

## SURFACE AND UNDERGROUND WATERS OF CRYOLITHOZONE

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**SOURCES OF RIVER FLOW FORMATION IN THE ZONE OF PERMAFROST:  
ESTIMATION BY THE METHODS OF TRACER HYDROLOGY ACCORDING  
TO THE DATA OF REGIME HYDROCHEMICAL OBSERVATIONS****T.S. Gubareva<sup>1,2</sup>, B.I. Gartsman<sup>1</sup>, N.G. Vasilenko<sup>3</sup>**<sup>1</sup> *Water Problem Institute, RAS, 7, Gubkina str., Moscow, 119333, Russia; Tgubareva@bk.ru*<sup>2</sup> *Pacific Institute of Geography, FEB RAS, 7, Radio str., Vladivostok, 690041, Russia*<sup>3</sup> *State Hydrological Institute, 23, 2<sup>nd</sup> line V.O., St. Petersburg, 199053, Russia*

The possibility of modeling the interaction among various sources of the river flow in the Nelka River basin using data from archival hydrochemical and hydrological regime observations based on a mixing model, including the principal component analysis, has been confirmed. Adaptation and testing of the mixing model for three water sources characterized by high accuracy of the chemical composition of river waters has been performed for five small watersheds. The results of the modeling made it possible to estimate the number of the dominant sources of the river runoff and clarify their nature – rain, soil water, and aufeis, reflecting the specificity of river runoff formation in the permafrost zone and associated with the presence of frozen ground. The proportions of each of them are estimated, with their inter-seasonal dynamics analyzed. The application of statistical evaluation criteria and the meaningful interpretation of the results confirm the high quality of the modeling performed.

*Runoff processes, permafrost zone, water sources, mixing model, principal component analysis, chemical tracers*

**INTRODUCTION**

Studying the water sources and the regularities of forming the river flow continues to be a fundamental problem of land hydrology, the content of which is essentially updated at each stage of its development. Complexity of such studies is caused by localization of the runoff processes in the underground part of the watershed, where direct observations are practically impossible. As the clue to understanding the hydrological processes lies under the ground [Sokolov, 1996], the tracer methods are a promising tool to be used in such investigations.

By now, significant progress has been reached in evaluating the water sources of rivers [Kirkby, 1978; Dunne, 1983; Anderson and Bert, 1988; Edelshtein and Smakhtina, 1991]. For the most part, this has been due to the use of the methods of genetic disintegration of the runoff hydrograph based on a mixing model, with the use of chemical tracers, which have been actively being developed since 1960s. After the pioneering study by P.P. Voronkov [1963], chemical tracers began to be successfully used for evaluating the contributions of different water sources to the river runoff [Pinder and Jones, 1969; Pisarsky and Khaustov, 1973; Christophersen et al., 1990; Hooper et al., 1990].

The methodological apparatus of trace hydrology has been realized as different variants of mixing models, based on solution of a system of equations for the balance of water and tracers. This area of studies

has been essentially developed over the recent twenty years, including the multivariate analysis methods, which resulted in transition from the simplest models of mixing two sources to the models of mixing three sources as the main working tool [Christophersen and Hooper, 1992; Bonell and Fritsch, 1997; Hooper, 2003].

Summarizing the results of the field studies using mixing models, conducted mostly in the humid temperate and tropical belts, demonstrated greater complexity of river runoff formation [Sokolov, 1996; Bonell and Fritsch, 1997]. For the permafrost zone, the level of understanding the runoff formation processes remains to be insufficient, and the coverage of studies is much less [Tetzlaff et al., 2015]. It is pointed out in the study indicated that there are no publications on tracer investigations conducted in Russia.

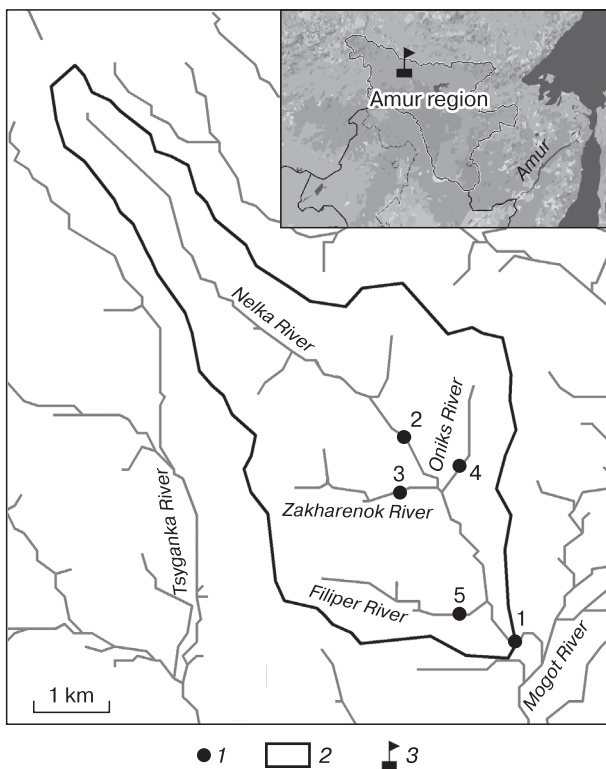
Currently the evaluations and interpretations of the results of trace studies vary considerably, and the review works state two key tasks for their development. The first key task consists in implementing targeted full-scale measurements at the modern level of science [Gartsman and Shamov, 2015; Tetzlaff et al., 2015]. The second task relates to adequacy of the applied models of mixing and the calculation methods of evaluating the flow resident time in the underground part of the system [Sokolov, 1996].

The goal of the study was to evaluate the possibility of identification of the water sources for the

river runoff in the permafrost zone by the data obtained using a standard software program for regime hydrological and hydrochemical observations (by the example of the Nelka River). The tracer model for mixing the water sources and the respective analytical procedures (End-Member Mixing Analysis – EMMA), as well as the procedures of modeling the chemical composition of the river water by the principal component analysis (PCA) constitute the methodological basis of the study [Hooper, 2003]. The main objective was to find out which chemical parameters could be considered as tracers, to determine the character (type) of the dominating water sources of the river flows, to reveal the specific features of the mixing processes in particular watersheds of the Nelka River basin, and to quantify the stream ratios and the behavior of the water sources.

