ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 13, pp. 2562–2571. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © T.T. Efremova, S.P. Efremov, N.I. Pavlenko, N.G. Maksimov, 2014, published in Ekologicheskaya Khimiya, 2014, Vol. 23, No. 2, pp. 63–73.

Elemental Composition and Structural Peculiarities of Humic Acids in Bog Waters of Taiga Zone

T. T. Efremova[a], S. P. Efremov[a], N. I. Pavlenko[b], and N. G. Maksimov[b]

[a] *Sukachev Institute of Forest, Siberian Branch, Russian Academy of Sciences,*
Akademgorodok 50/28, Krasnoyarsk, 660036 Russia
e-mail: efr2@ksc.krasn.ru

[b] *Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences,*
Akademgorodok 50/24, Krasnoyarsk, 660036 Russia
e-mail: pni@icct.ru

Received April 23, 2014

Abstract—Results of a complex studying the preparations of humic acids from bog waters by methods of IR spectroscopy, nuclear magnetic resonance and electronic paramagnetic resonance have been considered in the paper. Properties of humic acids are evaluated according to the elemental composition. Commonality and character of varying the composition of humic acids under forest oligotrophic and mesotrophic bogs are discussed hereaswell. The opinion about probable mechanisms of humic acid synthesis in bogs of different genesis is suggested.

Keywords: bog waters, humic acids, elemental composition, IR spectra, ^{13}C NMR spectra, electronic paramagnetic resonance (EPR)

DOI: 10.1134/S1070363214130131

INTRODUCTION

Swamp waters form a very special type of organogenic water properties and specificity of formation which still has not been well studied [1]. Meanwhile, this information is important in assessing the geochemical features of surface waters of the boreal zone and on a range of other scientific problems: geochemistry of organic substances, the general theory of humification, balance calculations of carbon fluxes in the sedimentary crust of the Earth, correct estimation of ways of carbon transformation under global climate change, etc.

In recent works devoted to the characterization of the bog water, it was shown that dissolved organic carbon is represented mainly by compounds of humic natures, mainly fulvic acids [2–10]. According to D.S. Orlov, fulvic acids represent a continuous series or group of compounds simultaneously existing in all soil conditions due to the fact they do not have sharply distinct specific features [11]. Therefore, if on the properties of water fulvic acids one can form a certain opinion, the nature of humic acids (in the classical understanding) remains virtually unexplored.

The purpose of current work – to characterize the elemental composition and structural features of humic acids of aqueous phase from the swamps of taiga zone of Western Siberia.

EXPERIMENTAL

The objects of study were chosen forest oligotrophic and mesotrophic bogs from southern taiga subzone of Western Siberia, situated between rivers Ob’ and Tom’. Water samples for chemical analysis were taken from the man holes in the autumn. Determination of the ionic composition of water, organic carbon content and isolation of humic acids was performed using standard techniques [12]. Since the content of HA in marsh water, usually no more than 10–20% of the dissolved carbon large amounts of water, generally 5–6 L were used for the isolation of which were concentrated on a steam bath, then acidified with 1.0 N H_2SO_4 to pH 1.5. The precipitate (gel) was filtered on a Buchner funnel, washed with

Table 1. Some chemical parameters of swamp waters from Taiga zone of Western Siberia

Entry no.	Sampling point	pH	M^a, mg/L	Carbon, mg/L			C_{HA}/C_{FA}
				total	HA	FA	
	Oligotrophic bog ”Kirgiznoe”						
3a	Northern slope	3.8	9.69	89.8	7.61	82.19	0.09
4a	Summit	3.6	8.31	94.7	7.98	86.72	0.09
5a	Eastern slope	3.5	12.56	107.1	9.5	97.6	0.10
	Mesotrophic mires						
11	Trapping channel, dry land–mire	6.8	75.12	55.4	5.5	49.9	0.11
14	76 Quarter, ploughed	5.2	26.33	94.7	15.76	78.94	0.20
16	Gazoprovodnoe	4.3	11.02	85.3	10.65	74.65	0.14
18	Maloe Elovochnoe	4.5	13.59	61.8	14.08	47.72	0.30

[a] (M) is a mineralization index.

acidified water and dried to constant weight at 60°C [13]. Mass of precipitated HA depending on the type of water and ranges from 40 to 480 mg, therefore no separate preparations covered all kinds of planned chemical analysis.

Elemental composition (C, H, O, N) was determined on the elemental analyzer FLASH TM 1112 (Thermo Quest, Italy). Calculations of atomic percent atomic ratios (H/C, O/C, C/N) and the degree of oxidation (ω) was performed according to the recommendations of D.S. Orlov and L.A. Grishina [14]. IR spectra were recorded on FTIR spectrometer Tensor-27 (Bruker) in 4000–400 cm^{-1} range. Processing of spectral information was carried out using the software package OPUS 5.0. Samples for IR spectra were prepared in the form of tablets in KBr matrix, with subtraction of self-absorption before processing. Interpretation of the spectra was performed using methods described previously [11, 13–15].

The distribution of carbon among structural fragments was determined by ^{13}C NMR spectroscopy. NMR spectra were registered on Bruker Avance III spectrometer with an operating frequency of 150 MHz for ^{13}C nuclei. D_2O (4.7 ppm) residual signal was used as an internal standard. For recording NMR spectra of humic acid samples were prepared by dissolving 60 mg of sample in 1 mL of 0.1 N NaOH solution in D2O. The resulting solution was centrifuged at 4000 rpm. for 10 minutes. Then, 0.5 mL of the filtrate was transferred to a NMR tube. Before the procedure of finding the integral intensities in the spectra, baseline correction was performed using linear function with zero angular coefficient. Integral intensities in the range of chemical shifts of assumpted functional fragments were calculated accordingly to [11].

