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Humic Acids and Their Migration Forms in the Waters of the Lakes of Eastern Transbaikalia

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Abstract

Results of the quantitative chemical analysis of waters in the lakes of the Onon-Borzya, Ingoda, Torey and Ivano-Arakhley limnic systems in Eastern Transbaikalia are systematized and analyzed. The content of humic acids in the waters under investigation was determined to vary within a broad range. Statistical interrelations between the determined concentrations of humic acids and the major physicochemical parameters of the medium were established. An increase in the concentrations of humic acids and fulvic acids is observed with an increase in pH, total dissolved solids (TDS), chemical oxygen demand, the content of carbonate, sulphate, nitrate ions, sodium and total phosphorus, while a decrease is observed with an increase in the redox potential (Eh). Taking into account the chemical composition of waters, thermodynamic calculations were carried out using MINTEQ software, and the major migration forms of humic acids were determined. It was revealed that humic and fulvic acids are present in lake water mainly in the anion and molecular forms, and in compounds with calcium and magnesium ions. The application of the Stockholm Humic Model (SHM) in thermodynamic calculations allowed us to establish the formation of the complexes of humic acids of different denticity with other metals, however, their content is insignificant for each element separately in comparison with the other forms of migration of the organic matter. Definite dependencies were demonstrated between migration forms and the characteristics of the environment. Molecular and anion forms of humic acids exhibit multidirectional correlations with TDS and pH. An increase in Eh of the system leads to inverse correlations with the molecular and anion forms in comparison with pH and TDS. It is stressed that all the established dependencies are interrelated with the properties of humic acids and their compounds with metals, mineralization and humification of organic substances, the formation of secondary minerals, and the types of studied waters.

Keywords: lakes, humic acids, migration forms, thermodynamic calculations

INTRODUCTION

Organic matter is widespread in nature and appears to be the inherent part of the hydrosphere and lithosphere of our planet [1–6]. Organic matter in natural waters is represented by a very complicated multicomponent system with an enormous number of individual chemical compounds [7–10]. The formation of the compounds of chemical elements with the organic matter of

natural waters is a widespread and generally recognized geochemical phenomenon, which acts as one of the most essential natural functions in controlling migration fluxes of metals. Many works of scientists in Russia and abroad have been published [11–16]. The overwhelming majority of the organic matter in aqueous ecosystems is represented by humic substances (HS); their percentage may reach 90 % of the total content of organic carbon [12, 17, 18]. This class of compounds,

in particular humus acids (HFA), which includes humic acids (HA) and fulvic acids (FA), hold special significance in the formation of joint complexes with metals because HA and FA are diverse and structurally randomized polyfunctional polyelectrolytes, which allows them to form colloid solutions and to enter ionic, molecular, oxidation-reduction, sorption and coordination interactions [15, 19–22].

For a more objective and integrated investigation of the migration processes of chemical elements, it is necessary to establish the forms in which HFA migrate in the aqueous objects of different landscapes and climatic conditions because it is still an urgent problem to predict their macroligand properties connected with the structure and functional features of FA and HA of different origins [20].

Thermodynamic calculations with the help of computer software complexes based on modern models [23, 24] allow highly reliable determination of the migration forms of chemical elements and modeling of geochemical processes participated by the organic matter of humus nature in the hydrosphere.

In the present paper, we consider the behavior of FA and HA in the lakes of different limnic systems of Eastern Transbaikalia depending on the chemical composition of water.

The major goal of the work was to carry out thermodynamic calculations in order to determine the migration forms of HFA in the lakes of Eastern Transbaikalia and to study their interrelations with different physicochemical characteristics.

EXPERIMENTAL

Objects of investigation

Samples were collected from 91 lakes during the years 2015–2019. The total number of water samples was 110. The objects under investigation spatially belong to the Ingoda, Onon-Borzya, Torey [25] and Ivano-Arakhley [26] lake systems in Eastern Transbaikalia.

Methods and procedures used in the chemical investigation

Sampling was carried out with special sampling devices into the vessels prepared according to the requirements [27]. Chemical analysis was carried out using generally accepted methods in

the certified Laboratory of Geoecology and Hydrogeochemistry at the Institute of Natural Resources, Ecology and Cryology, SB RAS (Chita) according to procedures with error norms corresponding to the standard [28]. The major cations in water were studied by means of atomic spectrometry: calcium, magnesium (atomic absorption spectrometry in flame); sodium, potassium (flame emission spectrometry). Titration was used to determine the permanganate value (chemical oxygen demand) and the concentrations of major anions: CO_3^{2-} and HCO_3^- (potentiometric titration); SO_4^{2-} (titration with the solution of BaCl_2 in the presence of metal indicator nitchromazo), Cl^- (argentometry). For low SO_4^{2-} content in waters under investigation, turbidimetry was used, while the low concentrations of Cl^- were determined by means of mercurimetric titration. Hydrogen ion exponent (pH), oxidation-reduction potential (Eh), the concentrations of F^- and NO_3^- were determined by means of potentiometry. The content of silicon, phosphorus, NO_2^- , NH_4^+ , S^{2-} , as well as chemical oxygen demand (COD) were determined using photometry. The total content of organic carbon (C_{org}) was estimated from oxygen demand with respect to dichromate-caused oxidation (COD) [29]. The concentrations of HA and FA were determined separately from the same sample according to the procedure described in [29]. After the sample was concentrated for the determination of HFA, the samples were treated with potassium pyrophosphate to separate HA from FA for their further determination by means of photometry at two wavelengths. In addition, the concentrations of elements in the samples under investigation were determined by means of mass spectrometry with inductively coupled plasma (ICP-MS) in the certified Analytical Department of A. P. Vinogradov Institute of Geochemistry, SB RAS (Irkutsk).