#### THE AREA OF THE STUDY AND THE OBSERVATION DATA USED

Small watersheds of the Mogot experimental hydrological site of the State Hydrology Institute (SHI), located within the central section of the BAM railway, approximately 60 km north of the town of Tynda, were chosen as the object of the study. The site which included the catchment of the Nelka River



**Fig. 1. A schematic map of the area under study.**

1 – stream gauges (see the names in Table 1); 2 – the borderline of the Nelka River basin; 3 – location of the site on a fragment of the map of Russia.

with tributaries (Fig. 1) is located in the middle part of the southern slopes of the Stanovoy and Tukuringra ridges. The watershed relief is that of medium-height mountains, with the absolute heights not exceeding 800–1000 m and the heights difference being 523 m. The northern and northeastern slopes are steep. There are frost mounds on the slopes and aufeis on river flows.

The soils are different combinations of frozen mountainous and taiga soils with shortened profiles and an abundance of gravel inclusions. Two types of soil ice are characteristic of them – cement (in macrofragmental cohesionless soils) and migrating ice (mainly in finely disperse soils, as interlayers and lenses 1–5 mm thick). Peat marshes rich in ice are commonly found at the bottom of the valleys. The continuous permafrost at the site is 100–250 m thick, and the average layer of seasonal thawing reaches 1.2–1.5 m. The forest cover of the watersheds is 80–90 %.

The detailed description of the catchments, the materials of the nature observations and the results of the studies of the hydrological regime are shown in [Vasilenko, 2013]. Hydrological observations over the runoff (measurements of the water levels and the flow rate) were carried out at five section lines (Fig. 1, Table 1) in the period from 1978 to 1983 according to the standard program of water balance stations; observations were carried out over precipitations from the meteorological station and the network of precipitation measurement sites. In the framework of the program of regime hydrochemical observations, samples of water were taken, analysis of which allowed elucidation of the main runoff phases: the beginning of runoff in the spring period, rise, peak, and decline of the high flow and of rainwater flow. The number of the samples taken is shown in Table 1, they were processed by the workers of the expedition of the Novocherkassk Hydrochemical Institute in accordance with [Semenov, 1977]. The results are provided in Table 2.

No consistent monitoring was conducted over the chemical composition of the water sources (except the soil water): there were only individual samples of atmospheric precipitation (snow) available. In 1982, samples were taken of aufeis water from the large aufeis on the Mogot River in several points, and in 1983, river flow and inundated valley aufeis samples were taken at different sites of the catchment of the Nelka River. No surface runoff was observed on the catchment slopes; the subsurface runoff, or the ‘stone tubes’ runoff, was predominant [Vasilenko, 2013]. To characterize the chemical composition of the soil waters, samples were used, taken from the slope water balance (w/b) sites from the typical slopes of the catchment: w/b 1 – on the deluvial foreslope, w/b 2 – in the lower part of the lighted slope, w/b 3 – on the shady slope of eastern exposure.

Table 1. The list of stream gauges, the hydrochemical parameters of stream water and the number of samples taken

Number	Stream gauge	F, km <sup>2</sup>	Hydrochemical parameters	Number of samples for the period					Total number
				1978-1979	1980	1981	1982	1983	
1	Nelka-2	30.8	Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> + K <sup>+</sup> , Σi	11	21	19	49	22	122
2	Nelka-3	16.0		3	24	22	43	21	113
3	Zakharenok-4	5.8		8	12	21	42	22	105
4	Oniks	3.0		12	19	19	38	21	109
5	Filiper-1	4.7		10	18	20	38	21	107

Note. F – catchment area at stream gauge; Σi – sum of major ions.

Table 2. The chemical composition of the natural waters of the Nelka River basin

Stream-gauge	Σi, mg/L	Content of ions											
		mg/L					%eq						
1	2	3	4	5	6	7	8	9	10	11	12	13	14
		Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> +K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> +K <sup>+</sup>
<i>In the stream waters during spring floods</i>													
Nelka-2	$\frac{11.1-44.6}{28.5}$	$\frac{0.9-3.7}{2.1}$	$\frac{5.2-26.4}{16.1}$	$\frac{0-7.2}{0.63}$	$\frac{1.0-3.8}{2.2}$	$\frac{0.6-2.3}{1.3}$	$\frac{0.3-12.8}{5.0}$	9.0	40.0	1.0	15.2	13.3	21.4
Nelka-3	$\frac{11.5-46.6}{27.3}$	$\frac{1.0-3.4}{2.1}$	$\frac{4.5-28.8}{16.7}$	$\frac{0-0.3}{0.001}$	$\frac{0.4-2.9}{1.8}$	$\frac{0.5-2.6}{1.2}$	$\frac{0.2-12.5}{5.5}$	7.9	42.0	0	11.2	12.9	25.9
Zakharenok-4	$\frac{10.3-47.2}{27.1}$	$\frac{1.4-5.9}{2.3}$	$\frac{3.7-28.2}{15.4}$	$\frac{0-6.5}{0.6}$	$\frac{0.8-3.5}{2.1}$	$\frac{0.5-2.8}{1.3}$	$\frac{0.5-9.3}{4.91}$	9.9	39.2	0.9	13.5	13.7	22.8
Oniks	$\frac{13.0-57.0}{32.5}$	$\frac{0.6-7.3}{2.3}$	$\frac{3.0-34.8}{18.7}$	$\frac{0-7.3}{1.1}$	$\frac{1.6-5.2}{3.1}$	$\frac{0.5-3.0}{1.6}$	$\frac{0.3-17.0}{5.2}$	8.9	39.0	2.1	15.2	13.5	21.3
Filiper-1	$\frac{12.1-61.6}{31.7}$	$\frac{1.2-6.8}{2.4}$	$\frac{4.5-40.8}{19.5}$	$\frac{0-0.9}{0.036}$	$\frac{1.2-3.9}{2.5}$	$\frac{0.7-3.3}{5.7}$	$\frac{0.2-13.2}{5.7}$	8.4	41.5	0.1	14.7	12.7	22.7
<i>In the stream waters during rain floods</i>													
Nelka-2	$\frac{11.8-39.2}{26.4}$	$\frac{1.2-8.4}{2.9}$	$\frac{4.5-24.0}{13.4}$	$\frac{0-9.2}{2.2}$	$\frac{1.2-3.3}{2.0}$	$\frac{0.3-2.0}{1.0}$	$\frac{0.8-9.7}{5.3}$	10.1	35.8	4.1	12.7	10.7	26.6
Nelka-3	$\frac{14.2-40.4}{24.7}$	$\frac{1.2-6.2}{2.6}$	$\frac{5.1-28.7}{14.4}$	$\frac{0-4.9}{1.1}$	$\frac{0.6-2.6}{1.5}$	$\frac{0.1-2.2}{0.9}$	$\frac{0.8-16.0}{6.1}$	9.4	38.5	2.1	10.0	9.7	30.3
Zakharenok-4	$\frac{11.1-40.3}{27.8}$	$\frac{1.0-6.6}{2.5}$	$\frac{5.1-25.8}{15.7}$	$\frac{0-4.3}{0.7}$	$\frac{1.0-3.0}{1.7}$	$\frac{0.5-1.9}{1.1}$	$\frac{0.5-10.2}{6.1}$	8.9	39.6	1.5	11.2	11.3	27.5
Oniks	$\frac{14.5-40.4}{31.5}$	$\frac{1.2-5.4}{2.3}$	$\frac{6.8-33.5}{16.9}$	$\frac{0-35.1}{2.5}$	$\frac{1.0-8.8}{2.4}$	$\frac{0.5-2.9}{1.3}$	$\frac{0.5-18.0}{6.2}$	7.3	39.3	3.4	13.3	11.7	25.0
Filiper-1	$\frac{10.6-37.0}{27.8}$	$\frac{1.2-9.1}{2.9}$	$\frac{6.4-24.0}{15.4}$	$\frac{0-6.1}{0.7}$	$\frac{0.9-3.3}{1.9}$	$\frac{0.1-2.3}{1.1}$	$\frac{0.3-10.5}{5.8}$	10.4	38.4	1.2	11.1	10.0	28.9

