ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 13, pp. 2226–2238. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © P.N. Linnik, V.A. Zhezherya, R.P. Linnik, Ya.S. Ivanechko, 2012, published in Ekologicheskaya Khimiya, 2012, Vol. 21, No. 2, pp. 98–111.

Concentrations of Aluminium, Iron, and Copper in Water of Some Shatskiye Lakes and Specificity of Their Distribution among Different Forms of Occurrence

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Received May 28, 2012

Abstract—The results of studies on the occurrence of aluminum, iron, and copper in water of Lyutsimir and Chernoe Bol'shoe Lakes belonging to the large group of Shatsk Lake system are discussed. Iron was shown to migrate mostly as suspended particles, and copper, as soluble species. The average annual fraction of suspended aluminum is about 40%. The ratio of suspended and dissolved aluminum depends not only on the concentration of suspended particles in water, but also on their nature. Anionic complexes predominate among soluble forms of the examined metals; their fractions in water of Lyutsimir and Chernoe Bol'shoe Lakes are on the average 86 and 70% (Al), 73 and 59% (Cu), and 60 and 47% (Fe). This is determined by the major contribution of humic substances to the total content of organic matter in water of both lakes and their participation in the complexation with metals. The metals compete for active centers in humic macroligands. Carbohydrates constitute the second important group of organic substances that participate in the complexation. Neutral complexes were found to consist mainly of iron compounds. Compounds with a molecular weight not exceeding 2.0 kDa predominate among anionic metal complexes.

DOI: 10.1134/S1070363212130087

INTRODUCTION

There is a large group of lakes in Volyn' region of Ukraine in the Shatsk National Natural Park which was created in 1983 to preserve the unique lake system and rare plant and animal species. The Lakes of Shatsk include 23 lakes with an overall area of about 65 km^2 [1]. According to their morphometric parameters, these are mainly small lakes, the area of only five of them exceeds 2 km^2. The largest lakes are Svityaz' Lake and Pulemetskoe Lake.

The Lakes of Shatsk belong to the West Bug basin. The input part of their water balance consists mainly of precipitation, surface runoff, and ground water, and the output depends mostly on the intensity of evaporation and runoff [1]. The lakes under study may be regarded as low-flow water bodies. Until recently they were not subjected to an appreciable anthropogenic impact, so that their state was believed to be environmentally safe. However, large-scale melioration started as early as 1960s and extensive recreation use of the lakes in recent time have led to a noticeable effect of human activity, which is reflected primarily in enhanced eutrophication [2, 3]. As compared to 1980s, the chemical composition of water in the lake system has changed significantly [2]. The mineralization of water in most lakes increased on the average by a factor of 1.2–1.4, the concentration of phosphate ions, by a factor of 5–11, the concentration of ammonium nitrogen, almost twice, and the concentration of iron, by a factor of 1.5–4. On the other hand, the concentration of silicon decreased by a factor of 4–6, which was attributed to extensive growth of diatoms. Increased in the mineralization of water was accompanied by variation of the salt composition [2]. Also, the ratio of the major nutrients (nitrogen and phosphorus) changed. Adverse effect on the gas conditions is reflected in reduced concentration of dissolved oxygen [2].

Though hydrochemical conditions of the Lakes of Shatsk were periodically studied, the concentration and forms of occurrence of metals as an important lake water component generally remained beyond the scope of these studies, except for a few examples [4]. Therefore, these issues were the subject of our studies which were performed in 2011 and included aluminum, iron, and copper as elements that strongly tend to complexation with organic substances dissolved in surface water; in addition, these metals are characterized by some specificities of their distribution and migration between abiotic components of water ecosystems.

MATERIALS AND METHODS

The studies were performed at two lakes, Lyutsimir and Chernoe Bol'shoe. Samples of water were withdrawn monthly from February to October, 2011, from the surface layer and were delivered to an analytical laboratory. Suspended substances were separated by membrane filtration using 0.4-μm Synpor membrane filters (Czechia). For this purpose, 0.5 l of lake water was passed through a filter under a pressure of about 2 atm, which was created using a UK 40-2M setup. The weight of the suspended substances was calculated by subtracting the weight of the filter from the weight of the filter after filtration dried at room temperature until constant weight.

The filtrate was passed in succession through glass columns charged with DEAE (diethylaminoethylcellulose) and KM (carboxymethylcellulose) ion exchangers (from Serva) to separate dissolved organic substances (DOS) into three groups with respect to their nature: acid, base, and neutral [5]. The first group contained mainly humic substances (HS), the second, protein-like compounds (PLC), and the third, carbohydrates. Metal compounds with the above DOS were classified as anionic, cationic, and neutral complexes, respectively. Cellulose ion exchangers ensured not only separation of DOS into particular groups but also their concentration, especially of acid and base substances (the concentration factor was 20–25).

The concentrations of DOS, as well as of aluminum, iron, and copper in the obtained fractions were determined with a view to analyze distribution of these metals among the examined groups of DOS.

The molecular weight distribution of anionic metal complexes (mostly with HS) was analyzed by gel chromatography. A 6-ml portion of the concntrated acid fraction was passed through a glass column charged with gel HW-50F (Japan), which was preliminarily calibrated against compounds with known molecular weight, namely poly(ethylene glycols) (*M* 1.0, 2.0, 15.0, and 20.0 kDa) and glucose (*M* 0.18 kDa). The column was eluted with a 0.025 M phosphate buffer (pH 7.0). We thus isolated 17 fractions, 15 ml each.

The concentration of HS in the acid fraction was determined by spectrophotometry. The electronic absorption spectra were recorded on a Unico UV 2800 spectrophotometer, and calibration curves were plotted in the coordinates optical density at λ 254 nm—HS concentration (mg l^{-1}). The water colority as a parameter indirectly characterizing HS content was evaluated on the Cr–Co scale [6].

The concentration of PLC was determined by the Lowry–Folin method, and the concentration of carbohydrates, by the anthrone method [7, 8].