The chemical composition of waters was studied using measuring tools: atomic absorption spectrophotometer SOLAAR M6 (Thermo Scientific, USA), high-resolution mass spectrometer with ionization in inductively coupled plasma ELEMENT 2 (Finnigan MAT, USA), single-beam spectrophotometer SPEKOL 1300 (Analytik Jena, Germany), analyzer of liquids Ekspert 001-3-0.1 (LC Ekoniks-Ekspert, Russia).

Statistical evaluation of the acceptability of results, control of their stability, as well as the procedures of analytical measurements and estimation of their uncertainty were carried out according to the international standardizing documents [30, 31].

Methods and means of thermodynamic investigation

The forms of HFA occurrence and the possibility for them to form complex compounds with inorganic components in waters were studied for all collected samples with the help of a MINTEQ software complex (version 3.1) [32] with the built-in database on stability constants for metal complexes with the organic matter of humic nature – Stockholm Humic Model (SHM) [33]. This model involves a discrete approach and electrostatic sub-model based on Stern theory. Parameters intended in SHM for the simulation of metal binding with HFA are: average radius of HA (1.8 nm) and FA (0.75 nm) molecules, the capacity of Stern layer (2 F/m²), the density of functional group distribution in HFA molecules (1.2 sp./nm²) and the equilibrium constant of the accumulation of screening counter-ions (100.8). Other parameters were calculated using experimental data [33]: the molar concentration (mol/g) of functional groups dissociating according to the acid type (carboxyl and phenol) and their dissociation constants; the specific surface area of HFA molecules (in m²/g), deduced from the assumptions concerning the geometry of dissolved and solid-phase HFA molecules, their radii and the density of functional group distribution; equilibrium constants for mono- and bidentate coordination of metal ions with HFA; an additional parameter depicting the fraction of HFA aggregated in gel-like structures – the gel fraction parameter (it is accepted to be equal to 1 for solid-phase HFA, while for dissolved species it is equal to 0.72).

Thermodynamic software MINTEQ with reaction constants built in it, the data on component concentrations and system parameters introduced into it, allows one to determine the ionic force of solution, activity coefficients and activities of system components, their molar ratios, the indices of water saturation with respect to different minerals, etc.

Thermodynamic calculations involved the concentrations of macrocomponents in water (Ca²⁺, Mg²⁺, Na⁺, K⁺, CO₃²⁻, HCO₃⁻, SO₄²⁻, Cl⁻, F⁻, Si), some microelements (Fe, Mn, Al, P, Cd, Zn, Pb, Cu, Co, Ni, As, Sr, Ba, U, Th), S²⁻, HA, FA, C_{org}, as well as pH and Eh of the system. The ratio of the active part of HFA in the processes of complexation and C_{org} were determined from the determined values of corresponding concentrations. Calculations were carried out for standard conditions.

RESULTS AND DISCUSSION

Quantitative chemical analysis

The results of quantitative chemical analysis revealed broad variability of the major physicochemical characteristics of waters in the studied lakes. Statistical data on the results of chemical analysis of lake waters are shown in Table 1; they are grouped in the selected types according to [34]. Separation on the basis of total mineralization (total dissolved solids, TDS) showed that there are 31 fresh-water bodies with TDS 0.083–0.938 g/L; other 79 water samples were characterized by increased salinity: brackish waters (44) with TDS 1.02–9.97 g/L, saline waters (30) – 10.1–49.0 g/L, brines (5) – 54.3–343.2 g/L.

In fresh water reservoirs, pH varies within the range 6.90–8.94, with the average value equal to 7.82. The content of major cations varies within the ranges, mg/L: Ca²⁺ 9.06–53.1 (the average value over the set of samples is 26.6); Mg²⁺ 3.23–59.5 (13.3); Na⁺ 5.66–215.8 (51.2); K⁺ 0.35–16.6 (5.52). Anions were detected in the amounts, mg/L: HCO₃⁻ 58.6–508.1 (average 219.1); SO₄²⁻ 1.0–162.9 (25.9); Cl⁻ 1.55–209.3 (22.8); F⁻ 0.12–7.74 (1.13). In addition, for five fresh-water lakes with pH above 8.3, CO₃²⁻ content within the range of 6.0–39.0 mg/L (average 18.1 mg/L) was established. As far as HS are concerned, the following ranges of carbon concentration in the organic matter were established for the lakes of this type, mg C/L: for HA, 0.02–0.64 (average 0.22); for FA, 0.52–31.3 (5.74). The minimal values were those determined for the surface layer of the Arey lake (pH 7.90, TDS 0.19 g/L); the maximal ones were those for the Solontsovoye lake (pH 7.52, TDS 0.11 g/L). Both objects belong to the Ingoda lake system.

Among the studied waters with TDS more than 1 g/L, soda lakes with pH > 9 in the amount of 69 are prevailing. In these lakes, pH values vary within the range 9.0–9.93, with the average value equal to 9.43. The cation composition of the lakes of this type is dominated by sodium (224.4–124 800 mg/L, the average value over the whole set of samples is 7043 mg/L). The content of other cations is small in comparison with sodium, mg/L: Ca²⁺ 2.72–182.1 (average 18.2); Mg²⁺ 1.08–395.2 (61.0); K⁺ 3.7–1467 (110.3). The major anions in this type of water are present in substantial concentrations, mg/L: HCO₃⁻ 41.1–11 041 (average value is 2334); CO₃²⁻ 6.0–16 140 (1901); SO₄²⁻ 36.0–62 340 (3330); Cl⁻ 13.2–133 740 (6317); quite contrary, F⁻ content in them is incomparably