Continuation tabl. 2

1	2	3	4	5	6	7	8	9	10	11	12	13	14
	<i>In the stream waters during the summer-autumn dry period</i>												
Nelka-2	$\frac{15.1-58.4}{28.4}$	$\frac{0.7-7.4}{2.2}$	$\frac{5.3-21.1}{10.7}$	$\frac{0-22.8}{7.5}$	$\frac{0.1-5.2}{2.4}$	$\frac{0.4-3.2}{1.3}$	$\frac{0.5-13.7}{4.5}$	7.1	28.7	14.2	15.2	12.8	22.0
Nelka-3	$\frac{11.0-42.2}{26.7}$	$\frac{0.5-9.1}{2.5}$	$\frac{6.4-23.3}{12.1}$	$\frac{0-18.6}{3.8}$	$\frac{0.5-4.0}{1.4}$	$\frac{0.2-2.3}{0.9}$	$\frac{1.0-11.5}{6.1}$	8.7	34.2	7.1	9.5	10.4	30.1
Zakharenok-4	$\frac{9.2-40.3}{23.6}$	$\frac{0.8-8.0}{2.7}$	$\frac{5.1-18.5}{11.2}$	$\frac{0-9.2}{2.7}$	$\frac{0.4-3.8}{1.5}$	$\frac{0.2-2.2}{0.9}$	$\frac{0.3-9.5}{4.8}$	9.9	34.8	5.3	11.3	11.5	27.3
Oniks	$\frac{15.0-41.5}{28.7}$	$\frac{0.7-6.9}{2.8}$	$\frac{4.1-20.2}{12.1}$	$\frac{0-17.1}{5.3}$	$\frac{1.4-4.0}{2.6}$	$\frac{0.2-2.8}{1.3}$	$\frac{1.0-8.7}{4.5}$	8.9	31.1	10.0	15.5	13.0	21.5
Filiper-1	$\frac{9.4-40.5}{23.9}$	$\frac{0.7-7.3}{2.8}$	$\frac{6.0-17.7}{12.0}$	$\frac{0-6.6}{1.7}$	$\frac{0.5-3.6}{1.5}$	$\frac{0.4-2.3}{1.1}$	$\frac{0.5-9.0}{4.6}$	10.5	35.9	3.7	11.2	13.7	25.2
	<i>In the samples of slope soil waters taken at water-balance sites</i>												
w/b 1	$\frac{15.4-67.9}{34.2}$	$\frac{1.2-17.5}{3.49}$	$\frac{4.4-34.2}{14.2}$	$\frac{0-23.4}{6.28}$	$\frac{2.2-6.7}{3.37}$	$\frac{0.5-4.0}{1.54}$	$\frac{1.0-15.1}{5.39}$	9.7	32.3	8.1	20.0	12.9	17.1
w/b 2	$\frac{17.9-76.9}{29.9}$	$\frac{1.0-3.8}{1.89}$	$\frac{5.2-28.2}{12.9}$	$\frac{0-41.6}{6.7}$	$\frac{1.2-4.7}{2.92}$	$\frac{0.4-5.0}{1.73}$	$\frac{0.5-15.5}{3.66}$	6.8	32.5	10.7	18.8	15.9	15.3
w/b 3	$\frac{18.9-88.3}{44.9}$	$\frac{0.9-2.6}{1.95}$	$\frac{7.2-29.4}{13.9}$	$\frac{0-52.0}{17.0}$	$\frac{2.7-15.1}{6.2}$	$\frac{0.3-2.7}{1.46}$	$\frac{0.8-9.0}{4.36}$	5.4	26.6	18.1	24.2	10.4	15.4
	<i>In the aufeis waters</i>												
Mogot	$\frac{34.8-88.3}{44.9}$	$\frac{2.3-5.9}{3.48}$	$\frac{15.4-31.4}{21.2}$	$\frac{0-9.6}{5.18}$	$\frac{0.6-3.1}{1.45}$	$\frac{1.0-1.7}{1.23}$	$\frac{6.8-19.5}{11.4}$	7.6	35.1	7.3	6.3	8.3	35.4
	<i>In the atmospheric precipitation samples (snow)</i>												
Gradient site	$\frac{17.4-23.4}{20.2}$	$\frac{1.7-4.1}{2.7}$	$\frac{8.3-13.0}{10.2}$	N/f	N/f	N/f	$\frac{6.3-8.2}{7.3}$	13.1	36.9	0	0	0	50.0

Note. Concentration expressed in mg/L; numerator – change limits, denominator – mean values; in %-eq – mean values; N/f – not found.

