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Humic Substances and Their Role in Migration of Metals in the High Colored Surface Waters: The Case Study of Rivers of the Pripyat' River Basin

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Abstract—The results of studies of humic substances and metals in rivers of the Pripyat' river basin are discussed. It is shown that concentration of these natural organic compounds is within a wide range of values – from 8.9 to 167.7 mg/L (0.4–7.0 mmol C L^{-1}). In river waters of the North Polessye it is above due to the predominance of peat and bog feeding in a forming of their runoff. In river waters of the Western Polesye the concentration of humic substances is in general much lower, but in some rivers it reaches approximately the same quantities as in the Northern Polesye. Humic substances are the predominant group of dissolved organic matter in studied river waters (73.3–88.3% C_{org}). In the humic substance composition the high molecular compounds are dominated. The relative content of fractions with a molecular weight of 5.0–20.0 and > 20.0 kDa is 59.0–82.3% of the total concentration of humic substances. Prevalence of high molecular fraction of humic substances is reflected on their weight average molecular weight (M_{w}), which is within 7.7–10.9 kDa. Humic substances in the high concentration have a significant influence on the behavior, migration and distribution of metals among their coexisting forms. In particular, the proportion of dissolved forms for such metals as iron and aluminum substantial increases because of complexation with humic substances which stabilize them in solution. Copper is found mainly as dissolved form due to complexation with humic substances. The close correlation between the content of titanium dissolved form and concentration of humic substances has not been established. The data on the distribution of metals among the complexes with dissolved organic substances of different chemical nature and also of anionic complexes with humic substances are given.

Keywords: humic substances, molecular weight distribution, iron, aluminum, copper, titanium, coexisting forms, complex compounds, the rivers of the Pripyat' river basin

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The main part of the Pripyat' river basin lies in the area of Polesye. Accordingly, the hydrochemical regime of the river basin is characterized by certain specific features due to the influence of a number of natural factors. In the first, significant rainfall promotes good soil washing and comparative improverishment of surface water in the content of mineral compounds. In second, due to significant wetlands in, the region, surface waters contain dissolved organic matter (DOM), mainly humic substances (HS), as well as iron and manganese compounds in relatively high concentrations [1–3].

Mostly right tributaries of the Pripyt' river are situated on the territory of Ukraine. Depending on the formation conditions of the DOM and therefore concentration of organic compounds and water colority, they are divided into two groups. The first group includes the rivers of the Western Polesye (Stokhod, Styr', Horyn', and others), and the second, the rivers of Northern Polesye, in particular the rivers Ubort', L'va, Stviga, Slovechna, and some others. The first group is characterized by the predominance of the ground feeding in the formation of their flow and relatively low levels of water colority. The second group of rivers is charac-

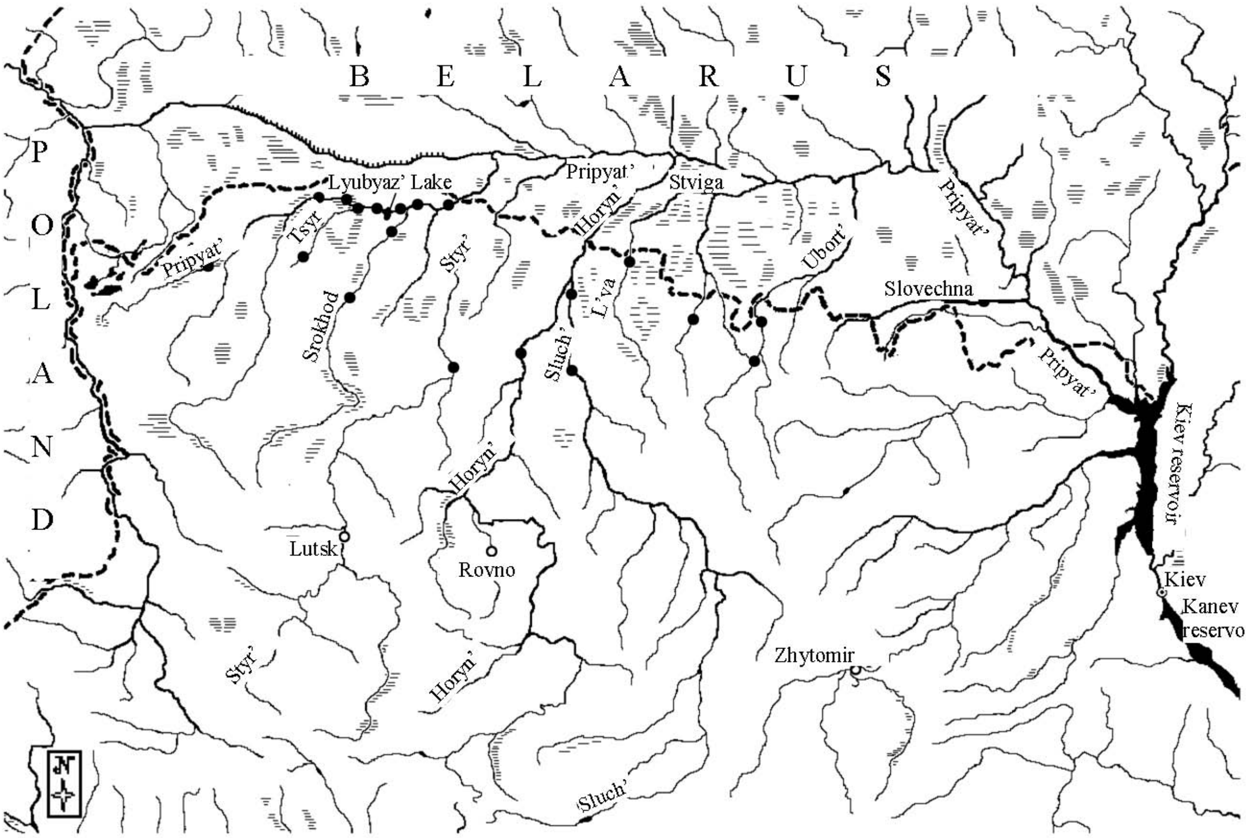


Fig. 1. Map of Pripyat' river basin (water sampling points in each of the studied rivers marked with black dots).

terized by a dominance of peat bog and marshland feeding and as a result, a high content of HS in water [3, 4].

It is known that HS are an integral and dominant component of DOM in surface waters [5]. They compose about 50–70% of the dissolved organic carbon content in fresh and coastal waters [6, 7]. HS play an important role in the functioning of aquatic ecosystems, determining the quality of water in them and the aquatic environment as a whole as a habitat for plants and animals [7–9]. First of all, they are an essential source of supply by many chemical elements. However it is known that high molecular fractions of HS are biologically indigestible, and their enzymatic hydrolysis is insufficiently effective [10]. In this regard, information on the ratio of different molecular weight fractions of HS are very important to assess their bioavailability. HS have protective function, because they are able to complexation, as well as reducing properties, which is very important from the standpoint of detoxification of toxic heavy metal ions [11–14]. Due to the binding capacity and the formation of adducts with hazardous organic toxicants, HS help to reduce the toxic effects of the latter on living organisms [15–19].

In recent years, more and more attention is paid to the study of this group of unique natural organic compounds from the standpoint of justification of their important ecological values, in particular their broader use for the recultivation of polluted areas, in agriculture and medicine [16].

The aim of this study was to investigate the content of HS, their molecular weight distribution and their role in the migration of metals such as iron, aluminum, copper and titanium in highly colored waters (for example, the rivers of Pripyat' basin).

EXPERIMENTAL

Researches on HS and metal content in the rivers of Pripyat' basin were performed in the summer–autumn period in 2010 and 2012–2013 and focused mainly on the right tributaries flowing through the territory of Ukraine. Water samples were collected from the surface layer of water (depth of ~0.5 m) in plastic

1.5 L containers and brought to the laboratory for further research. Map of the rivers mentioned basin and sampling points are shown in Fig. 1.