The concentration of metals in suspended matter was determined after wet combustion of filters in a mixture of concentrated sulfuric and nitric acids of chemically pure grade. The concentration of aluminum and iron in natural water filtrates, in solution after decomposition of suspended substances, and in particular fractions separated by ion-exchange and gel chromatography was determined by photometry [8, 9], and the concentration of copper therein, by chemilumine-scence analysis [10].

RESULTS AND DISCUSSION

As noted above, water samples from Lyutsimir and Chernoe Bol'shoe Lakes (Fig. 1) were used to study the concentration and seasonal variation of DOS and metals. These water reservoirs are characterized by the following morphometric parameters: length 3.1 and 1.4 km, maximal width 1.9 (average 1.4 km) and 0.8 km (average 0.6 km), maximal depth 11.0 (average 4.4 m) and 5.0 m (average 3.0 m), area 4.5 and 0.8 km^2, volume 19.8 and 2.4 million m^3, respectively. The lake retention time is 5.71 and 3.93 year, respectively [1]. The turbidity of water in Lakes of Shatsk is not high; as a rule, the concentration of suspended substances does not exceed 1–3 mg l^{-1}, and it may increase by a factor of 3–3.5 only in shoals of most lakes under strong wind-induced mixing. The limpidity of water in Lyutsimir and Chernoe Bol'shoe Lakes is estimated at 0.9 and 0.4 m, and the photic zone depth is almost 2.1 and 1.1 m, respectively.

Both lakes are subjected to the effect of nearby Shatsk urban village, and they may be classified as eutrophic lakes according to a number of trophosaprobiological indices [3].

Analysis of published data showed that microelement composition of lakes of the Shatsk National Park remains poorly studied. Only a few data on the

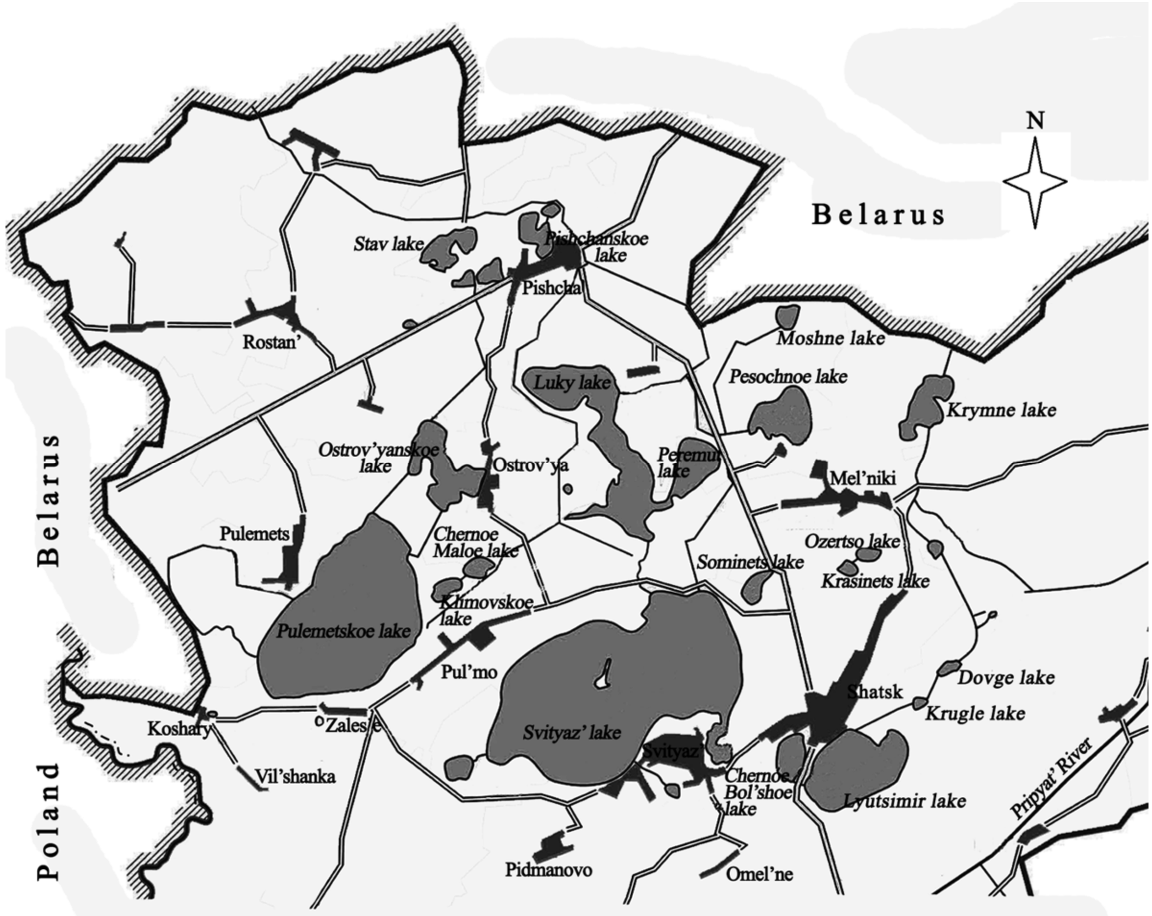

Fig. 1. Location of lakes in the Shatsk National Natural Park (Volyn' region, Ukraine).

concentration of some metals in water of the Lakes of Shatsk are available. For instance, limiting and average concentrations of iron, manganese, copper, zinc, and chromium in Svityaz' Lake over many years were reported [4]. The results of studying nutrient content (including iron) of water in some lakes of the Shatsk National Park were given in [2].

