Hydrologic conditions for chemical composition of the Siberian river waters

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Abstract. The influence of hydrologic conditions on the Siberian river waters chemical composition, their spatial and temporal changes are analysed. The dependencies between the hydrochemical and hydrological parameters are determined. It is shown that: 1) many hydrochemical parameter changes are defined by lognormal probability distribution; 2) variability of the chemical composition and elevated concentrations of some substances will be more likely to occur in the inter-annual and intra-annual runoff variability; 3) the main features of the water chemical composition are formed at the stages of the slope, subsurface and underground runoff formation.

1. Introduction

The chemical composition of natural waters is simultaneously an important characteristic of the ecological condition of water objects and the indicator and result of the processes that occur in these objects and their watersheds [1, 2]. Therefore, reliable knowledge about how and why the chemical composition of the waters is formed provides a basis for planning effective protection and use of water objects. Currently, some progress has been made in this direction, but many questions remain insufficiently studied. For example, it is not always clear how to determine the ratio of natural and anthropogenic components of the hydrochemical parameters and their values, the level of permissible anthropogenic impact on water objects, conditions for accumulation of certain substances in waters and sediments and so on. Tomsk Polytechnic University (TPU) and Tomsk State University (TSU) have studied these and other issues for several decades. The practical importance of these studies is to solve the following problems, especially important for Siberia: 1) development of geochemical methods for prospecting and exploration of underground resources, extraction and processing of which provide a basis for the economy of most regions from the Urals to the Pacific ocean; 2) development of methods for restoration of water objects that have been disturbed by mining. Understanding the mechanisms of geochemical anomalies formation in water objects is common for these tasks. Thus, the aim of the work is to determine the key aspects of the hydrologic conditions influence on the geochemical regime of Siberian rivers.

2. Initial data and research methods

The objects of study were primarily the medium-sized rivers in the Ob river basin with watershed area from 2,000 to 50,000 km$^2$; their watersheds are located within the same landscape zone, and the runoff of rivers is determined by zonal factors. Initial data were obtained from the stations of the state observational network (Roshydromet), as well as the field studies of TSU, TPU, JSC
“Tomskgeomonitoring” [3]. The hydrochemical data (pH, chemical oxygen demand (COD), the concentrations of main ions \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{Cl}^- \), the total dissolved solids TDS, \( \text{NO}_3^-, \text{NO}_2^-, \text{NH}_4^+, \text{PO}_4^{3-}, \text{Si}, \text{Fe}, \text{Al}, \text{Zn}, \text{Cu} \)) were selected in such a way that the concentrations were determined according to the standard comparable methods used in Roshydromet. Research methodology consisted of the collection of hydrological and hydrochemical data, their statistical analysis, and design of a model describing hydrological parameters influence on the chemical composition of the river waters. The thermodynamic calculations of the equilibrium relating to certain minerals in water were carried out to explain the parameters of the models [4]. The models were validated taking into account the recommendations [5] under the condition of \( R^2 > 0.36 \), where \( R^2 \) is the square of the correlation between the measured and calculated values.

3. Results and discussion

Analysis of the materials of our research, studies of other organizations and authors has shown the following: 1) the river waters in the Ob basin change from water with high mineralization, with sodium chloride in steppe to freshwater with very low and low mineralization, with hydrocarbonate calcium in tundra; 2) there is a pronounced increase in the content of the main ions in the direction from tundra in the north and north-east to steppes in the south-west; such tendencies in other hydrochemical parameters spatial distribution in lowland rivers are less pronounced; the TDS concentration in the rivers of highland area and piedmont is lower than in taiga and forest tundra and higher than in tundra; 3) empirical probability distribution of TDS in the river waters of the landscape zones in question corresponds mostly to the lognormal probability distribution (the best fit in comparison with the normal, gamma, and exponential distributions); 4) river waters of all landscape zones are generally undersaturated with the primary aluminosilicates and capable to dissolve them with the formation of clay minerals; the river waters are very often in equilibrium or supersaturated with the compounds of calcium and magnesium with humic acids; 5) the main differences between landscape zones are associated with different kinds of interaction of the river water with carbonate minerals (equilibrium or slight supersaturation with calcite and dolomite in forest steppe and steppe and undersaturation in other zones); 6) a portion of 37.4 % of the total main ions flux in the Ob river water and 16.3 % of organic carbon (C\(_{\text{org}}\)) are associated with atmospheric precipitation; 50.7 % of the main ions flux – with the interactions within the water-rocks system; 44.3 % of C\(_{\text{org}}\) – with the inflow from mires; 7) wastewater fluxes account for about 12.5 % of the total flux of main ions in the Ob river water and 6.6 % of C\(_{\text{org}}\); fluxes of petroleum hydrocarbons, some trace elements, and specific and organic trace components is mainly associated with anthropogenic influence; 8) the above features determine the feasibility of delimitating ecogeochemical areas corresponding to highland areas, steppe, forest steppe, taiga, forest tundra and tundra zones; each ecogeochemical area (ecoregion) has its specific values of hydrochemical parameters and the accessible quality indicators, the mean values of which are usually exceeded [4, 6–10]. To identify the general patterns of change in the chemical composition of the river waters, the relations between the hydrochemical and hydrological parameters were analyzed based on the following assumptions [7].

