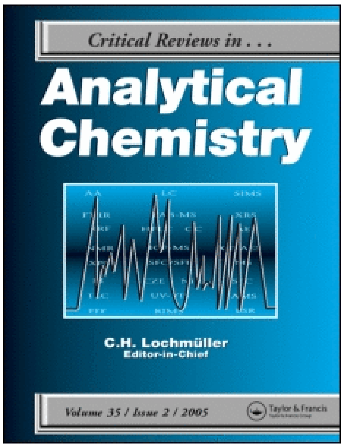

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HUMIC SUBSTANCES IN SURFACE WATERS OF LATVIA

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Introduction

The bulk of organic matter (60-85 %) in surface waters derived from natural sources consists of humic substances (HS) (Thurman, 1985), and their concentrations in bog waters can be very high (Heikkinen, 1990). Bog water humic substances were first isolated in 1836 by Berzelius, but major questions on bog water humus structure, properties, sources and sinks in environment, are still not answered. The properties of humic matter depend on their origin as has been found for soil and peat HS (Orlov, 1990), but origin cannot explain all of the observed differences in structure and properties of aquatic HS (Klavins, 1993; Peuravuori, 1992). However, humic substances from bog waters have not been studied in detail.

The aim of the present work was to study the properties of aquatic humic substances from bog waters in Latvia as the main factor determining natural acidity.

Materials and methods

Humic substances were isolated from bog lakes in Latvia. The hydrochemical parameters in waters of the sampling stations are briefly described and summarized in Table 1. Chemical analyses of water composition and determination of content of humic substances were conducted using standard methods (APHA, 1992). For isolation, a modified (Klavins and Cinis, 1989, Petterson *et al.*, 1994) XAD method was used (Malcolm and Thurman, 1982). The obtained fulvic acid solutions were transferred to the H^+ form and freeze dried, but the humic acid fraction was desalted by repeated washing with Milli-Q water. For comparison, Nordic Reference HA and FA samples were used.

The obtained humic substances were characterized as follows:

- elemental analysis: C, H, N and ash were determined by a Perkin Elmer 240/A CHN-Analyzer. Oxygen content was calculated by difference;
- content of functional groups was determined by standard methods (Klavins, 1993)
- molecular weight distribution (Town and Powell, 1992) was determined by gel filtration on a Sephadex G100 (bead diameter 40-120 μm) column (1x40 cm). The eluent, 0.001 mol/l $Na_2P_4O_7$, was pumped through the column at 1 ml/min, gathering 0.5 ml fractions. A standard set of proteins was used for column calibration. The void volume of the column was determined using Blue Dextran 20000. Detection was performed at 280 nm;
- 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;
- IR spectra were recorded in the 4000 to 500 cm wavenumber range using Perkin Elmer 400 IR spectrophotometer on KBr pellets obtained by pressing mixtures of 1 mg samples and 400 mg KBr, with precaution taken to avoid moisture uptake.

Results and discussion

The selected bog lakes are situated in raised moss bogs, which represent common bog waters in Latvia (Table 1). The waters can be characterized by comparatively low contents of hydrogencarbonates (< 25 mg/l compared to typical hydrogencarbonate concentrations in lakes of Latvia of about 120-250 mg/l) and inorganic salts, and they have high concentrations of humic matter. The reaction of bog waters is acidic. The selected water bodies have not been subjected to anthropogenic pollution and the concentrations of metals and nitrogen compounds in waters is low.

Table 1

Sampling locations and their hydrochemistry (mean annual values)

Lake	pH	Cond. µS/cm	HCO_3^-, mg/l	Cl^-, mg/l	Ca^{+2}, mg/l	NO_3^-, mg/l	Humic substances, mg/l.
Aces	6.3	51	16.6	5.71	7.07	0.8	120
Siguldas	6.2	68	21.5	4.43	5.21	0.9	62
Aklais	5.9	87	24.6	3.22	12.85	1.5	85
Certogs	5.7	65	13.5	4.48	8.76	0.3	170
Bažu	4.5	43	8.5	2.24	5.82	1.1	65
Islienas	5.1	76	12.8	9.63	7.12	0.9	104
Dubulkas	5.2	79	13.6	6.56	7.54	1.2	102
Vertežas	5.8	83	21.4	8.69	8.95	0.7	20
Lisenes	6.0	59	14.4	4.28	8.82	1.1	83
Pieslaistes	6.0	74	17.5	6.43	7.62	0.8	58
Liepājas	7.5	430	186.5	23.41	58.54	2.3	23
Rušonu	7.6	290	210.0	13.52	48.86	0.5	21
Burtnieku	7.3	225	195.5	10.32	35.61	1.4	32
Rāznas	7.4	230	180.5	8.38	36.75	0.6	21

