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GEOCHEMISTRY

Spatial Patterns of the Evolution of the Chemical Composition and Discharge of River Water in the Ob River Basin

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Abstract—The discharge of major cations and dissolved organic carbon (C_{org}) with water of the Ob River and its tributaries along the natural zones within the Ob River basin was calculated, and the contribution of the underground component to the volumes of total discharge of the Ob River basin was estimated. It was demonstrated that the total chemical composition of river water and the geochemical discharge in the Ob River basin were consistent with the zoned hydroclimatic conditions controlling the character and duration of interaction in the water–rock system. It was established that the average ionic discharge of the Ob River increased from 6–7 × 10^6 t/year near Barnaul to 46–47 × 10^6 t/year near Salekhard; the discharge of dissolved C_{org} increased from 0.1 × 10^6 to 3.8 × 10^6 t/year. Multiple enrichment of underground waters of the Ob River in dissolved organic matter from the upper to the lower reaches was revealed.

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Hydrogeochemical discharge is one of the basic indicators of state of a river and its basin. Solution of a complex of geoecological, geochemical, and hydrological problems in the Arctic system "land–shelf" requires information on outlets maximally close to the river mouths, as well as knowledge of the patterns of the intrabasin distribution of hydrochemical discharge and the chemical composition of river waters. An objective pattern of spatial variations is necessary for working out and realization of the methodologies for long-term hydrochemical predictions, geochemical prospecting for natural resources, and planning of events for use and preservation of natural resources. It is very important to determine the regularities of underground discharge for understanding the typical peculiarities of transport and transformation of organic material in the Arctic system "land–sea" as well [1–3].

The Ob River basin, one of the largest river basins in the world, is characterized by a variety of physical and geographical conditions: from the Altai mountain area and steppe in the south to the tundra and Arctic deserts in the north. This basin contains several large natural–technogenic systems including that related to the oil- and gas-producing complex of West Siberia (Fig. 1). Detailed study of the spatial heterogeneity in the distribution of hydrochemical characteristics of river waters was carried out for separate large areas of the Ob River only [4–7]. However, such investigations were not performed for the entire Ob River basin. This study is aimed at revealing the spatial patterns in the variations of the chemical composition of river waters and geochemical discharge in the Ob River basin with account for the different natural zones and tributaries of various orders. It is also important to compare the peculiarities of the hydrochemical regime of the Ob River, the basin of which is mostly located outside the permafrost area, with those of the Lena and Kolyma rivers located in the permafrost zone.

We applied the following methodologies: (1) collection and generalization of geochemical data obtained by Roshydromet and Tomsk Polytechnic University with account for (1.1) identity of sampling techniques and methods of chemical analysis, (1.2) heterogeneity of hydrological series, sometimes resulting from an increase in the underground component of river discharge from the early 1970s [8] (accordingly, we used the data obtained in the period of 1970–2010), (1.3) features of economic activity (the Irtysh River basin was not considered in this study due to the absence of reliable data on usage of water in the areas located in PRC and Kazakhstan; (2) interpolation and extrapolation of the totals of major cations and bichromate oxidation based on the data on water consumption and water discharge modules; (3) calculation of ionic discharge (the data on the concentration of major ions, such as Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^- +

