STRUCTURE AND PROPERTIES OF PEAT HUMIC SUBSTANCES Struktur och egenskaper för humus från torv

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Abstract

Humic substances are formed in very different environment and the relations between properties (and structure) and precursor biota composition still is far from being clarified. The aim of this study was to analyse relations between properties of the peat, peat humic acids and humification degree on example of analysis of three bog profiles in ombrotrophic bogs to identify the links between peat age, decomposition and humification degree, botanical composition and properties of peat humic acids (elemental, functional composition). The found variability of peat properties is much less than the significant differences in properties of peat forming living matter thus stressing the dominant impact of humification process on peat properties.

Key words - Humic substances; composition; soil; peat Humic substances; composition; soil; peat

Sammanfattning

Humusämnen bildas i mycket olika miljöer och förhållandet mellan deras egenskaper (och struktur) och det ursprungliga materialets är fortfarande långt från klarlagt. Syftet med denna undersökning har varit att analysera förhållandet mellan egenskaper för torv, humusämnen från torv och grad av nedbrytning för analyserade prover från tre olika mossar i ombrotrofiska mossar för att identifiera förhållandet mellan torvålder, nedbrytning och omvandling till humus, växtsammansättning och egenskaper för torvens humussyror (grundämnessammansättning, funktionell sammansättning). Den uppmätta skillnaden i torvens egenskaper är mycket mindre än skillnaden i de olika växter som bildar torv, vilket understryker betydelsen av torvbildningsprocessen för torvens humusämnes egenskaper.

Introduction

Humic substances are an operationally defined category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in colour, of high molecular weight and refractory. Humic substances form most of the organic components of soil, peat and natural waters; they influence the process of formation of fossil fuels, and play a major role in the global carbon biogeochemical cycle (Stevenson, 1994).

In the studies of humic substances, the issue of dependence of the properties of humic substances on their origin is still topical. It has been shown that the structure and properties of humic substances differ for HAs of dif-

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ferent origin (Stevenson, 1994; Klavins, 1998). At the same time, considering the great variability of properties of natural organic matter (plants, animals, microorganisms) and humification conditions (age of humic substances, impacts of climatic conditions, and other factors), the actual origin-properties relationship is far from being explained. A significant object of studies is role of humic substances during genesis of peat and fossil carbon deposits (Ghaly et al., 1999, Brown et al., 2000). Humification of living organic matter is a very complex subject of study considering the high variability of environmental conditions under which it decays, slow pace of humification reactions, and large number of organic molecules composing living organic matter and their structural differences. It can be supposed that humification conditions (temperature, redox conditions, pH, mineralization and other parameters) have impact on the structure and properties of refractory intermediate transformation products of living organic matter - humic substances (Cocozza et al., 2003). From this perspective, it is important to study humification processes in conditions where the transformation of living organic matter takes place in relatively homogeneous and stable environment - in bogs. During peat development even at one particular site, major changes in vegetation, temperature, amounts of precipitation and corresponding hydrological conditions of the bog, and land use in the basin of wetland can take place (Zaccone et al., 2007; Yeloff and Mauquoy, 2006), so that one can expect to find corresponding changes in properties of peat humic substances, identifying molecular descriptors of the organic matter diagenesis process. However, relations between peat properties (especially in full peat profiles: from the surface till underlying sediments) and properties of peat humic substances have not been studied much - in just a few studies (Anderson et al., 1986, Zaccone et al., 2008).

The aims of this study are to characterize HAs from raised bog peat using appropriate chemical and spectroscopic techniques (elemental and functional analysis, FTIR, ¹³C NMR), to evaluate the homogeneity of HAs isolated from the bogs, and to study peat humification impact on properties and structure of HAs.

Materials and Methods

Peat sampling, isolation of humic substances

Peat profiles were obtained from well-characterized, typical raised bogs (Kuske et al., 2010) – Eipurs, Dizpurvs and Dzelve. The ¹⁴C dating of peat samples was done at the Institute of Geology of the Tallinn Technical University (Estonia). Carbon, hydrogen, nitrogen and sulphur concentrations in peat and HA samples were determined by combustion-gas chromatography technique, using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference. HAs were extracted from peat and purified as suggested previously (Tan, 2005).