Table 2

Elemental and functional composition and molecular weight distribution of humic substances from surface waters of Latvia

Humic substances	C,%	H,%	N,%	O,%	COOH, mmol/g	ArOH, mmol/g	M_n	M_w
FA-Aces	54.13	3.68	1.15	39.61	3.75	1.24	1650	3450
HA-Aces	57.38	3.94	1.61	36.34	3.18	1.46	2700	5450
FA-Siguldas	55.48	3.75	1.07	38.12	3.88	1.22	1550	1800
HA-Siguldas	57.21	3.94	1.03	37.11	3.65	1.42	2000	3800
FA-Aklais	54.60	3.70	0.93	39.16	3.78	1.15	1480	2150
HA-Certogs	54.20	3.71	1.10	40.05	4.15	1.18	950	1340
HA-Bažu	54.33	4.23	0.96	37.63	3.85	1.25	3100	5750
FA-Bažu	51.02	4.72	0.87	41.90	5.32	1.21	1650	2800
FA-Vertežas	55.86	3.71	0.94	38.11	4.09	1.23	1150	1800

FA-Dubulkas	56.14	3.93	1.18	36.32	3.72	1.22	1100	1650
FA-Lisenes	58.34	4.72	2.64	32.67	3.46	1.38	860	920
HA-Islienas	57.18	4.12	0.63	36.83	3.75	1.64	1300	1920
FA-Islienas	56.41	3.85	0.87	37.12	4.17	1.43	1180	1350
FA-Pieslaistes	55.35	3.92	0.94	38.10	4.13	1.46	800	900
HA-Nordic Reference	55.20	4.12	1.04	39.02	4.12	1.21	4410	11190
FA-Nordic Reference	52.62	4.09	0.74	41.93	7.53	1.53	2180	3360
HA-peat	57.31	3.76	0.34	36.98	3.21	1.08	1790	2100
FA-Liepājas	49.38	4.22	0.61	45.34	5.78	1.36	1650	2700
FA-Rušonu	51.42	4.48	0.97	40.21	4.35	1.11	1800	3100
FA-Burtnieku	51.78	4.22	0.75	42.75	4.63	0.96	2200	3150
FA-Rāznas	49.68	4.25	1.45	43.51	4.94	0.85	2040	2550

For comparison, humic substances from other typical water bodies (Lakes Liepājas, Rāznas, Rušonu) of Latvia were isolated using the same modified XAD method. The elemental composition, atomic ratios and ash content of HA and FA are presented in Table 2, together with the corresponding data from Nordic Reference samples. The fulvic and humic acids isolated from bog waters of Latvia had very similar elemental composition. Humic substances from bog waters typically have high carbon content (C 54-58 %) especially in comparison with carbon content in other lakes of Latvia (C 49-51 %). Carbon content in humic acids generally is higher than in fulvic acids. Humic substances are low in nitrogen and oxygen content, but in fulvic acids oxygen content typically is higher than in humic acids. The values of elemental composition obtained for humic substances from inland waters of Latvia elemental composition are similar to those found for Nordic reference samples (obtained from marshwaters), but they differ from values found for other humic substances. For isolated humic substances, the content of carboxylgroups and oxygen are significantly correlated. The unique elemental composition of humic substances from bog waters can be explained by high metabolic activity of groups of specialized microorganisms (Tranvik, 1988).

The most important functional groups in the structure of AHS are carboxyl and phenolic hydroxylgroups. If the content of carboxylgroups higher is in fulvic acids (3.5-6 mmol/g), then content of phenolic groups higher is in structure of humic substances (1.0-1.5 mmole /g). In humic substances from bog waters, the content of carboxylgroups is lower and of phenolic hydroxylgroups higher than in humic substances from other water bodies of Latvia and reference humic substances. The acidity of humic substances can be characterized not only by total content of acidic functional groups, but also their distribution and properties.

The molecular weight distribution was characterized by number average molecular weight (M_n), weight average molecular weight (M_w) and their ratio (M_n/M_w) which characterizes the polydispersity of humic substances. According to the molecular masses, the humic substances can be arbitrarily divided depending on their type and origin. The determined molecular masses of humic substances were always higher than those of fulvic acids and they are more heterogeneous. The degree of heterogeneity can be regarded as estimate of humification degree (Pettterson *et al.*, 1994). Also, humic substances from eutrophic and mesotrophic lakes are more heterogeneous and have higher molecular mass than humic substances from dystrophic waters.