TABLE 1

Statistical data on the physicochemical parameters of lake water samples

Parameter	Water type		
	Fresh (<i>n</i> = 31)	Saline, pH > 9 (<i>n</i> = 69)	Saline, pH < 9 (<i>n</i> = 10)
pH	<u>6.90–8.94</u> 7.82	<u>9.00–9.93</u> 9.43	<u>7.60–8.99</u> 8.56
Eh, mV	<u>(–90)–(+289)</u> 147.2	<u>(–128)–(+209)</u> 67.3	<u>64–125</u> 94.1
M, g/L	<u>0.083–0.938</u> 0.369	<u>1.02–343.2</u> 21.1	<u>1.68–37.7</u> 11.8
mg O/L			
PO	<u>2.42–37.2</u> 13.5	<u>4.16–460.6</u> 68.5	<u>5.25–65.5</u> 31.0
COD	<u>9.50–126</u> 41.7	<u>13.0–4350</u> 315.1	<u>17.0–182.6</u> 93.6
mg C/L			
C _{org}	<u>3.56–47.3</u> 15.7	<u>4.88–1631</u> 118.2	<u>6.38–68.5</u> 35.1
HA	<u>0.02–0.64</u> 0.22	<u>0.03–13.8</u> 1.42	<u>0.02–2.81</u> 0.66
FA	<u>0.52–31.3</u> 5.74	<u>2.23–172.3</u> 30.0	<u>0.18–26.9</u> 9.86
mg/L			
CO ₂	<u>1.32–34.8^a</u> 7.99	–	22.7 ^b
CO ₃ ^{2–}	<u>6.0–39.0^c</u> 18.1	<u>6.0–16 140</u> 1901	<u>4.8–348.0^d</u> 65.4
HCO ₃ [–]	<u>58.6–508.1</u> 219.1	<u>41.1–11 041</u> 2334	<u>216.6–1696</u> 713.7
SO ₄ ^{2–}	<u>1.0–162.9</u> 25.9	<u>36.0–62 340</u> 3330	<u>80.0–7580</u> 2004
Cl [–]	<u>1.55–209.3</u> 22.8	<u>13.2–133 740</u> 6317	<u>79.1–22 334</u> 4807
F [–]	<u>0.12–7.74</u> 1.13	<u>0.49–414.0</u> 22.5	<u>0.36–7.74</u> 2.60
Ca ²⁺	<u>9.06–53.1</u> 26.6	<u>2.72–182.1</u> 18.2	<u>5.0–109.3</u> 42.9
Mg ²⁺	<u>3.23–59.5</u> 13.3	<u>1.08–395.2</u> 61.0	<u>11.9–333.2</u> 100.8
Na ⁺	<u>5.66–215.8</u> 51.2	<u>224.4–124 800</u> 7043	<u>313.4–13 835</u> 4017
K ⁺	<u>0.35–16.6</u> 5.52	<u>3.7–1467</u> 110.3	<u>13.9–247.9</u> 68.8
NO ₃ [–]	<u>0.20–9.60</u> 2.08	<u>0.75–1237</u> 65.4	<u>1.92–142.0</u> 43.7
NO ₂ [–]	<u>0.01–0.44</u> 0.13	<u>0.01–19.1</u> 1.71	<u>0.01–4.27</u> 0.84
NH ₄ ⁺	<u>0.19–1.90</u> 0.80	<u>0.09–100.3</u> 3.27	<u>0.02–7.87</u> 1.97
Si	<u>0.49–9.05</u> 3.15	<u>0.50–15.7</u> 3.07	<u>0.97–17.8</u> 4.59
P _{tot}	<u>0.05–1.93</u> 0.18	<u>0.05–12.8</u> 2.14	<u>0.05–2.85</u> 0.83
S ^{2–}	<u>0.06–0.40</u> 0.21	<u>0.03–223.0</u> 15.7	<u>0.05–278.5</u> 46.6
μg/L			
Al	<u>3.68–3109</u> 166.6	<u>2.32–8578</u> 537.8	<u>10.1–994.8</u> 190.6

TABLE 1 (End)

Parameter	Water type		
	Fresh (n = 31)	Saline, pH > 9 (n = 69)	Saline, pH < 9 (n = 10)
Mn	<u>1.50-435.1</u> 45.5	<u>0.10-4049</u> 127.9	<u>0.94-789.9</u> 111.3
Fe	<u>16.4-2446</u> 390.2	<u>3.64-3661</u> 522.2	<u>11.2-983.3</u> 271.3
Co	<u>0.03-1.47</u> 0.28	<u>0.01-109.4</u> 4.45	<u>0.20-14.9</u> 2.52
Ni	<u>0.21-15.8</u> 6.12	<u>1.30-248.1</u> 27.6	<u>1.36-24.5</u> 10.7
Cu	<u>0.47-93.6</u> 26.4	<u>1.19-437.6</u> 54.5	<u>4.12-236.3</u> 52.7
Zn	<u>2.05-330.7</u> 59.2	<u>0.78-791.9</u> 79.9	<u>3.43-231.2</u> 76.0
As	<u>0.59-76.5</u> 11.2	<u>4.44-6337</u> 588.4	<u>11.3-843.5</u> 166.7
Sr	<u>117.7-900.1</u> 351.1	<u>47.2-9194</u> 811.5	<u>197.4-7222</u> 1736
Cd	<u>0.05-3.55</u> 0.68	<u>0.07-587.1</u> 12.2	<u>0.18-6.65</u> 2.20
Ba	<u>9.00-70.0</u> 30.2	<u>4.98-1773</u> 74.3	<u>22.0-221.0</u> 64.7
Pb	<u>0.11-44.9</u> 4.26	<u>0.09-165.1</u> 8.43	<u>0.23-13.7</u> 4.02
Th	<u>0.002-0.64</u> 0.05	<u>0.003-209.3</u> 4.88	<u>0.02-2.67</u> 0.37
U	<u>0.04-10.9</u> 1.56	<u>2.27-10 855</u> 503.3	<u>0.88-456.2</u> 82.1

Notes. 1. n – number of samples. 2. M – TDS in water; PO – permanganate oxidizability of water. 3. Numerator – the range of values, denominator – average value. 4. Dash means the absence of a component.