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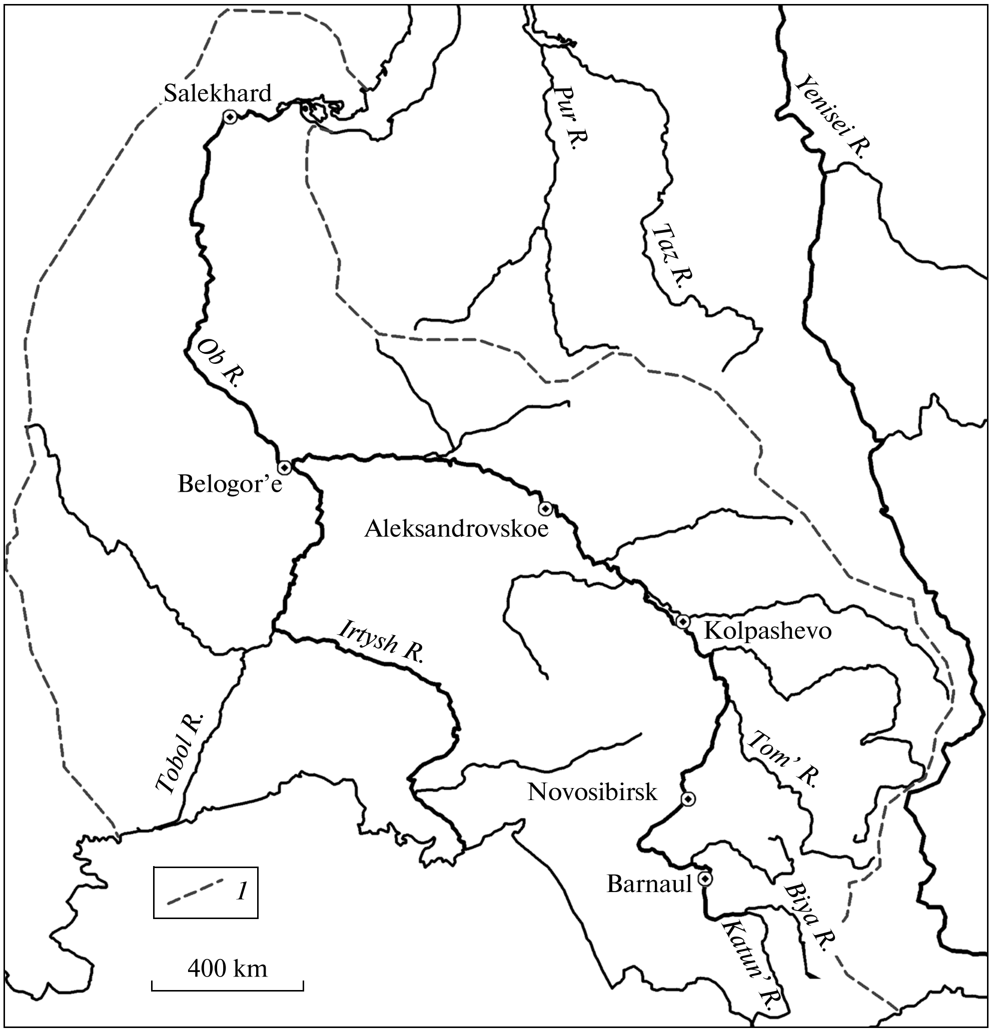

Fig. 1. Scheme of the boundaries (*1*) of the Ob River basin within the Russian Federation.

CO_3^{2-}, SO_4^{2-}, and Cl^-, were applied) and discharge of dissolved organic materials (by dissolved C_{org} [9]); (4) geographic and statistical analyses of variations of the chemical composition of river waters and hydrochemical discharge separately for large and medium rivers (with inclusion of the small ones).

The ionic discharge of the Ob River was determined for each year during the conventionally uniform period [8] (from 1970) as the sum of discharge values over 12 months; each value was calculated as the product of the monthly water discharge and the average monthly total of major ions Σ_i. The latter value was calculated by the dependence between the periodical values of Σ_i (mg/dm^3) and water consumption:

$$\Sigma_i = a \cdot Q + b, \quad (1)$$

where Q is the water consumption (m^3/s) and a, b are the coefficients obtained by the method of least squares. Similarly, we determined the underground ionic discharge (search for links by the winter periodical data and calculation of the series of average monthly values of water consumption), but the values of the monthly underground water discharge were used in the formula instead of the average monthly water consumption in the river. These values were accepted as equal to the river discharge in the winter low-water period; in other months, they were determined by the linear interpolation between the values in the first and last winter months (from November to April, for the Ob River near the village of Belogor'e, Salekhard, and rivers of the tundra and forest tundra; from December to March, in other cases).

The average long-term seasonal discharge of C_{org} with water of the Ob River, ionic discharge, and C_{org} discharge with medium rivers over the natural zones was determined as the product of the average seasonal (on average, over the long-term period) concentrations of matter and modules of water discharge. The annual discharge was calculated as the total of seasonal values, whereas its underground component is calculated as the product of the average long-term under-

