Pb and Co. These metals are markers of emissions from vehicles

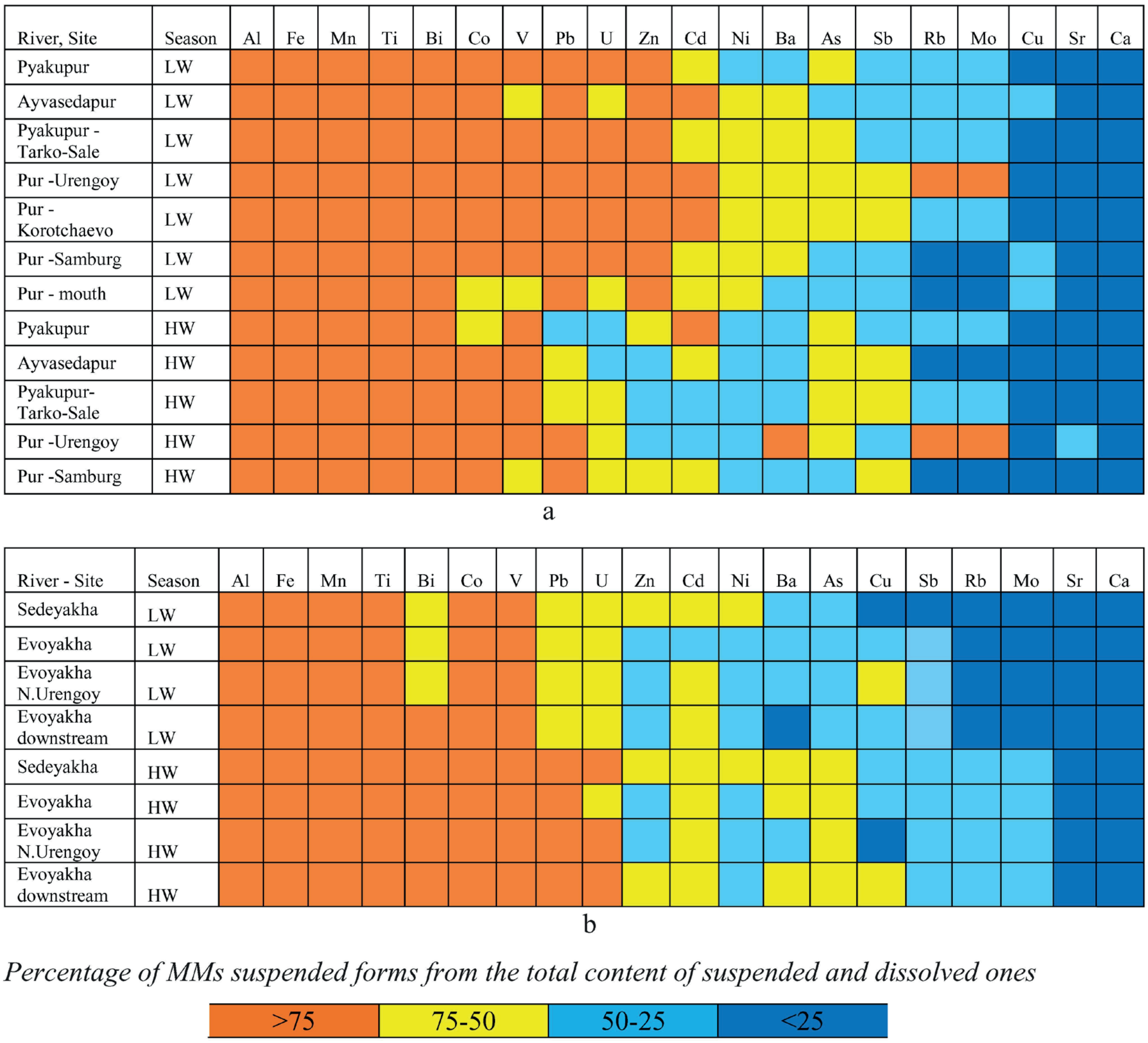


Fig. 12. Matrix of MMs migration forms in Pur (a) and Evoyakha (b) Rivers

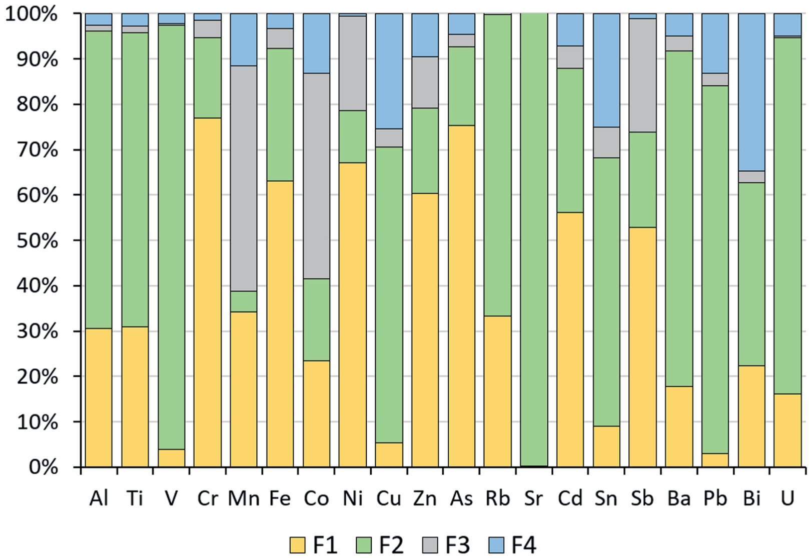


Fig. 13. Relative contribution of sources for suspended matter of the Evoyakha River, according to APCS-MLR model calculations: F1 – iron deposition, F2 – lithogenic, F3 – oil and gas production, F4 – vehicles emission

(Thorpe, Harrison, 2008). The coefficient of variation for some metals was close to or greater than 100%, and the maximum contributions of factors F3 and F4 were observed within the city and downstream. This confirms the input of MMs with F3 and F4 as anthropogenic. Thus, 4 main factors of MMs input into suspended particles were identified for the Evoyakha River. The greatest contribution is made by a mixed natural-anthropogenic factor associated with iron. The second source of MMs input is lithogenic. The third and fourth factors are caused by anthropogenic input and are defined as the influence of oil and gas production and vehicle emissions, respectively.