^a A set of 26 samples.

^b The parameter value exceeding the detection limit was established for one sample among the entire set of samples from the lakes of this type.

^c A set of 5 samples.

^d A set of 9 samples.

small – 0.49–414.0 mg/L (average value 22.5 mg/L). The content of HA in the waters of this type of lakes varies within the range, mg C/L: HA 0.03–13.8 (average value is 1.42); FA 2.23–172.3 (30.0). The minima of HFA concentrations were detected in the Kholvo-Torum-1 lake (Onon-Borzya system, pH 9.70, TDS 5.80 g/L), while the maxima were detected for the Grishkino lake (Torey system, pH 9.59, TDS 54.3 g/L).

Among the objects with increased salt content, lakes with pH < 9 may be distinguished, with prevailing anions Cl⁻ (79.1–22 334 mg/L, average 4807 mg/L) and SO₄²⁻ (80.0–7580 mg/L, average 2004 mg/L). The concentrations of the derivatives of carbonic acid in these lakes are several times lower than those of Cl⁻ and SO₄²⁻: HCO₃⁻ 216.6–

1696 mg/L (average 713.7 mg/L); CO₃²⁻ 4.8–348.0 mg/L (average 65.4 mg/L). Similarly to soda lakes, the dominating cation is Na⁺: 3134–13 835 mg/L (average 4017 mg/L). The content of other cations is low (see Table 1). For the lakes with increased TDS, pH varies within the range 7.60–8.99, with the average value equal to 8.56. The concentrations of HFA in the lakes of this type vary within the ranges, mg C/L: HA 0.02–2.81 (average 0.66), FA 0.18–26.9 (average 9.86). The minimal HA content was detected for the Kunkur lake (pH 8.80, TDS 2.03 g/L), while the minimal FA content was detected for the Gorbunka lake (pH 8.49, TDS 6.85 g/L). Both lakes relate to the Onon-Borzya system. The maximal concentrations of HA and FA were determined for the Barun-Shivertuy lake (pH 8.32, TDS 16.9 g/L) of

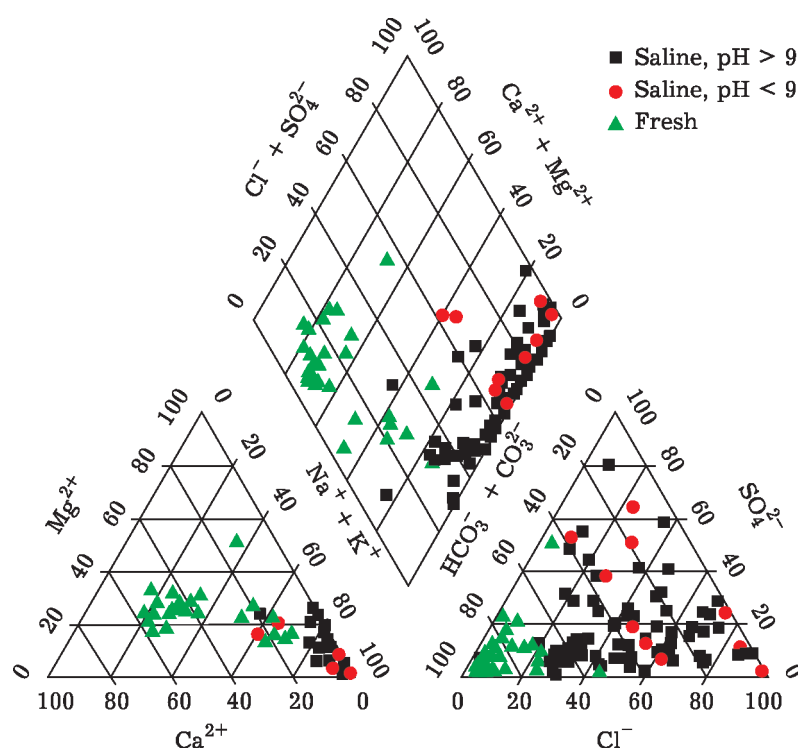


Fig. 1. Piper diagram with the results of quantitative chemical analysis of the macrocomponents for lakes with the indication of water types (equiv. %).

the Toray lake system. It should be noted that the number of the lakes of this kind is insignificant (10).

The relations of equivalent content (in equiv. %) of the major ions with the types of waters under study are shown in the form of a Piper diagram in Fig. 1.

The concentrations of all microelements in the objects under consideration vary within several orders of magnitude [35]. The broadest range was detected for all types of lakes for aluminium, iron, manganese, zinc; in addition, the concentrations of arsenic and uranium vary in saline lakes within broad ranges (see Table 1).

The concentrations of biogenic elements also vary within broad ranges. In particular, the content of inorganic nitrogen over the entire set of 110 samples was determined to be within the ranges, mg/L: NO_3^- 0.2–1237, NO_2^- 0.005–19.1, NH_4^+ 0.02–100.3. Silicon concentration varies from 0.49 to 17.8 mg/L, and the values are quite comparable for the three distinguished types of lakes (see Table 1). Total phosphorus content (P_{tot}) in waters varies from 0.05 to 12.8 mg/L. Judging from average values, its content increases as a sequence of lakes: fresh (0.18 mg/L) → saline with pH < 9 (0.83 mg/L) → saline with pH > 9 (2.14 mg/L).

The value of COD varies for the set of samples within the range 9.5–4350 mg O/L, the concentration of organic carbon C_{org} varies from

3.6 to 1631 mg C/L. The oxidation-reduction potential Eh increases from –128 to 289 mV.

