Mechanisms for Reduction of Natural Waters Technogenic Pollution by Metals due to Complexions with Humus Substances (Zoning: Western Siberia and the European Territory of Russia)

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Abstract. The article described the complexation of metal ions with humus substances in natural waters (small lakes). Humus substances as the major biochemical components of natural water have a significant impact on the forms and migration of metals and the toxicity of natural objects. This article presents the results of large-scale chemical experiments: the study of the structural features (zonal aspects) of humus substances extracted from soil and water natural climatic zones (more than 300 objects) in Russia (European Russia and West Siberia); the influence of structural features on the physico-chemical parameters of humus acids and, in particular, on their complexing ability. The functional specifics of humus matter extracted from soils is estimated using spectrometric techniques. The conditional stability constants for Fe(III), Cu(II), Pb(II), Cd(II), Zn(II), Ni(II), Co(II), Mn(II), Cr(III), Ca(II), Mg(II), Sr(II), and Al(III) are experimentally determined with the electrochemical, spectroscopic analysis methods. The activities of metals are classified according to their affinity to humus compounds in soils and water. The determined conditional stability constants of the complexes are tested by model experiments, and it is demonstrated that Fe and Al ions have higher conditional stability constants than the ions of alkali earth metals, Pb, Cu, and Zn. Furthermore, the influence of aluminium ions and iron on the complexation of copper and lead as well as the influence of lead and copper on complexation of cobalt and nickel have been identified. The metal forms in a large number of lakes are calculated basing on the experiments’ results. The main chemical mechanisms of the distribution of metals by forms in the water of the lakes in European Russia and West Siberia are described.

1. Introduction

Anthropogenic intake of metals ions in soil and water is a widespread phenomenon. Forms of finding metals in natural objects have varying degrees of toxicity. Especially dangerous are the ionic forms of occurrence for most metals.

A unique feature of metals distinguishing them from other pollutants is their potential toxicity and bioavailability in the environment depend to a large extent on their speciation [1–4]. In natural waters, metals migrate as free hydrated ions, complexes with organic and inorganic ligands, and compounds sorbed on the surface of solid mineral and organic particles.
The speciation of a metal is controlled by the conditions of the water systems: pH, concentration of various ligands, size and amount of suspended particles, etc. [3]. The prediction of biological activity (accumulation and toxicity) is based to some extent on the knowledge of equilibrium conditions in solutions and physicochemical properties of metal ions. The biological activity of a metal is defined as its ability to penetrate and accumulate in living organisms, as well as associated toxic effects [1-4]. For instance, the investigation of metal complexation showed that biological uptake and toxicity are in essence chemical processes: metal ions react with functional groups (sulphhydryls, amines, carboxyls, hydroxides, and oxides) on the surface of cells, in membranes, enzymes, etc. [5].

The metal ions in natural waters are capable of complexing with the anions of organic and inorganic nature. The most important organic anions, which make the largest contribution to the inactivation of most metals ions - humus substances (HS), extracted from the soil. Their concentration in the surface water is in the range of 1-100 mg / l and due to the specific structure of these compounds to possess excellent makroligands properties (Figure 1).

In order to investigate structure of humus-fulvic-acid (HFA) used and applied various analytical and physicochemical methods. For example, by NMR spectrometric analysis identified contents of elements in the Humus component (Table. 1.) of different soils. Reduction of acid groups and phenolic groups from the organic horizons to mineral may be explained by molecular microbiological degradation of FA and cleavage of the carboxyl groups. Phenolic fragments are more resistant to degradation and consequently accumulate in the structure of the photonic crystal. In contrast, less oxidized black soil, the main group is phenol fragment.

There are two main sources of the HS migration in surface water [3-6].