### TRACER ANALYSIS METHODS

The methods of analysis applied have been described by the authors in detail [Gubareva et al., 2015, 2016]. Quantification of the proportions of the water sources is possible on the basis of a two-tracer model of mixing three sources:

$$\begin{cases} Q_1 + Q_2 + Q_3 = Q_T, \\ C_1^1 Q_1 + C_2^1 Q_2 + C_3^1 Q_3 = C_T^1 Q_T, \\ C_1^2 Q_1 + C_2^2 Q_2 + C_3^2 Q_3 = C_T^2 Q_T, \end{cases} \quad (1)$$

where  $Q$  is the water discharge;  $C$  is concentration of tracers; the superscript indicates the tracer number; the subscript is the number of the water source; index  $T$  indicates the characteristics of the river flow. Solution of this set of equations is written as:

$$\begin{aligned} Q_1 &= \frac{(C_T^1 - C_3^1)(C_2^2 - C_3^2) - (C_2^1 - C_3^1)(C_T^2 - C_3^2)}{(C_1^1 - C_3^1)(C_2^2 - C_3^2) - (C_2^1 - C_3^1)(C_1^2 - C_3^2)} Q_T, \\ Q_2 &= \frac{C_T^1 - C_3^1}{C_2^1 - C_3^1} Q_T - \frac{C_1^1 - C_3^1}{C_2^1 - C_3^1} Q_1, \\ Q_3 &= Q_T - Q_1 - Q_2. \end{aligned} \quad (2)$$

As tracers, different chemical indicators of natural waters may be considered, for example: total dissolved solids (or conductivity), concentrations of the principal ions, micro components, isotopes of oxygen and hydrogen, dissolved organic matter, etc.

Individual chemical parameters rarely manifest good tracer qualities; therefore, a special statistical procedure of EMMA-analysis is currently used [Christophersen and Hooper, 1992]. It consists in forming two complex model tracers, the concentration values of which are a linear combination of the concentrations of the measured tracers. The principal components method, which projects the matrix of the measured data into the space of mutually orthogonal principal components ( $U$ -space), constitutes the core of the procedure [Esbensen, 2005].

Coefficients of transition from the original space to the  $U$ -space (loads) are applied to investigate the role of variables and to analyze their mutual dependences. The proportions of explained variance of data for each principal component are determined by the value of eigenvalues of  $\lambda$ . These values are calculated as sums of squares of projections of all the measurements on each axis of the  $U$ -space, demonstrating the contribution of the principal components to the total variability of the original data.

Further, in solving the model of mixing three sources, instead of concentrations of two measured tracers, the values of the first two principal components are used. The quality of the model of three sources is evaluated by the share of total variance of

data, explained by the first two principal components  $\lambda_{II}$ , which should constitute at least 90 %.

The hypothesis of tracer conservatism is tested with a technique based on modeling the chemical composition of water by PCA according to [Hooper, 2003]. Based on the described model of mixing three sources, concentrations of the original chemical parameters are calculated. If tracers are conservative, the differences between the measured and calculated values of concentrations (balances) should be random 'noise'. Verification of conservatism is performed by plotting a relation 'residuals against measured values' for each tracer.

Interpretation of the model of mixing three sources developed by using EMMA-analysis presupposes that the chemical composition of river waters is controlled by mixing three water flows of different and relatively stable compositions. To establish them, samples of water are taken from different sites characterizing potential water sources: atmospheric waters, different types of soil and underground waters are determined (by means of pyramidal funnels, lysimeters, boreholes, from springs, etc.). Points representative of the water sources are determined by analyzing mixing diagrams [Christophersen et al., 1990]. The mean values of tracer concentrations in each point are projected into points of 2-dimensional  $U$ -space of the model tracers.

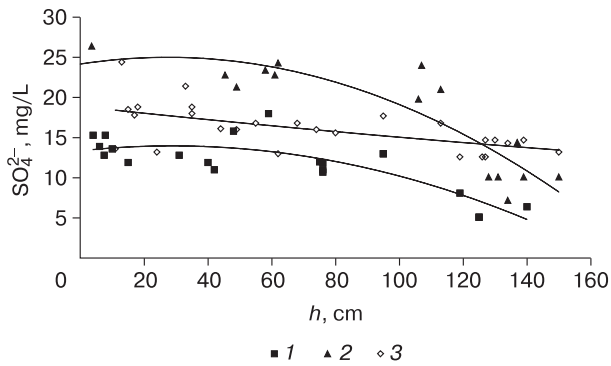
Points representative of the water sources form a field of mixing a subspace of a triangular shape, which encompasses all (almost all) the points corresponding to river samples, – given conservatism of mixing, correct choice of tracers and adequacy of interpretation of the water sources. Then, the shares of the water sources are calculated for each measured water discharge from equations (2). Finally, the model is validated by making calculations of tracer concentrations in river waters using the equations of the mixing model (1) and by comparing them with the observed concentrations.

### FORMATION OF THE ION COMPOSITION OF THE RIVER WATERS

The total dissolved solids (TDS) of the river water of the catchment is small and varies from 10 to 62 mg/L. During a year, there are two TDS peaks: the first one occurs in the period of the spring flood (the maximum values 40–62 mg/L), the second one takes place in the period before the freeze-up or through freezing (37–45 mg/L).

The content of  $\text{SO}_4^{2-}$  in the river waters is rather high – in the period of spring floods, it reaches the highest values 15–26 mg/L. When the spring flood is long and occupies vast territories, the maximum content of  $\text{SO}_4^{2-}$  is recorded when the first rain floods come, reaching 40–47 %-eq. The minimum content of  $\text{SO}_4^{2-}$  is recorded in August–September: 5–10 mg/L (25–28 %-eq).





**Fig. 2. Dependence of the content of  $\text{SO}_4^{2-}$  in the waters of the Nelka River on the depth of soil thawing  $h$  and the sum of precipitation for season  $X$  in the warm period.**

1 – 1979–1980,  $X = 350$  mm,  $R^2 = 0.58$ ; 2 – 1981,  $X = 495$  mm,  $R^2 = 0.78$ ; 3 – 1982,  $X = 595$  mm,  $R^2 = 0.35$ .

The seasonal variation of the content of  $\text{SO}_4^{2-}$  is caused by migration of unfrozen water and water-soluble compounds towards lower temperatures: in the winter period, towards the surface of the active layer, in the summer season, downwards along the soil profile [Popov, 1967; Ivanik, 1978]. This is especially noticeable in the regions of shallow bedding of sulfide ores, where intensity of the physico-chemical processes in the frozen ground increases due to oxidation of sulfides [Shvartsev, 1965]. For the  $\text{SO}_4^{2-}$  ion, statistically significant concentration reduction trends are observed as the thickness of the active layer and the amount of precipitation during the warm season increase (Fig. 2).