Table contains the concentrations of aluminum, iron, and copper, as well as of their suspended and dissolved forms, in water of Lyutsimir and Chernoe Bol'shoe Lakes, which were determined in the present work. It is seen that the concentrations of these metals vary over a wide range due primarily to seasonal variability, though we cannot speak unequivocally about its clearness. The largest concentration was found for iron, next followed aluminum and copper. It is noticeable that the concentration of Al(III) in lake water was fairly low (21.9–88.0 and 12.5–90.9 μg l^{-1} in Lyutsimir and Chernoe Bol'shoe Lakes, respectively) as compared to water bodies studied by us previously [11, 12]. The concentration of iron tends to decrease in spring and increase in summer, and this tendency is stronger for Chernoe Bol'shoe Lake. Somewhat increased concentration of Cu(II) in both lakes (15.2–30.5 μg l^{-1} in Lyutsimir Lake and 8.1–28.7 μg l^{-1} in Chernoe Bol'shoe Lake) should also be noted. The observed metal concentrations are likely to be determined by regional specific features, i.e., these concentrations may be regarded as some natural background. Appreciable anthropogenic impact is hardly probable.

1. Distribution of Metals between Suspended and Dissolved Matter

The ratios of suspended and dissolved metal-containing species indicate some seasonal variability of that parameter (see table). Suspended Al(III) predominates in autumn, whereas Fe(III), in summer. On the other hand, Cu(II) occurs mainly in the dissolved form. The data in Fig. 2 provide a more

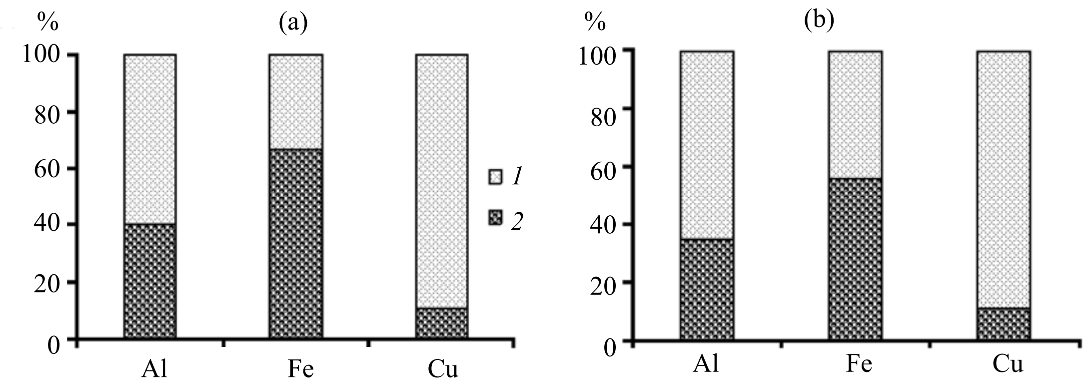

Fig. 2. Average annual ratios of (*1*) dissolved and (*2*) suspended forms of metals in water of (a) Lyutsimir Lake and (b) Chernoe Bol'shoe Lake.

distinct representation on metal distribution between the suspended and dissolved forms. It is seen that only iron occurs mainly in the suspended form (56–67% of its total concentration in water). These findings indicate predominant migration of iron as suspended particles in surface water.

The fraction of suspended aluminum was on the average ~40 and 34% in Lyutsimir and Chernoe Bol'shoe Lakes, respectively. It is known that this metal also migrates in surface water mainly as suspended particles. This is especially characteristic of river water where the fraction of suspended aluminum attains 97–99% [13, 14]. However, it may decrease considerably in going to river water with increased concentration of humic substances that effectively bind Al(III) to form coordination compounds. Analogous pattern was observed by us while studying rivers in the Pripyat' river basin, which displayed a high concentration of HS [11]. Humic substances also constitute the major part of DOS in the Lakes of Shatsk system, and their concentration is fairly high (see below). This is a reason for the occurrence of aluminum as water-soluble species. Relatively low concentration of suspended substances in the examined lakes (see table) is also a factor responsible for reduced concentration of suspended Al(III) particles. In addition, their origin strongly affects the ratio of suspended and dissolved forms of aluminum [15, 16]. If the major constituent of suspended substance is mineral, the major part of Al(III) occurs in the suspended form, for aluminum is a necessary component of many clay minerals. Prevalence of dissolved Cu(II) is typical of the behavior and migration of copper in natural surface waters. Copper migrates mainly in the dissolved form even in river water with high concentration of suspended particles, e.g., in the Danube river [17]. This is related to the complexation of copper with DOS in surface water, which is likely to prevent adsorption by suspended particles. Iron also forms coordination compounds with organic ligands present in natural water, and the concentration of its dissolved forms considerably exceeds that calculated on the basis of thermodynamic principles. Nevertheless, suspended iron often dominates over the dissolved form.

2. Effect of Dissolved Organic Substances on the Migration of Metals

Dissolved organic substances in natural surface water are very important in the fate, behavior, and migration of metals, for they form coordination compounds characterized by different stabilities and favor the occurrence of metals in the dissolved state, as well as detoxification [18–23]. Metal coordination compounds with humic substances are the most stable. They often predominate in surface water since humic substances themselves predominate among DOS [24–27].

The results of studying the distribution of Al, Fe, and Cu among complexes with different groups of DOS in Lyutsimir and Chernoe Bol'shoe Lakes are given below (Figs. 3, 4). As might be expected, HS play the key role in binding of the above metals. The fractions of metals bound to complexes with HS in water of Lyutsimir Lake are 63.9–94.4, 37.5–93.3, and 60.4–78.5% for dissolved aluminum, iron, and copper, respectively. The fractions of analogous complexes in Chernoe Bol'shoe Lake are slightly smaller, 59.3–82.1, 31.0–61.4, and 43.4–87.0%. Domination of anionic metal complexes (with HS) in the lake water also

Water colority, and concentrations of suspended substances, metals, and their suspended and dissolved forms in Lyutsimir and Chernoe Bol’shoe Lakes, 2011