1) leaching, and soil humus elastic oxidation of other organic substances;
2) synthesis of HA and FA in the reservoir due to enzymatic degradation of aquatic organisms

In the territory of Russia are widespread colored water with high concentrations of humus substances due to the nature of formation waters [6]. Increased concentrations of Fe(III), Al(III), Mn(II) due to humification watersheds are characteristic of feature of the natural objects chemical composition.

![Figure 1. Structure of humus acid [1]](image1.png)
The study of complexation in each natural object is a problem that requires a generalization of contradictory data in the literature, extensive experimental studies, mathematical calculations and accounting for many natural factors. An important task of our time is to develop methods that allow based on water chemistry to predict the speciation of metals and toxicity level of water.

### Table 1. The elemental composition of Humus components (wt.%)

| Components and soil | C   | H   | N   | O   | H/C | O/C |
|---------------------|-----|-----|-----|-----|-----|-----|
| Humic Acid (HA) sod-podzolic and gray forest soils |     |     |     |     |     |     |
| sod-podzolic soils (forest) | 51.1 | 4.2 | 5.2 | 39.4 | 1.0 | 0.6 |
| gray forest soils (forest) | 49.2 | 4.3 | 5.0 | 41.5 | 1.0 | 0.6 |
| gray forest soil (arable) | 48.3 | 4.2 | 4.8 | 42.7 | 1.0 | 0.6 |
| HA of black soil |     |     |     |     |     |     |
| black soil pratense | 54.3 | 3.9 | 4.6 | 37.2 | 0.9 | 0.5 |
| the typical black soil | 54.8 | 3.5 | 4.0 | 37.8 | 0.7 | 0.5 |
| pratense-gley black soil | 54.9 | 4.0 | 2.6 | 38.5 | 0.9 | 0.5 |
| Humus Substances of natural waters |     |     |     |     |     |     |
| r. Moscow | 51.2 | 4.9 | 1.6 | 42.3 | 1.2 | 0.6 |
| r. Istra | 52.7 | 5.0 | 1.6 | 40.4 | 1.14 | 0.58 |

The aim of the work was to study the complexation of metals with organic substances of water (small lakes), taking into account the zonal features of the territory: the zones of the northern taiga, mixed forests and steppes (forest-steppes) of European Russia (ER) and Western Siberia (WS). The following tasks were performed:

- the structural features of humus substances isolated from soils and waters of selected territories
- in the laboratory experiments the processes of complexation of metals with humus substances were modeled and the conditional stability constants of the complexes
- in natural waters (small lakes), the chemical composition of waters is analyzed and the forms of finding metals based on model equilibrium constants

2. Methodology of the research
The experiment consisted of the following steps (Figure 2):

1. Extraction of humus acids and fractions (acid groups) from the typical soils of different climatic zones;
2. The study of functional characteristics of HS and factions, and their acid-base properties;
3. Study of the interaction of HS metal ions, determination of appropriate stability constants of complexes;
4. Theoretical calculation of some of the forms of metals in natural water bodies.

In this work, we were investigated common soil humus substances (European Russia and West Siberia): the zone of northern taiga - gleepodzolisty soil, the zone of mixed forests - sod-podzolic soils, the steppe zone - black soil.

In the course of detailed experiments were studied (Figure 2). Humus substances - alkaline soil extractor; alkali-soluble and acid-soluble fraction of humus substances – fulvic acid; and humic acids + gimatomelanic (gimetomelanic) acids (HA-HmA) - alkoly-non soluble and. Electrochemical methods of analysis have been investigated processes of complexation of metal ions from the HS and their factions.

We have chosen the following metal ions: Fe (III), Cu (II), Pb (II), Cd (II), Zn (II), Ni (II), Co (II), Mn (II), Cr (III), Ca (II), Mg (II), Sr (II), Al (III).
Samples extraction was performed because the procedure of HS leaching from soils into water is the main source of organic matter. And, the structural features of organic matter of water similar to the composition of the soil humus substances. Also, HS of water contain in composition as the proportion of fulvic acids, which are readily soluble in water, and mixtures gimatomelanic and humic acids, which are soluble in alkali.

