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**EFFECT OF HUMIC SUBSTANCE COMPLEX FORMATION ON METAL
MIGRATION FORMS IN THE NATURAL WATERS OF THE NORTHERN
TAIGA AND FOREST-STEPPE ZONES IN THE TYUMEN REGION***

SUMMARY. The aim of this paper is to assess the effect of metal ion and humic substance complex formation on the metal form distribution in natural waters. To describe metal activity in the environment, the published data on conditional stability constant values of complexes are applied. A number of approaches to the assessment of metal ion complexing ability, metal ion toxicity and migration activity in natural waters are reviewed. The chemical characteristics of the waters in the northern taiga and forest-steppe zones are analyzed, and their effect on the metal form distribution is predicted. The calculations are performed taking into account the competitive reactions due to various cations and anions in the water system of the northern taiga and forest-steppe zones in the Tyumen Region. The obtained results are important for determining the toxicity in the case of metal ion pollution of waters and making adjustments to water quality standards (MAC) considering metal inactivation mediated by humic substances in the waters.

KEY WORDS. Humic substances, complex formation, forms of metal occurrence

Natural waters, as complex multicomponent heterophase polydisperse systems, are characterized by various forms of heavy metal (HM) occurrence in them [1-6].

Interactions between the components in waters are multi-various: hydrolysis, polymerization, formation of colloids and suspended matters, complex formation. These and many other reactions cause one of the main features of natural water composition — the occurrence of a number of coexisting chemical forms for each component [1-4]. Chemical forms of elements differ in migration activity, reactivity, and stability in natural waters.

Metal states in natural surface waters include different phases and biosystems; and metals rarely remain in one phase. The changes of physical and chemical conditions cause metal transition from one phase into another [1-4], [6-18]. Depending on the environmental conditions (pH, redox potential, ligand quantity, and other factors), metals exist in different oxidation states and are a part of

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various compounds. Moreover, all metals in the water phase tend to the equilibrium state in which metal forms coexist according to their physical and chemical properties.

Though the study of complex formation processes in metals with water humic substance (HS) does not give the complete picture of metal form distribution, it helps to predict the fraction of dissolved and colloidal forms of metals, and, consequently, the toxicity of waters. In the environment, the dissolved metal forms occur only in unpolluted waters with a low turbidity (the suspended matter concentration of less than 5.10 mg / l) [1-4], [9]. Truly dissolved metal forms are represented by free aqua-metal ions, ion pairs, organometallic and low-molecular organic compounds. Low pH and Eh values, small amounts of suspended matter, high concentration of HS [1-4], [10-18] facilitate the dissolution of metals and their existence in ionic forms.

Ionic forms of metals [6-8], as the most mobile and chemically active, are the most toxic ones. Therefore, abnormally acidic waters always contain many metal ions in large amounts. *Cr (III)* cations, for example, can only be transported and deposited in acidic waters with high alkalinity [5], [12-18]. It is possible to state that acidic and weakly acidic solutions with $\text{pH} < 6$ are favorable for the transportation of the majority of trace elements in the form of ions. Increasing pH reduces metal ion mobility due to sedimentation, as mentioned above.

Depending on the molecular weight, metal and HS complexes are exemplified by dissolved and colloidal forms, and, as mentioned above, each of them is characterized by a certain degree of stability. Stability changes of the HM and HS complexes are determined, first, by the physical and chemical properties of metals; second, by the quality of the organic component [12-13], and third, by the molecular HS weight [1-4], [9].

Reactant concentrations are significant for metal ion complex formation. In [9] some features of metal migration in soil waters are distinguished by means of mathematical modeling. It is stated that *Mn (II)* and *Cu (II)* migration is mainly determined by their organic compounds; the relation between mobile forms of *Pb (II)* and the humus content is high only in the reducing environment. Compounds of *Cr (III)* with organic matter are mobile and, therefore, they are removed from the soil into the water environment.

Summarizing the published data, we can state that one of the important processes determining the trace element migration ability in surface waters is the interaction of metal ion and water HS, which has a significant impact both on the mobility and the distribution of metals through forms.