Sampling date	Water colority, Cr/Co units	Suspended matter, mg l^{-1}	Al_{tot}, μg l^{-1}	Al_{sus}		Al_{dis}		Fe_{tot}, μg l^{-1}	Fe_{sus}		Fe_{dis}		Cu_{tot}, μg l^{-1}	Cu_{sus}		Cu_{dis}	
				μg l^{-1}	%	μg l^{-1}	%		μg l^{-1}	%	μg l^{-1}	%		μg l^{-1}	%	μg l^{-1}	%
Lyutsimir Lake																	
16.02	79.2	–	56.2	7.8	13.9	48.4	86.1	408.6	195.6	47.9	213.0	52.1	30.5	3.0	9.8	27.5	90.2
10.03	99.7	–	–	–	–	36.6	–	–	–	–	90.2	–	20.3	2.8	13.8	17.5	86.2
12.04	25.0	10.8	88.0	36.8	41.8	51.2	58.2	499.0	404.0	81.0	95.0	19.0	17.1	1.3	7.6	15.8	92.4
02.06	19.4	3.1	–	–	–	17.8	–	–	–	–	238.5	–	20.3	1.4	6.9	18.9	93.1
06.07	22.2	16.3	58.6	12.3	21.0	46.3	79.0	668.0	565.0	84.6	103.0	15.4	18.1	1.8	9.9	16.3	90.1
08.08	23.1	4.4	27.8	4.8	17.3	23.0	82.7	698.0	544.0	77.9	154.0	22.1	16.4	2.3	14.0	14.1	86.0
21.09	39.0	6.3	21.9	11.9	54.3	10.0	45.7	486.0	248.0	51.0	238.0	49.0	22.0	1.4	6.4	20.6	93.6
20.10	26.0	3.8	36.0	33.8	93.9	2.2	6.1	719.0	406.0	56.5	313.0	43.5	15.2	2.8	18.4	12.4	81.6
Chernoe Bol’shoe Lake																	
16.02	19.4	–	–	–	–	13.8	–	–	–	–	16.0	–	–	–	–	24.2	–
10.03	23.5	–	–	–	–	56.7	–	–	–	–	16.8	–	20.9	2.4	11.5	18.5	88.5
12.04	18.5	2.4	85.5	23.2	27.1	62.3	72.9	189.8	61.8	32.6	128.0	67.4	28.3	2.8	9.9	25.5	90.1
02.06	16.6	8.6	90.9	38.9	42.8	52.0	57.2	176.7	128.8	72.9	47.9	27.1	15.3	1.7	11.1	13.6	88.9
06.07	21.3	10.0	72.3	13.7	18.9	58.6	81.1	666.0	517.0	77.6	149.0	22.4	9.4	1.3	13.8	8.1	86.2
08.08	17.5	8.6	20.5	8.5	41.5	12.0	58.5	549.0	151.0	27.5	398.0	72.5	15.7	1.2	7.6	14.5	92.4
21.09	24.1	10.2	12.5	6.5	52.0	6.0	48.0	388.5	150.5	38.7	238.0	61.3	29.3	0.6	2.0	28.7	98.0
20.10	17.5	2.2	29.2	6.4	21.9	22.8	78.1	203.7	170.4	83.7	33.3	16.3	17.9	3.5	19.6	14.4	80.4

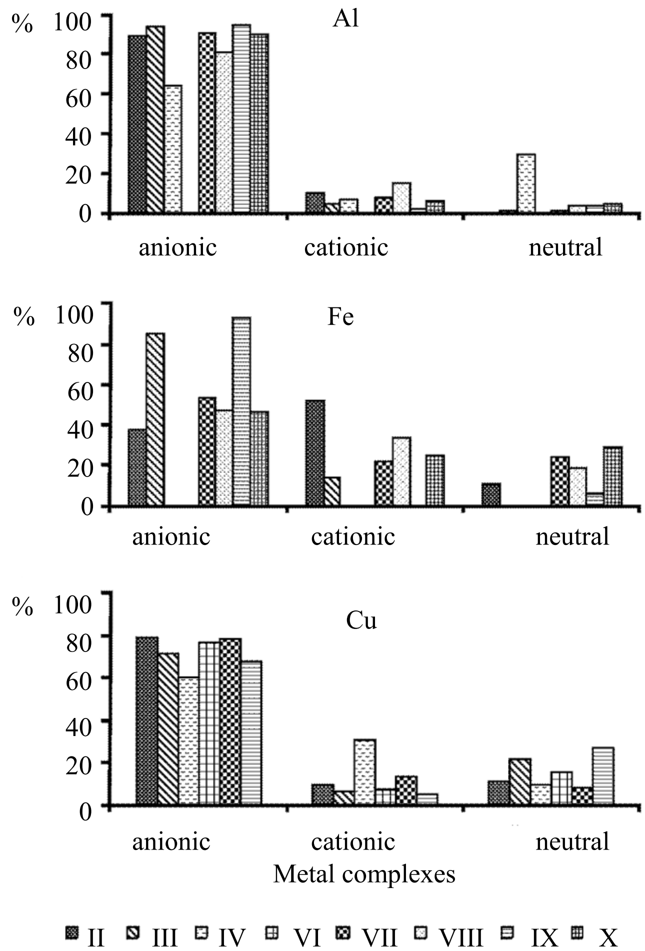

Fig. 3. Distribution of metals among complexes with dissolved organic substances of different chemical natures in water of Lyutsimir Lake, 2011. Here and in Figs. 4, 6, and 7 Roman numerals denote the month of water sampling.

follows from their average annual concentrations in particular groups of DOS (Fig. 5). On the other hand, it should be noted that the fraction of metal complexes with HS in Lyutsimir Lake is greater than in Chernoe Bol'shoe Lake. This is likely to be determined by higher concentration of HS in Lyutsimir Lake (Fig. 6).

Presumably, aluminum and copper complexes with HS are more stable than analogous iron complexes. In fact, the fraction of anionic Fe(III) complexes is smaller as compared to anionic complexes of Al(III) and Cu(II). Obviously, the examined metal ions compete with each other for binding (donor) centers in HS macromolecules. It is also important that in surface water bodies with increased concentration of HS iron migrates mostly in the form of coordination compounds with those natural organic acids, and the concentration of dissolved iron considerably increases in parallel with the water colority, the latter being an indirect indicator of HS concentration [28].