Analyzing the results of statistical data on the chemical composition of HS and taking into account three types of lakes, one may conclude that the concentrations of HA and FA, as well as C_{org} with respect to the average values increase as the sequence fresh lakes → saline lakes with pH < 9 → saline lakes with pH > 9 (see Table 1).

Analysis of the behavior of HFA in the objects under investigation shows that their content has definite statistical correlations with other parameters and components of water. Figure 2 shows a straight dependence of the concentrations of HA and FA on COD value characterizing the total content of organic carbon [29]. Pearson's linear correlation coefficients (r) between these components and COD are equal to 0.39 and 0.45, respectively. We also observe a trend to an increase in HFA concentrations with an increase in pH (see Fig. 2, b) and TDS (see Fig. 2, c). Similarly, the amount of HA and FA correlates with the concentration of major anions: with the sum of CO_3^{2-} and HCO_3^- concentrations (r is equal to 0.43 and 0.48, respectively); with SO_4^{2-} (r is equal to 0.23 and 0.31, respectively). As regards cations, the significant correlation is observed with sodium (r is equal to 0.20 and 0.26, respectively).

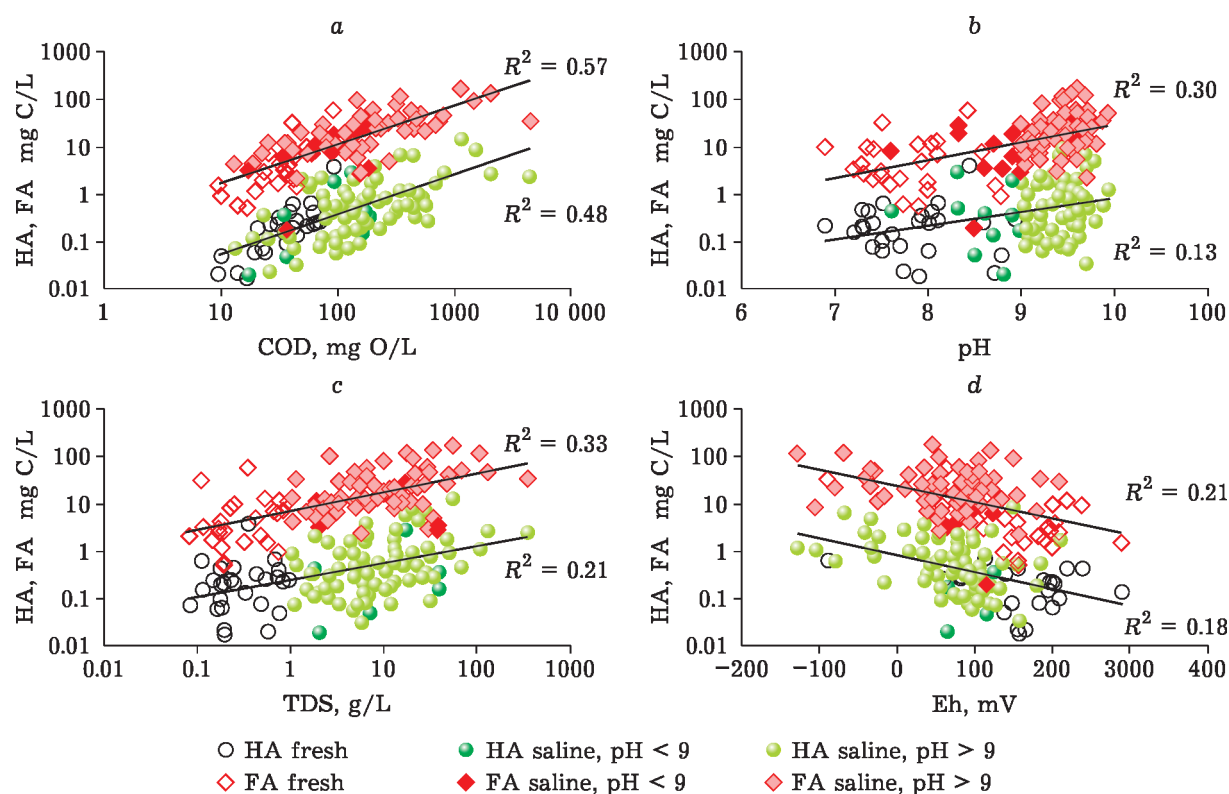


Fig. 2. Distribution of the content of humus acids (HA, FA) depending on the physicochemical parameters of lake waters: a – chemical oxygen demand (COD); b – pH; c – total dissolved solids; d – Eh. Here and in Fig. 3, 4: R^2 is the determination coefficient.

In addition, dependence was revealed between the concentrations of HFA and biogenic elements, namely phosphorus and some forms of nitrogen. For phosphorus, r values for HA and FA are 0.29 and 0.47, respectively; with NO_3^- – 0.19 and 0.23 m respectively.

The indicated dependences are due to a close correlation of HS with the inorganic compounds of carbon, nitrogen, sulphur, phosphorus, because all these compounds are inherent components of bioinert systems. An increase in the concentrations of HFA with an increase in the content of ionic derivatives of carbonic acid, NO_3^- , SO_4^{2-} and total phosphorus is connected with the fact that chemical elements incorporated into these anions act also as compulsory constitution elements of HS [36]. In turn, HA under the action of environment and biodestruction serve as one of the sources of these elements [37].

The dependence of HFA content on the value of oxidation-reduction potential (Eh) of the system is quite opposite by its nature: the concentrations of HA and FA decrease with an increase in Eh (see Fig. 2, d). Correlation coefficients r for them are equal to -0.25 and -0.33 , respectively. A decrease in HFA concentrations in water is ex-

plained by the transformation of organic components, which proceeds most intensely under oxidative conditions; this may be the evidence of the transition of HS into bottom sediments and humification or HFA mineralization to inorganic substances [5].