The purpose of this research was to make theoretical investigations to determine the forms of metal occurrence in the natural waters of the forest-steppe and northern taiga zones on the results of detailed studies of the natural water bodies in the Tyumen Region. The following variables were used: metal ion concentration, amount of organic matter, pH, and inorganic anion concentration. The competitive reactions, mass balance, and electrical neutrality of the system were considered. The data on the conditional constants of metal and humic substance complexes were taken from [18] taking into account the character of humic substances. Some general variables influencing the metal distribution are given in Table 1; Table 2 shows the metal concentration in the natural waters.

Results and discussion. Each natural water body is a separate chemical system where the forms of metal occurrence are affected by many factors. The main factors include pH, HS, and chemical composition of natural waters. The occurrence of inorganic anions and cations in the systems impacts on the process of complex formation with HS due to competitive reactions. The analysis of the data published and our experimental and computational results also reveal the impact of the functional features of humic substances in different soils on the forms of metal occurrence.

The natural waters of the northern taiga zone are characterized by lower pH and total alkalinity (Table 1) than the waters of the forest-steppe zone. This affects the distribution of the metals prone to hydrolysis, such as aluminum, copper, nickel, as well as the formation of carbonate complexes of alkali-earth metal ions. In the natural waters of the forest-steppe zone (Table 4), the major part of the alkali-earth metals is bound in carbonate complexes; and in the waters of the northern taiga zone, the ionic forms of metal occurrence prevail. According to the data obtained, strontium, as a representative of the alkali-earth metals, is in its ionic form in the natural waters of these zones. The low concentrations of the alkali-earth metals in the natural waters of the northern taiga zone (Table 2) and the high concentrations of aluminum and iron ($> 100 \text{ mg / L}$) facilitate low binding of calcium and magnesium ions to humic substances, especially, when the organic matter content is less than 10 mg O / l .

Table 1

The general variables affecting the metal form distribution in the natural waters of the northern taiga and forest-steppe zones (n is the number of water bodies, the numerator is a minimum-maximum value, the denominator is an average value)

Zone	n	COD Mn, mg O/l	pH	Colour, °	Alk, µeq/l	SO ₄ , mg/l	Cl, mg/l
Northern taiga	6	<10	5.7-6.4 5.9	9.4-134 38.0	112-305 182	0.3-0.7 0.4	0.5-8.2 1.9
	11	10-20	5.1-5.5 5.3	36.5-62.0 50.5	80-132 119	0.3-0.7 0.4	0.3-3.3 0.9
	6	20-30	5.0-5.6 5.2	130.0-170.0 151.3	0-100 78	0.5-2.3 1.4	0.5-5.5 2.8
Forest-steppe	1	<10	8.8 8.8	21.3 21.3	6079 6079	34.0 34.0	155.5 155.5
	6	10-20	7.5-8.3 7.6	29.1-41.1 34.5	5845-713 6363	2.0-42.0 14.4	24.0-210.0 139.6
	4	20-30	7.6-7.9 7.9	31.0-89.0 44.8	7296-12304 8012	0.5-324.0 64.7	22.5-911.0 247.1

Table 2

The concentrations of some metals (Ca, Mg, mg/l; others, μ /l) in the natural waters of the northern taiga and forest-steppe zones (the numerator is a minimum-maximum value, the denominator is an average value)