Registering spectra of electron paramagnetic–magnetic resonance (EPR) in preparations of HA was performed at room and low (100 K) temperatures in quartz ampoules on an ELEXYS E-580 (Bruker) instrument in CW mode. Radical contents was calculated by double integration of narrow signals in $g \approx 2.00$ range[16]. The relative intensity of the EPR signal of different metals were detected by the amplitudes of the strongest transition in the areas of: Fe^{3+}, $g = 4.3$ [17], Mn^{2+}, $g \approx 2.15$ [18], Cu(II)-porphyrin, $g + \approx 2.05$ [30], Fe(III)-porphyrin, $g + = 6.0$ [20].

RESULTS AND DISCUSSION

Swamp water of study objects are characterized by weak mineralization of 8.31–26.33 mg/L and acid reaction [pH 3.5–5.5 (Table 1)]. The main ingredients are compounds of humic nature 61.8–102.5 mg/L, clearly dominated by fulvic acids. $C_{HA} : C_{FA}$ ratio is 0.09–0.30. Water of mires is slightly less acidic compared to the oligotrophic and contain little more humic acids. More specific are water of trapping channel. It is laid on the perimeter of Bol’shoe (Greater) Elovochnoe mesotrophic bog and collects not only swamp waters, but also stock water from sandy ridges bordering the array. The water has neutral

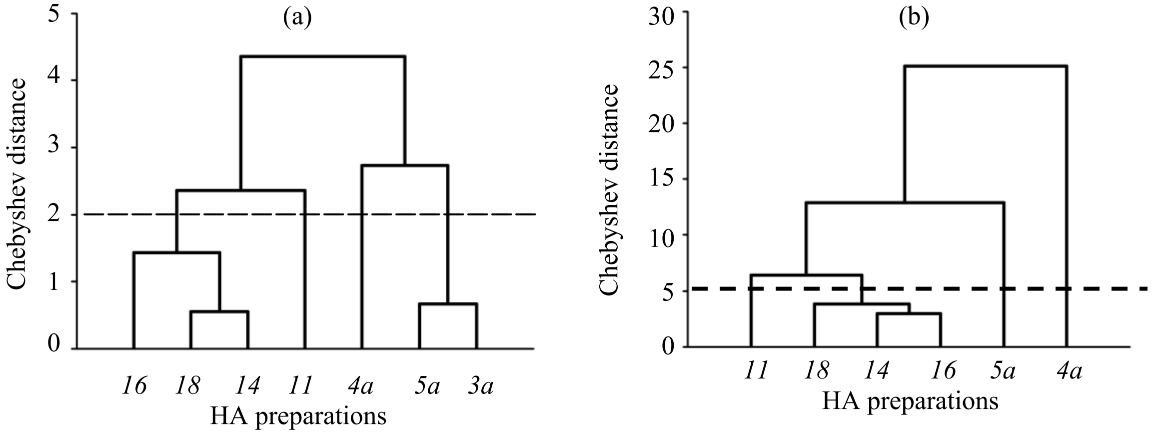

Fig. 1. Dendrograms combining aqueous preparations of humic acids by (a) elemental analysis and (b) ^{13}C NMR spectroscopy. HA preparations: (*4a*) oligotrophic bog–summit, (*3a*) northern slope, (*5a*) eastern slope, (*11*) trapping channel (dry land–mires border), (*14, 16, 18*) mires.

treaction, medium mineralization and relatively depleted of soluble carbon.

Elemental composition of humic acids. Humic acid of aqueous phase contain 47.06–53.47% carbon on a dry basis, 3.71–5.55% hydrogen, 38.07–47.11% oxygen, and 1.51–4.32% nitrogen (Table 2). The elemental composition expressed in atomic percent, quite clearly emphasizes the originality humic acids of different origins. HA from aqueous phase of oligotrophic bogs relatively to mesotrophic contain more carbon and oxygen, less hydrogen and nitrogen. Humic acid of trapping channel content of carbon and hydrogen close to the HA of oligotrophic bogs, the degree of oxidation, to mesotrophic and differ from both in high nitrogen content.

Aquatic humic acid of mires as reduced compounds ($\omega = 0.12$) with a higher ratio of H/C = 1.22, are fully consistent with the typical brown humic acids [13]. Oxidized ($\omega = 0.39$) HA of oligotrophic bogs with low H/C ratio = 0.95, form a special subgroup of brown humic acids. As such, they come close to fulvic acids: the average for the FC level of oxidation is in most cases about 0.33 [13].

For an objective assessment of the elemental composition of humic acid from bog waters formalized HA partition followed by cluster analysis has been done. As can be seen from Fig. 1a, 4 meaningful classes have been allocated. Humic acid from eastern and northern slopes of oligotrophic Kirgiznoe bog (entries *5* and *3a*), as well as HA of all mesotropic mires (entries *14, 16, 18*) were all combined into one specific cluster. Humic acid of bogs summits (entry *4a*) and trapping channel (entry *11*) were allocated to the individual clusters. The following data support high quality of the separation: Wilks lambda coefficient = 0.0267, F-criterion = 72.8, p-level < 0.0007.