Characterization of humic acids

Elemental composition

Carbon, hydrogen, nitrogen and sulphur concentrations in the peat and HA samples (elemental analysis of C, H, N, S) were determined by combustion-gas chromatography technique, using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). Ash content was measured after heating 50 mg of each peat sample at 750°C for 8 h. Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference.

Infrared spectra

Fourier transform infra-red (FTIR) spectra were recorded in the 4000 to 450 cm^{-1} wavenumber range using a Perkin Elmer 400 IR spectrophotometer. Spectra were registered on KBr pellets obtained by pressing mixtures of 1 mg samples and 400 mg KBr with precautions taken to avoid moisture uptake.

¹³C Nuclear magnetic resonance spectra

Solid-state ¹³C-NMR spectroscopy was carried out using the technique of cross-polarization with magic angle spinning (CP/MAS). The spectra were recorded on a Bruker Avance Wide bore 600 MHz Solid state NMR spectrometer equipped with a 4 mm MAS double resonance probe. A 2 ms contact time and 2 s repetition time were set. The sample magic angle spinning was 10 kHz, and chemical shifts were referenced to adamantane (left peak) at 38.48 ppm.

Results and Discussion

Characterization of peat

For the isolation of HAs, peat from 3 representative bogs were studied, covering major lithological classes of raised bog peat (Table 1). The bogs are covered by *Sphagnum* species, such as *S. fuscum, S. magellanicum* and some *S. rubellum.* Upper peat layers are common for raised bogs, whereas lower layers of peat profiles represent fen peat. Main part of the profile of the studied bogs consisted of different kinds of *Sphagnum* peat. Peat decomposition degree changes from 10% to 60%, and the age of the studied layers – from < 100 ¹⁴C years to ~ 9000 ¹⁴C years. If in upper peat layers humification degree is lower and, correspondingly, HA/FA ratio is < 10, then in more decomposed peat this ratio is >30, which means that peat humic matter is dominated by HAs, later selected as a major object of this study.

Basic peat properties can be analyzed using peat elemental (C, H, N, O, S) composition. The ash content of peat in the studied bogs ranges between 1.11% and >6%. The C concentration ranges from ~40 to 55%, H – from 5.4 to 6.2%, N – from 0.5 to >2%, and S – from 0.3 to 1.2%. The elemental composition of peat in Eipurs Bog is comparatively variable and reflects changes in peat decomposition degree and peat type. Starting from upper layers, C concentration in peat increases up

Table	1.	Pro	perties	of	peat	used	for	extraction	of	humic	acids	s.
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Bog	Peat depth from surface, cm	Peat decompo- sition degree ¹ , %	Peat age, ¹⁴ C years	Peat botanical composition	Peat type	Humifica- tion degree ²	HA/FA
Eipurs	0–25	10	70	Sphagnum fuscum	Raised	0.49	5.95
1	135-170	30	1300	Cotton grass-Sphagnum	Raised	0.84	25.53
	230-240	23	2660	Sphagnum fuscum	Raised	0.67	16.01
	320-358	41	6830	Pine, wood	Raised – transitional	1.29	33.49
	410-456	27	8800	<i>Hypnum</i> , sedge	Fen	1.27	38.52
Dzelve	30-40	12	75	Sphagnum fuscum	Raised	0.48	10.27
	190-200	10	1940	Sphagnum fuscum	Raised	0.38	6.80
	310-320	12	2230	Sphagnum fuscum	Raised	0.74	8.13
	340-350	>60	4810	Cotton-grass	Raised	2.99	71.76
Dizpurvs	0-20	13	50	Sphagnum - cotton grass	Raised	0.45	6.75
1	240-260	37	2300	Sedge - pinus	Fen	0.65	8.43
	400-430	40	5740	Sedge - hypnum	Fen	1.32	24.55

¹ – Determined as in (Lishtvan and Korol 1975)

² – Determined as in (Tan 2005)

to the level of 53%. Nitrogen concentrations are increased in the upper and lower horizons of the bog and the increased values coincides with changes in peat composition and formation conditions. Nitrogen concentration changes could be associated with changes in peat botanical composition and decomposition degrees. S concentrations are significantly lower just in the upper layer of the peat bog and are comparatively stable along the peat column. At the same time, the elemental composition of Dzelve Bog is to a great extent different and largely reflects the peat column composition: C content in the upper layers is much lower (- 45%) and comparatively uniform to the depth of 3.25 m; then, it rapidly increases, reaching 55% for highly decomposed peat. The same pattern of changes reflect elemental ratios (O/C, H/C, N/C).