Analysis of the  $\text{SO}_4^{2-}/\text{Ca}^{2+}$  ratio demonstrates that for all the stream water of the region under study, it is on average 4–6, reaching maximum values (10–16) in the period of floods. The increased relative content of  $\text{SO}_4^{2-}$  indicates the presence of sulfide ores in the region of the Mogot River watershed. In the catchments of the Timpton and Chulman Rivers, 40–60 km north of the region under study, these ores are quite widespread [Fotiev, 1965; Shvartsev, 1965]. Atmospheric precipitation containing up to 8–13 mg/L  $\text{SO}_4^{2-}$  and sulfur from protein substances formed during their decomposition as a result of oxidation of hydrogen sulfide may also be possible sources of  $\text{SO}_4^{2-}$  ions.

Another distinctive feature of the ion composition is the minimum content of  $\text{HCO}_3^-$  in the period of spring floods and further till the middle of summer, when it often decreases to analytical zero. The growth of the content of  $\text{HCO}_3^-$  is recorded in the low-water season to 10–20 mg/L, at times reaching 25–27 mg/L in the period of the deep dry season. We can suppose that the ground waters of the thawed active layer are the main source of  $\text{HCO}_3^-$  entry. As water seeps in in

the soil cover, the oxidation of organic matter results in the decrease of the oxygen content and in the reduction of the content of  $\text{CO}_2$ . Carbonic acid is a source for forming  $\text{HCO}_3^-$  ions, the presence of which in the river flows is the indicator of the beginning of active participation of the ground waters in the supply of water to rivers.

The change in the content of  $\text{Na}^+ + \text{K}^+$  ions is determined by the phase of the water regime. In the period of increased water content of the river, prevalence of  $\text{Na}^+ + \text{K}^+$  cations is recorded in all the sampling sites at increased content of  $\text{Ca}^{2+}$  cations. At relative values of  $\text{Na}^+ + \text{K}^+ < 15\%$ -eq,  $\text{Ca}^{2+}$  becomes the prevailing cation, which is best expressed in the winter dry period. Concentration of  $\text{Mg}^{2+}$  varies from 0.3 to 3 mg/L, and the trend of their increased content in the periods of floods and in the period of the low flow in autumn is visible. Concentration of  $\text{Cl}^-$  ions during the warm period is small and varies from 1 to 5 mg/L, not changing as the mineral content in the water changes.

In the spring period, when the active layer of the soil has not yet thawed, the source of water for the river flows is primarily determined by thawing of the snow cover and by vast aufeis. The falling liquid precipitation accelerates the thawing processes. Part of precipitation water comes to the river channel as surface-slope (overland) flow (according to the classification of P.P. Voronkov). The chemical composition of these waters is formed under the influence of daily variations in the soil temperature, migration of salts towards lower temperatures, their redistribution in the solution at periodic diurnal freezing and defreezing. The prevalence of the  $\text{SO}_4^{2-}$  ion in the river water may be considered as a tracer of the specific water mass associated with these processes.

In the periods of increased water supply (rain floods), water flows belong to the sulfate class of the  $\text{Na}^+ + \text{K}^+$  group at minimal content of  $\text{HCO}_3^-$  ions. Supply of water to the streams is provided primarily by surface-slope and soil-surface waters. In the dry periods, the basic flow is fed by soil waters formed in the lower part of the slope stratum of loose deposits contacting bed rocks, the indicator of which is the  $\text{HCO}_3^-$  ion.

#### ANALYSIS OF TRACERS AND OF WATER SOURCES IN THE MIXING MODEL

The number of chemical parameters determined according to the regular observation program for the water regime is small, and the possibilities of selecting natural tracers are limited. Nevertheless, we have been able to find the appropriate variant of decomposition by PCA for a set of measured hydrochemical parameters including ions  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+ + \text{K}^+$  and the sum of major ions ( $\Sigma i$ ), at which the cumulative proportion of explained variance by two first

Table 3. Values of explained variance ( $\lambda$ ) for each principal component (PC), cumulative variance explained by the first two PC ( $\lambda_{II}$ ), determination coefficients ( $R^2$ ) for the dependence “residuals against measured values”

Stream gauge	$\lambda$ , %					$R^2$			
	$\lambda_{II}$	PC1	PC2	PC3	PC4	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{Na}^+ + \text{K}^+$	$\Sigma$
Nelka-2	93.2	56.7	36.5	6.0	0.80	0.063	0.033	0.137	0.037
Nelka-3	94.5	62.6	31.9	4.8	0.70	0.060	0.019	0.114	0.026
Zakharenok-4	95.2	65.6	29.5	4.0	0.90	0.051	0.016	0.097	0.028
Oniks	91.4	58.4	32.9	8.0	0.70	0.107	0.006	0.195	0.133
Filiper-1	94.5	65.2	29.4	4.6	0.90	0.056	0.017	0.112	0.031

components is more than 90 % (Table 3). This indicates the possibility of determining three water sources and of quantifying the proportion of their mixing, accounting for the differences in the chemical composition of the stream water. Examples of mixing diagrams in the space of the first two principal components are shown in Fig. 3, and the load plots are shown on the insets. For all the streams, the maximum load for the first principal component is on  $\Sigma$  and  $\text{Na}^+ + \text{K}^+$ . The maximum load for the second principal component is always on the  $\text{HCO}_3^-$  ion.

Thus, the first principal component accounts for variation in the chemical composition of water, which manifests itself in the change of TDS concentration, whereas the second one is visible in the change of the content of  $\text{HCO}_3^-$  ion. We can suppose that the physical meaning of the first component consists in reflecting the changes in the positions of the water source area (surface, soil supply, etc.), which is closely related to the phase of the water regime, whereas the physical meaning of the second component is to reflect the changes in the thickness of the active layer as a result of melting. This statement agrees with the previously obtained interpretation of the principal components for the waters of the Baikal region provided in [Semenov and Snytko, 2013].

Analysis of the plots ‘residuals against measured values’ (Fig. 4) for each tracer demonstrates a random structure and small dependence (Table 3), which does not allow us to accept the hypothesis of conservatism for each tracer. The use of the generally accepted set of tracers in the mixing model is statistically well-founded and rationally interpreted.

The configuration of the mixing field in the space of the principal components demonstrates a triangular shape for all the rivers. Consider the mixing diagram for the Nelka-2 gauging station (Fig. 3, a). The sides of the triangle are drawn as a field envelope of the points, and the triangle vertices represent the positions of hypothetical water sources, interpretation of which is possible on the basis of analyzing the character of stream samples close to each of them.