Zone	COD Mn, mg O/l	Ca	Mg	Al	Fe	Cu	Ni	Co	Zn	Mn	Sr	Pb	Cr	Cd
Northern taiga	<10	0.8-1.6 1.7	0.2-1.5 0.7	6.5-30.0 19.7	92.6-150.0 111.4	0-4.5 2.8	0-9.0 5.2	0-0.1 0.1	0.2-1.0 0.5	0-2.0 1.0	0-14.0 8.6	0-7.7 7.7	0-0.3 0.2	0.0 0.0
	10-20	1.3-2.1 1.8	0.4-0.7 0.6	26.0-202.0 92.5	311.0- 1416.0 647.6	2.6-4.5 3.3	0-5.2 1.9	0-0.3 0.0	0-0.7 0.3	0-6.2 3.5	6.3-14.0 8.7	0-6.0 5.6	0.1-0.4 0.3	0.0 0.0
	20-30	2.1-2.9 2.5	0.6-0.9 0.7	50.2-204.0 126.0	112.0- 1416.0 758.7	0.2-7.6 2.1	0-1.2 1.0	0-0.15 0.2	0.1-1.7 0.7	0.1- 15.2 5.7	0.8-12.7 8.3	0-0.3 0.2	0.3-0.9 0.6	0-0.11 0.1
Forest- steppe	<10	27.5 27.5	34.5 34.5	55.9 55.9	40.7 40.7	5.7 5.7	4.0 4.0	0.0 0.0	6.7 6.7	4.3 4.3	3827.0 3827.0	8.7 8.7	0.8 0.8	0.0 0.0
	10-20	28.0-81.0 42.2	32.0-75.5 42.9	6.0-29.3 12.9	11.0-87.0 79.4	2.0-5.5 4.2	0.5-1.5 0.9	0.0 0.0	0.8-3.0 1.5	4.0-8.0 5.4	315.0-394.0 340.1	0-0.4 0.4	0.3-4.2 2.2	0-0.2 0.2
	20-30	27.0-35.0 41.0	8.0-35.5 38.4	6.7-21.2 14.3	45.0-147.5 74.3	4.0-5.0 4.6	0.5-5.0 1.5	0.0 0.0	0.1-3.5 1.4	1.1-24.0 7.4	343.5-700.0 392.2	0-1.0 0.4	1.2-14.2 3.5	0.0 0.2

Fe (III) and *Al (III)* ions are in high concentrations (more than 100 mg / l) in the natural waters of the northern taiga and forest-steppe zones (Table 2). The high binding of ions to humic substances in all studied water bodies should be noted (Table 3-4). *Al (III)* ions are less studied; it is impossible to compare our results with the works by other authors. It is known that *Al (III)* ions are able to form complexes with HS along with *Fe (III)* ions [6-8], but ion binding to HS can greatly vary because of different chemical composition of water bodies.

For example, in the natural waters of the forest-steppe zone (Table 4), the difference between the aqua ion and complex forms of *Al (III)* is more than 50-70%. The low concentrations of copper, zinc and lead ions (less than 2 mg / l) in the natural waters of the forest-steppe zone, according to Le Chatelier's principle, predominantly determine the aqua ion type of metal migration, but in the water bodies of the northern taiga zone, copper ion binding to humic substances is as high as 20%. Cadmium in the natural waters of the northern taiga and steppe zones is in an ionic form because of low conditional stability constants of the complexes [18] and a low cadmium content in the natural waters. The complex formation of nickel ions in some water bodies of the steppe and northern taiga zones in the condition of low competitive environment and the humus contents of more than 10 mg O/l is as high as 70%; this is the result of the low competition for the humic substances in these water bodies. *Mn (II)* in the natural waters of the Tyumen Region is in an ionic form; that can be explained by the low stability constants of the complexes and the low metal concentrations. *Cr (III)* in the natural waters is mainly in hydroxocomplexes and practically does not form compounds with humic substances.

After the analysis of the metal form occurrence, we can conclude that the great variability in the metal form distribution in natural waters is determined by the composition and concentration of trace elements and the features of humic substances. The chemical HS properties in natural waters depend on the soil properties in the reception basin, and, therefore, they have zonal particularities.

On the basis of metal form distribution, we can state that the hazardous properties of some metals, such as aluminum, iron, copper, occur in the natural waters with low humus content and high total alkalinity. The toxic properties of cadmium, lead, nickel and zinc occur over large amounts of iron, copper, and aluminum ions, i.e., if in the system there are strong competitors in the humic substance complex formation.