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Basic peat humic acid properties

Preparative amounts of HAs were isolated from each of the studied bog layers. There were significant variations in the elemental composition of HAs within the peat profiles. Depending on the bog and the intervals of changes, the elemental compositions of the studied peat HAs were highly variable: C was 49–57%; H was 4.6– 5.7%, N was 1.6–2.8%, S was 0.5–1.5%, and ash was 0.1–1.2%. The O content range of 32–42% was determined by mass balance (Table 2). In general, C and H concentrations increased with depth. N concentrations decreased with depth, whereas S concentration was very variable down the profile. The elemental composition of HAs from peat in Latvia is similar to that of peat HAs from other regions of the world. Peat HAs were analyzed using van Krevelen graphs that are frequently applied for

Humic acid	Depth, cm	С, %	Н, %	N, %	S, %	O/C	H/C	N/C
	0.05	52 (0	5.00	2 (2		0.550	1.00	0.0/
Lipurs HA	0 - 25	52.40	5.39	2.43	1.50	0.550	1.23	0.04
Eipurs HA	135 – 170	53.20	4.80	2.13	1.05	0.547	1.07	0.03
Eipurs HA	230 - 240	54.70	5.04	1.87	0.87	0.514	1.10	0.03
Eipurs HA	320 - 358	52.70	4.34	2.25	0.83	0.567	0.98	0.04
Eipurs HA	410 - 456	55.30	4.49	2.48	1.01	0.498	0.97	0.04
Dzelve HA	30 - 40	52.25	4.51	2.59	0.77	0.573	1.03	0.04
Dzelve HA	190 - 200	56.17	5.11	2.29	0.84	0.476	1.08	0.03
Dzelve HA	310 - 320	57.05	5.16	2.66	0.80	0.452	1.08	0.04
Dzelve HA	340 - 350	59.49	3.98	2.02	0.68	0.427	0.80	0.03
Dizpurvs HA	0 - 20	56.54	5.71	3.24	0.88	0.446	1.20	0.05
Dizpurvs HA	240 - 260	56.05	4.35	2.14	0.89	0.490	0.93	0.03
Dizpurvs HA	400 - 430	58.11	4.78	3.10	0.90	0.428	0.98	0.05

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Fig. 1. Van Krevelen (H/C vs. O/C atomic ratio) graph of living organic matter elemental composition changes during humification: bog plants (\bullet); humic acids isolated from peat samples from bogs in Latvia (\bullet); reference peat humic acid and peat humic acid (\star); soil humic acid (\bullet); humic acids from different coals and lignite (\blacksquare), sedimentary humic acid (\star) and aquatic humic acid (\blacktriangle).

studies of HAs and the C biogeochemical cycle. The index of atomic ratios O/C, H/C and N/C is useful in identification of structural changes and the degree of maturity of HSs obtained from different environments. The relation between H/C atomic ratio and O/C atomic ratio of HAs of differing decomposition degrees – beginning with bog plants up to brown coal, lignite and coal – reveals changes in the associated elemental composition (Fig. 1). Figure 1 graphically represents the humification process, indicating the degree of maturity and intensity of degradation processes, such as dehydrogenation (reduction of H/C ratio), decarboxylation (reduction of O/C ratio), demethylation occurring during the decay of peat-forming plants, and peat humus re-



Fig. 2. Fourier transform infrared spectra of peat humic acids from Dzelve Bog, depending on the depth of the sample.

sidual enrichment (mass loss of easily degradable compounds) continuing up to formation of coal. These changes are especially evident if the atomic ratios of peat-forming plants (Sector 3 in Fig. 1) are compared to the atomic ratio of organic matter of a high decomposition degree (low moor peat, coal) (Sector 1 in Fig. 1). From the point of view of chemistry, peat HAs have an intermediate position (Sector 5 in Fig. 1) between the living organic matter and coal organic matter, and their structure is formed in a process in which more labile structures (carbohydrates, amino acids, etc.) are destroyed, while thermodynamically more stable aromatic and polyaromatic structures are formed. Comparatively, the studied peat HAs are at the beginning of the living organic matter transformation process due to the residual enrichment of refractory compounds, but including also polymerization of low molecular weight compounds and microbial metabolites.