1. The change in the concentration of substance \( C \) in the river waters depending on the water runoff \( Q \) is approximately described by equation (1):

\[
\frac{dC}{dQ} = \frac{k_C}{k_Q} \frac{C}{Q},
\]

where \( k_C \) and \( k_Q \) are the values of specific rate of change in concentration of substance and water runoff, respectively; \( k_C \) is an exponential or power function of water temperature and/or flow rate [2]; \( k_Q \) is generally a nonlinear function of water runoff, although it is often used as a constant. Taking it into account in [7], the ratio of \( k_C \) and \( k_Q \) is given as a nonlinear function of water runoff (2), which allows obtaining (3) by integrating (1):
\[ \frac{k_C}{k_Q} = k_0 + k_1 \left( \frac{Q}{Q_0} \right)^{k_2}, \]  

\[ Y = X^{k_0} \cdot \exp \left( \frac{k_1}{k_2} \left( X^{k_2} - 1 \right) \right), \]  

where \( k_0, k_1, k_2 \) are empirical coefficients; \( Y = C/C_0 \) and \( X = Q/Q_0 \) are modulus coefficients of concentration and water runoff; \( C_0 \) and \( Q_0 \) are the expectations of concentration and water runoff; the expectations of \( Y \) and \( X \) are equal to one [7].

2. The expected concentrations of the studied substances are approximated by the geometric mean \( C_G \), on the basis that the water–rock system conditions can be generally described by equation (4):

\[ \Delta G_T = R \cdot T \cdot \sum_{i=1}^{N} \ln \Pi_i - \ln K_T^0, \]  

where \( \Delta G_T \) and \( K_T^0 \) are a general change in free energy of the system and the total equilibrium constant at a given temperature \( T \); \( \Pi_i \) is the total product of the component activities involved in each of the reactions; \( N_i \) is the number of chemical reactions. The equation (4) may be simplified to (5):

\[ \ln C_x \approx b_0 - \sum_{j} b_j \cdot \ln C_j, \]  

where \( b_0, b_j \) are constants. The concentration of the target substance \( C_x \) can be considered as a random variable, and the parameter \( N_i \) possesses generally quite large values. Taking it into consideration, it may be assumed that a normal probability distribution of \( \ln C \) with the mathematical expectation \( E(\ln C) \), which is calculated as the arithmetic mean of some \( N_p \) values of \( \ln C \) (\( N_p \) is a number of actually considered substances; as a rule, \( N_p < N_i \)). Accordingly, the probability distribution of concentration \( C \) can be roughly considered as lognormal with the expectation \( C_G \), which is confirmed by the statistical analysis [7]. Using the Taylor series decomposition and taking the expectation of water runoff equal to its arithmetic mean, we obtain the equation for the standard deviation \( \sigma(C) \):

\[ \sigma(C) \approx |k_0 + k_1| \cdot C_0 \cdot C \sigma(Q). \]  