Suspended matters were separated from the dissolved ones by membrane filtration of water samples using Synpor filters (Czech Republic) with a pore diameter of 0.4 microns. DOM in the filtrates thus obtained were subjected to fractionation with isolation of acidic, basic and neutral groups, which are dominated respectively, by HS, protein-like compounds and carbohydrates [20]. In order to separate the above mentioned DOM fractions glass columns packed with DEAE (diethylaminoethyl) and CM (carboxymethyl) cellulose sorbents produced by “SERVA” were used. Water filtrates of 1.0–1.5 L volume were passed successively through these columns. Desorption from the DEAE-cellulose column was performed in three stages in order to ensure the most complete extraction of HS [21]. For the first stage 0.3 M solution of KOH was used as an eluent, in the second, 0.02 M solution of H2SO4 and third, again 0.3 M of KOH. Elution rate was approximately 1.0 mL/min. Desorption of protein-like compounds from the column with CM-cellulose was performed with 0.1 M HCl. During adsorption process on column organic substances were concentrated 25–40 times. Neutral group of DOM was concentrated 10–12 times frozen out [11].

Since HS are the dominant group of DOM in river waters of Pripyat’ basin, we focused on their study. This applies, in particular, to the study of molecular-weight distribution of HS and their metal complexes. For these purposes, a method of gel-chromatography was applied. Concentrate of HS (6.0 mL) was passed through a glass column packed with TOYOPEARL HW-50F gel (Japan). Column parameters, the rate of elution, substance used to calibrate the column, eluent type wer described in details previously [5].

Absorption spectra of HS in concentrates and in fractions after gel-chromatographic separation were recorded with a Unico UV 2800 spectrophotometer. The concentration of HS were determined from the calibration graph “the optical density at 254 nm—concentration of HS, mg/L.” We also used an indirect method determination of HS, based on the definition of the colority of natural water or their solutions using a simulation dichromate-cobalt scale. [22] The results of gel-chromatographic studies were used to calculate the weight average (M_w) molecular weight of HS.

The pH of natural waters and solutions in fractions containing separated groups of DOM was measured with a pH-150MI pH meter (Russia). Permanganate oxidizability of water and chemical oxygen demand (COD by dichromate) were determined by standard methods [23]. The total concentration of dissolved organic carbon (C_{org}) was calculated from the results of determination of the COD according to the formula $C_{org} = 0.375COD$.

The metal concentration in the individual groups of DOM and in HS fractions after gel-chromatographic separation was determined after photochemical destruction of organic compounds with UV-light.

Solutions, 15–25 mL, containing the individual groups of DOM (HS, protein-like compounds, carbohydrates) or HS fractions with different molecular weight were placed in a 50 mL quartz glasses, pH was adjusted to 1.0–1.5 with concentrated H_2SO_4, 3–5 drops of 35% of H_2O_2 solution was added thereto and the whole was irradiated with a mercury-quartz lamp DRT-1000 for 2.0–2.5 h.

Weight of suspended matters needed to calculate their content in 1 L of water was determined by the difference between the weight of filter with a suspended matters and filters, dried and weighed at room temperature. In order to ensure the constancy of weight filters were stored in a desiccator with anhydrous calcium chloride. The metal content in the composition of suspended matters was determined after “wet combustion” of filter with a suspended matters in a mixture of concentrated HNO_3 and H_2SO_4 and the subsequent hydrothermal treatment of undecomposed residual of suspended matters at 230°C for 5 h.

To determine metal concentration photometric (Al, Fe and Ti, by reaction with chromazurol S,O-phenanthroline and chromotropic acid respectively) and chemiluminescence (Cu) analysis techniques were used [22, 24, 25].

RESULTS AND DISCUSSION

Humic substances. Table 1 summarizes data on the pH values, colority and oxidizability of studied waters of Pripyat’ river basin. pH values of water were within a range of values 6.63–8.06 and depended largely on the concentration of HS. As it increases, pH value is decrises, that quite clearly shows the course of the curves of pH and water colority as a approximation of HS content (Fig. 2). As such, there is an inverse relationship.

Table 1. The values of pH, colority and oxidizability of the water of the rivers of the Pripyat' basin, 2012–2013

Water bodies	pH	Water colority, °Cr-Co-scale	Permanganate index, mg O L^{-1}	COD, mg O L^{-1}
Pripyat'	6.63–7.96 7.43	34.0–173.6 85.5	24.7–80.6 48.2	40.2–168.5 90.8
Tsyr	7.12–7.60 7.23	72.8–234.8 141.2	40.3–92.5 66.8	76.8–206.0 140.7
Styr'	7.24–7.88 7.53	12.5–29.6 20.8	14.5–18.7 16.2	24.5–32.6 27.3
Sluch'	7.40–7.86 7.68	30.5–48.5 35.7	20.7–31.2 24.5	36.5–42.6 40.5
Stokhod	6.88–7.98 7.56	56.6–150.2 108.7	29.4–78.7 60.5	56.5–142.5 107.9
Horyn'	7.72–8.05 7.88	14.7–69.5 36.8	11.8–44.6 24.8	18.6–74.5 40.3
Lyubyaz' Lake	7.42–8.06 7.84	46.7–120.5 91.5	29.8–70.4 51.5	52.4–123.0 93.8

As follows from the data in Table 1 and Fig. 2, the highest rates of water colority and, accordingly, the content of HS (Table 2) are characteristic for rivers Tsyr, Pripyat', Stokhod, Slovechna, Ubort', Stviga and L'va, as well as the Lyubyaz' Lake located in the Pripyat' area. Oxidizability of water in these rivers is also characterized by high values. The maximum values of permanganate oxidizability of water reach 70.4–92.5 mg O L^{-1}, and COD 123.0–206.0 mg O L^{-1}.

The concentration of HS in the water of the rivers of the Pripyat' basin and in Pripyat' river itself undergoes seasonal changes due to a change in feeding in some seasons of the year. Most commonly the increase of HS content is observed from winter to spring, and a decrease in their concentration in the autumn. [1] Our researches were conducted in the summer and autumn, and showed that in the summer a relatively high content of HS is also observed, which is significantly higher than in the autumn. Thus, in June 2010, the average concentration of HS was about 1.8 times higher than in September, that support by corresponding data on water colority and HS content in studied rivers (Figs. 2 and 3a). In 2012, this difference

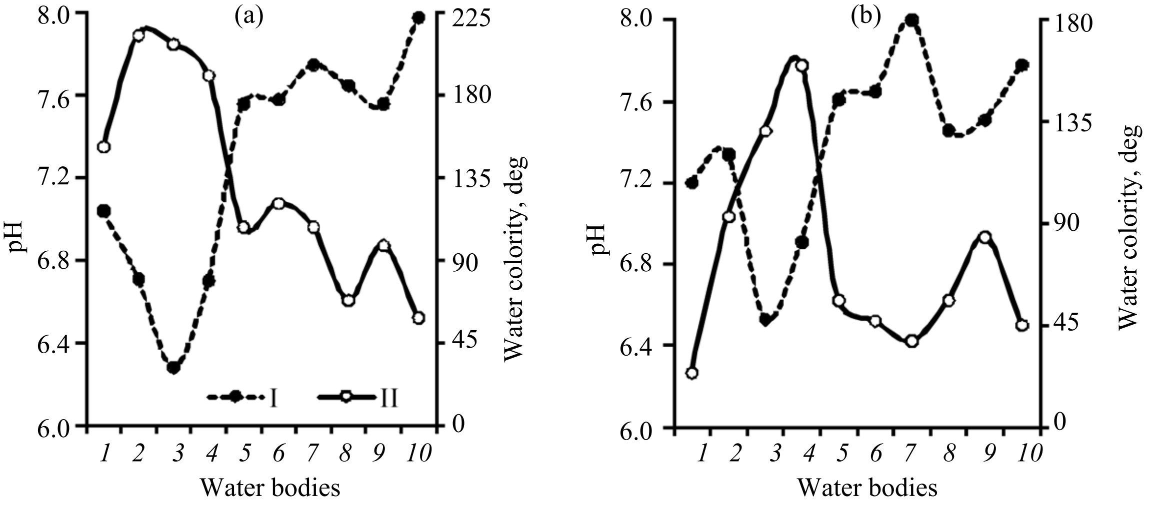


Fig. 2. The change in pH of water (I) of the Pripyat' river basin, depending on its colority (II) in summer (a) and autumn (b) of 2010. Water colority is expressed in degrees of simulation dichromate–cobalt scale. Here, and in Fig. 3: (*1*) Slovechna, (*2*) Ubort', (*3*) Stviga, (*4*) L'va, (*5*) Horyn', (*6*) Styr', (*7*) Prostyr', (*8*) Stokhod, (*9*) Pripyat' (village Senchitsy), and (*10*) channel Habarische.