The UV-Vis spectra of the FA and HA examined (Fig. 1) are featureless and monotonically decreasing with increasing wavelength with a more or less pronounced shoulder at about 270 nm exhibited by all HA. The slope of the adsorption curves, as measured by the ratios of absorbance at 465 and 665 nm, has been traditionally suggested to be inversely related to the amount of condensation of aromatic groups (aromaticity) and to particle size and molecular weight. This was found to be true also in our case. The differences in UV spectra of humic substances depend on their origin.

The IR spectra (Fig. 2) of the FA and HA examined are similar in the principal positions of adsorption, but differences are apparent in the relative intensity of some bands, depending on the origin and nature of the sample. The IR spectra of the FA samples can be tentatively classified as type II spectra, while those of HA samples resembles type I spectra. All of the spectra are characterized by a strong band at 3390-3370 cm^{-1} (stretch of hydrogen bonded OH), which is relatively more intensive for HA than for FA of any origin, and broadens widely towards lower wavelengths (aromatic C-H stretching modes) for bog water FA. The presence of aliphatic groups is shown by a peak at 2920 cm^{-1}, with decreased intensity in humic substances from bogwaters in comparison with humic substances from other sources. The peak at 1618 cm^{-1} and broad band at 1400 cm^{-1} indicate the presence of C=C stretching of substituted aromatic rings. Intense sorption is observed at 1717 cm^{-1} and 1210 cm^{-1} indicating protonated carboxylic acids and ketonic C=O groups, C-O stretching vibration, and OH bending deformations of the COOH groups. Humic substances from bog waters do not show sorption common for carbohydrate residues.

Conclusion

The elemental, functional, mass-molecular and spectral characterization of bog humic substances, indicates the major role of their origin on the properties. Humic substances from different water bodies principally differ in properties, indicating variable intensity of processes of biological transformation of organic matter. The obtained results demonstrate that, even in a small territory such as Latvia, it is impossible to isolate one reference sample which could be able to represent a typical humic substance.

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References

Heikkinen, K.: 1990, *J. Environ. Qual.*, **19**, 649-657

Klavins, M. and Cinis, U.: 1989, *Izv. AN Latv. SSR. Khim. Ser.*, **(3)**, 341-347

Klavins, M.: 1993, *Humic substances from inland waters of Latvia*, LU, Riga, p. 86.

Orlov, D.S., 1990: *Soil humic acids and general humification theory*, MGU, Moscow, p.324 (in Russian)

Pettersson, C., Ephraim, J. and Allard, B.: 1994, *Org.Geochem.*, **21(5)**, 443-451

Peuravuori, J.: 1992, *Finnish Humus News*, 4(1), 1-334

Thurman, E.M.: 1985, *Organic geochemistry of natural waters*: Martinus Nijhoff/Dr.W.Junk Publishers : Wageningen, p.234

Thurman, E.M. and Malcolm, R.L.: 1981, *Env. Sci. Technol.*, 15, 463-466

Town, R.M. and Powell, H.K.J.: 1992, *Anal. Chim. Acta*, 256, 81-86

Tranvik, L.J.: 1988, *Microb. Ecol.*, 16, 311-322

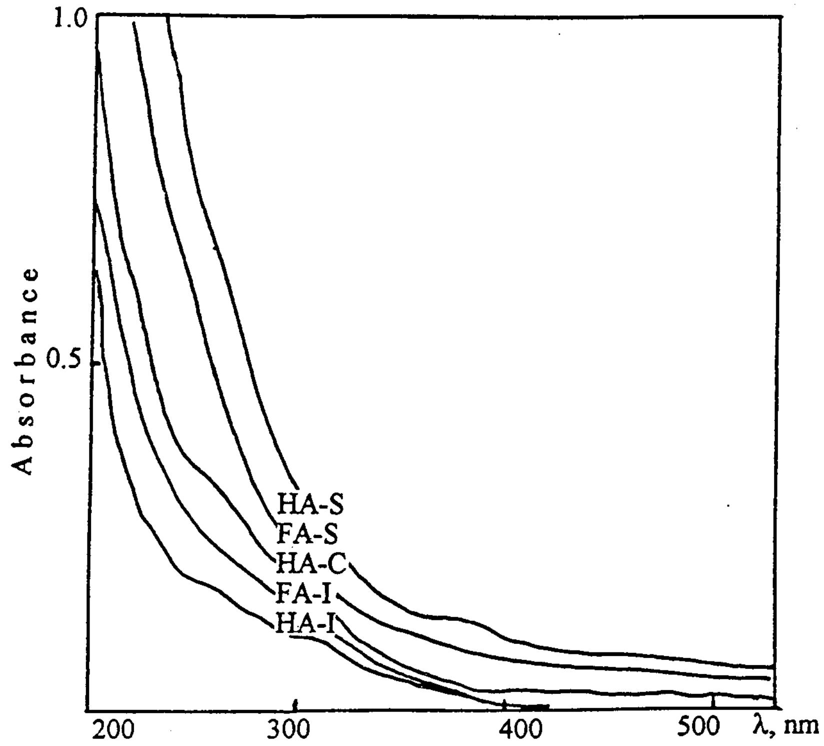

Fig. 1. UV-Vis spectra of aquatic humic substances from waters of lakes Siguldas (HA, FA-S), Islienas (HA, FA-I), Certogs (HA-Z)