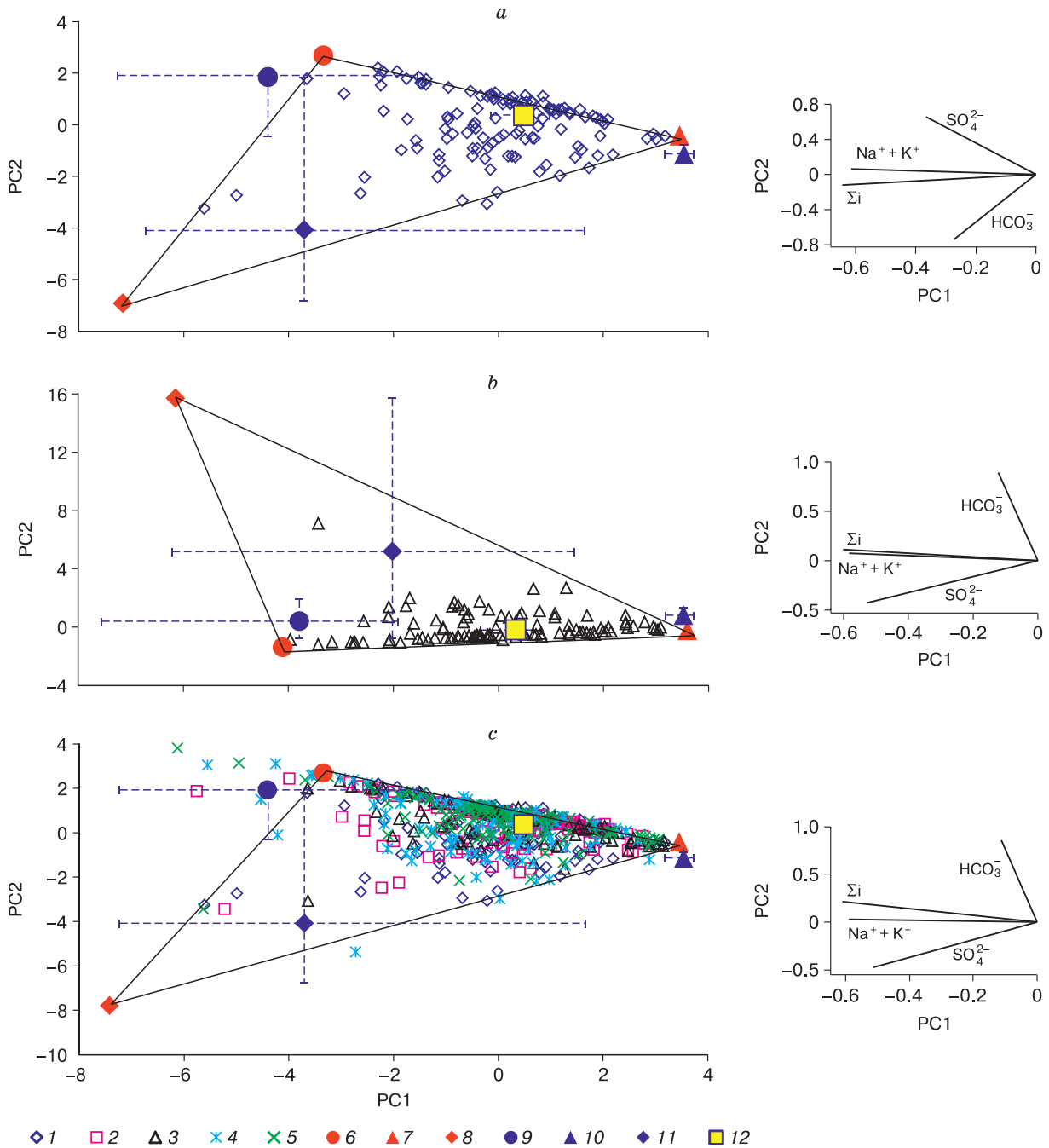
Near the first source, there are mostly river samples taken during spring floods. We will briefly refer to this source as a thawed cryogenic source, as it represents the water mass related to thawing of soil ice,

channel and floodplain aufeis and snow cover. The presumed chemical composition of this source includes the maximum (compared to other sources) content of  $\text{SO}_4^{2-}$  – 20–36 mg/L, while the minimum (at the level of the analytical zero) content of  $\text{HCO}_3^-$ , the content of the  $\text{Na}^+ + \text{K}^+$  ion content equals 7.0–8.5 mg/L, the TDS concentration 35–40 mg/L.

The supposed origin of the second source is rainwater. Near this vertex, there are river water samples taken at the peak of rain floods, primarily August floods. It is evident that during regular and heavy rainfall (in August, total precipitation reaches its maximum and constitutes 130–200 mm), rainwaters flow down to the river over the rill channel network, which drains the water-saturated soil layer. The presumed chemical composition of the rainwater source is the following: the content of  $\text{SO}_4^{2-}$  compared to the other sources is minimal and constitutes about 4.5–7.0 mg/L, the content of  $\text{HCO}_3^-$  is low – from the analytical zero to 3 mg/L, the TDS content is 10–12 mg/L, the content of  $\text{Na}^+ + \text{K}^+$  varies within 0.1–1.5 mg/L.

Source 3 is poorly represented by river water samples (Fig. 3, a); however, samples taken in the dry periods tend to be close to it. The origin of this water mass is presumably related to water-logged soils, which form the base inflow of water to the rivers in the dry periods. The conditional chemical composition of the waters from this source is the following: the content of  $\text{SO}_4^{2-}$  is low and constitutes 9–13 mg/L, the content of  $\text{HCO}_3^-$  is maximal compared to other sources – 15–50 mg/L, the content of  $\text{Na}^+ + \text{K}^+$  is 7–15 mg/L, the TDS content is 40–70 mg/L. There is a visible trend for location of a certain number of river water samples on a straight line between the second and third sources, indicating the inflow of water to the river only from these two types of water sources.

