



Characterization of peat humic substances from Latvia

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Summary

The acidity, elemental, functional and spectral characteristics of peat humic substances isolated from peat of different origin in Latvia are described. Structure of humic substances has been analyzed GC-MS and ^1H NMR, ^{13}C NMR. The GC-MS analysis reveals dominance of aromatic structures in the humic substances. Humic substances isolated from peat of more recent origin are more similar to humic substances from soil, but for humic substances originating from older sources greater degree of humification is evident.

Key index words: humic substances; acidity; peat

Introduction

Humic substances are the dominating naturally occurring organic substances. Humic substances (HS) form most of the organic component of soil, peat and natural waters, they influence the process of formation of fossil fuels and they play a major role in the global carbon geochemical cycle. About 60–85 % of the organic matter in peat consists of humic substances and their concentrations changes depending on the peat origin. Interaction of humic substances with xenobiotics may modify the uptake and toxicity of these compounds, and affect fate of pollutants in environment. The peat humic substances may be regarded as a valuable substance which may find manifold uses for different purposes.

The major questions are about the dominant structures in humic matter depending on their origin. It has been shown, that the structure and properties of peat humic matter evidently differ between peat humic matter of different properties. Unless spectroscopic methods have been most widely used for chemical characterization of peat humic substances, degradative methods has demonstrated their powerfulness in the studies of the peat humus structure (Lu *et al.*, 2000).

The aim of the present paper is to describe the properties peat humic substances isolated from peat in Latvia to evaluate the impact of the character of biological processes during the humification process.

Materials and Methods

Humic substances were isolated from peat of Latvia, representing different peat types and mechanisms of their formation. The peat was characterized by standard methods. The obtained humic substances were characterized as follows:

- elemental analysis: C, H, N and ash concentrations were determined by a Model EA-1108 (Carlo Erba Instruments) CHN-Analyzer. Oxygen concentrations were calculated by difference;
- concentrations of functional groups were determined by standard methods (Tan, 2005);

- molecular weight distribution was determined with gel filtration on Sephadex G-100 (bead diameter 40–120 μm) column (1 \times 40 cm). Detection was performed at 280 nm;
- acid-base properties were determined by potentiometric titration in aqueous media using HACH One pH combination glass/reference electrode. Equilibrium was allowed to take place after each addition of acid before the pH was recorded;
- UV-Vis spectra were obtained over a range of 200 to 700 nm using a Specord UV 40 UV-Vis spectrophotometer on 0.05 N NaHCO_3 solutions at a concentration of 50 mg/l for FA and 33 mg/l for HA and a pH between 8 and 9. E_4/E_6 ratios were measured as in Chen *et al.* (1977);
- fluorescence spectra were recorded using a Hitachi 850 fluorescence spectrometer, on aqueous solutions of each sample at a concentration of 100 mg/l, adjusted to pH 8 with 0.05 M NaOH. Emission spectra were recorded (scan speed 60 nm/min, response 2 sec) over the wavelength range 360 to 640 nm at a fixed excitation wavelength of 335 nm.
- IR spectra were recorded, in the 4000 to 500 cm^{-1} wavenumber range using a Perkin Elmer 400 IR spectrophotometer, of KBr pellets obtained by pressing mixtures of 1 mg samples and 400 mg KBr with precautions taken to avoid moisture uptake;
- ^{13}C NMR spectra were obtained using XL-300 Varian NMR spectrometer at 75.429 MHz. The number of scans for each spectrum varied, but typical value was 2000. All spectra were obtained using the methyl resonance of hexamethylbenzene as an external reference (17.36 ppm). The acquisition time was 1.5 ms, with recycle time of 0.3 s and a contact time of 1000 μs .

Results and Discussion

The composition of major elements, atomic ratios and ash contents of HA and FA, and Nordic Reference samples, examined are presented in Table 1. The elemental composition of humic substances from peat of Latvia is generally similar to that of Nordic countries.