The Pur River

Four factors (F1-F4) were also identified for the Pur River dataset. They explained 74% of the total variance in MMs content (Supplementary 3). The first factor F1 accounted for 36% of the total variance. It was responsible for the input to

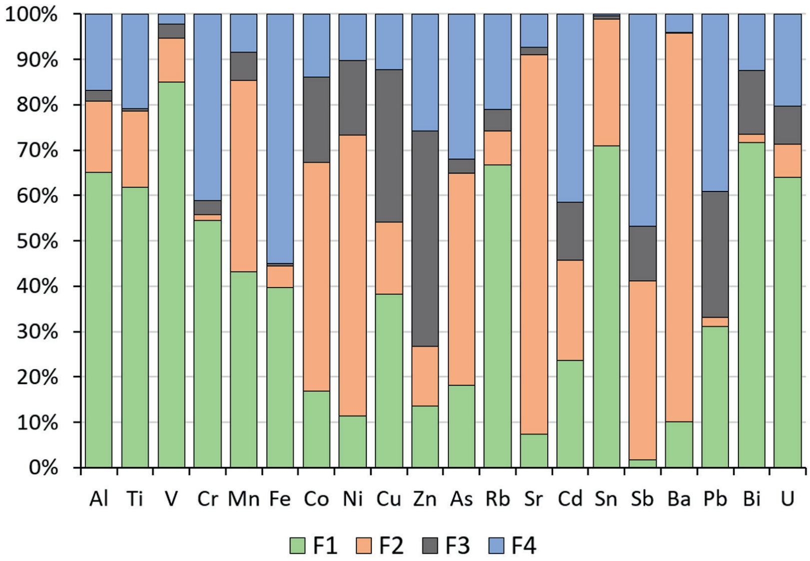


Fig. 14. Relative contribution of sources for suspended matter of the Pur River, according to APCS-MLR model calculations: F1 – lithogenic, F2 – oil and gas production, F3 and F4 – vehicles emission (F3 – wear of tires, F4 – wear of brake pads)

the suspended particles of 85% of the total mass of V, more than 60% of Rb, Al, U, and Ti. The similar association of elements was noted for the lithogenic factor in Evoyakha, suggesting a regional bedrock influence. The coefficient of variation of the MMs did not exceed 50%, in addition, these elements had the lowest EF values, hence factor F1 can be interpreted as a lithogenic factor.