In natural waters, there are complex mechanisms of binding and distributing metal form occurrence, which are determined by the general chemical properties of waters including the whole complex of metal contents, as well as by the individual features of humic substances, rather than the properties of the metal ions. Each water system has a unique set of chemical components and HSs. The physical and chemical properties of metal ions, their contents and the concentrations of cations and anions cause specific trends in metal migration.

The metal form occurrence in the natural waters of the northern taiga zone
(the numerator is a minimum-maximum value, the denominator is an average value)

Metal	COD Mn, mg O/l	pH	M-HS	M-OH	M-SO ₄	M-Cl	M-HCO ₃	M ^{m+}
Ca(II)	<10	5.7-6.4 5.9	0-0.03 0.02	0	0-08 0	0 0	0-1.5 0.94	98.5-99.0 99.04
	10-20	5.1-5.5 5.3	0-0.02 0.02	0	0-07 0.01	0 0	1.3-1.4 1.36	98.6-99.0 98.62
	20-30	5.0-5.6 5.2	0-0.06 0.05	0	0-08 0	0 0	0-1.5 0.67	98.6-99 99.28
Mg(II)	<10	5.7-6.4 5.9	0-0.02 0.01	0	0 0	0 0	0-2 1.16	98-99 98.82
	10-20	5.1-5.5 5.3	0-99 9.01	0	0 0	0 0	0-1.5 1.03	0-99 89.97
	20-30	5.0-5.6 5.2	0-100 33.25	0	0 0	0 0	0-0.7 0.32	0-99 66.43
Fe(III)	<10	5.7-6.4 5.9	98-99.5 99.23	0.1-1.5 0.48	0 0	0-0.5 0.30	0 0	0 0
	10-20	5.1-5.5 5.3	99-100 99.84	0 0.10	0 0	0-0.2 0.06	0 0	0 0
	20-30	5.0-5.6 5.2	99-100 99.98	60-90 0.02	0 0	0-0.06 0.02	0 0	0 0
Al(III)	<10	5.7-6.4 5.9	0-85 15.17	0-99 37.68	0-05 0	0 0	0 0	0 0
	10-20	5.1-5.5 5.3	4-100 20.64	0-100 54.23	6 0	0 0	0 0	0 0
	20-30	5.0-5.6 5.2	3-100 31.66	0-100 16.25	3 0	0 0	0 0	0 0

Table 4

The metal form occurrence in the natural waters of the steppe zone (the numerator is a minimum-maximum value, the denominator is an average value)

Metal	COD Mn, mg O/l	pH	M-HS	M-OH	M-SO4	M-Cl	M-HCO3	M ^{m+}
Ca(II)	<10	8.8	0	0	6.0	0	46.4	47.9
		8.8			6.0		46.4	47.9
	10-20	7.5-8.3	0	0	5.2-6.4	0	6.0-77.3	17.3-88.0
7.6		5.9			38.7		55.4	
20-30	7.6-7.9	0	0	3.4-5.3	0	3.5-27.0	68.0-93.0	
	7.9			4.3		16.1	79.6	
Mg(II)	<10	8.8	0	0	0	0	100	0
		8.8			0		0	100
	10-20	7.5-8.3	0	0	0	0	9-100	0-90
7.6		0			0		75.0	25.0
20-30	7.6-7.9	0	0	0	0	5.5-39.0	61.0-95.0	
	7.9			0		0	24.0	76.0
Fe(III)	<10	8.8	97.0	0	6.0	2.3	0	0
		8.8	97.0	0	6.0	2.3	0	0
	10-20	7.5-8.3	78-99	0	0	0-22	0	0
7.6		92.0	0	0	7.3	0	0	
20-30	7.6-7.9	0-99	60-90	0-36.0	0-1	0	0	
	7.9	26.0	63.0	9.4	0.4	0	0	
Al(III)	<10	8.8	100	0	0	0	0	0
		8.8	100	0	0	0	0	0
	10-20	7.5-8.3	0-100	0-100	0	0	0	0
7.6		50	50	0	0	0	0	
20-30	7.6-7.9	0-100	0-100	0	0	0	0	
	7.9	25.0	25.0	0	0	0	0	

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