Investigation of fractions HS such as fulvic and humic and gimatomelanic mixture of acids were carried out for more in-depth examination of complex formation taking into account functional characteristics of each faction. Research complexation FA as the dominant component of HS revealed the metal ions that have an affinity for oxygen-containing functional groups, as well as to compare the obtained stability constants of metal complexes with FA with numerous data in the literature, most of which is devoted to the study of this fraction HS.

Study of complex formation of metal ions with a mixture of humic acids and gimatomelan acid which are necessarily present in natural waters, but in lower concentrations compared to FA, revealed differences in the mechanisms of complex formation for these fractions.

Physical and chemical methods used to study the complexation of metal ions with the HS, are shown in Figure 3. As the figure shows, the qualitative features of the soil acids were studied by IR and NMR spectrometric methods [1-5] (information on the functional groups, causing the connection to a specific metal ions). According to Moiseenko [6-8] observed a significant correlation (99%) between the amount of organic matter in waters humic nature and values of permanganate oxidation, therefore the method of permanganatometric concentrations were used for analyzez HS, FA and HA-HimA and in following, for calculated concentrations [7].

The average molecular weight of humus substances were found by sedimentation equilibrium [1-8]. Using the obtained molecular weights were calculated molar concentrations of acid and fractions, which are used in further for asses conditional stability constants of the complexes.

The stability constants of metal complexes with HS have been determined by various physical and chemical methods. The main physical and chemical methods used in the work - a method of voltammetry (VA) [3-6]. Potentiometric titration method was used to study the interaction of the ions Ca (II), Mg (II), Sr (II), Al (III) with FHS.

Application of ionometry to determine the stability constants of metal complexes with HS was implemented in the form as direct ionometry and potentiometric titration [8]. Using these methods
have been studied species complexation processes ions Ca (II), Mg (II), Pb (II), Zn (II), Cu (II), Cd (II) with HA and fractions.

In the final stage of the experiment, as shown in Figure 3, was conducted of the testing stability constants of the complexes by preparing systems containing multiple metal cations and HS. They also discussed the processes of complexation of metal ions with HS in a competitive binding, ie, in the presence of several cations or anions, close in composition to the waters of the natural systems. The concentrations of cations and anions were chosen according to the chemical composition of natural waters, reflected in [6-8].

The basis of the methodology used in isolation of humic substances fractionation is the process that was reflected in the D.I.Orlov [1-4]. Known extraction method was supplemented by a few steps, namely: HS. Undergoes a process of desalting cation-exchange resin and purification of low molecular weight organic substances with activated carbon; mixture during the isolation of HA and HimA not divided into lower molecular weight fraction by adding an alcohol, and has been considered as a set of acids falling into water in the leaching process.

Figure 3. Scheme of investigation of metal complexation with humus substances and factions.

According to these amendments, a detailed soil sample preparation system and the allocation of HS and fractions consisted of the following steps. We used infrared spectrometric analysis and NMR spectrometry analysis for evaluating qualitative features of humus substances and their fractions - IR-spectrometr NicoletTM380, NMR-spectrometr JEOL. To evaluate the properties of the organic components of potentiometric method using potentiometric titration.

Analyses of water lakes (chemical composition):

The concentrations of dissolved elements Li, Si, Na, Mg, Al, P, S, K, Ca, V, Mn, Fe, Cu, Zn, Sr, and Ba were determined using ICP-AES (ICAP-61 Thermo Jarrell Ash, Institute of Problems of Microelectronics Technology and Superpure Materials RAS, Chernogolovka). The measurements were conducted with the following spectrometer parameters: an RF generator output power of 1200 W; an angular nebulizer; a plasma-forming Ar flow rate of 18 L/min; an auxiliary Ar flow rate of 0.9 L/min; an Ar flow rate into the nebulizer of 0.6 L/min; an analysed sample flow rate of 1.5 m L/min;
and a plasma observation zone height of 14 mm. The integration time of the spectra during each run was 5s. The element contents in aqueous solutions were determined by the quantitative method using calibration solutions (High Purity Standards, USA) of 0.5 and 10 mg/L of each element. Element contents in the water were calculated out using the spectrometer software (ThermoSPEC, version 4.1).