The factor F2 accounted for 22% of the total variance. It contributed more than 80% of Ba and Sr, and most of the mass of Ni, Co, As, Mn and Sb. This factor is most likely related to the sorption of the elements by Mn (hydr)oxides (Zheng et al., 2020). For all the elements associated with the F2 factor, a high correlation was displayed particularly by Mn (0.6-0.8). This association of MMs is similar to the F3 group for the Evoyakha River, which we linked to oil and gas production. The significant contribution of Ba and Sr may be due to their use in drilling fluids. Each of the two factors F3 and F4 contributed 8% to the total variance. Factor F3 was responsible for the input of Zn, Cu and small portions of Pb (Fig. 14). Zn is one of the markers of car tires abrasion, with Cu and Pb often found with it (Thorpe, Harrison, 2008; Alves et al., 2020). The factor F4 accounted for half of the Fe, Sb, Sn and Pb input. This association of elements may be due to the wearing of the vehicles brake pads (Pant, Harrison, 2013). High EF values for the elements associated with factors F3 and F4 (EF>5), indicate the anthropogenic nature of these factors. In addition, the maximum contribution of both factors was observed at sites within cities. Hence, it can be assumed that these metals enter the urban environment through motor vehicles and are transported to rivers by storm water drainage systems.

Thus, 4 factors of MMs input were determined for suspended particles of the Pur River waters. The first factor explains the lithogenic input, the second one is related to oil and gas production. The third and fourth factors are defined as the vehicle influence, at that, the third factor is related to input from wear of tires, the fourth factor - with wear of brake pads.

CONCLUSIONS

1. Waters of the Pur River and its tributaries are characterized by generally low content of dissolved metals and metalloids, not exceeding the world average values, except for Fe and Zn. A high variability of Al, Fe, Mn, Co, Cu, Zn, Pb and Cd contents was observed, caused by seasonal factor and anthropogenic impact. The median contents of metals can be used as the baseline values.

2. Median levels of metals and metalloids in the suspended matter of the Pur River are lower than the global averages, except for Fe and Mn. According to the seasonal dynamics two groups of elements can be distinguished: the first group - Fe, Mn, Ni, Co, As, Sb, Cd, Sr and Ba - is characterized by an increase in concentrations during low-water, the second group - Al, V, Pb, Sn, Bi, U and Rb - during high-water seasons. Near cities, the maximum concentrations of Zn, Cd, Cu and other metals in suspended matter are 3-5 and more times higher than the baseline values. Analysis of EF values for median contents of MMs allowed us to identify the association of elements with considerable and high enrichment of suspended matter: Fe, Mn, Sb, As, Cd and Zn.

3. On the basis of D,S-analysis, we identified three groups of chemical elements in the Pur River basin: D-elements – Ca, Sr, Cu, Mo, Rb; D,S-elements – Sb, As, Ba, Ni, Cd, Zn, and U; S-elements – Al, Fe, Mn, Ti, Bi, Co, V, Pb. The position of chemical elements within a particular group is determined by properties of the elements themselves, while their behavior within groups is determined by external factors, mainly hydroclimatic and anthropogenic.

4. On the basis of PCA/APCS-MLR method, we determined 4 main factors with different contributions to the total content of metals and metalloids in river sediment: lithogenic, iron oxidation, urban wastewaters, and motor vehicle emissions.

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SUPPLEMENTARY 1

Table 1. Sampling points in 2021-2023 (numbering corresponds to Fig. 1)