This grouping is most likely explained by the geomorphological features of the modern phase of bogs development: phytogenic forms of surface topography and the direction of flow of the waters. Mires are characterized by even terrain relief, which is a flat surface [21]. As a consequence, over the entire area similar parameters set for flowing water, which are very small. Because of this aqueous medium in most of the area is almost leveled. Oligotrophic bog form a characteristic dome-shaped surface, as a result, water goes down slopes from the center to the periphery of the array in the form of limited concentric circles, where the conditions of permanence degree in flow and moisture content of the active layer keep constant. While central elevated part of wetlands (dome) is in conditions of just rainfall feeding.

Humic acid of peaks of oligotrophic bogs, forming separate clusters, featuring a high degree of oxidation ($\omega = 0.41$), the lowest carbon content of 34.84%, the highest oxygen content of 26.18% and the lowest nitrogen-enrichment level C/N = 36.37 (Table 2). Combined into one cluster humic acids of slope waters, are as well oxidized, with the highest carbon content of 39.29% and the lowest hydrogen of 34.61%. Grouped humic acid of mires waters are belong to reduced compounds, which distinguishes them from HA of other formation conditions. Humic acid of trapping channel—of oxidation nature with peculiar feature of which as an independent cluster is highly enrichment with nitrogen C/N 13.98.

Table 2. Elemental compositions of humic acids from swamp's water phase[a]

Entry	Mole fraction, %				Atomic percents				Atomic ratio			ω
	C	H	O	N	C	H	O	N	H/C	O/C	C/N	
Oligotrophic bog "Kirgiznoe," summit												
4a	47.06	4.32	47.11	1.51	34.84	38.02	26.18	0.96	1.09	0.75	36.37	0.41
Oligotrophic bog "Kirgiznoe," slopes												
3a	51.47	3.71	43.05	1.81	39.74	34.11	24.95	1.20	0.86	0.63	33.26	0.40
5a	50.95	3.87	43.04	2.15	38.85	35.12	24.63	1.40	0.90	0.63	27.68	0.36
$\bar{x}$	51.21	3.79	43.05	1.98	39.29	34.61	24.79	1.30	0.88	0.63	30.47	0.38
Trapping channel (dry land–mesotrophic mire)												
11	51.78	4.18	39.72	4.32	38.36	36.81	22.09	2.74	0.96	0.58	13.98	0.19
Mesotrophic bogs												
14	53.05	5.36	38.07	3.52	35.76	42.95	19.26	2.03	1.20	0.54	17.58	–0.12
16	53.47	5.55	38.84	2.13	35.53	43.89	19.37	1.21	1.24	0.55	29.31	–0.14
18	52.11	5.34	39.63	2.92	35.23	42.96	20.12	1.69	1.22	0.57	20.84	–0.08
$\bar{x}$	52.88	5.42	38.85	2.86	35.51	43.26	19.58	1.65	1.22	0.55	22.58	–0.11

[a] (ω) is an oxidation degree, (x) is an average in clusters.

IR spectra of humic acids. Water HA of different origins (Figs. 2a–2c) contain absorption bands characteristic of humic acids [13, 14]. The IR spectra of all preparations (samples) present intense broad absorption band at 3300–3500 cm^{-1} due to stretching vibrations of OH groups, mainly binded by intermolecular hydrogen bonds. Bands at 2960, 2925, and 2854 cm^{-1}, relating to the stretching vibrations of aliphatic CH_3- and CH_2 groups, proving the presence of aliphatic structures as part of the studied substances. Presense of strong band at 1725 cm^{-1} characteristic to stretching vibrations of C=O group in combination with the bands in the region 1100–1030 cm^{-1} may serve as evidence for the presence of aldehydes, ketones and carboxylic acids in the composition of humic acids from bog water. In humic acids, this band is presented mainly due to the carboxyl groups. Absorption bands at ~ 3300, 1620, 1510, and 770 cm^{-1} suggest the presence of aromatic structures as part of the HA, while low intensity of the bands at 3300, 1510, and 770 cm^{-1} characterize their low content. High intensity of absorbtion at 1620 cm^{-1} is caused by the superposition of two absorption bands: the bending vibration of adsorbed water and the stretching vibration of C=C bonds. This situation corresponds to the idea about the properties of HA formed by a free-radical mechanism from the degradation products of biopolymers and fulvic acids, capable to interact with chemically similar compounds, forming the superstructures diffusely permeable to small molecules of water [22]. In the 1150–1050 cm^{-1} range there are two well-defined bands at 1158 and 1050 cm^{-1}, to alcoholic hydroxy groups. A similar band is characteristic to carbohydrates.

On the background of generality of IR spectra of aqueous humic acids were identified and some special features of the structure of the HA, combined into clusters on the basis of the elemental composition. In particular, the spectral pattern of humic acid from northern (sample *3a*) and eastern (sample *5a*) slopes of oligotrophic bog are identical, that indicates similarity of the structure (Fig. 2a). However, the decrease in the intensity of all the absorption bands in the HA series of northern slope > eastern slope (subjected in the past to forest-peat fires) suggest a different number of functional groups. The value of the integral in the range of 3000–2700 cm^{-1}, which characterizes the amount of alifatic structures changes from 4.2 to 2.4, respectively, for the samples *3a* and *5a*. Moreover, in our opinion, judging by the very low intensity of the band at 2960 cm^{-1}, aliphatic structures are presented, mostly by –CH_2– groups. The same intensity decrease is observed for the bands at 1158 and 1050 cm^{-1}, corresponding to alcoholic hydroxy groups.