The detection limits of the various elements were: Li 0.5 mg/L; Si 0.05 mg/L; Na, Mg, Al, Ca 0.01 mg/L; K, Zn 0.15 mg/L; P 0.8 mg/L; Fe, Cu, Sr 0.003 mg/L; Mn, Ba 0.0003 mg/L. The detection limits for ICP-AES measurements were calculated as follows: $DL_i = C_i + 3\sigma$, where $C_i$ is the mean content of an element of interest for measurement in control samples, and $\sigma$ is the standard deviation of its determination in control samples. The accuracy of analyses was better than 5% for elements with $C > 5$ DL and did not exceed 20% for elements with $C < 5$ DL. For most of the above elements analyzed, the concentrations were higher than 5 DL. Contents of B, Li, Be, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rh, Sr, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Tb, W, Re, Os, Ir, Pt, Au, Hg, Ti, Pb, Bi, Th and U in the samples were determined by ICP-MS (X-7 ICP-MS Thermo Electron, Institute of Problems of Microelectronics Technology and Superpure Materials RAS, Chernogolovka). The measurements were conducted with the following spectrometer parameters: an RF generator output power of 1250 W; a PolyCon nebulizer; a plasma-forming Ar flow rate of 12 L/min; an auxiliary Ar flow rate of 0.9 L/min; an Ar flow rate into the nebulizer of 0.9 L/min; a resolution of 0.8 mL/min. The following parameters were used for mass-spectrum estimation: detector mode– double (pulse counting and analogous); scanning modes: Survey Scan and Peak Jumping. The detection limits for the ICP-MS measurements ($\leq 0.1–1$ ng/L for Cd, Ba, Y, Zr, Nb, REE, Hf, Pb, Th, U; 1 mg/L for Ga, Ge, Rb, Sr, Sb; $\leq 10$ mg/L for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As) were calculated as follows: $DL_i = C_i + 3\sigma$, where $C_i$ is the mean content of an isotope of interest for measurements in control samples and $\sigma$ is the standard deviation of its determination in control samples. For elements with several isotopes, DL was used for the most abundant isotope. The accuracy of analyses was better than 10% for elements with $C > 5$ DL and did not exceed 20% for elements with $C < 5$ DL. For most elements analyzed, the concentrations were higher than 5 DL.

3. Result and discussion

3.1. Spectrometry Research

According to NMR spectrometry analysis HS steppe zone characterized by a predominance of substituted aromatic and aliphatic hydrocarbon fragments of the oxygen-containing fragments, HS of northern taiga soil – oxygen and nitrate group.

Analysis of IR-spectrograms revealed for both territory WS and ER:

1. Humus substances isolated from soil of typical northern taiga zones are characterized by a high content of oxygen-containing groups. Humus substances derived from soil zone typical mixed forests contain about the same amounts as oxygen and aromatic aliphatic hydrocarbon fragments. Variability oxygenated fragments large compared to the rest of submitted samples. Humus substances isolated from soil of typical steppe zone, characterized by a predominance of aromatic and aliphatic hydrocarbon fragments.

2. Fulvic acids isolated from soils of the taiga, represented the most extensive part of the spectrum corresponding to the presence of large amounts of oxygen-containing groups. For fulvic chernozems is characterized by narrow spectra. Part of the spectrum of humic acids of chernozem, reflecting the widest aromatic moieties, unlike of humic acids of soils of northern taiga zone.