Some amounts of metals were also detected in cationic and neutral complexes. Therefore, there are reasons to contend that PLC and carbohydrates participate in complexation as well. However, the concentration of these organic substances in lake water is largely determined by the biotic factor, and it is incomparably lower than the concentration of HS (Fig. 6). Calculation of the average annual relative concentrations of particular groups of organic compounds in the total DOS concentration showed that the fraction of HS in Lyutsimir Lake is about 84%, and in Chernoe Bol'shoe Lake, 78% (Fig. 7). In addition both protein-like compounds and carbohydrates are fairly unstable (they readily undergo bacterial degradation). Taking the above stated into account, it may be presumed that

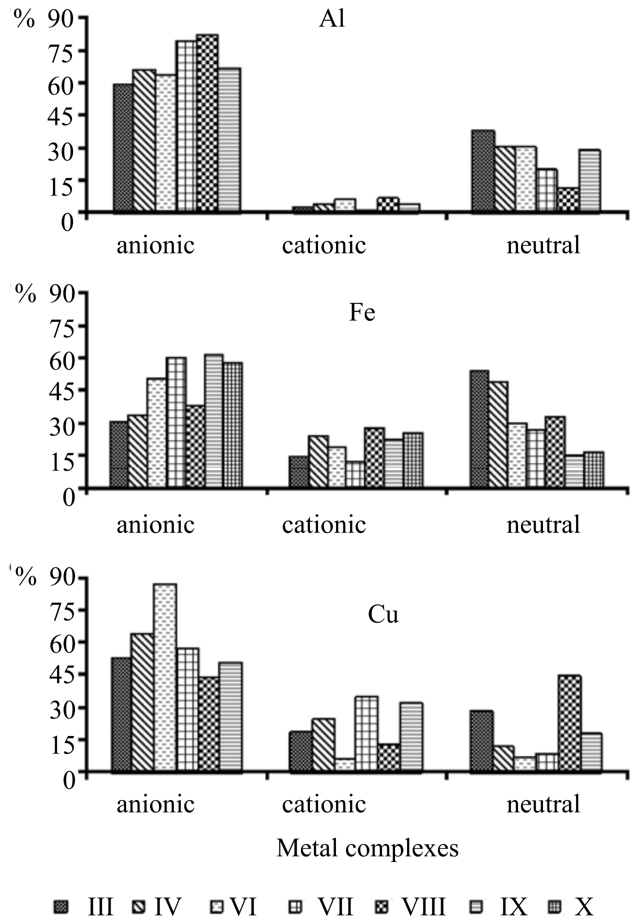

Fig. 4. Distribution of metals among complexes with dissolved organic substances of different chemical natures in water of Chernoe Bol'shoe Lake, 2011.

metal complexes with PLC and carbohydrates are less stable than metal complexes with HS. The occurrence of metals in the form of complexes with carbohydrate and PLC is more typical of iron and copper (Figs. 3–5), and the fraction of these complexes in Chernoe Bol'shoe Lake is appreciably higher while the relative concentration of anionic complexes is lower (Fig. 5).

3. Molecular Weight Distribution of Anionic Metal Complexes

Insofar as metal complexes with acid DOS were found to predominate in water in the examined lakes, complexes of this group were studied by gel chromatography. The results showed that molecular weights of anionic complexes vary over a wide range (Fig. 8–10). On the other hand, it is obvious that the complexation with HS having lower molecular weights prevails. This is illustrated more clearly by Fig. 10 where the generalized data are presented. Presumably, low-molecular-weight humic acids exhibit a stronger ability to bind metal ions.

Until present there are no generally accepted views on the complexing ability of humic substances with different molecular weights. It is known that fulvic acids (FA) constitute no less than 90% of humic substances in total. Fulvic acids have relatively low molecular weight, though high-molecular weight compounds are also present among them [29, 30]. Our results showed that compounds with a molecular weight of more than 5.0 kDa dominate among humic substances in water of the Lakes of Shatsk. Their relative concentration in Lyutsimir Lake is on the average ~54%, and in Chernoe Bol'shoe Lake, about 60%. Nevertheless, humic substances with a molecular weight of no more than 2.0 kDa ensure more efficient binding of metals to complexes (Fig. 10), though their fraction is smaller.