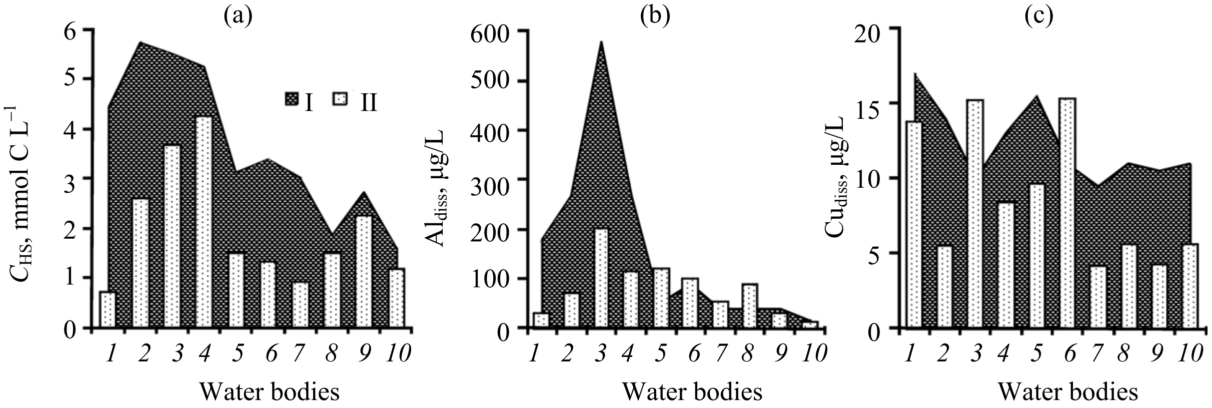


Fig. 3. The content of humic substances (a) and the dissolved forms of aluminum (b), and copper (c) in the river Pripyat' in summer (I) and autumn (II) of 2010.

was even more pronounced (almost 3 times) the an average of 82.9 mg/L in July and 28.9 mg/L in October. The average concentration of HS in the water of Pripyat' basin rivers in October 2013 amounted to 50.3 mg/L, and in June of the same year 74.6 mg/L, i.e. was higher by almost 1.5 times.

The dynamics of the HS content in waters of Pripyat' river and its tributaries is significantly affected by surface runoff, which depends in turn on the year water level [1]. In dry and average years water level, water colority and the concentration of C_{org} in the water are characterized by significant seasonal variations. In wet years indicators characterizing content of DOM, do not differ between baseflow and freshet.

In the waters of the Pripyat' river basin, as one would expect, the HS are the dominant group of DOM. Their relative content is in average 73.3–88.3% C_{org} with a maximum of 96.4% C_{org} (Table 2). High concentrations of HS causing a substantial increase in the water colority in the rivers of Pripyat' basin, can cause depression of photosynthesis and, as a consequence, the limitation of primary production, the reduction of the depth of the photic zone [7]. Therefore, it can be

Table 2. Concentration of HS in the water of the rivers of Pripyat' basin and their relative content as a part of the DOM, 2012–2013

Water bodies	C_{HS}		C_{org}, mmol C L^{-1}	HS fraction in DOM, C_{org}, %
	mg/L	mmol C L^{-1}		
Pripyat'	24.3–124.0 62.3	1.0–5.2 2.6	1.3–6.7 3.2	54.4–96.4 81.3
Tsyr	33.0–167.7 98.0	1.3–7.0 4.1	2.4–7.7 4.4	74.7–96.3 88.3
Styr'	8.9–76.4 34.7	0.4–3.2 1.4	0.8–3.9 1.9	51.6–87.5 73.7
Sluch'	21.8–34.6 25.6	0.9–1.4 1.1	1.2–1.8 1.5	67.0–81.2 73.3
Stokhod	34.0–107.0 60.5	1.4–4.5 2.5	1.7–4.8 3.1	72.4–95.2 80.6
Horyn'	10.5–49.8 26.7	0.4–2.1 1.1	0.6–2.5 1.5	68.8–82.7 73.3
Lyubyaz' Lake	33.4–86.0 56.8	1.4–3.6 2.7	1.6–5.3 3.4	66.7–93.2 79.4

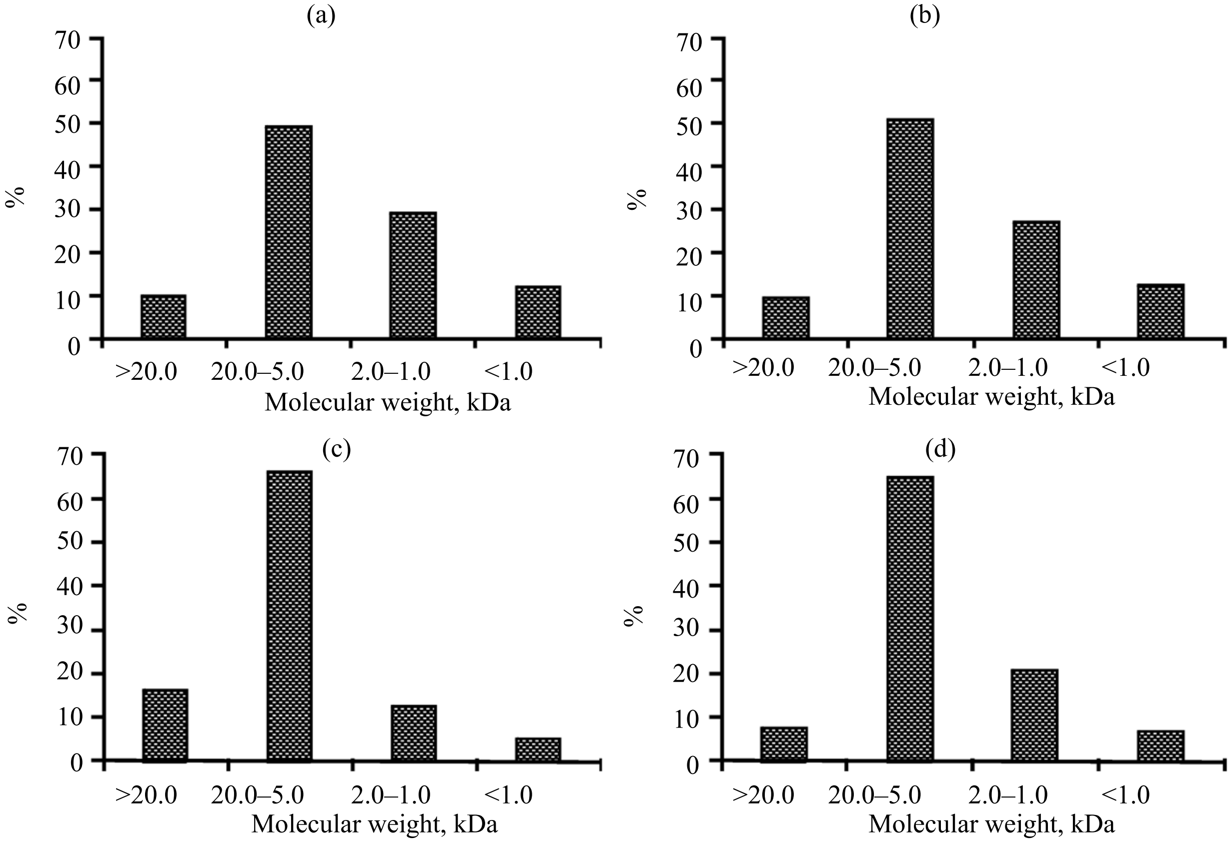


Fig. 4. The relative content of different molecular weight fractions of HS (C_{HS}, %) in the water of rivers Pripyat' (a) and Tsyr (b, c, d). (a, b) July 2012; (c, d) June and September of 2013; HS concentration in the original natural water: (a) 69.4, (b) 124.6, (c) 121.4, and (d) 41.5 mg/L.

argued that the role of biotic component in forming DOM component composition in this case is expressed to a lesser extent than, for example, in waters with a significantly lower content of HS.