3. Change in the value \( C_0 (C_G) \) can be roughly described by the equation (7) of substance dispersion mainly due to the advective transfer:

\[ \frac{1}{Q_0} \cdot \frac{\partial}{\partial x} \left( C_0 \cdot Q_0 \right) = -k_c \cdot C_0 \cdot \frac{w}{Q_0}, \]  

where \( w \) is the cross-sectional area of the current, \( x \) is the spatial coordinate. If the watershed with an area \( F \) may be represented as a part of the annulus inside the sector with radius \( L \) and movement of water masses from the arc inside the sector, then the equation (7) takes on form (8), and its analytical solution becomes the form (9):

\[ \frac{\partial C_0}{\partial x} + \left( \frac{1}{Y_0} \cdot \frac{\partial Y_0}{\partial x} + \frac{2 \cdot (L - x)}{L \cdot x - x^2} \cdot \eta \right) C_0 = 0, \]  

\[ C_0 = C_U \cdot \frac{Y_U}{Y_0} \left( \frac{F_U}{F_0} \right) \eta, \]  

where \( Y_0 \) is the expectation of water runoff depth, mm; \( C_U \) and \( Y_U \) are the expectations of substance concentration and water runoff depth in the headwaters of the river (the watershed area without the delineated channel with an area \( F_U \)); \( \eta = 1 + \frac{k_y \cdot k_c \cdot T}{a} \), where \( k_y \) is a coefficient of transition from the runoff depth to the nominal mean depth of the current; \( a \) is a coefficient of dimension; \( T \) is a calculation period [11].
The research [12] proposed to describe the runoff on a basis of the Schreiber formula:

\[ Y_0 = \mu \cdot H_0 \cdot \exp \left( -\frac{E_0}{H_0} \right) \left( 1 + \frac{C_{VH}^2 \cdot E_0^2}{2 \cdot H_0^2} \right), \]

(10)

\[ \mu = k_{y,1} \cdot k_{y,2} \cdot \left( f_p + 1 \right)^{y,3} \cdot \left( f_M + 1 \right)^{y,4}, \]

(11)

\[ k_Z = \begin{cases} Z_b - 500, & Z_b > 500 \\ 1, & Z_b \leq 500 \end{cases}, \]

(12)

where \( Y_0 \) is the mean annual water runoff depth, mm/year; \( H_0 \) - the mean total annual depth of water income from liquid atmospheric precipitation, snow and ice melt; \( C_{VH} \) is the variation coefficient of the total annual depths of water; \( E_0 \) is the mean annual value of potential evaporation, mm/year; \( \mu \) is a function of the physiographic conditions influence on the water runoff; \( Z_b \) is the mean altitude of the watershed, m; \( f_p \) is the proportion of swamped area in the watershed, \%; \( f_M \) is the proportion of forested area in the watershed, \%; \( k_{y,1}, k_{y,2}, k_{y,3}, k_{y,4} \) are the empirical coefficients (the value \( k_{y,4} \) is usually negative). It allows eliminating time-consuming work of defining water runoff depth and making (9) become the form:

\[ C_0 = C_U \cdot \frac{\mu_U}{\mu} \left( \frac{F_U}{F} \right)^{\eta} \]

(13)

where \( \mu \) and \( \mu_U \) are the functions of the physiographic conditions influence on the water runoff in the watershed in question as a whole and its top part without the delineated channel network, respectively.

The model (3), (6), (9), (13) was tested using the joint hydrological and hydrochemical monitoring observational data, mainly in the basins of the Ob, Yenisei (Central Siberia) and Hồng Hà (Vietnam) rivers. In particular, the parameters of the equation (3) were obtained for the 28 medium-sized rivers in the Ob river basin: \( k_0 = -0.376 \pm 0.011; \ k_1/k_2 = -0.010 \pm 0.002; \ R^2 = 0.63 \). A fragment of the relation between the \( Y \) and \( X \) values is presented in Figure 1. The most part of it corresponds to the relationship: \( \ln Y = (0.348 \pm 0.009) \cdot \ln X \), which characterizes the reduction of dissolved salts with an increase in the water runoff [7]. Analysis of the equation (3) showed that the most significant changes in the chemical composition of water are located within the range of water runoff 0.5–1.0 \( \text{l s}^{-1} \text{ km}^2 \) taking into account the specificity of landscape zones. Thus, the changes of more than 5% are connected to modules of water runoff less than: 0.03 \( \text{l s}^{-1} \text{ km}^2 \) in forest steppe; 0.05 \( \text{l s}^{-1} \text{ km}^2 \) in taiga; 0.04 \( \text{l s}^{-1} \text{ km}^2 \) in highland areas (Figure 2). This suggests that the underlying chemical reactions and physicochemical processes that define the basic features of the chemical composition of water are determined at the stages of formation of surface, subsurface and underground flow. In turn, they quite often correspond to the initial section of the curve of relation between the \( Y \) and \( X \) values (Figure 1) when there is an increase in the total dissolved salts with a rise in water runoff. For example, it is specific for the Aktru River, the flow of which is formed in the mountain-glacial region of the Altai.