3. The acid-base properties of fulvic and humic acids differ due to the influence of oxygen, nitrogen and hydrocarbon-containing functional groups in the fractions. These differences lead to different processes of dissociation of acids. The biggest acidity constants have acid soil humus, acid soil lowest gleypodzolic soil.

4. The metal ions have different affinities to specific functional groups. As shown in Figure 6-7. For the ions Fe (III) is most typical bond formation through an oxygen bridge. Alkaline earth metal
ions - Hard Pearson acids form strong bonds through oxygen and nitrogen atoms. Cu (II) and Pb (II) can bind to the HS via a soft center - sulfur-containing groups.

Based on the results of experimental studies of the qualitative composition of humic substances and fulvic acids of sod-podzols and chernozem of WS and ER (samples isolated from soils of the catchment and natural waters), the significant differences in the content of active functional groups were revealed. Organic acids isolated from sod podzols of ER contain approximately equal amounts of both oxygen-containing and aromatic, aliphatic hydrocarbon fragments; Organic acids isolated from sod-podzols WS contain a large amounts of nitrogen groups and are characterized by the predominance of Pearson's hard acids over soft acids. This specificity is associated with the peculiarities of the biochemical formation of soil humus in the territory of the WS and, possibly, the specificity of the technogenic activity of the region. The variability of oxygen-containing fragments (hydroxo groups, carboxyl groups, carbonyl groups) is large for HS of sod-podzols of WS soils in comparison with ER samples, which affects their acid-base characteristics. Organic acids of chernozems ER are characterized by the predominance of aromatic and aliphatic hydrocarbon fragments over oxygen-containing fragments; for the samples of chernozem WS, the predominance of aromatic fragments over aliphatic structures, nitrogen-containing fragments of purine and pyrimidine nature was revealed.

Significant contents of sodium ions were found in the structure of the HS of the chernozem WS, which promotes the displacement (shift) of the bands of the spectrum of the carboxyl groups. An important process that influences the mechanism of complexation of HS with metals for sod-podzols WS is gleying (which is manifested in a larger content of Fe (II) in natural waters), and for chernozems - solonetzation.

3.2. Complexation with humus substances

As was found for both region (WS and ER), alkaline earth metal ions: Sr (II), Ca (II) and Mg (II) to form complexes with humic substances gleelpodzolisty soil in a ratio of 1: 1. The strength of the formed complexes is low (about $10^3$) and the degree of formation of complexes with alkaline earth metal ions depends on the degree of humification and mineralization of the water lakes. Ions Fe (III) form with HS gleelpodzolic monodentantnye soil complexes. Complex Fe(III) with HS northern taiga zone are characterized by high stability constant ($K_1 = 1 \times 10^{10}$), due to the predominance of oxygen-containing groups (Pearson hard grounds) in them.

The stability constant of the complex Al (III) is equal to 106 HS, the stoichiometry of the complex - 1: 1. Ions of Ni (II) and Co (II) exhibit high ability to form complexes with HS gleelpodzolic soil: according to the data obtained from the stability constants of the compounds HS (in the ratio 1: 1) are 4.4 and 5.8, respectively. Ni (II) and Co (II) - intermediate acid Pearson different from Fe less affinity for oxygen atom and Cu (II) - a lower affinity for soft grounds Pearson. Therefore, the obtained values of stability constants of the complexes is lower than complexes ions Fe (III) with HS. Ions Zn (II) in the process of complexation form complexes in a ratio of 1:1 with a log constant equal to 3.7. Ions Zn (II), possess an affinity for oxygen-containing groups, but due to the size of the ionic radius having steric hindrance and stability constants of the complexes is lower than that for other metal ions.

Mn (II) and Cr (III) by reaction with HS complexed in a ratio of 1: 1 with low values of stability constants, because of low power for ions and a sufficiently large radius. Based on these results, we can conclude that such metal ions as Fe (III), Pb (II), Cu (II) capable of forming a complex with HS gleelpodzolic soil in a ratio of 1: 2. For the Mn (II), Cr (III), Cd (II), Ni (II) and Co (II), Ca (II) and Mg (II) - 1: 1.