Composition of the HS is dominated by fulvic acids (FA), the relative content of which reaches 90–92% of the total concentration of HS (C_{HS}). Despite the fact that the proportion of humic acid (HA) in most cases does not exceed 10.8% of C_{HS}, their concentration in the studied rivers lies in a wide range from 0.9 to 13.7 mg/L [26].

The results of gel-chromatographic studies have shown that in the composition of HS of the Pripyat' basin rivers dominate macromolecular compounds (Fig. 4). The total share of fractions with a molecular weight of 5.0–20.0 and >20.0 kDa is 59.0–82.3% of CHS. This can be explained by the following reasons. In the first, for fractionation were used HS undivided into fractions of HA and FA, that is in a state in which they were removed from the column with DEAE-cellulose. Only pH of HS concentrates were adjusted to the values characteristic of the source water of studied rivers Pripyat' and Tsyr. This means that they also contain HA typically with a molecular weight greater than FA [5, 9, 15]. At the same time, sufficiently "soft" HS extraction method, as in our case, and no exposure to acidic conditions and heating during fractionation for HA and FA, created conditions

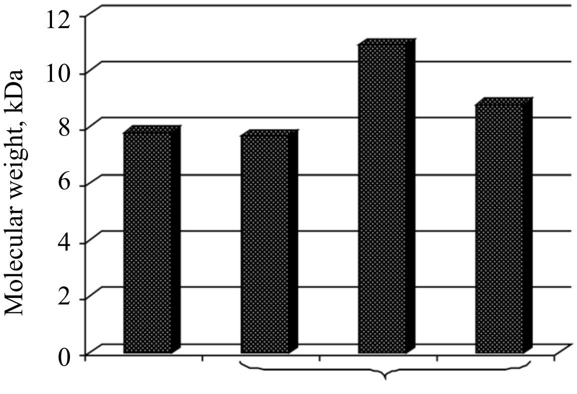


Fig. 5. The weight average molecular weight of HS extracted from the waters of the rivers Pripyat' (July 2012) and Tsyr (July 2012; June and September of 2013).

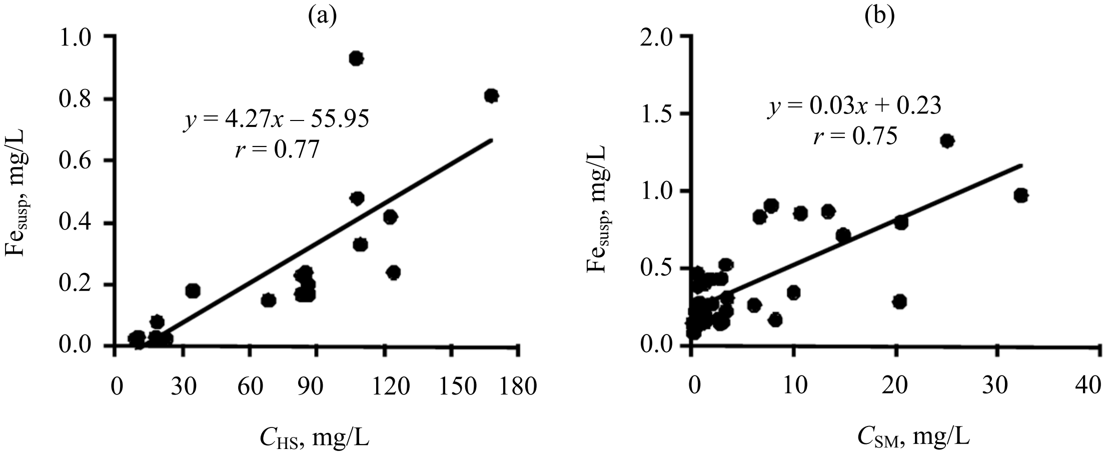


Fig. 6. The relationship between the concentration of dissolved iron (Fe_{diss}) and the content of HS (a) and concentration of suspended iron (Fe_{susp}) and suspended matters (SM) (b) in the water of the rivers of the Pripyat' basin. Here, in Figs. 7, 8 and 12: r is a correlation coefficient with a significance level of 0.01.

that do not allow the destruction or splitting HS to form compounds with lower molecular weights. Secondly, investigated river waters are characterized by relatively high concentrations of HS from 41.5 to 124.6 mg/L (Fig. 4). Apparently, in this case the effect of concentration is observed, leading to aggregation or consolidation of macromolecules. It is likely that this phenomenon is reflected in the value of the molecular weight of HS as a whole and the individual fractions in particular [21]. The prevailing fraction of higher molecular weight, resulting in an increase in the value of M_w of HS as a whole. This can be judged on the basis of the data presented below (Fig. 5) of the M_w HS, calculated on the results of gel-chromatographic separation. It can be seen that the investigated HS are the high molecular weight compounds with M_w in the range from 7.7 to 10.9 kDa.

Metals. The study of metals were focused on the study of coexisting forms of iron, aluminum, copper and titanium. Their concentration in the water of the rivers of Pripyat' basin, as well as data on the ratio of suspended and dissolved forms are given in Table 3. In a slightly lesser extent we had previously investigated manganese and chromium [27].

Iron. Iron is one of the most common and the most important bioelements necessary for the development and vital activity of algae and higher aquatic plants and many other representatives of aquatic organisms [11]. As part of porphyrin and proteins molecules as the main carriers of oxygen iron is actively involved in the biochemical redox reactions occurring in living organisms [28, 29].

In the waters of the Pripyat' river basin concentration of iron is in a wide range from 178.0 to 3898.0 μg/L (Table 3), due primarily to its high content in the marsh waters. According to [30], the total concentration of Fe(II) and Fe(III) therein is typically 1.1–6.7 mg/L, and sometimes reaches 8.8 mg/L. A direct dependance between C_{org} and iron concentration has been established.

Assessing the ratio of suspended and dissolved forms of iron, we can see that most often this metal is prevalent in the composition of suspended matters (Table 3). The abundance ratio of this form of iron (Fe_{susp}) varies in the average from 40.0 to 80.6% of Fe_{tot}. Although one would expect its existence predominately in the dissolved state, as in the river waters of the Pripyat' basin HS are in relatively high concentrations, and Fe^{2+} and Fe^{3+} ions form with them stable complexes [11, 31]. In addition, our results showed that there was a direct correlation between the content of dissolved iron (Fe_{diss}) and the concentration of HS (Fig. 6a). Nevertheless, a significant, and in some cases even overwhelming, part of the iron is found in the composition of the suspended matters. At the same time there is also a direct correlation between the concentrations of iron (Fe_{susp}) and suspended matters in the water of studied rivers (Fig. 6b). Preferential migration of iron in suspended state is usually characteristic for river waters. In this case, it may be explained by the adsorption of high molecular complexes of iron with HS on finely-dispersed particles of suspended matters. It is known that iron compounds are often used in the water treatment plants

Table 3. The content and the ratio of suspended and dissolved forms of metals in the water of the rivers of Pripyat' basin, 2012–2013[a]