N	River	Description	2021	2022		2023	
			Aug	Jun	Aug	Jun	Aug
1	Pyakupur	upper reaches (30 km south of Muravlenko, 50 km north-west of Noyabrsk)			+	+	+
2	Pyakupur	at the latitude of Muravlenko and Khanymey					+
3	Pyakupur	at the latitude of Purpe and Kharampur		+	+	+	+
4	Ayvasedapur	at the latitude of Purpe and Kharampur		+	+	+	+
5	Pyakupur	near Tarko-Sale (above the confluence with the Ayvasedapur)		+	+	+	+
6	Ayvasedapur	near Tarko-Sale (above the confluence with the Pyakupur)		+	+	+	+
7	Pur	near Tarko-Sale (below the confluence of the Pyakupur and the Ayvasedapur)			+		+
8	Pur	above Korotchaevo (left branch)			+		+
9	Pur	above Korotchaevo (right branch)			+		+
10	Pur	between Korotchaevo and Urengoy			+		+
11	Pur	below Urengoy		+	+	+	+
12	Pur	below Samburg		+	+	+	+
13	Pur	15 km from the mouth, left branch			+	+	
14	Pur	15 km from the mouth, right branch			+	+	
15	Khanto (lake)	northern boundary of Noyabrsk			+		+
16	Khanayakha	0.2 km from the source			+		+
17	Khanayakha	0.6 km from the source			+		+
18	Khanayakha	1.1 km from the source			+		+
19	Nankpyokh	mouth			+		+
20	Evoyakha	above Novy Urengoy	+	+		+	+
21	Sedeyakha	above Novy Urengoy	+	+		+	+
22	Evoyakha	confluence with the Sedeyakha	+	+		+	+
23	Sedeyakha	confluence with the Yevoyakha	+	+		+	+
24	Evoyakha	below the confluence with the Sedeyakha	+	+		+	+
25	Evoyakha	below Novy Urengoy	+	+		+	+
26	Sedeyakha	upper reaches	+	+		+	+
27	Evoyakha	Novy Urengoy, eastern industrial zone	+	+		+	+
28	Evoyakha	eastern border of Novy Urengoy town	+	+			+
29	Evoyakha	7 km below Novy Urengoy	+	+			+
30	Evoyakha	21 km below Novy Urengoy	+	+			+
31	Evoyakha	10 km from the mouth	+	+		+	+

SUPPLEMENTARY 2

Table 1. Hydrochemical characteristics and content of major ions in water bodies of the Pur River basin during the 2023 flood

Station	Date	River	HCO_{3^-}	SO_4^{2-}	Cl^-	Ca2+	Mg^{2+}	Na^+	K^+	M,mg/l
			mg/l							
1	04.06.2023	Pyakupur	7,57	0,25	0,60	1,17	0,68	0,98	0,30	12
3	05.06.2023	Pyakupur	6,96	0,97	1,32	0,87	0,56	1,52	0,45	13
4	05.06.2023	Ayvasedapur	7,94	0,42	0,20	1,06	0,50	0,64	0,23	11
5	04.06.2023	Pyakupur	6,58	0,57	1,20	0,74	0,48	1,47	0,44	11
6	05.06.2023	Ayvasedapur	8,73	0,31	0,34	1,20	0,73	0,52	0,40	12
11a	03.06.2023	Pur	4,76	0,49	0,58	0,58	0,36	0,51	0,20	7
11a	10.06.2023	Pur	5,98	0,37	0,33	0,85	0,58	0,81	0,27	9
11b	03.06.2023	Pur	7,38	0,42	0,40	0,78	0,55	0,79	0,35	11
11b	10.06.2023	Pur	7,81	0,54	1,03	1,04	0,64	0,99	0,25	12
12a	10.06.2023	Pur	6,35	0,50	0,64	0,70	0,49	0,84	0,32	10
13	10.06.2023	Pur	7,93	0,47	0,56	0,87	0,60	0,86	0,40	12
14	10.06.2023	Pur	6,71	0,50	0,73	0,70	0,48	0,87	0,37	10
21	02.06.2023	Sedeyakha	3,66	0,39	0,71	0,44	0,24	0,67	0,45	7
21	07.06.2023	Sedeyakha	3,60	0,90	0,38	0,61	0,34	0,81	0,35	7
22	01.06.2023	Evoyakha	5,98	1,00	0,19	0,75	0,35	0,61	0,38	9
22	08.06.2023	Evoyakha	5,49	1,78	0,31	1,00	0,54	0,62	0,23	10
23	01.06.2023	Sedeyakha	4,15	1,12	0,63	0,57	0,27	1,12	0,69	9
23	08.06.2023	Sedeyakha	2,87	1,20	0,29	0,65	0,39	0,77	0,33	6
24	01.06.2023	Evoyakha	3,30	0,82	0,38	0,49	0,23	0,80	0,38	6
24	08.06.2023	Evoyakha	2,75	1,67	0,61	0,79	0,37	0,91	0,43	8
25	02.06.2023	Evoyakha	2,14	1,07	0,49	0,54	0,32	0,78	0,57	6
25	08.06.2023	Evoyakha	2,93	1,58	0,74	0,71	0,41	1,02	0,56	8
26	31.05.2023	Sedeyakha	2,81	0,53	0,35	0,35	0,17	0,46	0,26	5
31	03.06.2023	Evoyakha	5,19	0,63	0,81	0,90	0,39	1,01	0,62	10
27a	06.06.2023	Evoyakha	2,99	1,57	0,50	0,54	0,25	0,58	0,40	7
27b	06.06.2023	Evoyakha	4,15	1,30	0,50	0,51	0,27	0,59	0,52	8
27c	06.06.2023	Evoyakha	2,93	1,49	0,75	0,51	0,30	0,81	0,40	7