According to the calculations of the stability constants of complexes was built following "a range of active metals»: Fe (III)> Cu (II)> Pb (II)> Al (III)> Co (II)> Ni (II)> Cd (II)> Zn (II)> Cr (III)> Mg (II)> Sr (II)> Ca (II)> Mn (II).

Complexes of alkaline earth metal ions with HS from zone of mixed forests is characterized by lower values of stability constants compared with complexes with HS zone of northern taiga. For ions Ca (II) and Mg (II) values of stability constants are much lower - average lgK = 2.2 instead of 3.3. The
stability constants of complexes of Sr (II) c HS of sod-podzolic soils are equal. The values of the stability constants of the complexes HS zone of mixed forests with ions of calcium and magnesium, as reflected in the work [9], and also show a low ability of metals to form complexes (lgK <3). The stability constant of complexes of Fe (III) -HS is 10⁻⁷.⁶ which is lower than the stability of the complexes of Fe (III) with HS zone of northern taiga. The reasons for this difference can serve as a smaller proportion of oxygen-containing groups, which is not advantageous from the viewpoint of the formation of complexes for hard acids Pearson. Ions Cu (II) form complexes with HS, characterized by stability constant (lgK) about 6.5, which is slightly higher than for systems with HS zone of northern taiga. According to a preferred functional groups for ions Cu (II), as the bond is formed through the rigid center - oxygen and nitrogen, as well as through the soft center - sulfur. Comparison of the stability constants of metal complexes with HS describes the following series: Cu (II)> Fe (III)> Al (III)> Ni (II)> Pb (II)> Co (II)> Cd (II)> Sr (II)> Mn (II)> Cr (III)> Ca (II)> Mg (II)

Humic substances of black soil have an increased content softer centers Pearson (sulfur-containing groups, aromatic moieties) compared with podzolic soils. These features create favorable conditions for complexion milder acids Pearson.

Ions Ca (II) and Mg (II) to form complexes with stability constants of the logarithms of 3.8 and 2.7, respectively; that is different from the values obtained for the previous bands, but as well as in the area of the northern taiga Ca (II) is more constant than the Mg (II). Fe (III) forms complexes at a ratio of 1: 1 and 1: 2, with the logarithms of the stability constants of 8.2 and 15.9, that could be due to the presence of HS in the sample zone steppe contribution complexion oxygenates and nitrogen containing groups. It can be assumed that the dominance of the substituted aromatic groups in the structure HS determines various mesomeric and inductive effects in the aromatic ring.

For ions Cu (II), obtained stability constants of complexes with black soil HS higher than for systems with HS podzolic soils. As milder acid Pearson, unlike Fe (III) and Al (III), Cu (II) complexes with better milder bases Pearson, which dominate the samples submitted. Pb (II) complexes with HS in the ratio 1: 2, which differs from the process flow of chelation complexes with other soil HS (C = 10⁴.⁵ and 10⁷.²).

Comparing the values of stability constants of metal complexes with HS can form the following series: Fe (III)> Cu (II)> Al (III)> Pb (II)> Ni (II)> Zn (II)> Co (II)> Ca (II)> Cd (II)> Sr (II)> Mg (II)> Cr (III)> Mn (II)

Complexes of alkaline-earth metal ions with HS of sod-podzols ER are characterized by lower values of the stability constants compared to complexes with HS of sod-podzols WS (LgK = 2.4 and 3.6, respectively), which can be explained by more active hard centers in HS of WS. The stability constant of the complexes Fe(III)-HS of ER is 10⁻⁷.⁶, which is an order of magnitude lower than for the sample of WS.