Water bodies	M_{tot}, μg/L	M_{susp}		M_{diss}	
		μg/L	M_{tot}, %	μg/L	M_{tot}, %
Iron					
Pripyat'	178.0–3898.0 556.0	137.0–3640.0 353.0	24.8–93.4 63.5	41.0–792.0 203.0	6.6–75.2 36.5
Tsyr	324.0–2214.0 924.0	156.8–908.0 399.0	24.4–61.3 43.2	168.0–1306.0 525.0	38.7–75.6 56.8
Styr'	307.0–783.0 530.0	172.6–758.0 371.0	56.3–96.8 70.0	25.0–218.0 159.0	3.2–43.7 30.0
Sluch'	584.0–1355.0 939.0	269.0–1330.0 757.0	46.0–98.2 80.6	25.0–315.0 182.0	1.8–54.0 19.4
Stokhod	327.0–1405.0 692.0	153.0–474.0 277.0	33.7–55.9 40.0	158.0–931.0 415.0	44.0–66.3 60.0
Horyn'	1057.0	978.0	92.5	79.0	7.5
Lyubyaz' Lake	285.0–990.0 542.0	151.0–857.0 375.0	53.0–86.6 69.2	133.0–236.0 167.0	13.4–46.9 30.8
Aluminium					
Pripyat'	7.6–277.0 47.8	2.2–261.8 28.3	15.5–94.6 59.2	4.2–83.9 19.5	5.4–82.7 40.8
Tsyr	17.9–68.0 44.8	8.0–29.0 14.8	22.8–72.0 33.0	5.0–43.9 30.0	27.9–77.2 67.0
Styr'	279.0–947.0 484.0	189.0–939.0 428.0	67.7–99.2 88.4	7.8–101.0 56.0	0.8–32.3 11.6
Sluch'	316.0–1078.0 809.0	305.0–1051.0 788.0	96.7–97.7 97.4	10.5–27.0 21.0	2.3–3.3 2.6
Stokhod	14.8–119.0 57.5	3.2–79.2 23.3	19.8–66.4 40.5	11.6–89.0 34.2	33.6–80.2 59.5
Horyn'	832.0–1433.0 1039.0	712.0–1395.0 959.0	85.6–97.3 92.3	38.0–120.0 80.0	2.7–14.4 7.7
Lyubyaz' Lake	21.3–247.0 63.7	5.5–218.0 44.0	25.8–41.0 69.0	15.8–28.6 19.7	65.4–74.2 31.0
Copper					
Pripyat'	3.6–59.5 16.6	0.4–21.0 2.6	2.8–51.0 15.7	2.3–43.4 14.0	49.0–97.2 84.3
Tsyr	4.4–45.8 19.7	0.7–17.6 3.9	3.5–38.4 19.8	3.5–30.4 15.8	61.6–96.5 80.2
Styr'	15.0–24.0 19.0	2.4–4.0 3.2	12.9–26.7 16.8	11.0–20,9 15.8	73.3–87.0 83.2
Sluch'	8.7–21.6 13.6	0.5–1.8 1.2	5.0–18.4 8.8	7.0–19.8 12.4	85.6–95.0 91.2
Stokhod	5.4–14.7 10.3	0.5–3.2 1.4	4.8–31.0 13.6	4.5–14.0 8.9	69.0–95.0 86.4
Horyn'	11.3–21.5 15.0	2.1–6.0 3.5	18.6–28.0 23.3	9.2–15.5 11.5	72.0–81.4 76.7
Lyubyaz' Lake	3.9–19.7 13.5	0.7–2.8 1.7	8.7–17.9 12.6	3.2–16.9 11.8	82.0–91.3 87.4

Table 3. (Contd.)

Water bodies	M_{tot}, μg/L	M_{susp}		M_{diss}	
		μg/L	M_{tot}, %	μg/L	M_{tot}, %
Titanium					
Pripyat’	n.d.–70.0 24.6	n.d.–32.0 7.6	n.d.–100 31.0	n.d.–65.4 17.0	n.d.–100 69.0
Tsyr	14.8–44.0 23.0	n.d.–10.8 4.5	n.d.–60.0 19.6	7.2–44.0 18.5	40.0–100 80.4
Styr’	5.3–115.0 52.4	5.3–92.0 45.0	79,8–100 86.0	n.d.–23.0 7.4	n.d.–20.0 14.0
Sluch’	25.5–151.8 81.2	8.4–92.4 55.3	33.0–98.0 68.0	1.3–59.4 25.9	2.0–67.0 32.0
Stokhod	1.5–39.3 19.0	1.5–30.0 12.8	43.8–100 67.4	n.d.–9.3 6.2	n.d.–56.2 32.6
Horyn’	117.0	101.8	87.0	15.2	13.0
Lyubyaz’ Lake	6.0–25.9 18.0	4.2–25.9 12.0	18.6–100 66.7	n.d.–18.0 6.0	n.d.–81.4 33.3

[a] (n.d.) not detected by photometric method with chromotropic acid. (M_{tot}, M_{susp}, M_{diss}) total metal concentrations and its concentrations in suspended and dissolved form, respectively.

for water purification from HS by coagulation. Therefore, it is possible that a similar process may occur in the natural environment at high concentrations of iron and HS, some of which may pass into suspended state.

Aluminum. Investigation of coexisting aluminum forms in natural surface waters are of special interest due to the fact that this metal is one of hazardous toxicants [32, 33]. Particularly toxic are hydroxocomplexes $[AlOH]^{2+}$ and $[Al(OH)_2]^{+}$, whose existence especially probable is high at pH 4.5–5.5. However, the toxicity of said hydroxocomplexes substantially reduced in the presence of various complexing agents, in particular, HS that actively bind Al(III) [33]. It is therefore of interest to examine the state of the metal in the river waters, where HS are the dominant group of DOM and are in high concentrations.

It was found that the aluminum concentration in the studied river waters is characterized by very wide range of values from 7.6 to 1433.0 μg/L (Table 3). We can confidently assert that the high concentrations of aluminum, as well as iron, are caused by the presence in water of rivers high content of HS. It is sufficiently confirmed by the above data on the concentration of HS and dissolved aluminum (Al_{diss}) in the studied rivers in 2010 (Figs. 3a and 3b). Maximum concentrations of Al_{diss} were marked in summer, when the water colority reached its maximum. In the autumn it was significantly lower and this is reflected in the decreaseing the content of Al_{diss}. At the same time, in 2012–2013 even at high concentrations of HS in the summer (108.0–168.0 mg/L) the content of Al_{diss} was not so high (21.9–41.9 μg/L), as observed in 2010 in rivers Ubort’, Stviga, L’va (268.0–580.0 μg/L), that also are caracterized by about the same concentrations of HS. And this is despite the fact that there is a direct correlation between the concentration of Al_{diss} and HS content (Fig. 7). Consequently, this dependence is also affected by other factors. In our view, among them the biggest impact has the pH of the aquatic environment. On reducing pH value the concentration of Al_{diss} in water increases. Thus, we can talk about the feed-back between pH and Al_{diss} (Fig. 8). Most likely both factors (HS content and pH) together influence on the concentration of Al_{diss}. pH values of the water in rivers Ubort’, Stviga and L’va in June 2010 were in the range of 6.28–6.71, and pH value of water for rivers in Table 3, in the 2012–2013 were higher 7.07–8.00. This is what can be one of the biggest factors that make a noticeable difference in the concentrations of Al_{diss} in waters of studied rivers. Apparently, in the 2012–2013 for some reason there was no significant leaching of Al(III) from the bog waters. Therefore, complexation occurred to a lesser extent.

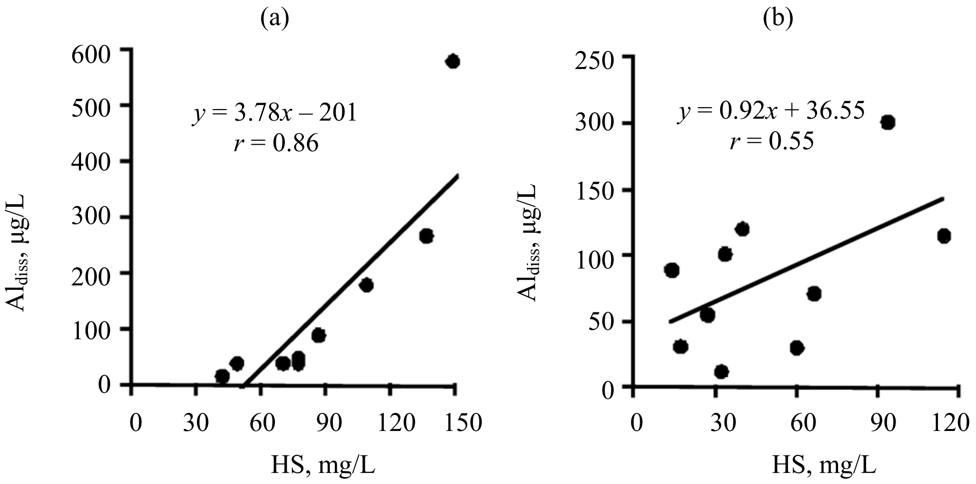


Fig. 7. The relationship between the concentration of dissolved aluminum and HS content in river waters of the Pripyat' basin in (a) summer and (b) autumn in 2010.