Table 1. Main properties of the peat humic acids

Sample	C,%	H,%	N,%	S,%	O, %	Ash content, %
Dižais Veikenijs 0-25	54,80	5,09	2,19	0,83	36,48	0,61
Dižais Veikenijs 25-52	54,11	5,07	2,10	0,95	37,30	0,47
Dižais Veikenijs 52-75	54,38	5,72	2,46	0,90	35,92	0,62
Dižais Veikenijs 75-98	54,31	5,44	2,59	0,82	36,37	0,47
Dižais Veikenijs 98-118	56,36	5,59	2,23	0,66	34,99	0,18
Gāgu 0-20	49,94	4,68	2,11	0,34	41,49	1,45
Gāgu 20-40	54,32	5,03	2,36	0,89	36,78	0,62
Gāgu 40-60	54,87	4,93	2,10	0,55	36,93	0,62
Gāgu 60-80	58,76	5,20	2,15	0,74	32,53	0,62
Gāgu 80-100	57,75	4,50	1,98	0,39	35,26	0,12
Gāgu 100-120	52,09	4,94	1,66	1,27	39,42	0,62
Gāgu 120-140	53,80	5,34	1,96	0,78	37,83	0,29
Kaigu 0-25	57,05	5,06	2,62	0,57	34,45	0,25
Kaigu 25-45	54,52	5,42	2,52	0,85	36,39	0,30
Kaigu 45-70	55,14	5,07	1,96	0,87	36,85	0,11
Kaigu 70-95	57,61	5,35	2,22	0,59	33,93	0,30
Kaigu 95-125	57,60	5,19	1,82	1,59	33,50	0,30
Kaigu 125-145	56,26	5,43	2,37	0,09	35,33	0,52
Mazais Veikenijs 0-30	54,10	5,33	2,24	1,55	36,68	0,10
Mazais Veikenijs 30-60	57,51	5,35	2,73	0,81	32,94	0,66
Mazais Veikenijs 60-90	55,36	5,29	2,56	0,80	35,33	0,66
Mazais Veikenijs 90-125	54,89	5,23	2,76	0,79	35,11	1,22
Ploce 0-30	51,51	4,80	2,12	1,03	40,30	0,24
Ploce 30-60	51,13	4,81	2,06	0,78	40,97	0,25
Ploce 60-85	51,12	4,87	2,05	0,92	40,78	0,26
Ploce 85-110	52,11	4,61	1,60	0,73	40,70	0,25
Ploce 110-130	57,50	4,94	1,92	0,78	34,61	0,26

The most dominant functional groups in the structure of AHS are carboxyl and phenolic hydroxyl groups. The concentrations of carboxyl groups are higher in fulvic acids (3.5-6 mmole/g), while humic acids have more phenolic groups (1.0-1.5 mmole/g).

The molecular weight distribution of HS can be characterized by number average molecular weight (M_n), weight average molecular weight (M_w) and their ratio, which indicates the polydispersity. According to the molecular masses, the humic substances can be arbitrarily divided, depending on their type and origin. In all cases, the found molecular masses of humic substances are higher than those of fulvic acids and they are more heterogeneous. Also, humic acids from more young peat are more heterogeneous, but with lower molecular mass, than humic substances from deeper peat layers. Fractionation of isolated humic substances in Tris-HCl buffer confirmed that humic acids are more heterogeneous, since more individual fractions were evident.

The Fourier transform infrared (FTIR) spectra of HA's isolated from the peat column using the IHSS procedure (Fig. 1) shows high degree of similarity. It can be seen that the shapes of the FTIR spectra of HA's very similar in the range 500-4000 cm^{-1} . The wide and intense band at around 3400 cm^{-1} is the -OH stretching vibration of acid, protein and polysaccharide groups. The bands at 2950 and 2850 cm^{-1} are the stretching vibration of -CH₃ and -CH₂- in the saturated aliphatic chains. The band at 1720 cm^{-1} is attributed to the -C=O stretching vibration, due mainly to carboxyl groups

and it could partially overlap the -C=O stretching vibration of amides (around 1620 cm^{-1}). The band within 1600-1500 cm^{-1} is related to stretching vibrations of aromatic -C=C- bonds. Finally, the band at *ca.* 1040 cm^{-1} is the -C-OH stretching vibration. The band at around 1700 cm^{-1} , attributed to the result of partial oxidation.

The UV-Vis spectra of FA and HA examined are featureless, and they monotonically decrease with increasing wavelength, with a more or less pronounced shoulder at about 270 nm exhibited for all HA. The ultraviolet spectra of both humic and fulvic acids are similar, differing only slightly in optical density. The slope of the adsorption curves as measured by the ratios of UV absorbency at 465 and 665 nm, have been suggested to be inversely related to the condensation of aromatic groups (aromaticity), and also to particle size and molecular weight (Chen *et al.*, 1977). The higher E_4/E_6 ratios measured for the FA, and particularly HA in Latvia, with respect to those of their terrestrial compartments, are in general agreement with data in the literature and suggest a lower degree of condensed aromatic systems and smaller particle sizes or molecular weights for younger peat HS. The E_4/E_6 ratio for fulvic acids is higher than for humic acids, thus this ratio correlates with the changes in molecular mass of humic substances.

The studies of structure of humic matter are confirmed using ¹³C NMR spectroscopy (crosspolarization/magic angle spinning (CP/MAS) technique) which allows direct evaluation of the dominant structural units of HS.