The spectrum of humic acids from oligotrofic bog's central dome saped part (sample *4a*) in the region of 4000–1480 cm^{-1} identical to that of HA from the slopes of the bog (Fig. 2b). The value of the integral in the range 3000–2700 cm^{-1} is 2.9. Differences are observed mainly in 1400–816 cm^{-1} range. The most revealing is region about 1100 cm^{-1}, where there are intense absorption bands at 1050 and 1080 cm^{-1} characteristic of polysaccharides, that is confirmed by ^{13}C NMR spectroscopy (Table 3). Vibrations in this area are among the most characteristic features of IR spectra of fulvic acids. Possibility of HA formation in natural waters from fulvic acids via free radical condensation under the action of sun's ultraviolet light was shown by Yu. Skurlatov and G. Duc [22]. The closeness of humic acids from summits of oligotrophic bog to fulvic acids based on their high degree of oxididation was marked in the discussion of the

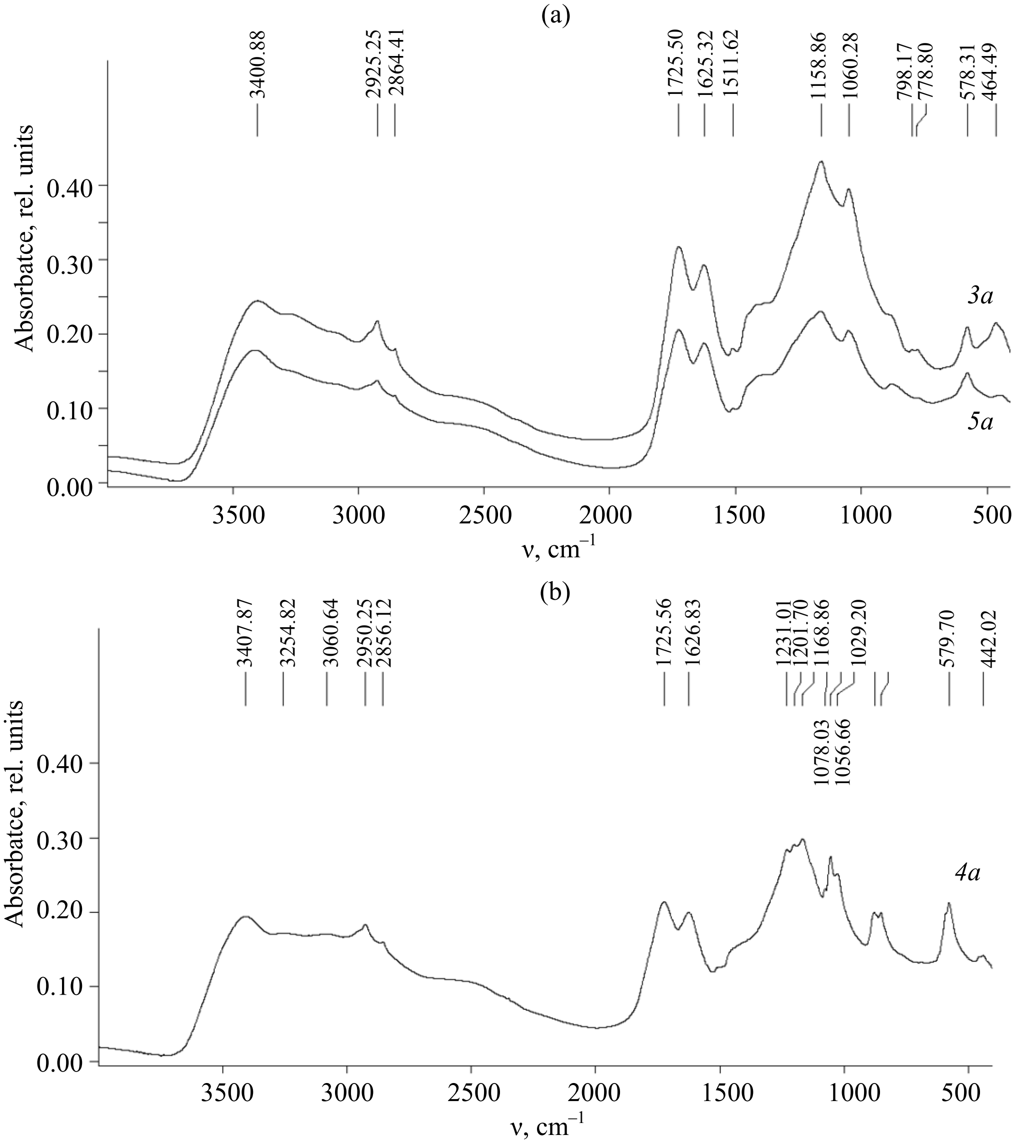

Fig. 2. Infrared spectra of aqueous preparations of humic acids grouped into clusters according to the elemental composition: (a) slope areas of oligotrophic bogs, (b) the top of oligotrophic bogs, (c) mires, and (d) trapping channel. For HA numbering see Fig. 1.