Thermodynamic calculations

It was established as a result of thermodynamic calculations carried out with the help of the MINTEQA software that under the given conditions HFA form compounds almost with all the considered metals but the major forms of their migration are anion and molecular, as well as compounds with calcium and magnesium ions. The statistical data on calculation results are presented in Table 2. One can see that the major prevailing forms of humus acids are the anions formed in water through the electrolytic dissociation of HFA:



where RH is an HFA molecule; R^- is an HFA anion.

According to the average values, the molar fractions of these forms increase as a sequence: fresh lakes $\rightarrow$ saline lakes with $\text{pH} < 9 \rightarrow$ saline

lakes with $\text{pH} > 9$. An inverse picture in this sequence is observed for molecular forms.

HFA in compounds with calcium and magnesium are present in smaller amounts. The average values of the molar fractions of HFA–Ca associates (summed up) decrease in the above-indicated sequence of lakes. For all HFA compounds with magnesium, somewhat different regularity is observed: the concentrations of complexes increase as a sequence: fresh lakes $\rightarrow$ saline lakes with $\text{pH} > 9 \rightarrow$ saline lakes with $\text{pH} < 9$.

As far as the structure of the coordination compounds of metals with the organic matter originating from humus is conserved, it is known that the HS of soil form chelate complexes with polyvalent cations [2, 36]. The structure of these compounds in natural waters has not been studied thoroughly by the present, but an assumption was made that these may be either chelate formations or other forms [18]. The presence of complex compounds of different denticity with two- and three-valent cations was established with the application of the SHM model. The formation of monodentate complexes proceeds according to generalized equations [33]:



The formation of bidentate coordination compounds may be also presented in the general form:



Results showed that monodentate organic complexes of HA are formed in the studied waters under given conditions in the amounts from 15 to 30 mol. % (over average parameters). For FA, the total content of all monodentate complexes is 12–22 mol. %. The model determined the presence of bidentate complexes in smaller amounts. The average values of their content for HA and FA are comparable (see Table 2).

The results obtained in thermodynamic calculations have statistical interrelations with the geochemical parameters of the environment, which is depicted in Table 3 and is shown in Fig. 3 for HA as an example. Thus, a strong negative correlation is observed between pH and the content of the molecular forms of HFA. In the case of the anion forms of HA, a trend to increase with an increase in pH is observed (see Fig. 3, a). This

TABLE 2

Major forms of humus acid migration in typified lake waters (mol. %). Statistical data according to MINTEQ

Designation of form	Migration form	Water type		
		Fresh	Saline, $\text{pH} > 9$	Saline, $\text{pH} < 9$
HA	Molecular form of humic acids	<u>16.88–23.31</u> 21.22	<u>7.03–16.37</u> 11.28	<u>13.21–22.61</u> 17.92
HA^-	Anion form of humic acids	<u>42.39–49.26</u> 45.04	<u>45.07–89.85</u> 69.09	<u>46.69–66.55</u> 56.50
HA–Ca	Compounds of humic acids with calcium ions	<u>9.46–27.47</u> 21.76	<u>0.21–17.62</u> 4.52	<u>2.14–21.17</u> 8.79
HA–Mg	The same, with magnesium ions	<u>4.16–20.49</u> 8.32	<u>0.06–24.12</u> 9.37	<u>6.64–18.34</u> 11.98
HA(1)–Me	Monodentate complexes of humic acids with metal ions, total amount	<u>27.62–32.05</u> 30.68	<u>0.22–30.83</u> 14.79	<u>15.47–29.22</u> 22.08
HA(2)–Me	Bidentate complexes of humic acids with metal ions, total amount	<u>0.37–7.43</u> 3.05	<u>0.38–13.06</u> 5.94	<u>2.02–9.23</u> 4.75
FA	Molecular form of fulvic acids	<u>14.69–22.76</u> 20.11	<u>6.66–14.83</u> 10.25	<u>12.60–21.30</u> 16.26
FA^-	Anion form of fulvic acids	<u>51.38–58.42</u> 54.06	<u>49.35–90.82</u> 73.16	<u>51.70–70.69</u> 61.85
FA–Ca	Compounds of fulvic acids with calcium ions	<u>7.33–20.53</u> 15.74	<u>0.17–12.78</u> 3.43	<u>1.98–17.88</u> 7.03
FA–Mg	The same, with magnesium ions	<u>3.16–16.13</u> 6.19	<u>0.30–23.30</u> 7.69	<u>5.07–15.90</u> 10.22
FA(1)–Me	Monodentate complexes of fulvic acids with metal ions, total amount	<u>19.69–24.38</u> 22.35	<u>0.15–26.68</u> 11.75	<u>11.39–24.81</u> 18.26
FA(2)–Me	Bidentate complexes of fulvic acids with metal ions, total amount	<u>0.48–8.58</u> 3.47	<u>0.06–14.38</u> 5.84	<u>2.19–9.11</u> 4.67

Note. The value range is indicated in numerator, the average value is in denominator.

phenomenon is explained by the good solubility of HA at higher pH due to the formation of soluble humates with monovalent cations, such as Na^+ [36]. A decrease in the fraction of the molecular form is due to an increase in the degree of dissociation of acid functional groups with an increase in pH [20]. Similarly, the formation of soluble fulvates with sodium cations leads to a decrease in the concentrations of the molecular form of FA and an increase in the concentrations of their ionic forms.

For HFA compounds with calcium cations, a decrease in the content of these associated with an increase in pH is detected (see Fig. 3, *a*), which may be connected with the competing processes: the formation of chemogenic calcite in alkaline waters [38]. The concentrations of HFA associates with magnesium cations do not have a clear correlation with this physicochemical parameter (see Table 3).