The direct confirmation of the adequacy of making the mixing diagram is the location of some available measured samples from the assumed water sources on it. Single samples of aufeis waters sampled on April 9, 1982 in several points of the vast aufeis on the Mogot River are located near the vertex of the first source, corroborating its cryogenic character. The same is evidenced by three samples of atmo-



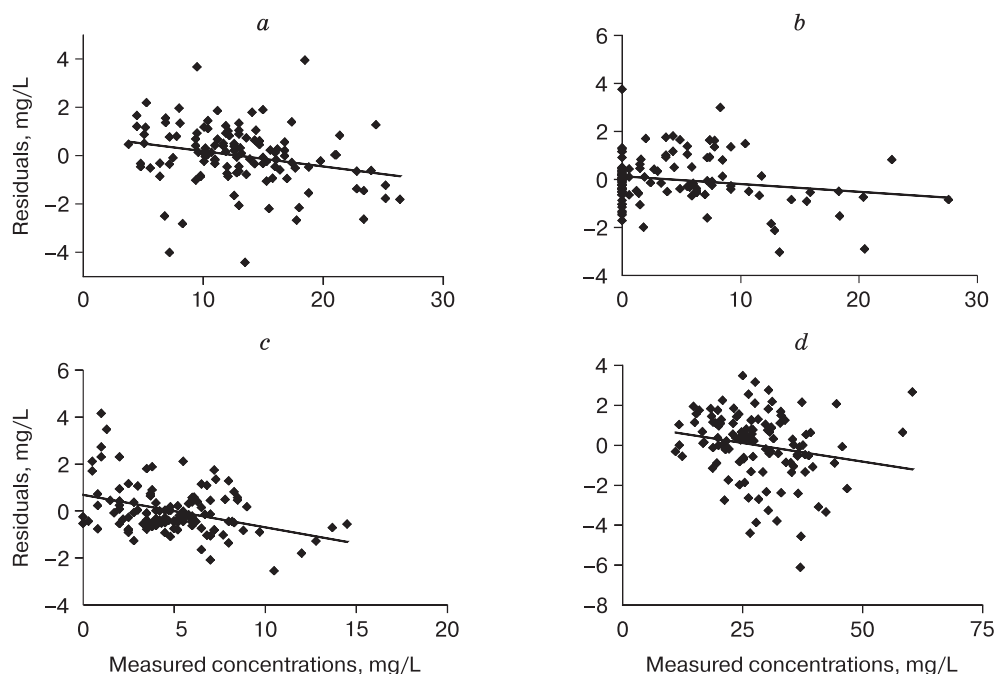
**Fig. 3. Diagrams of mixing the waters of the Nelka-2 River (a), Zakharenok-4 River (b), the aggregated sample of the river water samples (c).**

Water samples from the stream gauges: 1 – Nelka-2; 2 – Nelka-3; 3 – Zakharenok-4; 4 – Oniks River; 5 – Filiper-1; model sources: 6 – thawed-cryogenic; 7 – rain water, 8 – slope soil water; source water samples (averaged values): 9 – aufeis, 10 – precipitation [Fotiev, 1965], 11 – soil water from the water balance site No. 3; 12 – snow. Dashed lines with stops – variation limits for respective data samples.

spheric precipitation in the form of snow (Table 2), sampled in the catchment of the Nelka River and located at the border of the mixing triangle between the thawed-cryogenic source and the rainwater source.

As there were no observations of the chemical composition of liquid atmospheric precipitation in the catchment, we used the data of such observations around the settlement of Chulman [Fotiev, 1964]. The





**Fig. 4. Dependences “residuals against measured values” for the Nelka-2 River.**

*a* –  $\text{SO}_4^{2-}$ ; *b* –  $\text{HCO}_3^-$ ; *c* –  $\text{Na}^+ + \text{K}^+$ ; *d* –  $\Sigma i$ .

averaged values of concentrations for 8 samples taken in July and August 1960 provided a point in the mixing diagram which practically coincided with the position of the hypothetical rain source.

Among the samples of the soil-slope waters taken at three water balance sites, the samples taken from site 3 proved to be most representative ones. The averaged chemical parameters of these samples in the space of the principal components are logically located on the side of the triangle connecting the rain and soil sources (Fig. 3). Certain samples taken in the dry period coincide with the position of source 3 (soil-ground) established by the shape of the mixing diagram.

The mixing diagrams of other streams are not essentially different. However, in making them, uncertainties arise in establishing the position of the soil source due to lower coverage with the observation data. The identical view of the mixing diagrams in the *U*-space, as well as of the load plots for all the water flows, allows us to state that the processes of mixing of the assumed water sources controlling the chemical composition of the river waters are similar.

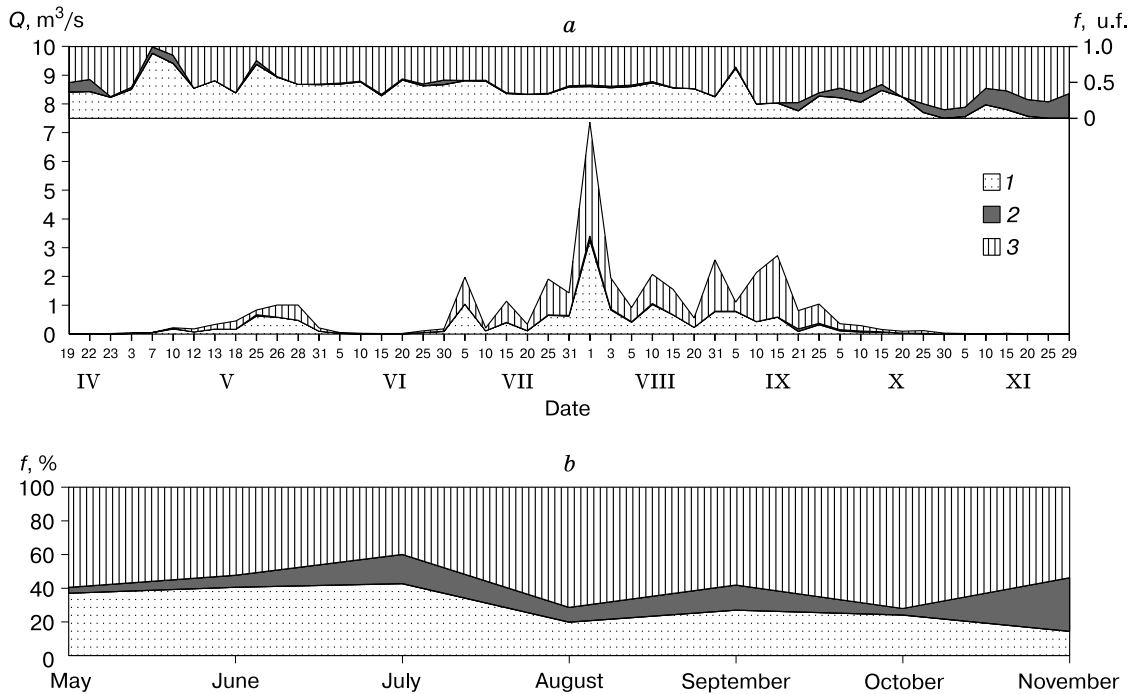
In addition, analysis of the combined mixing diagram for the outlet of the Nelka-2 gauge station (Fig. 3, *c*), where the water samples of nested catchments are also plotted in accordance with the technique of [Hooper, 2003], shows that practically the aggregated series of the water samples of all the streams forms the integrate mixing space limited by

the already identified water sources. All this indicates the homogeneity of the river runoff processes and the similarity of the factors controlling its chemical composition, for the entire catchment of the Nelka River.