Table 2. Hydrochemical characteristics and content of major ions in water bodies of the Pur River basin during the 2023 low-water season

Station	Date	River	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	M, mg/l
			mg/l							
1	21.08.2023	Pyakupur	37	0,60	2,63	7,79	2,78	2,32	0,38	53
2	20.08.2023	Pyakupur	35	0,84	4,34	7,41	3,23	4,62	1,20	57
3	21.08.2023	Pyakupur	29	0,97	1,32	6,08	2,66	2,73	0,45	44
4	22.08.2023	Ayvasedapur	42	0,56	1,19	10,18	3,63	1,77	0,32	60
5	22.08.2023	Pyakupur	34	0,58	3,01	5,66	2,54	2,70	0,59	49
6	22.08.2023	Ayvasedapur	33	0,44	1,16	6,21	2,76	1,74	0,25	45
7	22.08.2023	Pur	33	0,76	3,49	6,13	2,68	2,90	0,37	49
8	23.08.2023	Pur	17	0,86	1,65	2,50	1,21	0,89	0,18	24
9	23.08.2023	Pur	17	0,81	1,70	2,08	1,88	0,69	0,17	25
10	23.08.2023	Pur	16	0,86	0,63	3,07	1,54	1,11	0,23	23
11a	23.08.2023	Pur	31	1,58	2,03	5,94	2,79	1,90	0,50	46
11b	23.08.2023	Pur	51	1,23	4,13	7,62	3,36	6,07	2,31	75
12a	29.08.2023	Pur	35	1,48	3,10	6,19	2,80	2,12	0,36	51
12b	29.08.2023	Pur	31	1,17	2,98	6,63	3,16	2,22	0,36	47
20	18.08.2023	Evoyakha	15	5,85	0,28	2,89	1,64	0,85	0,35	27
21	18.08.2023	Sedeyakha	13	5,28	0,50	2,44	1,40	0,87	0,28	24
22	16.08.2023	Evoyakha	11	6,58	0,56	2,38	1,42	0,74	0,24	23
23	16.08.2023	Sedeyakha	13	4,53	0,91	2,39	1,41	0,79	0,24	23
24	16.08.2023	Evoyakha	13	7,26	0,78	2,88	1,72	1,11	0,29	27
25	19.08.2023	Evoyakha	13	4,48	1,70	3,51	1,93	1,23	0,41	27
26	25.08.2023	Sedeyakha	14	3,77	0,62	3,47	1,43	1,18	0,42	25
27	25.08.2023	Evoyakha	19	4,38	0,82	4,64	2,22	1,58	0,40	33
28	25.08.2023	Evoyakha	14	2,28	1,55	2,39	1,26	2,31	0,80	25
29	25.08.2023	Evoyakha	12	2,84	0,92	2,54	1,25	1,51	0,47	21
30	25.08.2023	Evoyakha	16	3,58	2,81	3,76	1,78	3,19	1,52	33
31a	25.08.2023	Evoyakha	16	4,51	2,80	2,75	1,53	1,60	0,60	30
31b	25.08.2023	Evoyakha	17	2,61	1,09	2,39	1,39	1,15	0,22	26
15	21.08.2023	Lake Hanto	53	1,17	1,33	8,22	3,52	1,63	0,29	69
18	21.08.2023	Khanayakha	49	7,60	0,88	8,80	3,69	1,27	0,34	71
19	21.08.2023	Nankpyokh	50	1,88	1,34	10,18	3,59	1,95	0,32	69

MAJOR ION CONTENT

Hydrochemical studies during flood and low-water seasons in 2023 made it possible to determine the content of the main ions (HCO^{3-}, SO_4^{2-}, Cl^- anions and Ca^{2+}, Mg^{2+}, Na^+, K^+ cations) in the waters of the Pur River and its tributaries, as well as to trace their seasonal dynamics. A total of 57 water samples were processed. Chemical analyses were made according to the methods set out in (Komarova, Kamentsev, 2006; RD 52.24.493, 2020).

During the study period the average mineralization of the Pur River water was 10.8 mg/l in spring, and increased to 49 mg/l during the summer low water period, that corresponds to literature studies for other large rivers in the Arctic region (Geoecological ..., 2007). The maximum values of mineralization (75 mg/l) at this time were observed in the area of the village of Urengoy. Average mineralization of the water of the tributary of the Pur River – Evoyakha River during flood is 7.4 mg/l and in summer low water period - 26 mg/l. Meltwater and rainwater share in water supply plays an important role in mineralization and major ions content formation.