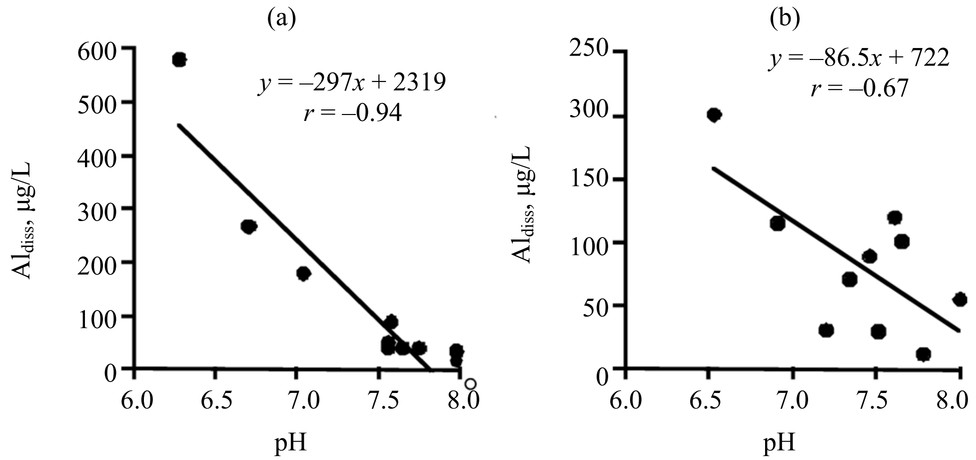


Fig. 8. The relationship between the concentration of dissolved aluminum and pH of the water in the rivers of the Pripyat' basin in (a) summer and (b) autumn in 2010.

Previously, it was experimentally established that the binding of Al(III) in complexes with HS of natural water, including HA and FA, most activity occurs at pH 4.0–6.0, i.e., in a weakly acidic medium [34, 35]. The decrising of pH at the boundary of water and bottom sediments also contributes to increasing of aluminum migration from the latter [36]. Therefore, leaching of aluminum from bogs in higher amounts will facilitate its binding to complexes with HS in a weakly acidic medium and increasing concentrations of $\mathrm{Al_{diss}}$ in water.

The predominant form of migration of aluminum turned to be suspended (see Table 3). Only in rivers Tsyr and Stokhod aluminum prevailed in the dissolved state. In general, aluminum migration in the river waters is characterized mainly in the composition of suspended matters (95–99% $\mathrm{Al_{tot}}$) [37, 38]. A significant increase in the proportion of $\mathrm{Al_{diss}}$ in water of the rivers of Pripyat' basin is caused by the increased content of HS. However, in those rivers where suspended matter content was higher (Fig. 9), the proportion of Alsusp increased significantly. In this case, important factor is the nature of the suspended matters. The greater proportion of mineral particles, the higher the concentration of $\mathrm{Al_{susp}}$.

Copper. Copper is, from the one hand, an essential trace vital element, and from the other—one of the toxic metals [11]. However, its toxicity as well as for many other toxic metals depends largely on its state in natural water. The greatest toxicity exhibit so-called

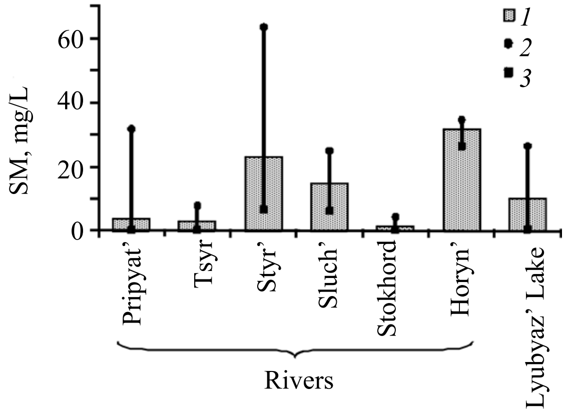


Fig. 9. Minimum (*1*), maximum (*2*), and average (*3*) content of suspended matters (SM) in the rivers of the Pripyat' basin and the Lyubyaz' Lake.

free (hydrated) ions of Cu^{2+} and hydroxocomplexes $[CuOH]^+$ and $[Cu(OH)_2]^0$. Complexation with natural organic substances, in particular with HS, reduces the toxicity of ions Cu(II) till its complete loss [39].

The copper content in the water of the rivers of Pripyat' basin is within 3.6–59.5 μg/L range, although the average concentration is much lower (Table 3). Most of it is in dissolved form, accounting for an average 76.7–91.2% Cu_{tot}. The dominance of dissolved copper (Cu_{diss}) is characteristic for other surface water of Ukraine, including those where the content of HS is much lower than in the Pripyat' river waters [40]. This is due to the fact that Cu(II) forms a stable complexes with organic ligands of natural surface waters, thereby stabilizing it in the dissolved state [11]. In the water of investigated rivers this stabilization is achieved by preferential binding of Cu(II) in complexes with HS. However, we did not find such a close relationship between the concentration of HS and Cu_{diss}, as in the case of iron and aluminum. Although with the increasing of HS concentration in water dissolved copper content is slightly increases (Fig. 3c). In general, the low concentration of copper in most of the rivers of the Pripyat' basin witness the absence of anthropogenic sources of pollution of this metal.

Titanium. Among the metals of natural surface waters titanium is the least studied. This is apparently due to the fact that practically till now biological role of this element has not been established. It is believed that titanium oxide TiO_2 is relatively non toxic. However, TiO_2 nanoparticles have a specific biological properties due to their photocatalytic activity. Toxic effects of nanoparticles of TiO_2 on fish is associated with oxidative stress and some other effects [41, 42]. There are also data on the toxicity of TiO_2 nanoparticles for microalgae [43], however, significantly reduced in the presence of HA, as was found in experiments with culture of green algae *Chlorella Sp.* [44].

Titanium is one of the most abundant elements in the earth's crust (the ninth of all the elements and the second after the iron in transition metal group), and found in the rocks, soils and bottom sediments [41, 45]. The results of the determination of titanium in natural surface waters show its relatively low concentration due to poor solubility of TiO_2. In the pH range of 4.0–10.0, according to the results of thermodynamic analysis, it does not exceed 0.05 μg Ti L^{-1} [46]. However, in the natural surface waters, titanium concentration may be higher because of the presence of its colloidal particles.

In estuarine and coastal waters, the concentration of titanium is often in the range per 1 L. For example, in Amazon estuary, content of dissolved titanium (Ti_{diss}) does not exceed 0.16–0.34 μg/L. [45] About the same range (0.55–0.69 μg/L) is Ti_{diss} concentration in the upper reaches of the river Severn (UK) [41]. However, in the river waters of agricultural and industrial regions of the UK average content of Ti_{diss} increases to 0.87–6.48 μg/L, and in times of storm water discharge up to 1.42–13.05 μg/L [41].

In natural surface waters, rich in organic matter, Ti_{diss} concentration is 1.2–5.5 μg/L [45]. Hence, the importance of complexation with natural organic ligands. A number of studies [47] experimentally shown that the presence of natural organic matter, including HA and FA, contributes to the stabilization of TiO_2 particles. It becomes more noticeable when the concentration of natural organic substances increases from 10 to 25 mg/L. This in turn increases the mobility of the TiO_2 nanoparticles in an aquatic environment. Dissolved titanium in natural surface waters found in the form of hydrated oxide $TiO(OH)_2$. Therefore, it is possible that in natural water with a high content of FA titanium can form hydroxofulvic complexes like hydroxofulvic iron complexes [31]. Although this is only an assumption, requiring relevant studies.

In some surface waters such as some Ethiopian rift-walley lakes and their in-fows, titanium concentration reaches tens or even hundreds of micrograms per 1 L [48].