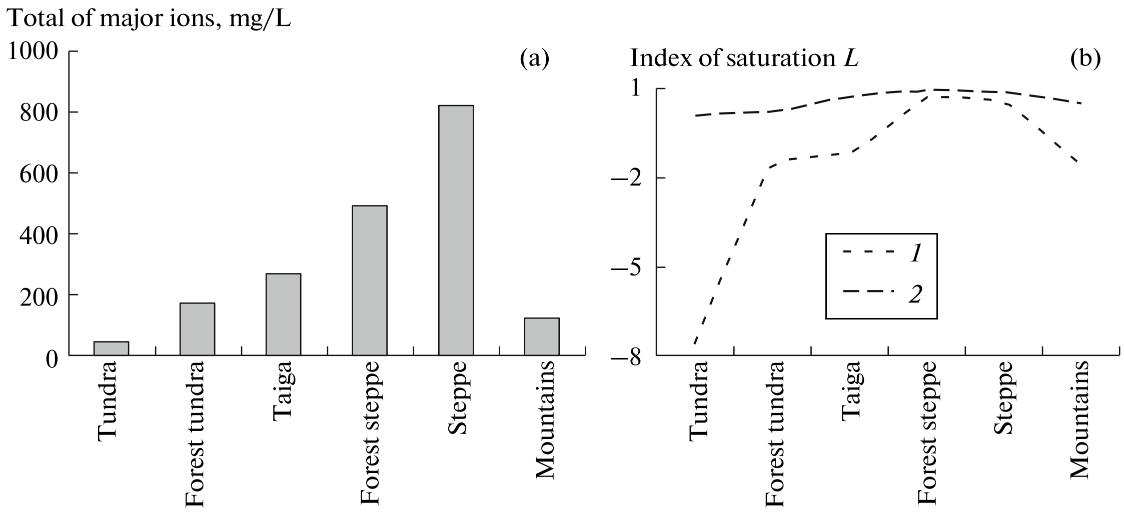

Fig. 2. Average long-term values of total major ions (a) and index of saturation in relation to dolomite (*1*) and calcium humate (*2*) (b) (negative value *L* indicates potential undersaturation; positive value indicates oversaturation of the solution in relation to the material) in river waters of the different natural zones.

ground discharge and (1) average long-term matter concentration over December–March for the zones of the taiga, forest steppe, steppe, and mountain regions and (2) the average long-term matter concentration in underground waters on the basis of the data [10] for tundra and forest tundra.

Combined analysis of the data obtained and materials of previous investigations [6, 11] allows us to conclude that, according to the classification [12], river waters in the Ob River basin range from fresh with a high mineralization or brackish, sodium chloride in the steppe zone to fresh with a very low and low mineralization, and calcium hydrocarbonate in tundra. As a whole, in spatial relation, a clear increase in the concentration of major ions is observed the from tundra in the north and northeast to the steppes in the southwest (Fig. 2). The trends for other hydrochemical indicators are much poorer or are absent. The concentration level of dissolved salts in river waters of mountain and foothill areas is lower than that in the taiga and forest tundra and higher than that in the tundra (Fig. 2). It is established that, as a whole, river waters in all natural zones are undersaturated in relation to primary aluminosilicates and may dissolve them with the formation of clay minerals. Equilibrium or slight oversaturation of river waters in relation to the compounds of Ca and Mg with humic acids is one more common feature of the rivers in the Ob basin (Fig. 2). The main differences between the natural zones are related to the different character of interaction of river waters with carbonate minerals (equilibrium or slight oversaturation in relation to calcite and dolomite in forest steppe and undersaturation, in the other zones) (Fig. 2).

Based on the performed hydrochemical generalizations and with account for the revealed links between the hydrochemical and hydrological indicators, we established average long-term values of the integral ionic discharge in the Ob River basin, which is ~47 × 10^6 t/year for the Ob River and 0.5–4.4 × 10^6 t/year for its main tributaries. Ionic discharge is

Average long-term (1970–2010) discharge of major ions (Σ_i) and dissolved organic carbon (C_{org}) in the Ob River basin, $\times 10^3$ t/year

River–locality, natural zone	Discharge	Discharge of materials	
		Σ_i	C_{org}
Ob–Salekhard	1	46545.66	3807.72
	2	29221.08	1250.72
Ob–Belogor'e	1	37553.00	2838.72
	2	26035.32	901.65
Ob–Aleksandrovskoe	1	23862.20	1177.70
	2	13840.08	329.74
Ob–Kolpashevo	1	17893.04	470.21
	2	8392.69	102.67
Tundra	1	617.60	472.99
	2	268.51	28.88
Forest tundra	1	5215.03	264.37
	2	3398.00	161.64
Taiga	1	144090.73	7765.39
	2	30007.64	1058.29
Forest steppe	1	91071.49	1164.68
	2	12924.97	130.55
Steppe	1	5351.80	89.84
	2	190.00	1.47
Mountain regions	1	62294.35	1241.31
	2	6248.66	70.53

(1) Total; (2) underground.

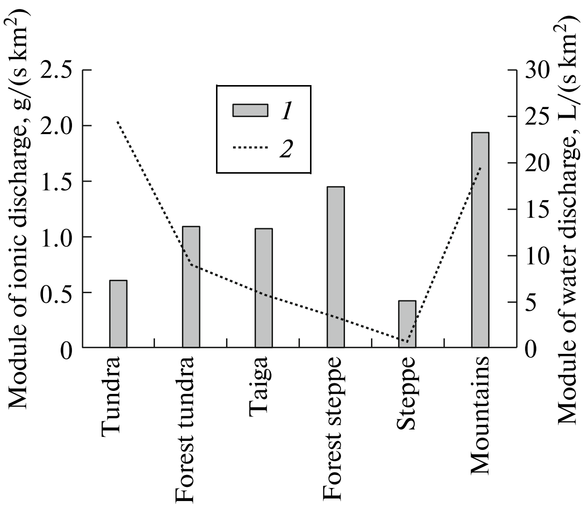

Fig. 3. Distribution of average long-term values of the modules of ionic (*1*) and water (*2*) discharge in the Ob River basin over the natural zones.

mostly represented by major components (85–90% and more) (Table 1).