Characterization of peat humic acid structure

The IR spectra (Fig. 2) of the HAs examined are in general similar to one another in the main position of absorption. Differences of the intensities of absorption maximums are apparent in the relative intensity of some bands, depending on the origin and nature of the sample. IR spectra of the analyzed HAs can be divided by regions, depending on informativity and the presence of important functional groups. Absorption bands in the spectral region 3600–2800 cm⁻¹ are very broad and typical not only for humic substances but also for mineral constituents. Absorbance in this spectral region is determined by the presence of -OH groups. Sorption at wavelengths 2920 and 2860–2850 cm⁻¹ identifies the presence of CH_3 - and CH_2 - groups. The IR spectra data of soil humic substances show that methylene groups - $(CH_2)_n$ - exist in the form of comparatively short alkane chains ($_n < 4$). Intensive sorption lines are typical for the region around 1700 cm⁻¹ (1725–1700 cm⁻¹), which is characteristic for carbonyl groups in aldehydes, ketones and carboxylic acids.

The actual sorption maximum greatly depends on the degree of conjugation, presence of substituents and hydrogen bonding. In the spectral region 1690-1500 cm⁻¹, it is possible to identify the sorption maximum of amide bonds (1650-1640 cm⁻¹ and 1550-1540 cm⁻¹). In the region 1625–1610 cm⁻¹, the sorption value indicates the presence of aromatic C=C and carbonyl groups and quinones. At the wavelengths 1470-1370 cm⁻¹, there are bands typical for C-H and O-H bending and sorption maximums typical for C-O. For the wavelengths below 1000 cm⁻¹, fingerprint patterns are evident. Sorption values in this spectral region provide information about a possible role of carbohydrate content in the structure of humic molecules. Sorption at 1080 cm⁻¹ shows OH deformation or C-O stretch of phenolic and alcoholic OH groups, and 1040 cm⁻¹ indicates C-O stretch of polysaccharide components. The studied HAs demonstrate significant changes in major functional groups during the diagenesis process of humic matter. Decomposition process might first of all be associated with the decrease of signals related to the presence of carbohydrate hydroxyl groups and appearance of intensive sorption lines around 1700 cm⁻¹ (1725–1700 cm⁻¹) common for carboxylic acids.

Solid-state cross-polarization with magic angle spinning (CP/MAS)¹³C NMR spectra provides direct evidence of structural features of peat HAs. Signals in these NMR spectra represent different types of carbon atoms. In general, the spectra of all studied peat HAs show similar characteristics, presenting signals that can be associated with different functional aliphatic (C-H, C-N, O-CH3 and other groups and carbon in polysaccharides) and aromatic groups. The use of cross-polarization (CP) and magic angle spinning (MAS) techniques resulted in better resolved spectra, thus allowing their division into eight main regions attributed to carbon atoms in major structural units. The ¹³C NMR spectra can be divided into several chemical shift ranges (Fig. 3), indicating the presence of different major structural elements in the structure of HA. Analysis of ¹³C CP MAS NMR spectra allow direct evaluation of substantial differences between peat HAs of different origin and development of their structure during peat humification process. The dominant structures are characterized by resonance at 50–0 ppm, and they are common for CH_n in aliphatic (alkyl) fragments. The second most signifi-

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cant structural carbon atom group is ring carbon in carbohydrates (resonance signal 90-60 ppm) as well as carbon atoms in alkenes or aromatic structures (resonance signal 160-140 ppm). From the functional perspective, carbon atoms in carboxylic groups (determining acidity of peat humic substances) are important structural elements of HAs, and these carbon atoms constitute ~ 10% of the total carbon atom amount. A major discussion with respect to structures of HAs concerns their aromaticity vs. aliphaticity. A cornerstone for this discussion is the fact that aromatic substances are nearly absent in peat-forming mosses (commonly different Sphagnum species). This fact is also proven by Py-GC/MS analysis, indicating that lignin residues are nearly absent. Thus, it can be assumed that a dominant part of the HAs isolated from upper layers of peat contain alkene structures. However, in the HAs isolated from deeper layers of peat bog, where residues of higher vegetation prevail in peat composition, aromatic structures have lignine residues as a precursor material.