The reasons for this difference can be a smaller share of Fe(III) and an increase in the proportion of Fe(II), which is a less hard Pearson acid and forms connection with other functional groups. The Ni(II) and Co(II) ions are characterized by various affinity to organic substances of WS and ER. For the Co(II) complex with HS of chernozems ER the constant decreases by an order in comparison with the samples of WS. For the Ni(II) complex with HS ER the stability constant of the complexes is opposite. Complexes of Mn(II) and Cr(III) with HS of sod podzolic soils ER have low stability constants, although their activity in samples with HB WS (common for all oxidation states) is higher.

3.3. Metals forms in water

The calculations of the forms of metals in natural waters lay study of small lakes in the European part of Russia, from the tundra to the steppe zone, held at the Institute of Water Problems of RAS. The method of sampling and analysis is described in detail [10]. The concentrations of cations and anions, which were carried out according to the calculations, as reflected in [10] in the process of calculation takes into account the effect of these anions - humus substances, sulfate ions, chloride ions, sodium ions, hydroxide ions, as well as in the presence of other cations metals.
Analysing the forms of occurrence of metals can be concluded about the great variability of forms of distribution of metals in natural waters, which are determined by the composition and concentration of trace elements and characteristics of humus substances. The chemical properties of GW in natural waters depends, in turn, the properties of the soils located in the catchment area and therefore have a zonal specifics.

There are complex mechanisms of binding and distribution of the forms of metals in natural waters, which are defined not only by the properties of metal ions as the overall chemistry of the waters, including the entire range of metal content, as well as individual quality features of humus substances in them.

The distinctive features of the chemical composition of the waters of the northern taiga zone are low salinity and high variability of the concentrations of HS, Fe (III) and Al (III) due to the presence of lakes are located in the mountainous landscape, as well as among the wetlands and woodlands. Natural waters boreal forest characterized by a large variety of metal ions, the simultaneous presence which, together with sufficient alkalinity, cause the following pattern in an advantageous distribution of metal ions bound in organic complexes:

$$Fe > Al > Pb > Co > Ni > Zn > Cd > Cu > Mg > Ca > Cr > Mn > Sr$$

Based on the chemistry of the waters of this natural area, structure and properties of metals HS, one can conclude that Fe (III) and Al (III) are the main competitors for binding into organic complexes and other metals inactivation probability is very low, most of them will be in ionic form.

The natural water areas of forests are characterized by a high content of mineral salts, a fairly wide range of alkalinity and pH, the presence in the waters of a large group of metals. The general rule in the distribution:

$$Fe > Cu > Al > Zn > Cd > Pb > Ni > Co > Mg > Ca > Cr > Mn > Sr$$

In this zone, as in the taiga, Fe (III) is the main binding elements. Cu (II) is located at the second position due to the possibility to communicate with HS in the absence of Fe (III). Al (III) is in third place due to the difference between the stability constants of Cu-Al-HS and HS.

Natural water steppe zone characterized by the presence or absence of aluminum ions, Fe (III), Cu (II), a high total alkalinity. These features are manifested in changes in the extent of binding metals. The presence of all the metals in the system generally shown in the following patterns:

$$Al > Fe > Cu > Zn > Ni > Co > Mg > Ca > Sr > Mn > Cr$$

Lack of Fe (III), aluminum and Cu (II) several changes this pattern. In this case, a number of substantially unchanged, but increases the degree of binding metals in the following sequence:

$$Ni > Co > Zn > Sr > Ca > Mg > Mn > Cr$$

Every water system has a unique set of chemical components. Physicochemical properties of metal ions and their content as well as the concentration of cations and anions cause specific trends metal migration. Therefore, each of the proposed series is quite arbitrary and generalized to specific conditions. It should be noted that the patterns of distribution of metals according to the calculations do not repeat the pattern of the values of stability constants of complexes - this confirms the finding of an impact on the form of metals of many factors. Therefore, the stability constants of metal complexes with humus substances - an important but not the only factors affecting the speciation of elements in natural waters.

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