With an increase in TDS, correlations similar to those for pH values are observed for the indicated compounds (see Fig. 3, *b*), but the correlation dependence is pronounced weaker (see Table 3). Similarly to the previous case, these dependences are explained by the processes of the formation of HFA salts and carbonate complexes with the cations of alkaline metals, as well as secondary minerals, because saline lakes with $\text{pH} > 9$ dominate in the set of samples under consideration. It should be noted that the dependence of HFA complexation with magnesium ions on TDS

has a more clearly expressed negative nature than the dependence on pH because the formation of carbonate minerals with magnesium proceeds after the formation of calcite, when waters are characterized by higher salt content and alkalinity [39].

Considering the dependences of the content of all HFA migration forms on the oxidation-reduction potential of the system over the entire set of samples, we generally see the correlations that are opposite to those obtained for TDS and pH (see Fig. 3, *c* and Table 3), because an increase in Eh promotes humification [2, 5]. These dependences are connected with water saturation with calcium and magnesium, the formation of poorly soluble compounds of these metals with HA [36], the transformation of ionic forms into molecular ones and their transition into bottom sediments. An identical picture for the associates formed by FA that are soluble within the whole pH range may be connected with the genetic affinity of HFA [40], as well as with the fact that FA may be not only the products of HA transformation but they may also be their precursors [37].

Ion and donor-acceptor interactions between chemical elements and HFA in waters accompany each other, their mechanisms are very complicated and depend not only on the properties of metals but also on the properties of the entire set of substances in general, on their quantitative content and on the structural features of HS [15].

TABLE 3

Pearson's coefficients (*r*) of the linear correlation between the major forms of migration of humus acids and some physicochemical parameters of lake waters

Designation of form	Forms of migration	pH	M	Eh
HA	Molecular form of humic acids	-0.93	-0.37	0.52
HA^-	Anion form of humic acids	0.78	0.51	-0.56
HA-Ca	Compounds of humic acids with calcium ions	-0.87	-0.54	0.48
HA-Mg	The same, with magnesium ions	0.05	-0.29	0.22
HA(1)-Me	Monodentate complexes of humic acids with metal ions, total amount	-0.75	-0.50	0.56
HA(2)-Me	Bidentate complexes of humic acids with metal ions, total amount	0.41	-0.21	-0.02
FA	Molecular form of fulvic acids	-0.95	-0.34	0.52
FA^-	Anion form of fulvic acids	0.77	0.49	-0.55
FA-Ca	Compounds of fulvic acids with calcium ions	-0.87	-0.54	0.49
FA-Mg	The same, with magnesium ions	0.08	-0.22	0.17
FA(1)-Me	Monodentate complexes of fulvic acids with metal ions, total amount	-0.68	-0.49	0.53
FA(2)-Me	Bidentate complexes of fulvic acids with metal ions, total amount	0.32	-0.22	0.05

Note. M is TDS in water.

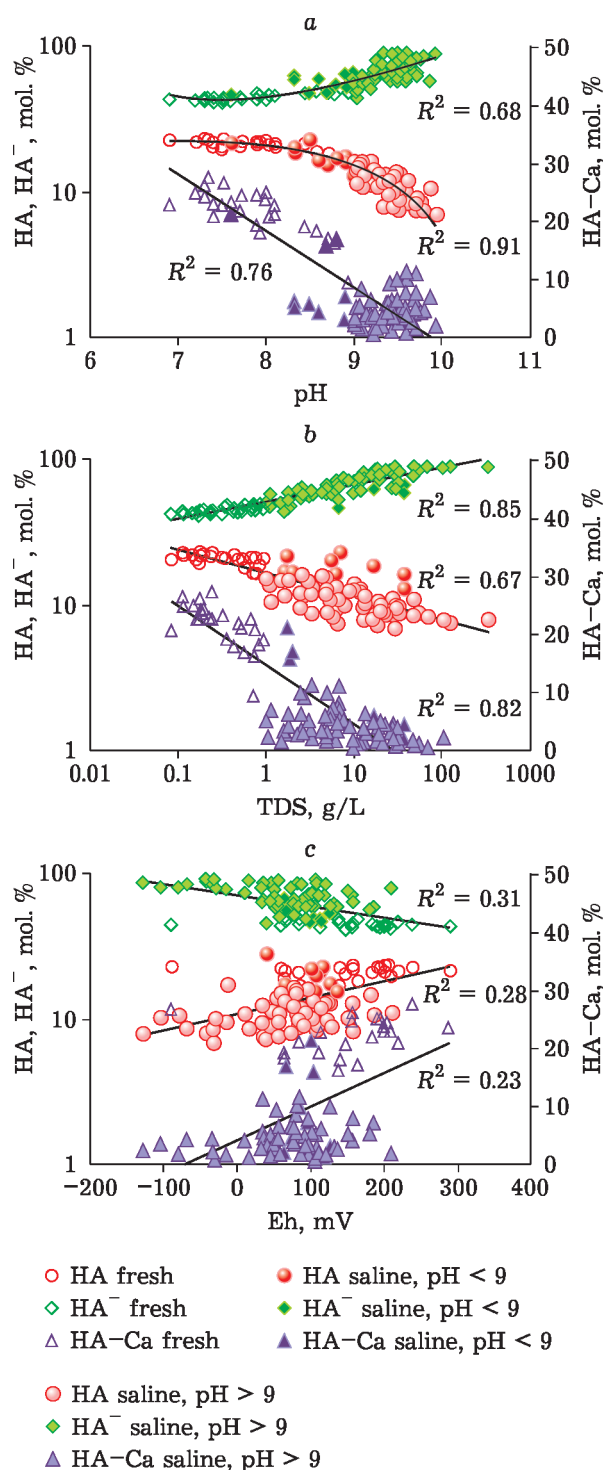


Fig. 3. Distribution of some migration forms of humic acids depending on the physicochemical parameters of lake waters: a - pH; b - total dissolved solids; c - Eh. For designations, see Table 2 and Fig. 2.