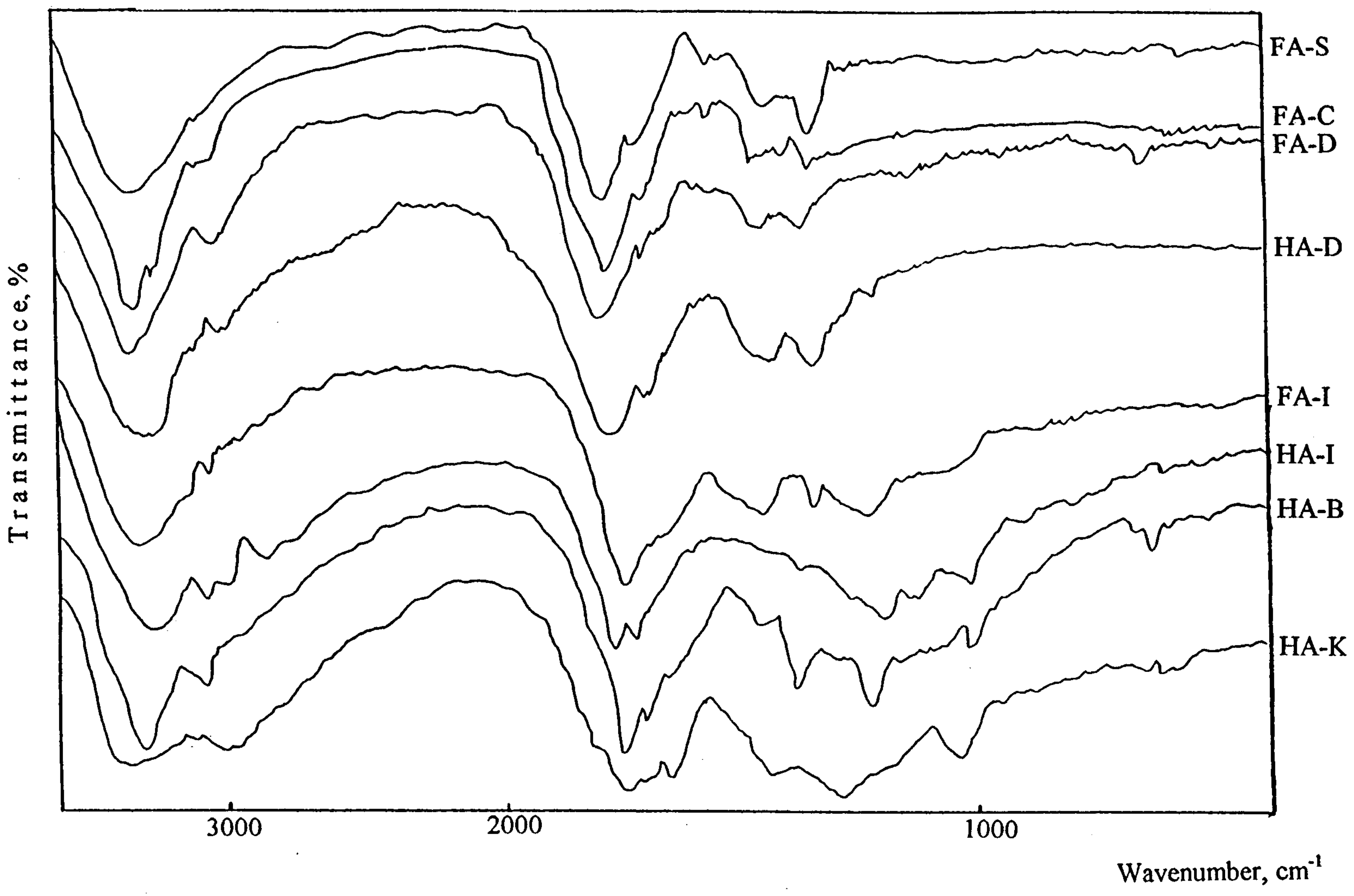

Fig. 2. IR spectra of aquatic humic substances from waters of Lakes Siguldas (FA- S), Certogs (FA-C), Dubulkas (HA, FA-D), Islienas (HA, FA-I), Burtnieku (HA-B), peat humic acid (HA-K)