At the stage of channelled runoff a list of these reactions, apparently, changes depending on the water velocities (e.g. within a year), but not so much. Moreover, the flow velocity in turn depends on the roughness and slopes of the surface (taking into account the typical values of these parameters for different landscape zones). As a result, if the water runoff module is fixed in a taiga zone, the water travel time and, therefore, the list of reactions and dissolved salts content in river water will be greater than the corresponding values in the highland taiga areas (due to smaller slopes) and less than in forest tundra and tundra (due to lower roughness of the watershed surface). It should be noted that almost equal flow travel time (in other words, the basic chemical reactions) may be determined by a combination of different factors, and no matter taken individually or together, they are in general random variables. Accordingly, the random variable is the substance concentration that, on the one hand, leads to the formation of blurred boundaries between the landscape zones and hydrochemical year seasons, and on the other, justifies application of the statistical distribution parameters for assessment of water quality, modelling, prediction and regulation of the rates of permissible impact on the water objects, but not single values of hydrochemical parameters. An example of such indicators is...
the geometric mean, which, taking into consideration (9)–(13), in general depends on the geochemical state of the watershed (particularly its part in the headwaters of the rivers, where there is no permanent channel network), and the intensity of water exchange that determines the time and nature of the interactions in the water-rock system. If the geometric mean is estimated for a statistically homogeneous sample after eliminating extreme values (not typical for the studied conditions), it can be used as a “geochemical background” of the investigated water object or its part: in the presence of the predominantly natural factors of conditional equilibrium state formation (4), (5) – as “natural background”; and in the presence of the natural and anthropogenic factors – as “natural-anthropogenic background”.

The feasibility of this definition is confirmed by comparing the geometric means of the total main ions in water of 28 medium-sized Siberian rivers and the results of the thermodynamic modeling using the Solution software complex [4, 7]. The mean values of pH, water temperature, and concentrations of Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, HCO$_3^-$, SO$_4^{2-}$, Cl$^-$, Si, Fe, fulvic and humic acids are taken as the initial water composition. As a result, the total main ions $C_{eq}$, which correspond to the minimum Gibbs energy in the system (4), are the closest to the geometric mean ($C_{eq}=(0.840\pm0.010)\cdot C_g$; $R^2=0.91$). Deviation of hydrochemical parameters from the background values (the geometric means) also depends on the water runoff and hydrological regime that determine the parameters of the release, transport and concentration of chemical elements and their compounds (Figure 1, 2). A numerical parameter of these deviations is the standard deviation, which increases (according to the formula (6)) with a rise in the geochemical background values and variation of water runoff. Another factor such as conjugation within the watershed river network with tectonic disturbances also plays an important role here. This parameter may be estimated by the difference $P(rf)-P(r)\cdot P(f)$, where: $P(r)$ is the density of the river network (as the probability of the channelled surface waters movement); $P(f)$ is the density of tectonic disturbances within the watershed; $P(rf)$ is the joint probability of the river network and tectonic disturbances [7].

4. Conclusions
The concentration of the dissolved substance in the water environment is determined by a combination of different factors, and no matter taken individually or together, they are in general random variables. Accordingly, the substance concentration in the river water is the random value. Analysis of observational data for the Siberian rivers has shown that variations in the hydrochemical parameters are well matched by the lognormal probability distribution. The expected concentrations of the substance are approximated by the geometric mean and considered as the background value, which reflects the conditional equilibrium state of the water–rock system in the statistically homogeneous conditions. The higher geochemical background is determined if the following conditions occur: 1) the smaller the intensity of water exchange; 2) the greater the relative area of the watershed without the delineated channels ($F_u/F$); 3) the closer the relation between the location of the river network and
tectonic disturbances (the higher the value $P(rf)=P(r)*P(f)$). The standard deviation increases with a rise in the geochemical background and variation of water runoff. Accordingly, the variability of the chemical composition and elevated concentrations of some substances will be more likely to occur due to inter- and intra-annual runoff variability. Therefore, the main features of the water chemical composition are formed at the stages of the surface, subsurface and underground runoff formation. At the stage of the channelled water flow, changes in water chemistry also occur, but to a lesser degree. They are associated with changes in the time and nature of the interactions in the water–rock system and the proportion of water masses formed as the channel, surface, subsurface and underground flows.

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