Because of this, the molar fractions of complex compounds of HFA with different structures, in turn, exhibit definite dependences on pH, Eh and TDS in waters (see Fig. 4). In particular, the content of monodentate complexes decreases

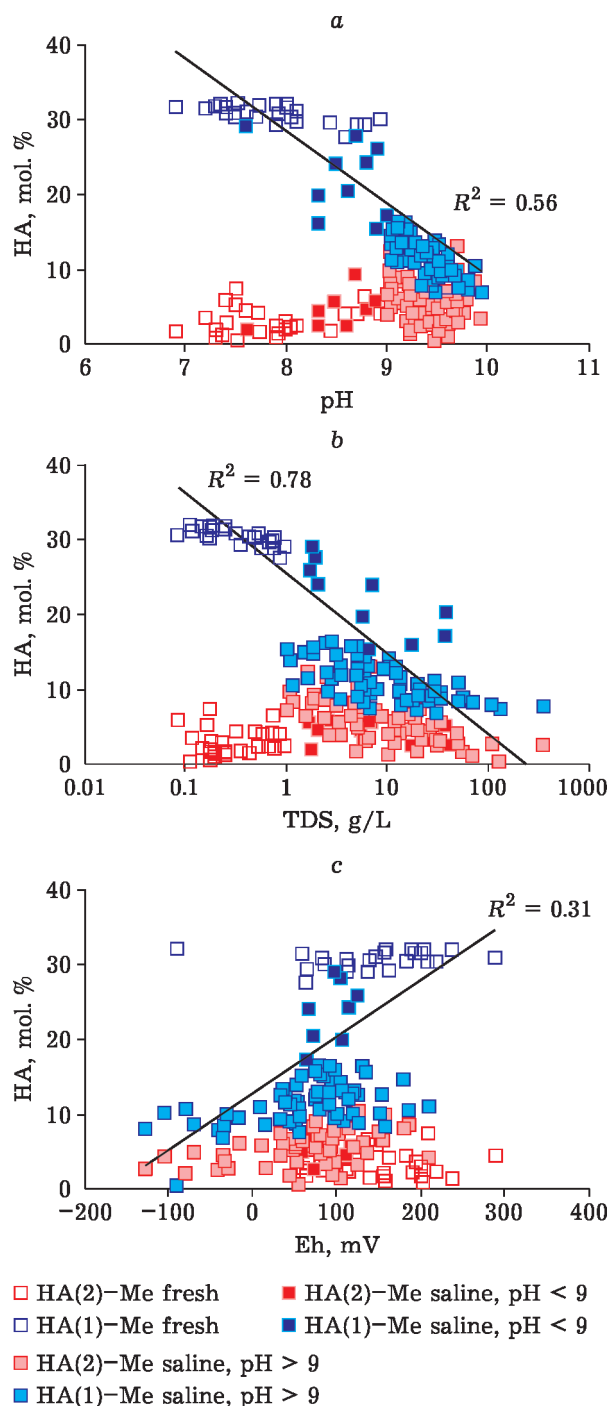


Fig. 4. Distribution of mono- and bidentate complexes of humic acids depending on the physicochemical parameters of lake waters: a - pH; b - TDS; c - Eh. For designations, see Table 2 and Fig. 2.

with an increase in pH and TDS, while, quite contrary, it decreases with an increase in Eh. The effect of physicochemical parameters on the formation of complexes is clearly demonstrated in agreement with the accepted water types by the

example of monodentate compounds (see Fig. 4). Bidentate complexes have positive but less clearly expressed correlations with TDS and pH, while any dependences on Eh are absent (see Table 3).

CONCLUSION

Chemical studies showed a broad variability of the content of components, parameters and properties of the studied lake waters from different limnic systems of Eastern Transbaikalia. Both fresh and saline lakes are distinguished among the studied objects. Over the entire set of samples, the number of saline lakes dominates ($\text{pH} > 9$), and the species dominating in the ion composition are CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-} , Na^+ . The range of HA content in all the studied lakes is 0.01–13.8 mg C/L, and FA content is an order of magnitude higher: 0.18–172.3 mg C/L.

The data obtained over the results of thermodynamic calculations using MINTEQ showed that HFA form the compounds with almost all metals that were taken into account by the model. The major forms of HFA migration in the studied waters turned out to be ion and molecular forms, as well as the compounds with calcium and magnesium. The formation of mono- and bidentate coordination compounds of HFA with metals was established by calculations; the amounts of these compounds with every element separately is insignificant with respect to the major forms of HS migration.

The established positive correlation dependences between HFA content and such parameters as pH, TDS, CO_3^{2-} , HCO_3^- , SO_4^{2-} , NO_3^- , P_{tot} content provide evidence of their close interactions and the transition of organic substances into inorganic ones, occurring in bioinert media. A negative correlation of HFA with an increase in Eh is caused by the favourable conditions for the transformation of organic components and provides evidence of the removal of HS from water into bottom sediments or their mineralization to inorganic components. Interconnections established between the content of the major forms of HFA and physicochemical parameters of waters are due to the acid properties of the former, the properties of their compounds with metals, as well as competitive processes of the formation of secondary minerals proceeding in the system, and the genetic affinity of HS. In addition, the associates of HFA with metals having specific structure may be present in different concentrations in dif-

ferent types of waters, which once more confirms the dependence of the formed complexes on the geochemical parameters of the medium.

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