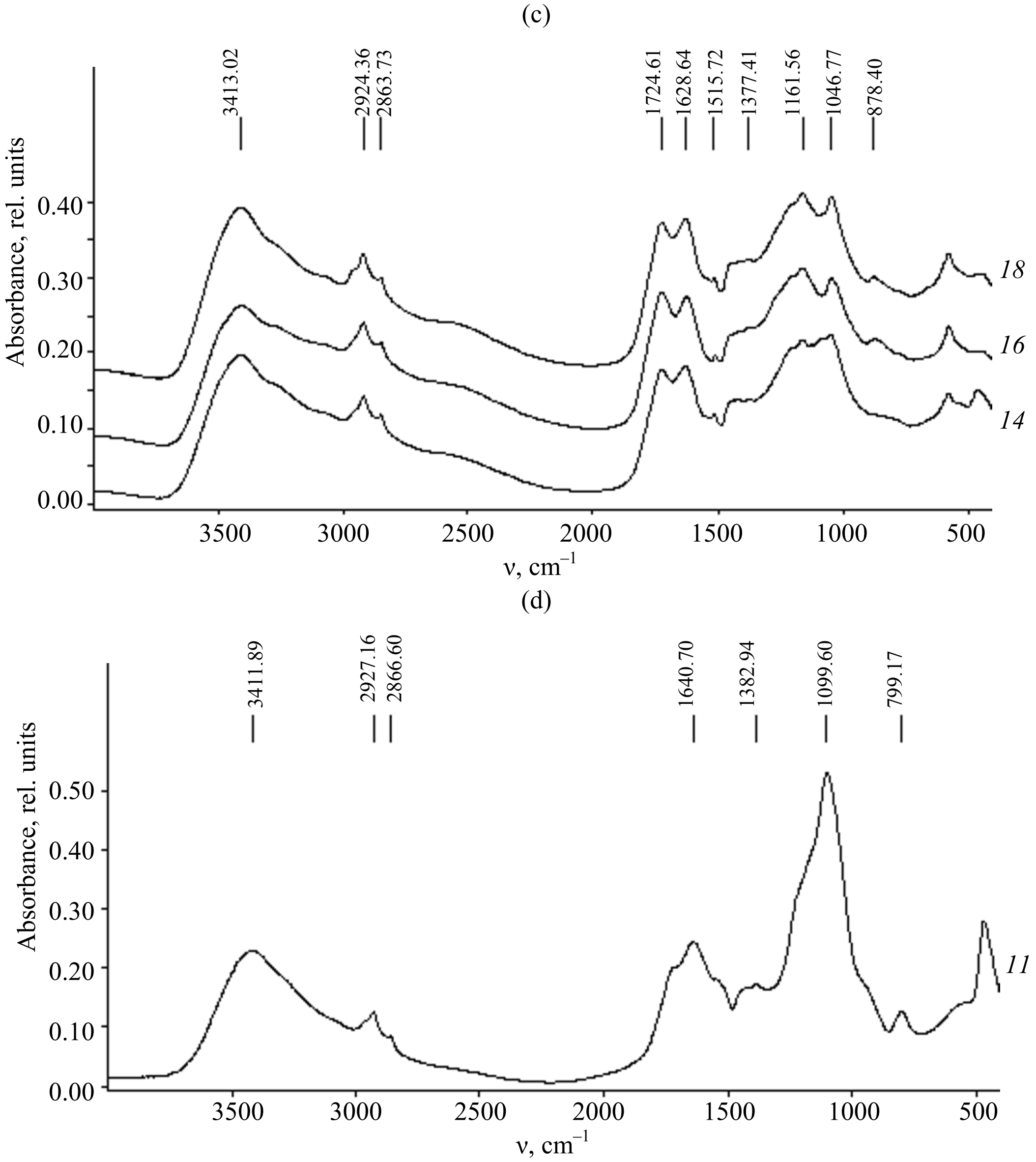

Fig. 2. (Contd.)

elemental composition of the HA. In the spectrum of aquatic humic acid from the top of bog, there are two rather intense band at about 900 cm^{-1}, corresponding to the deformation vibrations of C–H bond in the aromatic rings. This suggest relatively low content of aromatic components, which is confirmed by ^{13}C NMR spectra.

IR spectra of humic acids from water phase of mires (samples *14, 16, 18*) are identical and similar to the IR spectra of oligotrophic bogs (Fig. 2). Originality is manifested in the fact that in the spectra of HA from mires appear bands of medium intensity at 2960 cm^{-1} and about 1380 cm^{-1}, respectively, due to the valence, and deformation vibrations of methyl groups. This fact, as well as the integral of samples *14, 16, 18* in the range of 3000–2700 cm^{-1}, which is equal to 4.0, 4.8, 5.2, indicate more advanced peripheral structure of aquatic humic acid from mires compared with oligotrophic HA.

IR spectra of humic acid from trapping channel (sample 11) are identical to HA from bog waters in the 4000–1480 cm^{-1} range (Fig. 2d). The value of the integral in the range 3000–2700 cm^{-1} is 3.6. The differences are related to the presence of the band at

Table 3. Structure fragment composition of HA according to ^{13}C NMR spectroscopy(relative to integral, %)

HA[a]	Spectral ranges, ppm				
	0–45	45–60	60–110	110–165	165–210
	aliphatic		sugars, primary alcohols, acetales, polysaccharides	aromatic	carbonyl
	alkyl	methoxyl			
4a	11.65	16.76	44.46	17.33	9.80
5a	27.08	10.72	22.54	28.14	11.52
11	13.08	10.02	24.33	41.01	11.56
14	20.12	8.06	15.87	38.60	17.35
16	17.54	6.36	17.65	41.56	16.89
18	15.41	8.63	20.19	41.86	13.91

[a] For HA numbering see Fig. 1.