Changes in the intensities of resonance signals in the CP MAS ¹³C NMR spectra of peat HAs allow to trace the structural changes of organic matter during humification process. At first, a major decrease of aliphatic (alkyl) structures (resonance at 50-0 ppm) occurs with an increasing depth (nearly by a half for HAs from Eipurs Bog, and significantly also for other HAs). Peatforming carbohydrates are commonly considered to be labile and rapidly destroyable during peat formation process, whereas our results show that the ring carbon atoms of carbohydrates do not change significantly in the structure of HAs in the main body of the bog during humification process. At the same time, a comparison of carbohydrate amount in peat-forming mosses with carbohydrate content in the HAs isolated from upper peat layers shows significant differences, which means that



Fig. 3. CP MAS ¹³C NMR spectra of humic acids from Dizpurvs Bog.

only a part of carbohydrate structures so abundant in mosses are incorporated into the structure of peat HAs. On the other hand, Sphagnum carbohydrates in the structure of peat HAs are refractory and are not much degraded during humification process. One of the major structural features common for humic substances is their acidity - presence of carboxylic groups. Our results show that C of carboxyls and esters (resonance at 160-190 ppm) indeed belongs to major structural groups, and changes in the amount of these structures within the bog profile are not very significant. Again, if compared with the presence of carboxyl functional groups in the composition of peat forming mosses, major differences can be found, as their concentration is low in the structure of the samples of living peat-forming biota. It means that carboxyl groups appear at the first steps of living organic matter degradation in the upper peat layers (acrotelm).

The 0–50 ppm region consists primarily of aliphatic carbon (CH_n) resonances (methyl, methylene and methine carbons). The 50–60 ppm region consists of methoxylcarbon (-OCH₃) resonance signals. The 60–90 ppm region consists of carbon atom resonance line bound by a simple bond to heteroatom and mainly entering into the composition of carbohydrate units. The 90–110 ppm region consists primarily of a carbon atom bound by simple bonds to two heteroatoms (oxygen or nitrogen), mainly acetal carbon in cyclic polysaccharide (OC-O, N) resonances. The 110–140 ppm region is as-

signed to the resonance of unsubstituted and alkysubstituted aromatic carbons (C_{Ar}). The 140–160 ppm region consists of the resonance of aromatic carbons substituted by oxygen and nitrogen (e.g., phenols, aromatic ethers or amines). The 160–190 ppm region consists of the resonance of carbon in carboxyl, ester and amide groups. The 190–220 ppm region consists of the resonance of carbons in quinone and ketone groups substituted by oxygen and nitrogen (e.g., phenols, aromatic ethers or amines).

Major differences in the ¹³C CP MAS NMR spectra of raised bog peat-forming bryophytes (SM - Sphagnum magellanicum), peat from the depth 0-25 cm and HA isolated from the same depth can be seen in the spectral regions of 0 - 50 ppm, 60-90 ppm, and 90-110 ppm. At the early stages of humification of bog-forming plants (bryophytes) and diagenesis of HA molecules, structures containing aliphatic carbon appear first, and the number of methoxylcarbon (-OCH3)-containing structures reduces. Moreover, the number of such structures reduces again with ongoing humification process (Fig. 3). Major changes take place in the 60-90 ppm spectral region characterizing the carbon atoms of carbohydrate units. The number of these units drops already at the early stage of humification and continues to decrease during humification process. The 90-110 ppm region consists primarily of a carbon atom bound by simple bonds to two heteroatoms (supposedly oxygen), probably in the form of cyclic polysaccharides, and these structures are