In surface waters of Ukraine titanium content was little studied previously. In the water of the Pripyat'

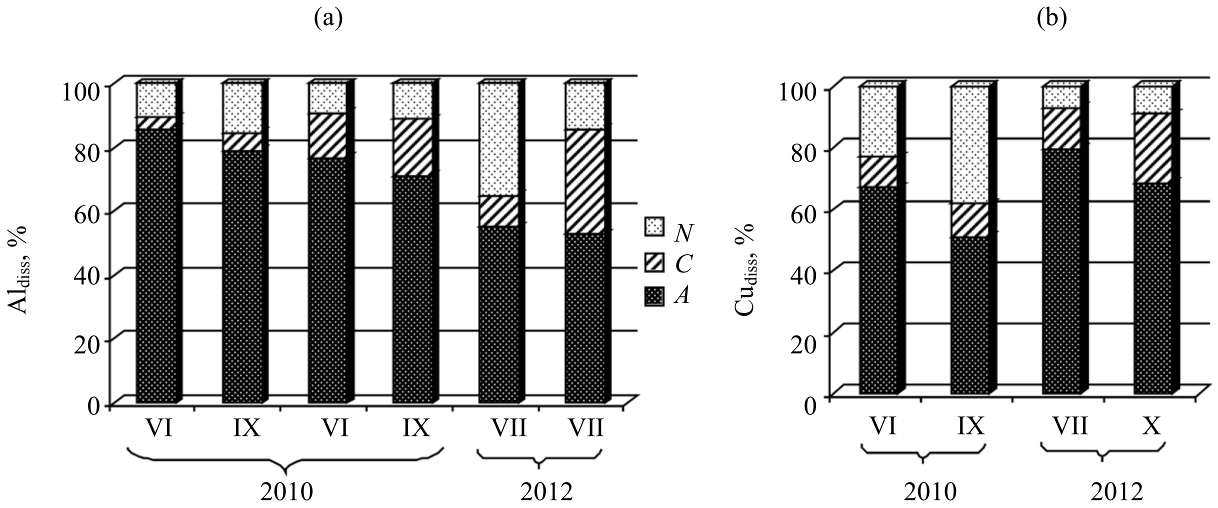
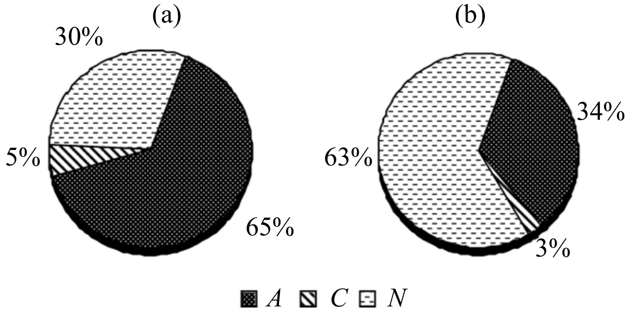


Fig. 10. Distribution of the dissolved aluminium (a) and dissolved copper (b) among complex compounds with different chemical nature of DOM in water of rivers Pripyat', Stviga and Tsyr. Here, in Fig. 11: (*A, C, N*) anionic, cationic, and neutral complexes, respectively. (a) 1st, 2nd, 5th columns: Pripyat', 3rd and 4th columns: Stviga, 6th column: Tsyr; (b) Pripyat'.

river basin we found wide variations of titanium (Ti) concentration—from trace amounts not detectable by photometric method with chromotropic acid up to 151.8 μg/L (see Table 3). The highest content of Titot is characteristic for Sluch' and Styr' rivers, that connected, most likely, with a consistently high levels of suspended matters in these rivers (Fig. 9) and the determination in their composition most of detected titanium. It is characteristic that in all studied water bodies, except the rivers Pripyat' and Tsyr, titanium prevalates in suspended form (an average of 66.7 to 86.0% Ti$_{tot}$). Most likely, suspended matters are mineral particles. Perhaps some of the fine suspended particles contained on their surface adsorbed HS, which have been binded to titanium. At the same time, the mean values of the concentration of dissolved titanium (Ti$_{diss}$) were relatively low and close to the concentration of Cu$_{diss}$ (Table 3), i.e., they were about the same order. Slightly higher they were in the water of the rivers Pripyat', Tsyr, and Sluch' due to the maximum values of Ti$_{diss}$ oncentration which is associated with the presence of high concentrations of HS in these rivers.

Distribution of dissolved metal among the complex compounds with DOM. The predominance of HS in the composition of DOM in the Pripyat' river basin is significantly reflected in the ratio of metal complexes with natural organic ligands. As showed the results of research, often anionic metal complexes with HS were dominated. As part of these complexes were detected 52.9–85.6% Al$_{diss}$ (Fig. 10a) and 50.7–79.5% Cudiss (Fig. 10b). Sometimes in summer and more often in autumn the abundance ratio of these complexes is somewhat reduced with a simultaneous increase in the proportion of neutral complexes. Most likely, this phenomenon is associated with a change in the component composition of DOM, and a noticeable increase in the concentration of organic compounds of neutral group—carbohydrates. Seasonal changes in the ratio of metal complex com-pounds can be seen, for example, for copper (Fig. 10b). Separately should be said on cationic complexes of Cu(II). Most likely, it is positively charged hydroxo complexes $[CuOH]^+$, as they are determined, as a rule, in filtered natural water prior to photochemical degradation of DOM with UV-light. Frequently their concentration coincide with the content of Cu(II) in the composition of basic (cationic) groups of DOM. If between these indicators there is a difference, in this case, we can assert the existence of positively charged complexes of Cu(II) with a protein-like substances, dominant in the basic group of DOM. Often, however, their share in the total content of complex compounds of copper with DOM is relatively low.

Most of the dissolved iron is also found in the composition of anionic complexes with HS (Fig. 11a). The iron concentration in natural water often simultaneously increases with increasing content of HS, as we have noted previously [49]. This is also confirmed by a positive relation between the concentrations of Fe$_{diss}$ and HS (Fig. 6a).



Fif. 11. Distribution of the dissolved iron (a) and the dissolved titanium (b) among DOM complexes with different chemical nature in water Tsyr river in July 2012. Contents of each metal in the composition of individual fractions of the complex compounds is expressed as % of the total soluble metal concentration.

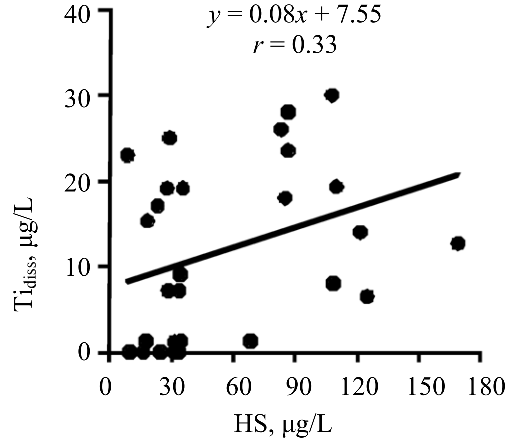


Fig 12. The relationship between the concentration of dissolved titanium and HS content un the water of the rivers of the Pripyat' basin, 2012–2013.

However, the distribution of dissolved titanium among complexes with DOM significantly differ (Fig. 11b). The predominant part of it was in the complex composition with neutral compounds (63.0%) and only 34.0% Ti_{diss} was associated with HS. This suggests that the concentration of titanium is less dependent on HS content in waters. Therefore, there is no such a close correlation between the concentrations of Ti_{diss} and HS (Fig. 12), as in the case of iron or aluminum (Figs. 6, 7). Apparently, the interaction of the hydrated titanium oxide $TiO(OH)_2$ with HS is more complicated than in case of Fe(III) and Al(III), due to the strong bonding of titanium and oxygen. In addition, it is unknown at what pH complexation (if any) occurs more actively. Indeed, in the case of aluminum, the most active complexation with HS occurs in weakly acidic medium at pH 4.0–6.0, as already was noted above. We can not exclude the fact that neutral nanoparticles of TiO_2, adsorbing HS on the surface as a result acquire negative charge [47]. Based on the foregoing, it can be assumed that the presence of titanium in the composition of the acid group of DOM may be due either to the complexation with HS or adsorption of the latter on the surface of nanoparticles of TiO_2. Further in depth investigations needed to obtain a clear answer to this question. Domination of the so-called "neutral" complexes of titanium is likely due to the presence of the same nanoparticles of TiO_2 with a neutral charge, which also requires proof.