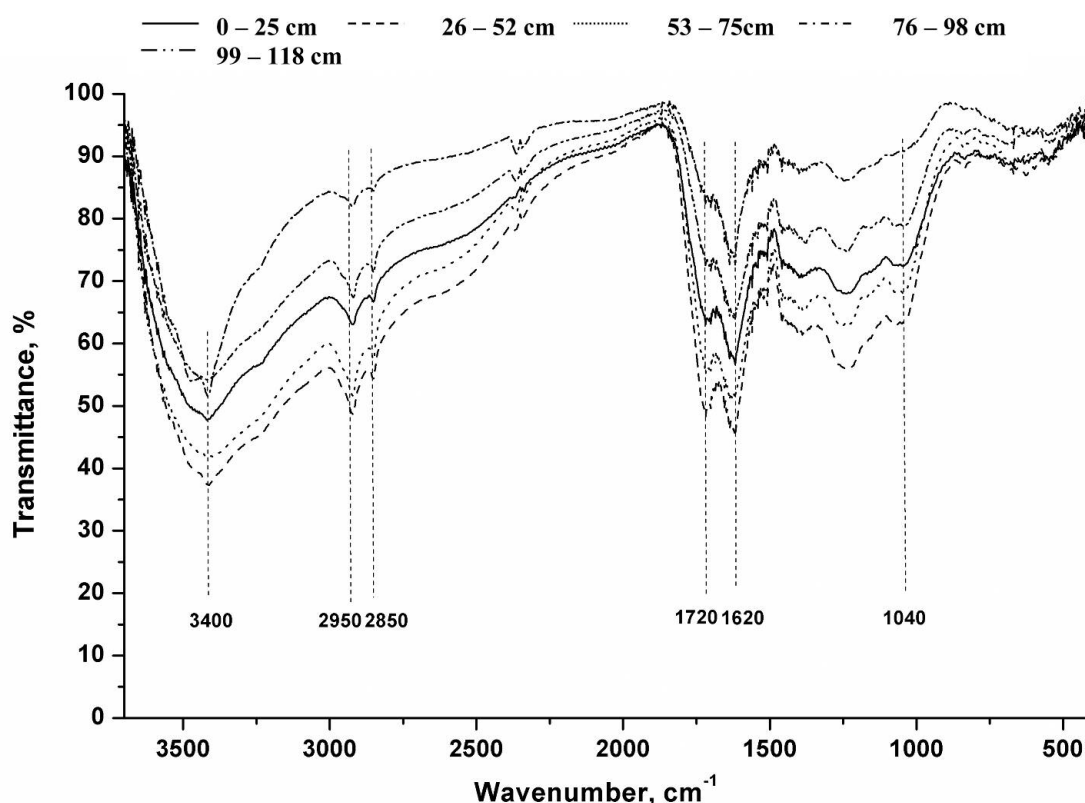


Figure 1. FTIR spectra of humic acids isolated from a peat column in bog Dižais Veikēnieks.

Comparison of ^{13}C CP/MAS NMR spectra allows directly determining major structural units of humic substances. The signals in these NMR spectra represent different types of carbon atoms and allow to determine their concentrations. The ^{13}C NMR spectra can be divided into eight chemical shift ranges. Analyzing ^{13}C NMR spectra of analyzed HS are evident differences in their structure: namely higher aromaticity of humic acids, in comparison with fulvic acids, but higher content of aliphatic structures in the molecules of the latter. In general, the pattern of ^{13}C NMR spectra confirms the information provided by elemental, functional and other spectroscopic studies of humic substances and the proportions of aliphatic structures calculated basing on the spectral properties of HS.

Fluorescence emission spectra (excitation at 335 nm) of humic and fulvic acids (Fig. 6) are differentiated by broad bands centered around $\lambda = 435$ nm and between $\lambda = 435$ nm and $\lambda = 465$ nm, respectively. Some samples show also shoulders at lower wavelengths. Although the exact nature of the fluorescing groups is still far from clarified, fluorescence at the higher wavelengths, typical of bog humic substances, may be attributed to either highly substituted aromatic nucleus, possibly bearing at least one electron-donating group, and/or conjugated unsaturated systems capable of high degrees of resonance (Ghosh and Schnitzer 1980).

Conclusions

The elemental, functional, mass-molecular and spectral characterization of peat humic substances stresses the role of their origin on the properties of humic substances. Humic substances from different bogs bodies differ in properties.

The pattern of regional samples, and differences between Latvian, peat, soil and Nordic Reference samples, demonstrates that even within small territory as Latvia it is impossible to isolate one reference sample that would be representative of peat humic substances.

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