	220-190	190–160	160-140	140-110	110-90	90–60	60–50	50-0
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	C=O	>CO -O, N	C _{Ar} -O, N	C_{Ar}	OC-O, N	C-O, N	-OCH ₃	CH_n
Dzelve 30-40	2.5	12.4	6.2	13.8	7.9	19.8	6.7	30.6
Dzelve 200–210	2.5	10.2	5.7	12.6	6.5	18.8	6.1	37.6
Dzelve 310–320	2.7	10.7	4.9	13.1	5.5	18.3	6.6	38.2
Dzelve 340-350	4.7	12.4	7.5	21.3	4.0	8.4	5.1	36.4
Eipurs 0–25	2.1	10.7	4.6	9.2	6.0	17.6	6.4	43.3
Eipurs 170–187	1.8	9.0	6.5	13.1	6.6	19.2	6.0	37.7
Eipurs 230–240	1.8	8.8	5.7	12.1	5.0	16.7	6.2	43.6
Eipurs 320–358	3.1	11.4	7.6	18.5	5.1	14.9	7.6	31.9
Eipurs 362–410	2.8	10.0	8.4	19.6	5.3	15.1	9.1	29.8
Eipurs 410–456	3.7	9.6	8.8	21.1	5.3	15.0	10.6	25.9
Eipurs 456–462	4.4	13.0	8.3	19.0	4.6	15.2	7.1	28.4
Dizpurvs 20–40	1.9	10.3	4.1	8.9	8.2	23.2	6.4	37.0
Dizurvs 140–160	3.2	12.6	7.4	16.4	6.9	16.7	7.3	29.6
Dizpurvs 180–200	3.3	12.9	8.7	18.6	8.5	15.0	6.4	26.7
Dizpurvs 220–240	3.2	11.8	8.0	18.1	7.5	17.0	7.3	27.2
Dizpurvs 280–300	3.3	10.3	7.9	19.1	5.7	17.6	9.7	26.3
Dizpurvs 300–320	3.4	9.5	9.5	22.0	6.3	15.2	10.6	23.5
Dizpurvs 380–400	3.3	9.1	9.7	24.1	6.0	14.2	10.6	23.1

Table 3. Integrated areas of the main signal regions of CP MAS¹³C NMR spectra of peat humic acids.

Table 4. Integrated areas of the main signal regions of the CP MAS ¹³C NMR spectra of peat-forming bryophytes.

	212-190	190–160	160–140	140-110	110–90	90–50	50–0
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Sphagnum magellanicum	0.1	4.0	0.6	0.5	15.0	70.0	9.9
Ŝphagnum girgensohnii	0.8	4.7	0.9	5.0	14.0	65.2	9.3
Pleurozium schreberi	0.5	5.2	0.6	3.4	13.2	65.9	11.2

also destroyed during humification process. Whereas the intensity of signals in the 160–190 ppm region (resonance of the carbon of carboxyl, ester and amide groups [>CO -O, N]) as well as in the 190–220 ppm region (resonance of the carbons of quinone and ketone groups) does not change significantly in the early stages of humification process, a significant increase of signal intensity in these regions takes place in later stages of humification process.

Thus the distinctive distribution of functional groups and the major building blocks of peat HAs reflect the way of their production and structure alteration due to microbial degradation and geochemical alteration. HA formation occurs through reactions involving compounds from precursor organic materials driven by their microbial degradation. For peat HAs, lignin is not included in the set of precursor materials, and carbohydrates and aliphatic structures are relatively abundant.

Further comparison of the CP MAS ¹³C NMR spectra of raised-bog-forming bryophytes with those of the samples of common species in bogs (*Sphagnum girgensohnii, Sphagnum magellanicum, Pleurozium schreberi*) (Table 4) as well as comparison of CP MAS ¹³C NMR spectra of bryophytes, peat and peat HAs were performed.

Conclusions

Peat humic acids (HAs) have an intermediate position on the diagenesis scale between living organic matter and coal organic matter, and their structure is formed in a process where more labile structures (carbohydrates, amino acids, etc.) are destroyed, while thermodynamically more stable aromatic and polyaromatic structures emerge. Comparatively, the studied peat HAs are at the beginning of the transformation process of living organic matter. Concentrations of carboxyl and phenolic hydroxyl groups change depending on the peat age and decomposition from which HAs have been isolated, and carboxylic acidity increases with peat location depth and humification degree.

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