1640 cm^{-1} due to the C=O of the amide group or a OCN group. This band is characteristic of humic acids with high content of nitrogen, which is consistent with the elemental composition of the HA from trapping channel, most nitrogen-rich. Furthermore, in the 1340–400 cm^{-1} range there are two absorption bands: a broad band of very high intensity at 1099 and 800 cm^{-1} due to mineral Si–O groups and amorphous SiO_2, which is understandable. Silicon enters the trapping channel (border of dryland and wetland) from sandy ridges, surrounding mire. Possibly, silicon is involved in the migration in the composition of humic acids as an impurity in a true and (or) a colloidal form. However, there is an opinion that the silica fragments of soluble humic acids, in particular, from podzolic soil are tightly bound to humic substances, and are not mechanical impurities [23]. In epy preparations of HA from bog water of different genesis occur band of variable intensity in the 1168–1159 cm^{-1} range. The range of 1180–1160 cm^{-1} is associated with a large group of related mineral components [13].

Electron paramagnetic resonance (EPR). The study of HA using electron paramagnetic resonance confirmed the existing of interaction of humic acid from aqueous phase of mires with metals. Along with a narrow ($\Delta H \leq 10$ G) and structureless signal (at $g \sim 2.00$), characteristic to humic substances as high molecular weight disordered systems [24], in EPR spectra are observed characteristic signals of paramagnetic centers (PMC) of cations Fe^{3+}, Cu^{2+}, and Mn^{2+} . As example, the spectra of the PMC of aqueous humic acids from the top of the oligotrophic mire are shown in Fig. 3.

Relative concentration of paramagnetic metal centers, due to water sorption capacity of the humic

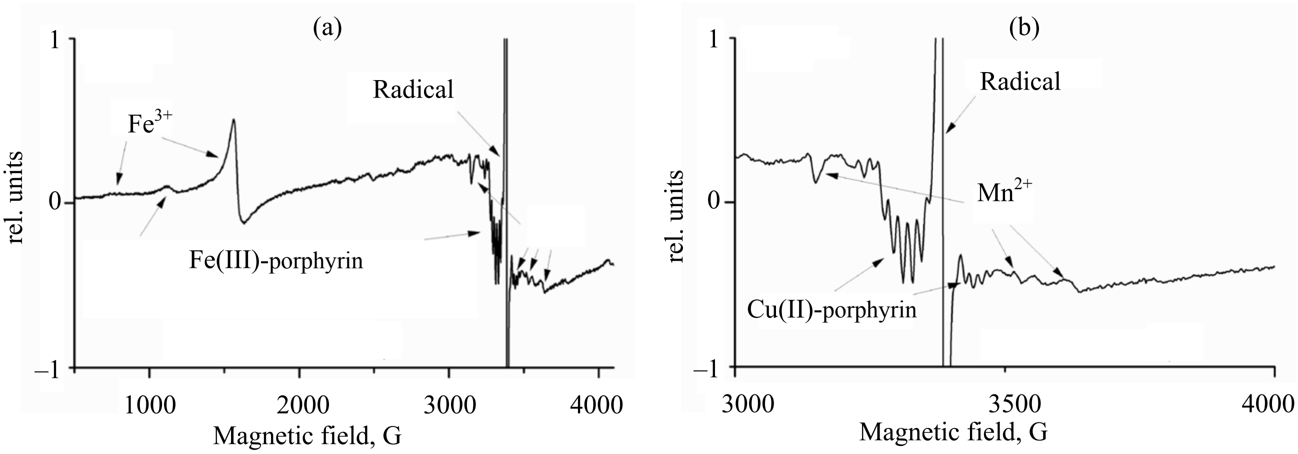

Fig. 3. The spectra of electron paramagnetic resonance (EPR) (a) of aqueous humic acid from summit of oligotrophic bogs and (b) high-field spectra of the Cu(II)-porphyrin and Mn^{2+}.

Table 4. The relative signal intensity of paramagnetic centres of transitional metals in humic acids

HA[a]	Paramagnetic centres, *g*-factor			
	Fe(III), $g = 4.3$	Mn(II), $g \approx 2.15$	Cu(II)-porphyrin, $g_\perp \approx 2.05$	Fe(III)-porphyrin, $g_\perp = 6.0$
4a	40	10	6.5	3.4
5a	140	15	Not	Not
11	30	Not	Not	Not
14	360	1.1	1	Not
16	240	Not	2	Not
18	270	Not	Not	Not

[a] For HA numbering, see Fig. 1.

acids varies greatly depending on the type of mires, i.e. HA formation conditions. The most revealing in this respect, are iron ions, the content of which varies widely (Table 4). This shows the different contents of carboxylic acids inpreparations of aqueous humic acids, which is confirmed by correlation–regression analysis. A highly significant positive regression relationship ($R^2 = 0.79$) of Fe^{3+} signal intensity and carboxilic carbon spectrum according to ^{13}C NMR (Fig. 4) and a positive correlation of carboxylic and aromatic carbon ($r = 0.69$) have been revealed. Established correlations suggest that in humic acids appearance at low fields a signal ($g \sim 4$) caused by the presence of Fe^{3+} compounds with purely ionic bond mainly due to the aromatic portion of the functional groups of humic acids [25].