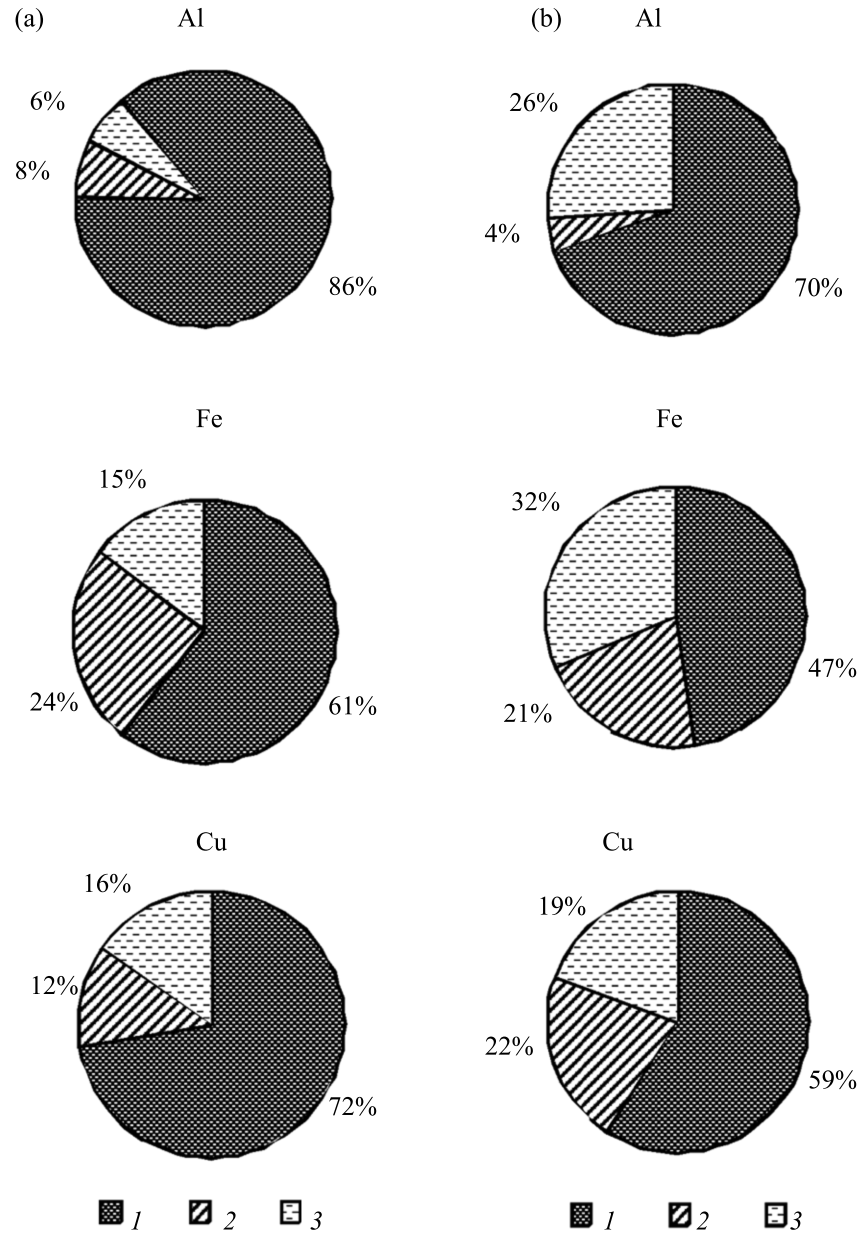

Fig. 5. Ratios of chemically different metal complexes in water of (a) Lyutsimir Lake and (b) Chernoe Bol'shoe Lake with account taken of their average annual relative concentration in each DOS group: (*1*) anionic, (*2*) cationic, and (*3*) neutral complexes.

Presumably, metal ions form complexes mainly with fulvic acids since the concentration of humic acids (HA) is generally insignificant. According to the results of our previous studies, the relative concentration of HA in water bodies in Ukraine does not exceed 5–10% of the overall HS content [11, 12]. Domination of anionic complexes with lower molecular weights indicates that low-molecular-weight fractions of HS (2.0–1.0 and <1.0 kDa) exhibit stronger complexing ability than those with higher molecular weight. We also found that copper is efficiently bound to complexes by high-molecular-weight HS (20.0–5.0 kDa), especially in water of Lyutsimir Lake (Fig. 6).

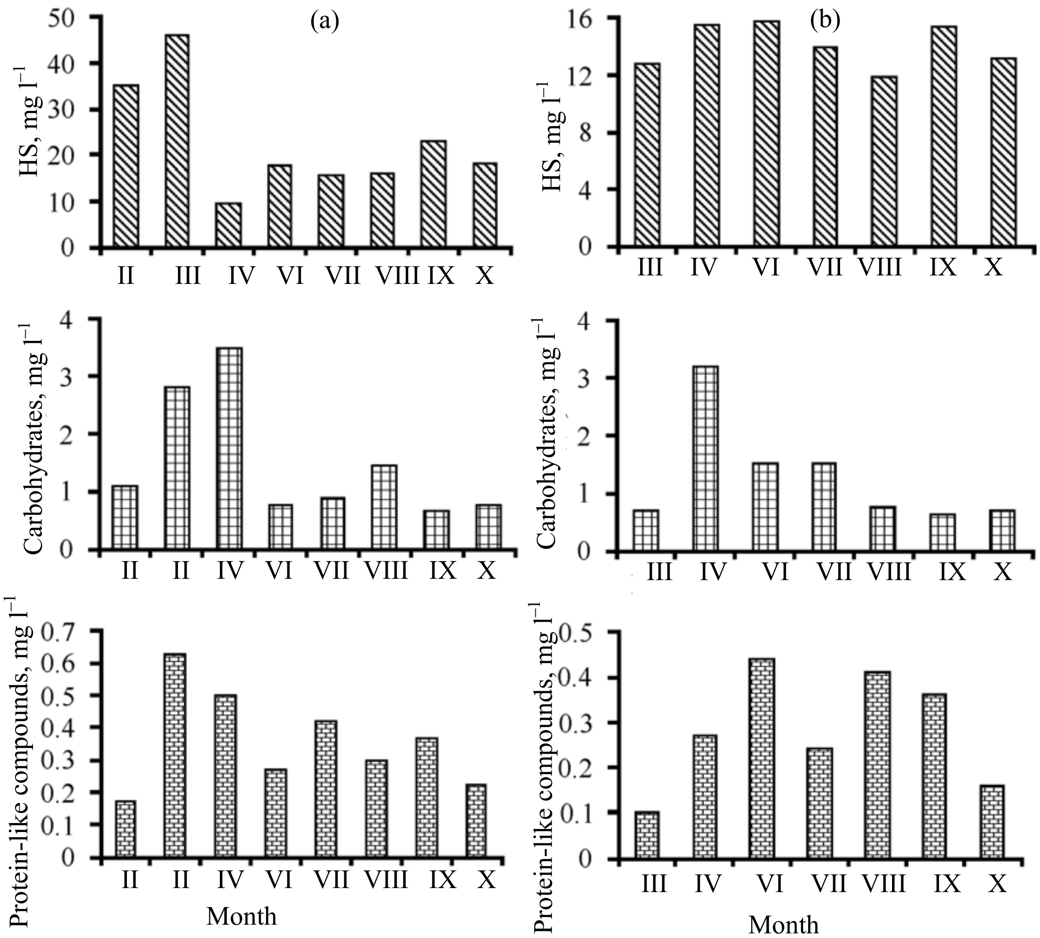

Fig. 6. Concentrations of DOS in water of (a) Lyutsimir Lake and (b) Chernoe Bol'shoe Lake, 2011.