#### QUANTIFICATION OF NATURAL WATER SOURCES

Calculation of the proportions of water sources was made using the mixing model for the Nelka River at the outlet gauge 2 for each date of sampling of the river water for the entire observation period (Fig. 5, *a*). Monthly averaging of the calculated values across all the observation years allowed us to plot the runoff hydrograph separation by water sources (Fig. 5, *b*), on which the specific features of interaction between thawed-cryogenic, rain and soil water sources are demonstrated. The proportion of the thawed-cryogenic water source is significant and varies from 20 to 40 % throughout the entire period at maximum values in June–July. Its reduction has been observed since September (from 27 to 14 %), but complete depletion does not occur.

The proportion of the rain waters in river prevails throughout the year – from 40 to 70 %. Its largest values are recorded in August, and the increased proportion of rain water source remains till the runoff ceases, with the precipitation in the autumn period decreasing. Solid precipitation falling in September–October melts at positive day air temperatures, seeping into the yet unfrozen active layer of soil, partly



**Fig. 5. An example of hydrograph separation of the Nelka-2 River by water sources:**

*a* – for 1982, *b* – typical hydrograph. Sources: 1 – thawed-cryogenic, 2 – soil water source, 3 – rain water source.

flow from the catchment to streams and partly accumulate in the active layer.

The proportion of soil waters is insignificant and varies from 3 to 30 % (Fig. 5, *b*). For this type of water source, a trend of increase of soil water towards autumn is typical, with maximum values recorded in November. At maximum depth of thawing of the active layer in September and insignificant atmospheric

moisture, the contribution of the soil water source may be significant – 10 % (Fig. 5, *b*), and in some years, 20 %. This trend is regularly violated by rain floods, often occurring in September, and the accumulated rainwater in the catchment exhaust in October–November (Fig. 5, *a*). Until the table of seasonal freezing and permafrost closes, the dynamics of the contributions of water sources is determined by the

**Table 4. Evaluation of the quality of simulating tracer concentrations by average ( $\bar{x}$ ), standard deviation ( $s$ ), correlation coefficient ( $r$ ) between the measured and simulated values**

Characteristic	$\bar{x}_{meas}$	$\bar{x}_{sim}$	$s_{meas}$	$s_{sim}$	$r$	$\bar{x}_{meas}$	$\bar{x}_{sim}$	$s_{meas}$	$s_{sim}$	$r$
<i>Aggregated series of water samples for Nelka-2</i>						<i>Aggregated series of water samples for Oniks</i>				
SO <sub>4</sub> <sup>2-</sup>	13.0	14.1	5.05	5.09	0.93	15.4	15.1	6.24	6.55	0.95
HCO <sub>3</sub> <sup>-</sup>	4.31	4.95	5.71	5.81	0.98	3.51	5.37	5.06	5.24	0.98
Na <sup>+</sup> + K <sup>+</sup>	4.98	4.75	2.77	1.89	0.90	5.08	4.27	2.97	1.29	0.90
Σi	28.2	28.1	8.70	8.97	0.98	30.6	30.6	8.76	9.13	0.97
<i>Aggregated series of water samples for Nelka-3</i>						<i>Aggregated series of water samples for Filiper-1</i>				
SO <sub>4</sub> <sup>2-</sup>	13.9	12.9	5.16	3.51	0.94	15.0	13.1	5.94	3.14	0.95
HCO <sub>3</sub> <sup>-</sup>	2.07	4.04	2.07	3.79	0.98	1.39	3.60	3.57	6.05	0.99
Na <sup>+</sup> + K <sup>+</sup>	5.75	3.77	3.09	1.20	0.91	5.38	4.06	2.85	1.14	0.92
Σi	26.7	28.6	8.87	8.89	0.97	27.6	32.2	9.08	7.99	0.94
<i>Aggregated series of water samples for Zakharenok-4</i>										
SO <sub>4</sub> <sup>2-</sup>	13.9	13.8	5.54	4.20	0.95					
HCO <sub>3</sub> <sup>-</sup>	1.51	2.31	3.01	3.57	0.93					
Na <sup>+</sup> + K <sup>+</sup>	5.25	4.36	2.64	1.53	0.91					
Σi	25.9	28.8	8.73	8.38	0.97					

ratio of the rain and soil sources at a relatively small content of the thawed-cryogenic source.

Testing the quality of simulated tracer concentrations provided good results (Table 4). The correlation coefficients of all the relations between measured and modeling tracers are higher than 0.9, and the values of statistical sample parameters are very close. This indicates the high accuracy of the simulation values of the water sources of the rivers.

### CONCLUSIONS

As a result of the study, it was established that EMMA modeling can be performed using data observed according to the standard hydrological and hydrochemical monitoring programs. Compared to special studies of the water sources of the river runoff, such data are characterized by the infrequent sampling and the limited number of the analyzed chemical parameters.

Nevertheless, processing the data observations of several years, we have been able to develop mixing models which are characterized by the high accuracy of simulating the chemical composition of the river waters. The correlation coefficients between the simulated and observed series of concentrations proved to be higher than 0.9 for all the tracers. Using the EMMA-analysis and the additional data of observations over the background chemical composition of precipitation, three main water sources have been identified – the thawed-cryogenic source, rain and soil sources.

Calculation based on the mixing model for the cross section 2 of the Nelka River has shown that the proportion of the rainwater in the river water prevails throughout the entire period and varies from 40 to 70 %, with the maximum observed in August. The proportion of the thawed-cryogenic water source varies from 20 to 40 %, with the maximum in June–July and significant reduction in September; however, no complete cessation of the runoff occurs. The proportion of the soil water source varies from 3 to 30 %, with the maximum in October–November, with the common reduction tendency of the stream flow. The number and the type of the sources, and also the patterns of their mixing are stable in terms of space and the annual trend, which allowed us to carry out the typical hydrograph separation by water sources for the cross section of the Nelka-2 River.

An essential result of the study reflecting the specific characteristic of the permafrost zone consists in identification and quantification of the significant content of the thawed-cryogenic source throughout the entire period of the runoff, which is related to the presence of permafrost in the catchment. This result agrees with the data obtained previously for the Baikal Region [Kichigina *et al.*, 2016]. The study results

indicate the high efficiency of the methods of tracer hydrology in the permafrost zone and the possibility of expanding their database by using the river regime information of Rosgidromet monitoring network.

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