The results obtained are in tune with the views of L.N. Alexandrova about the process of humification as an oxidizing acid production. [26] On this basis, water HA from mires, and among them the dried version (preparation *14*) with the highest content of Fe^{3+} and acid functional groups can be considered a product of the deepest biochemical oxidation of organic remains. Water HA of oligotrophic bogs are probably the result of less profound transformation of peat-forming plants. Evidence of this, in our opinion, are the paramagnetic Mn^{2+} centers and porphyrin complexes of iron and copper, which registered mainly in aquatic humic acids from top of the bog. As known, the group of porphyrins, heterocyclic natural nitrogen compounds include chlorophyll. The presence of plant pigments and manganese known to be involved in the formation

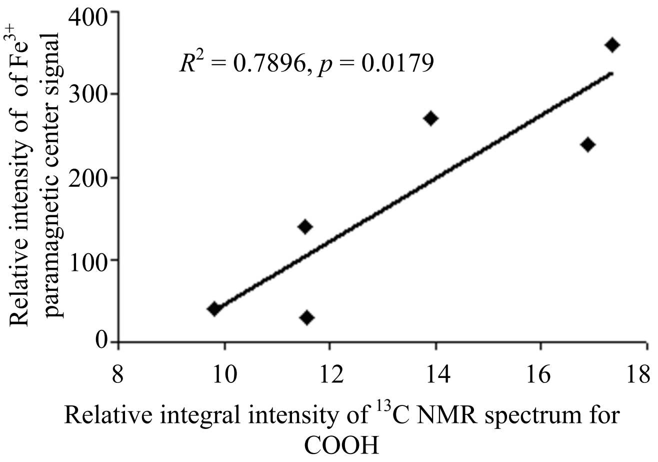

Fig. 4. The regression relationship between paramagnetic centers Fe^{3+} and the carboxyl carbon in humic acids from bog waters.

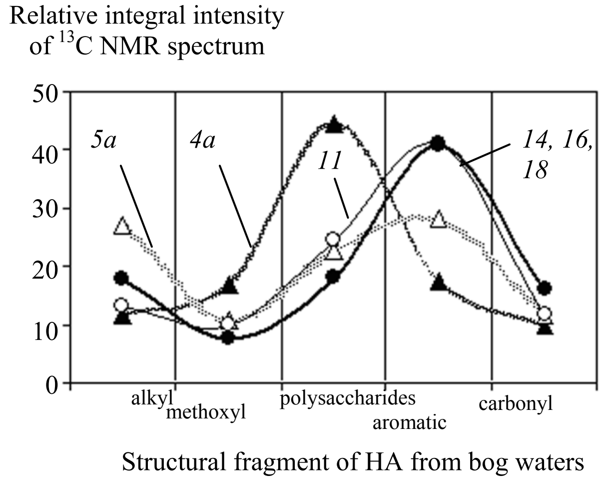

Fig. 5. Structural fragments of aquatic humic acids grouped into clusters according to ^{13}C NMR spectroscopy. For HA numbering see Fig. 1.

of chlorophyll indicates the stability of nitrogen aromatic macrocycles of chlorophyll during humification.

Thus, used methods of chemical analysis of aqueous humic acids (elemental composition, IR spectra, ^{13}C NMR, EPR) showed quite good comparability of results. Thus, the cluster analysis groups humic acids according to the elemental composition and the results of ^{13}C NMR spectroscopy in a similar manner. HA of mires are combined into a single cluster, HA from trapping channel, top and slopes of oligotrophic bogs form separate clusters (Figs. 1a, 1b). Meaning differences in the structure of HA from allocated clusters relate primarily to the content of carbohydrate moieties (polysaccharide) and aromatic structures (Fig. 5). In aqueous HA from mesotrofic bogs and trapping channel (mires perimeter) dominate aromatic moieties, in humic acids from the top of oligotrophic bog, polysaccharides. In structure of HA from slope areas a certain originality due to locale factors is maintained. First of all, a form of bog surface relief, runoff direction and perhaps the influence of pyrogenic layers at a depth of 30–40 cm, i.e., in the active horizon of peat deposits, which is characterized by intensive moisture exchange with the atmosphere and the surrounding areas [21].

CONCLUSIONS

It was established that the aqueous humic acid from mires belong to the reduced compounds to a greater extent enriched with aromatic structures, carboxyl groups, the aliphatic carbon and characterized by a relatively deeper biochemical transformation as compared to HA from oligotrophic bogs. Humic acid of oligotrophic bogs belong to a group of oxidized, compounds with lowest nitrogen enrichment but contain more methoxy carbon and carbohydrates (polysaccharides).

Identified structural features of macromolecules of water-soluble HA of different origins are likely to be determined by several factors. Firstly, by geochemical pecularities of the waters feeding the bog, which, along with the degree of mineralization and the medium reaction, determine their redox potential depending on the content of organic substances and dissolved gases. The main source of water supply to oligorophic bogs is, as known, precipitation, oxygen-enriched from air. Mires, in addition to atmospheric moisture, nourishes from soft water of gley aquifers, a characteristic feature of which is the presence of methane, hydrogen, various hydrocarbons and reduced iron [27]. Secondly, the structural features and characteristics of the elemental composition of the HA may be due to specific mechanisms of synthesis of humic acids. In mire soils, which in numbers, biomass and species composition of the group of biota richer than oligotrophic, is likely to prevail biochemical mechanism of humus formation. Water humic acids from mires, identified by the elemental composition as brown HA, are formed in the process of humification of peat forming plants mainly in the upper active layer the area of contemporary soil formation [28]. In the process of decomposition of litter and peat in the surface horizons humic substances with primarily hydrophilic properties are formed [29]. Due to low content of mineral components in the peat, ie the deficit of cations, humification products are unsaturated and actively enter the aquatic environment.

In oligotrophic bogs, where the role of animals in the decomposition of peat is small, and the activity of microorganisms in the conditions of the highly acidic environment is strongly suppressed [30], is likely to dominate the chemical way of humic acids formation [31]. According to the concept [22], as these processes act free-radical reactions of polycondensation of degradation products of biopolymers, low molecular weight organic compounds and fulvic acids. Reactions of polycondensation caused mainly by OH radical dominant in ground waters and in topsoil layer, as well as by other products of exposure to ultraviolet radiation, fell down with precipitation.