Such a distribution of dissolved titanium by the charge, as described above, was found and for other water bodies. For example, in the Kanev Reservoir anionic fraction of Ti_{diss} in some seasons of the year (for example, in May 2012 and 2013) was 37.9–47.4%, while the share of neutral fraction reached 46.8–52.6%. In the same reservoir, in some cases Ti_{diss} was detected mainly in the composition of the anionic fraction (80.8 and 89.4% respectively in April 2012 and 2013), which was associated with an increase in the concentration of HS.

Molecular weight distribution of anionic metal complexes. Given the fact that in the rivers of the Pripyat' basin dominate anionic metal complexes with HS, we investigated their molecular weight distribution. It was found that metals were in complexes with both high- and low-molecular HS fractions (Fig. 13). In particular, as complexes with molecular weight > 5.0 kDa were found 37.6–68.4% Al(III), 31.9–58.7% Fe(III) and 32.2–84.0% Cu(II) content in the total composition of anionic complexes (M_{anion}). At the same time, the results of molecular weight distribution of HS showed that their composition is dominated by high-molecular fractions (Fig. 4), as already was mentioned above. Therefore, it was logical to expect preferential existence of metals in the composition of these fractions. However, this is not always the case, as can be seen in the example of the Tsyr river. Thus, in July 2012, the total content of fractions with a molecular weight of HS 5.0–20.0 and >20.0 kDa in the water of this river was 60.5% (Fig. 4b). Accordingly, they have been binded with 68.4% Al(III), 58.7% Fe(III) and 84.0% Cu(II) of the anionic complexes (Fig. 13c). In June 2013, the total content of the above-mentioned HS fractions in the same river water reached 82.3% (Fig. 4c), but it was associated with only 34.4% Al(III), 31.9% Fe(III) and 32.2% Cu(II). Consequently, most of the metals contained in the fractions of HS with lower molecular weight (≤ 2.0 kDa), despite their little proportion in the total balance of these organic compounds.

CONCLUSIONS

A characteristic feature of the Pripyat’ river basin is the high content in their waters humic substances whose concentration is in a wide range from 8.9 to 167.7 mg/L (0.4–7.0 mmol C L^{-1}). The highest content of humic substances have rivers of the Northern Polesye as the formation of dissolved organic matter in them is mainly of the peat reach and swamp sources. In the rivers of the Western Polesye concentration of humic substances on average 2.8–3.8 times lower. Although in the rivers Tsyr and Stokhod flowing through the Western Polesye, the content of humic substances in the summer of 2012–2013 was also high (122.5–167.7 and 89.3–107.3 mg/L, respectively) and commensurate with their concentration in the water of the rivers of the Northern Polesye (Ubort’, Stviga, L’va), observed in the summer of 2010 (136.4–152.0 mg/L).

In total content of dissolved organic matter share of humic substances ranging from 51.6 to 96.4%. Given the average value of the relative content of this group of natural organic compounds (73.3–88.3% C_{org}), it can be considered as dominant.

The concentration of humic substances undergoes seasonal changes. In summer, it is substantially higher than in the autumn (1.5 or even 2.9 times higher). Among the humic substances high molecular weight compounds are dominated, in particular the total content of fractions with a molecular weight of 5.0–20.0 and >20.0 kDa reaches 59.0–82.3% C_{HS}. Proportion of these fractions especially increases, when the concentration of humic substances reaches its maximum values. This is likely to be explained by consolidation (aggregation) of macromolecules. Dominance in high-molecular fractions in the humic substances is reflected in the value of their weight average (M_{w}) molecular weight, which is 7.7–10.9 kDa.

High concentrations of HS in the rivers of the Pripyat’ basin influence the behavior and migration of metals. This effect manifests itself primarily in the form of an increase in the concentration of dissolved metals such as iron and aluminum, which are transported by river waters mainly as part of suspended matters. Thus, the average content of dissolved iron in the water of the studied rivers was 19.4–60.0% Fe_{tot}. In the rivers with the highest concentration of humic substances dominate dissolved form of iron. A positive correlation between the content of Fe_{diss} and humic substances content ($r = 0.77$) has been established.

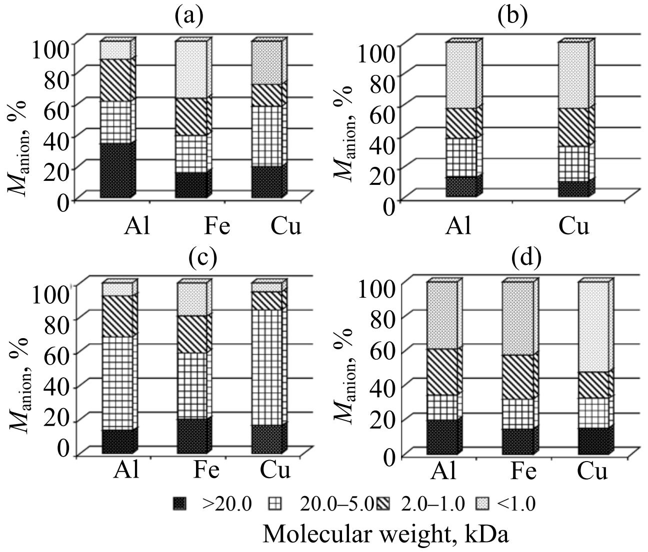


Fig. 13. Distribution of metals (M_{anion}, %) among the anionic HS complex compounds with different molecular weights in the water of the rivers (a) Ptipyat’, (b) Stviga, and (c, d) Tsyr. (a, c) in July 2012, (b, d) in June 2010 and 2013, (M_{anion}) is the total content of metals in acidic (anionic) group of DOM.

The same can be said with regard to aluminum. Although there are some particularities of its behavior in highly coloured river waters of the Pripyat’ basin. Despite the existing correlation between the concentration of Al_{diss} and humic substances, the content of dissolved forms of this metal also depends to a large extent on the pH of the aquatic environmental. At low pH (within 6.28–6.71) and high concentrations of humic substances, as observed in the water of the rivers Ubort’, Stviga, L’va in summer 2010, the contents of Al_{diss} was 268.0–580.0 μg/L. At the same time, in a number of other rivers of the Pripyat’ basin at higher pH values of water and a high concentration of humic substances content of Aldiss was considerably lower. This indicates that the pH of the water plays a pivotal role in the accumulation of dissolved form of aluminum in an aquatic environment because binding of this metal in complexes with humic substances more active occurs in the weakly acidic at pH 4.0–6.0.

Most of the copper in the investigated river waters exists in dissolved form, which is typical for this metal, even in lakes and rivers, which are characterized by comparatively not so high content of humic substances.

No such close correlation between the content of Ti_{diss} and the concentration of humic substances has been established. Most likely, it may be due to certain difficulties in the course of complexation with humic substances. Because titanium is in the aqueous phase exists in the form of hydrated oxide $TiO(OH)_2$, in which it has a very strong bond with the oxygen. Therefore, we can assume, on the one hand, the hydroxofulvic titanium complexes, and on the other, existence of other aggregates related to the adsorption of humic substances on the surface of nanoparticles of TiO_2, which requires additional studies to prove their existence. At the same time, in rivers with maximum content of humic substances titanium prevails in dissolved form, and its high total concentration in some rivers was associated with the high content of mineral suspended matters.

For all the metals, except titanium, is characteristic dominance of anionic complexes with humic substances. Most of the Ti_{diss} was found in the group of neutral DOM. Apparently, these are particles of hydrated oxide $TiO(OH)_2$, that has a neutral charge.

The binding of metal ions in complexes with humic substances takes place with the participation of both high-molecular and low-molecular fractions, although the high-molecular fractions prevail in the composition of this natural organic acids.

Given the above it can be argued that the humic substances in the river waters of the Pripyat' basin have a significant impact on the behavior, migration and distribution of metals among their co-existing forms.

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