CONCLUSIONS

The results of the present study showed that distribution of metals among different forms of their occurrence in water of the Lakes of Shatsk strongly depends on the concentration of suspended substances and their nature, as well as on the concentration and composition of dissolved organic substances. Low turbidity of the lake water and the presence of humic substances therein are the main factors responsible for predominant occurrence of metals in the dissolved state. This applies primarily to copper and aluminum. Domination of dissolved Cu(II) is typical of natural surface water. Unlike many other metals, Al(III) as component of many clay minerals migrates in surface water (including river water) mostly in suspended particles. However, the fraction of dissolved Al considerably increases if water contains increased amount of HS. A significant part of aluminum in the Shatsk lake system occurred in the dissolved state, for the concentration of suspended substances in water was low while the concentration of HS was sufficiently high to bind Al to complexes. The concentration of Al (III) in suspended particles depends on their origin. In lake systems with extensive development of phytoplankton the fraction of suspended Al is generally small despite high concentration of suspended matter which is mostly of biotic origin (it consists of algal biomass). The lakes under study are not characterized by strong eutrophication. On the other hand, most iron occurred in suspended matter, which also differentiates the behavior and migration of this metal in surface water from many other metals, including aluminum and copper.

The dissolved forms of Al(III), Fe(III), and Cu(II) are mostly coordination compounds with different DOS. These metals form fairly strong complexes with organic ligands present in surface water. Anionic complexes, i.e., metal compounds with HS, dominate

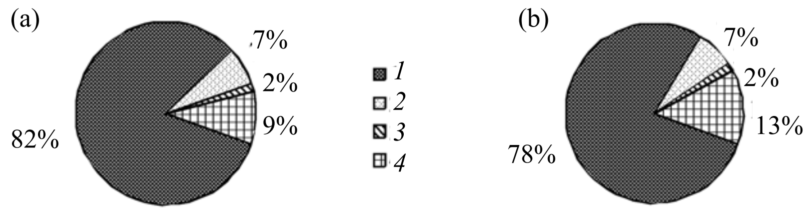

Fig. 7. Average annual relative concentrations of DOS (in percent of C_{org}) in water of Lyutsimir and Chernoe Bol'shoe Lakes: (*1*) humic substances, (*2*) carbohydrates, (*3*) protein-like compounds, and (*4*) other organic compounds.

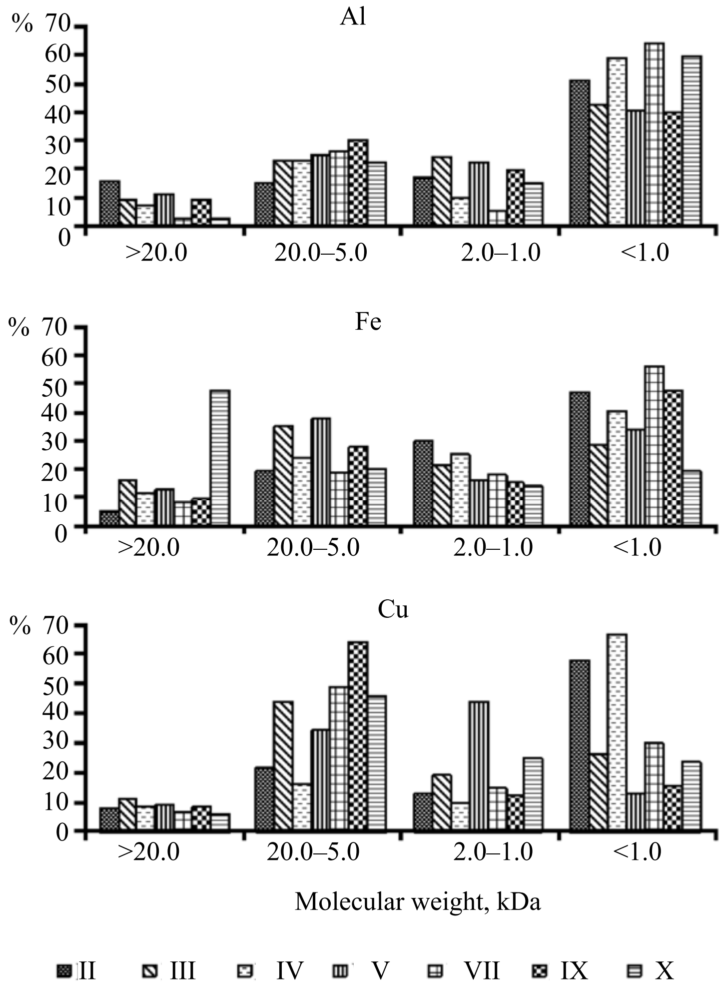

Fig. 8. Molecular-weight distribution of metal complexes with acid DOS in water of Lyutsimir Lake.

in the lake water, for HS dominate among other groups of DOS. Our data indicate competition between the examined metals for binding sites in HS macromolecules. Anionic complexes are most typical for Al(III) and Cu(II). The fraction of anionic Fe(III) complexes is somewhat lower, though iron ions are known to be effectively bound by HS. Carbohydrates and protein-like compounds also contribute to the complexation, but they bind a much smaller amount of metals. This may be due to lower concentration of these organic substances in surface water, which is determined completely by the development of biotic component. In addition, carbohydrates and PLC are readily assimilated by hydrobionts, unstable, and liable to biodegradation. Therefore, the corresponding metal complexes are less stable than those derived from HS.