ACKNOWLEDGMENTS

This work was financially supported by the International Science and Technology Center (ISTC) (project no. 4079).

REFERENCES

1. Shvartsev, S.L., Rasskazov, N.M., Sidorenko, T.N., and Zdvizhkov, M.A., in *Bolshoe Vasyuganskoe boloto. Sovremennoe sostoyanie i protsessy razvitiya* (Great Vasyugan Swamp. Current State and Development Processes), Kabanov, M.V., Ed., Tomsk: Inst. Optiki Atmosfery Sib. Otd. Ross. Akad. Nauk, 2002, pp. 139–149.
2. Dubrovskaya, L.I. mand Brezhneva, E.S., *Vest. TSPU*, 2010, vol. 93, no. 3, pp. 108–112.
3. Efremova, T.T., Efremov, S.P., and Melent'eva, N.V., *Vod. Res.*, 1993, vol. 20, no. 2, pp. 206–211.
4. Efremova, T.T., Efremov, S.P., and Melent'eva, N.V.,

Pochvoved., 1997, no. 12, pp. 1470–1477.

5. Efremova, T.T., Efremov, S.P., and Melent'eva, N.V., *Geograf. i Prirodn. Resurs.*, 1998, no. 2, pp. 79–84.
6. Ivanova, E.S., Voistinova, E.S., and Kharanzhevskaya, Yu.A., *Trudy V vreross. Conf. "Guminovye veshchestva v biosfere"* (Proc. V All-Russia Conf. "Humic Substances in the Biosphere"), Part 2, St. Petersburg: S.-Peterburg. Univ., 2010, pp. 511–518.
7. Inisheva, L.I. and Inishev, N.G., *Vod. Res.*, 2001, no. 4, pp. 410–417.
8. Rasskazov, N.M., *Izv. Tomsk. Politekh. Univers*. 2005, vol. 308, no. 4, pp. 55–58.
9. Savichev, O.G., *Izv. Tomsk. Politekh. Univers*, 2009, vol. 314, no. 1, pp. 72–77.
10. Haiber, S., Herzog, H., Burba, P., and Gosciniak, J., *Fresenius J. Anal. Chem.,* 2001, no. 369, pp. 457–460.
11. Orlov, D.S., *Gumosovye kisloty pochv i obshchaya teoriya gumifikatsii* (Humic Acid Soils and the General Theory of Humification), Moscow: Mosk. Gos. Univ., 1990.
12. *Unifitsirovannye metody analiza vod* (Unified Methods for Water Analysis), Lurie, Yu.Yu., Moscow: Khimiya, 1973, 2d ed.
13. Orlov, D.S., *Gumosovye kisloty pochv* (Humic Acid Soil), Moscow: Mosk. Gos. Univ., 1974.
14. Orlov, D.S. and Grishina, L.A., *Praktikum po khimii gumusa* (Workshop on Humus Chemistry), Moscow: Mosk. Gos. Univ., 1981.
15. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, New York: John Wiley & Sons, 1975.
17. Brodbeck, C.M., *J. Non-Cryst. Soc.*, 1980, vol. 40, nos. 1–3, pp. 5–313.
18. Tsay, F.D., Manatt, S.L., and Chan, S.I., *Chem. Phys. Lett.*, 1972, vol. 17, no. 2, pp. 223–226.
19. Hakasson, P., Nguyen, T.N., Nair, P.B., Edge, R., and Stulz, E., *Phys. Chem. Chem. Phys.,* 2013, vol. 15, pp. 10930–10941.
20. Chaudhary, A., Patra, R., and Rath, P., *Indian J. Cem.*, 2011, vol. 50A, pp. 432–437.
21. Ivanov, K.E., *Vodoobmen v bolotnykh landshaftakh* (Water Exchange in the Mire Landscapes), Leningrad: Gidrometeoizdat, 1975.
22. Knyazev, D.A. Fokin, A.D., and Ochkin, A.V., *Pochvoved.*, 2009, no. 9, pp. 1061–1065.
23. Kulikova, N.A. and Perminov, I.V., *Vestn. Mosk. Univ., Ser. 17*: *Pochvoved.*, 2010, no. 4, pp. 16–19.
24. Strigutsky, V.P., Navosha, Yu.Yu., Bambalov, N.N., and Liogon'sky, B.I., *Pochvoved.*, 1989, no. 7, pp. 41–51.
25. Bazarova, O.V., Dudarchik, V.M., Prokhorov, S.G., Strigutskii, V.P., and Zhdanov, V.S., *Pochvoved.*, 1992, no. 1, pp. 155–158.
26. Alexandrova, L.N., *Organicheskoe veschestvo pochvy i processy ego transformatsii* (Soil Organic Matter and Processes of Its Transformation), Leningrad: Nauka, 1980.
27. Perelman, A.I. and Kasimov, N.S., *Geokhimiya landshafta* (Feochemistry of Landscape), Moscow: Astreya-2000, 1999.
28. Efremova, T.T., *Pochvoved.*, 1992, no. 12, pp. 25–35.
29. Milanovsky, E.Yu. and Shein, E.V., *Pochvoved.*, 2002, no. 10, pp. 1201–1213.
30. Kozlovskaya, L.S., *Rol' bezpozvonochnykh v transformatsii organicheskogo veschestva bolotnykh pochv* (The Role of Invertebrates in the Transformation of Organic Matter Marsh Soils), Leningrad: Nauka, 1976.
31. Efremova, T.T., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Biol.*, 1988, no. 1, pp. 38–44.