According to Alekin's classification (1970), all samples of water of the studied area belonged to the bicarbonate class and mixed type. During the flooding in the Pur River the proportion of Mg^{2+} among the cations was slightly increased (by 1-2%-eq.). Samples from Evoyakha River also belonged to bicarbonate class. They have an increased share of sulfates (8-13%-eq.). An increased proportion of sodium was observed among the cations (12-21%-eq.). During the autumn period the share of SO_4^{2-} uprise to 9-22%-eq. Ca^{2+} prevailed among the cations, but the share of Mg^{2+} was also relatively high, which makes it impossible to distinguish the predominant type.

The major ions content changes along the rivers reflect the sources of water supply. The relative content of Na^+, Mg^{2+}, Cl^- was increased in the water of the Pyakupur River (stations 1, 3) during the flooding period. These elements come from atmospheric precipitation of marine origin and enter into rivers with meltwater. The share of $HCO3^-$ and Ca^{2+} was reduced in comparison to the low-water season, since there was a strong dilution of river water by meltwater from the catchment area. In the samples of the Ayvasedapur River (stations 4 and 6), the proportion of HCO^{3-} was higher by 6-8%-eq., which indicates a lower amount of meltwater in the water runoff. On Pyakupur River in the Tarko-Sale area, increased shares of Na^+ and Cl^- were found, which may indicate the presence of human-made pollution. Downstream, the ratio between the main ions changed slightly.

I n the Evoyakha River basin during the flooding, smaller proportions of HCO^{3-} were observed in comparison with the Pur River. The river is mainly fed by meltwater, as well as the waters of lakes and swamps, which are gradually thawing. The intake of swamp waters in the upper reaches contributes to an increase in the share of SO_4^{2-} as well as K^+. In the middle and lower reaches of the river. The third factor that increased the amount of Na^+, Cl^-, SO_4^{2-} in the ion composition of water is the anthropogenic influence of the city of Novy Urengoy, from where these chemical elements come from wastewater and from storm sewers. The influence of the city weakened in the lower reaches of the river (station 31) as a result of dilution by tributaries.

During the low water period, an increase in the content of HCO^{3-} and Ca^{2+} was observed in the Pur River as a result of the predominant supply of groundwater to water bodies, in particular, as a result of melting of permafrost. The share of Mg^{2+} changed slightly. The SO_4^{2-} and K+ ions content accounted for 1-3%-eq, which indicated a weak contribution of swamp waters to the total water runoff. The increase in Na^+ content observed in station 11b water is probably due to the influence of the river port of the settlement Urengoy.

In the Evoyakha River basin more heterogeneous macro-component composition was observed in the low water period. Compared with the flooding, the share of HCO^{3-} has changed slightly, but the amount of SO_4^{2-} has increased significantly, especially in the upper reaches of the Evoyakha and Sedeyakha Rivers (up to 23%-eq). This may occur due to the intensive flow of water from the swampy part of the river basin. Close to the sampling station 27 (below the treatment facilities and industrial sites of Novy Urengoy city), an increase in the share of Na^+ and Cl^- was observed, which can be attributed to human influence, which can be traced throughout the entire middle and lower reaches of the river.

SUPPLEMENTARY 3

Table 1. Source contributions of MMs (%) by the MLR-APCS model in suspended matter of the Evoyakha River

Factor	F1	F2	F3	F4	R^2
Al	31	**65**			0,97
Ti	31	**65**			0,97
V		**94**			0,74
Cr	77	18			0,72
Mn	34		**50**	11	0,88
Fe	**63**	29			0,93
Co	23	18	**45**	13	0,81
Ni	**67**	12	21		0,90
Cu		**65**		25	0,49
Zn	**60**	19	11	9	0,80
As	**75**	17			0,60
Rb	33	**67**			0,97
Sr		**97**			0,69
Cd	**56**	32		7	0,54
Sn	9	**59**	7	25	0,64
Sb	**53**	21	25		0,46
Ba	18	**74**			0,88
Pb		**81**		13	0,66
Bi	22	**40**		35	0,62
U	16	79			0,89
Eigenvalue	7,9	4,6	1,5	1,4	
% Total	39,7	22,9	7,7	7,1	