The value of ionic discharge obtained by the authors for the Ob River is higher than the estimates in [12] by a factor of ~1.4, which is mostly explained by the heterogeneity of hydrochemical series controlled by the evolution of water discharge, as well as by the higher "specific weight" of the samples collected from a network of observations of Roshydromet during the high water periods before 1970. The increased anthropogenic influence is important as well, although its role seems to be less important in the case of ionic discharge than in the case of removal of oil products and pesticides [13] due to the existence of geochemical and biogeochemical barriers [6]. We should emphasize that an improved value of ionic discharge for the "non-permafrost" Ob River is comparable with discharge of the Yenisei River, the basin of which is mostly located outside the permafrost zone as well, but is significantly lower than discharge of the "permafrost" Lena River [12]. This issue requires further studies.

The distribution of ionic discharge modules (1.0–1.2 g/(s km^2)) over the territory of the Ob River basin is the following: >2 g/(s km^2), for the Ob and Chulym rivers, ~1.5 g/(s km^2), for the Tom' River and some of its tributaries, which are the forest steppe rivers; ~1.0 g/(s km^2), for the lowland rivers of taiga and forest tundra; <0.5 g/(s km^2), for rivers of the steppe zone. Such a distribution is controlled by the latitudinal zoning in water discharge and mineralization of river waters (Figs. 2 and 3).

The underground component of hydrochemical discharge of the rivers of the Ob basin varies in quite a wide range (Fig. 1, Table 1). For ionic discharge, it varies from 3–4% in the steppe and forest steppe to 60% and higher for lowland tributaries of the Ob River with waterlogged watersheds. The underground ionic discharge of the Ob River progressively increases from 47–58% of the total near Kolpashevo (middle reaches) to 60% and higher near the village of Belogor'e and Salekhard (lower reaches) (Table 1). This confirms the necessity of a complex geochemical approach to tracing the output of the underground river discharge on the Arctic shelf.

Our calculations of matter introduction into the Ob River basin in the area of its middle reaches allowed us to obtain a general pattern and distinguish the most important sources and processes, which influence on hydrochemical discharge. Among them, first of all, is matter precipitation from the atmosphere (37.4% for major ions; 16.3% for C_{org}). Matter introduction as a result of interactions in the "water–rock" system (50.7% for major ions), as well as income of materials from swamps (44.3% for C_{org}), contributes significantly to the formation of hydrochemical discharge as well. Anthropogenic influence at the expense of discharges from concentrated and disordered sources is estimated as 12.5% for major ions and 6.6% for C_{org}. The anthropogenic influence mostly controls release of oil hydrocarbons, a number of minor elements, and specific organic minor impurities [13, 14]. Estimation of this influence requires further investigations with specification of the forms of migration and estimation of solid discharge.

As a result of the study performed, we estimated the values of hydrochemical discharge of the Ob River and its tributaries and estimated the contribution of the underground component to the volumes of total discharge of rivers in the Ob basin. The total chemical composition of river waters in the Ob River basin is characterized by regular decrease of the concentration of major ions from steppe to tundra being consistent with zoned hydroclimatic conditions, which control the character and periods of interaction in the "water–rock" system and, consequently, the relationships between the processes of matter accumulation and removal from various environmental components. The average ionic discharge of the Ob River increases from 6–7 × 10^6 t/year in the upper reaches near Barnaul to 46–47 × 10^6 t/year in the mouth zone near Salekhard, whereas discharge of dissolved C_{org} varies from 0.1 to 3.8 × 10^6 t/year, respectively. We revealed multiple enrichment of underground waters of the Ob River in dissolved organic matter from the upper reaches (70.53 × 10^3 t/year) to the Ob Bay (1250.72 × 10^3 t/year). Note that the removal of dissolved salts (by the total of major ions) at the outlet of the Ob River near Salekhard is lower by 262 × 10^6 t/year than the total discharge medium rivers over natural zones within the Ob basin; C_{org}, by 8.1 × 10^6 t/year. This provides evidence for more significant chemical denudation of drainage systems, as was suggested previously [15].

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