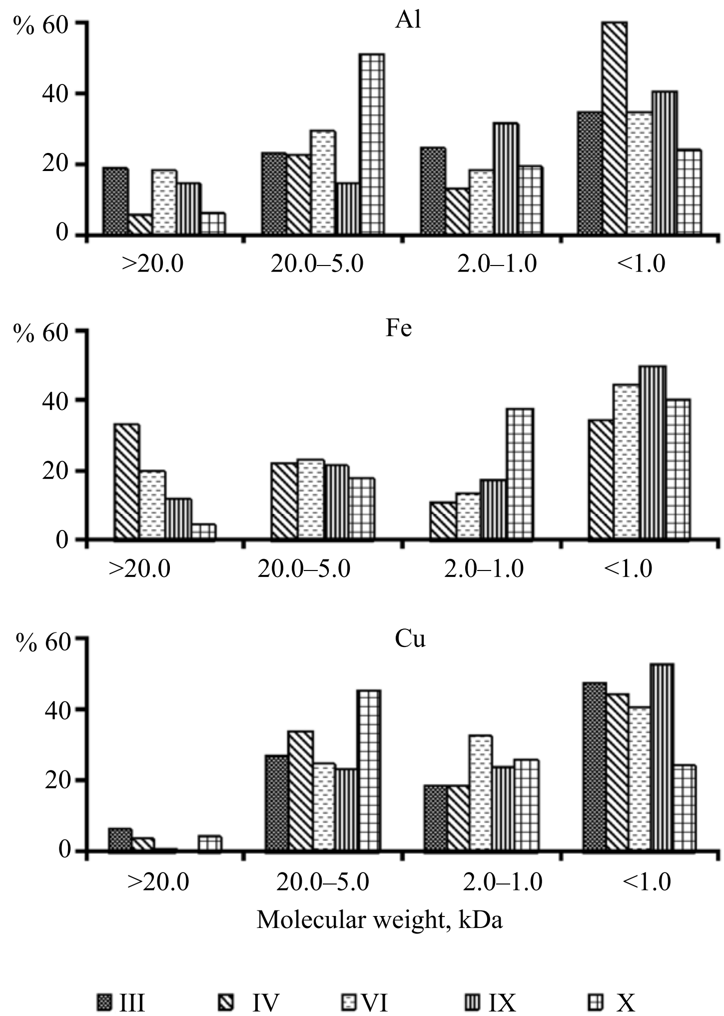

Fig. 9. Molecular-weight distribution of metal complexes with acid DOS in water of Chernoe Bol’shoe Lake.

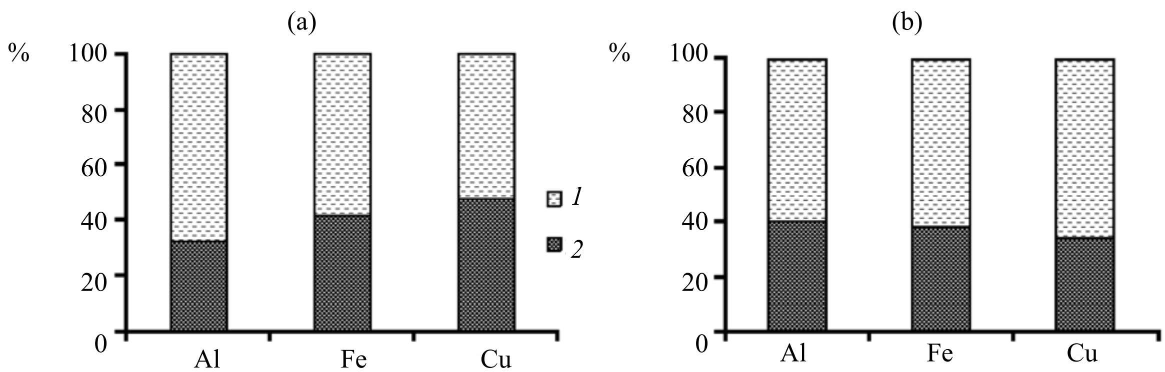

Fig. 10. Ratios of anionic metal complexes with different molecular weights in water of (a) Lyutsimir Lake and (b) Chernoe Bol’shoe Lake; (*1*) $M \leq 2.0$ kDa, (*2*) $M > 5.0$ kDa.

Compounds with a molecular weight not exceeding 2.0 kDa predominate among anionic complexes of Al (III), Fe(III), and Cu(II). This suggests different complexing abilities of particular HS fractions. The major HS fraction in water of the Lakes of Shatsk had a molecular weight of more than 5.0 kDa (54 and 60% in Lyutsimir and Chernoe Bol'shoe Lakes, respectively). Nevertheless, low-molecular-weight fractions, especially those with a molecular weight of less than 1.0 kDa, bind metal ions more effectively than do high-molecular-weight fractions. In some seasons, the latter exhibited a higher complexing ability than fractions with lower molecular weights. This is seen most clearly with Al(III) and Cu(II). Taking into account that HS in natural surface water consist mainly of fulvic acids, these acids are presumed to play the key role in the complexation.

Thus our results indicated that predominant occurrence of metals in a bound state (in suspended particles or as complexes with DOS) in water of the Lakes of Shatsk, as well as of other water bodies, should be considered as a positive factor which reduces chemical and biological activity of metals and hence their toxicity for living organisms. In our case, this is important for Al(III) and Cu(II) as elements possessing pronounced toxicity. The results of long-term studies showed that the presence of free (hydrated) ions of the examined metals (as the most toxic form) in appreciable concentrations in surface water bodies with extensive adsorption and complex formation is improbable. The concentration of free Al (III) and Fe(III) is so low that it cannot be detected even by highly sensitive methods. The fraction of free Cu(II) ions is also small (generally not higher than 10–15%). Humic substances present in water of the Lakes of Shatsk system bind metal ions to form complexes, which may be regarded as an important factor responsible for their detoxification. Furthermore, the concentration of HS in the aqueous phase is considerably higher than the concentration of metals. Therefore, the lake water has some potentialities to bind metals to complexes.

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