

## COMPARATIVE STUDY OF PEAT HUMIC ACIDS BY USING UV SPECTROSCOPY

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### Abstract:

Studies of the living organic matter humification process are essential for understanding of the carbon biogeochemical cycle. The aim of this study is to analyze relations between the properties of peat humic acids and peat humification degree using UV spectroscopy. The analysis has been done on samples of humic substances extracted from peat profiles in three ombrotrophic bogs and relations between peat age, decomposition and humification degree, botanical composition and properties of peat humic acids (elemental, functional composition) were studied.

The found variability of peat properties is less significant than differences in the properties of peat-forming living matter, thus revealing the dominant impact of humification process on the properties of peat. Correspondingly, composition of peat humic acids is little affected by differences in the composition of precursor living organic material. UV spectroscopy and used absorbance ratios can be successfully used for describing organic matter properties and diagenesis.

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**Key Words:** UV spectroscopy, peat, humic acids

### Introduction

Peat is a light brown to black organic material, which is formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees (Cocozza et al., 2003). The interest in peat properties is growing, as peat is a substance that supports and influences bog and wetland ecosystems, while peat profiles can serve as “archives” indicating conditions in past environments (Yeloff and Mauquoy, 2006; Zaccone et al., 2007). Significant amounts of organic carbon are stored in the form of peat. Therefore, peat reserves play a major role in the carbon biogeochemical cycling, which is of key importance in the context of the on-going process of climate change (Falkowski et al., 2003; Borgmark, 2005). Industrial and agricultural uses of peat are growing (Ghaly et al., 1999; Brown et al., 2000), and significant amounts of peat are mined industrially. Considering this, there is an increasing interest into studies of peat properties and their diagenesis.

In the carbon biogeochemical cycle, the transformation of living organic matter into refractory part of organic matter (humic substances, such as humic acids, fulvic acids, and humin) or humification is of key importance. Humification can be defined as the transformation of numerous groups of substances (proteins, carbohydrates, lipids etc.) and individual molecules present in living organic matter into groups of substances with similar properties (humic substances) (Francioso et al., 2003). To characterize the humification process, an important tool is the development of humification indexes that link the rate of transformation of living organic matter, development of humic substances with parameters that describe the properties of formed materials (Lu et al., 2001). Several humification indexes have been suggested to study the humification process during composting to evaluate maturity of compost (Jerzykiewicz et al., 1999; Domeizel et al., 2004) and to study soil formation processes (Zsolnay et al., 1999; Cavani et al., 2003; Ikeya and Watanabe, 2003; Rosa et al., 2005; Corvasce et al., 2006). Usually the humification process is evaluated using indirect measurements that describe structural changes occurring during the humification process. Several methods have been suggested, such as measurement of  $E_4/E_6$  ratio that indicates the development of condensed macromolecules, the amount of organic/aliphatic carbon estimated with  $^{13}\text{C}$  nuclear magnetic resonance spectra. Furthermore, measurements of presence of free radicals, determined

using electron spin resonance spectra and studies of fluorescence properties of humic macromolecules, have been used to describe humification processes (Milori et al., 2002). However, only a few articles study the humification process of peat (Schnitzer and Levesque, 1979; Preston et al., 1989; Hargitai, 1994; Baran, 2002; Francioso et al., 2003; Štíre et al., 2008) despite the fact that bogs and wetlands form one of the largest sources of refractory organic matter.

The aim of this study is to analyze relations between the properties of peat humic acids and peat humification degree using UV spectroscopy.

## **Materials and methods**

### **Site location**

In-depth study of peat composition, humification degree and peat humic acid properties was carried out in three ombrotrophic bogs located in Latvia. Full peat profiles were obtained and cut into 5-cm layers for analysis of peat properties and isolation of humic acids.

### **Isolation of peat humic acids**

HAs were extracted and purified, using procedures recommended by the International Humic Substances Society (IHSS) (Tan, 2005).

### **Analysis of peat and humic acid properties**

The <sup>14</sup>C dating was done at the Institute of Geology of the Tallinn Technical University (Estonia). Carbon, hydrogen, nitrogen and sulphur concentrations in the peat and humic acid 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.

The analysis of botanical composition was performed microscopically, using a Carl-Zeiss binocular microscope, thereby determining the decomposition degree (Listvan, 1975).

For estimation of carboxylic groups and total acidity, an automatic titrator TitroLine easy (Schott-Geräte GmbH) was used. The known Ca-acetate method (Tan, 2005), based on the formation of acetic acid, was used for determining the total number of carboxylic groups. To estimate the total acidity, Ba(OH)<sub>2</sub> method was used (Tan, 2005).

Humification degree (according to (Blackford and Chambers, 1993) and modified by (Borgmark, 2005)) was estimated as absorption at 540 nm after treatment of 1.00 g of peat sample for 1½ hrs with 25 ml of 8 % NaOH in 25 ml plastic tube in a boiling water bath (95 °C) and filtration.

### **UV spectroscopy**

UV-Vis spectra were recorded on a Thermospectronic Helios  $\gamma$  UV (Thermolectron Co) spectrophotometer in a 1-cm quartz cuvette. The UV-Vis spectral ratios  $E_2/E_3$  (Peuravuori et al., 1997) and  $E_4/E_6$  ratio (Chen et al., 1977), i.e. the ratio of absorbance at 280 and 360, and 465 and 665 nm respectively, was determined for humic acid solutions 10 mg/l diluted in 0.05 M NaOH.

Absorbance ratios  $E_{280/472}$ ,  $E_{280/664}$ ,  $E_{472/664}$  were calculated from UV-Vis absorbance at 280, 472 and 664 nm (Albrecht, 2011). Absorbance ratio  $E_{270/400}$  were calculated from UV-Vis absorbance at 270 and 400 nm (Uyguner and Bekbolet, 2005). Absorbance ratio  $E_{254/436}$  were calculated from UV-Vis absorbance at 254 and 436 nm (Shirshova et al., 2006).

Specific absorbance  $A_{280}$  (Chin et al. 1994),  $A_{254}$  and  $A_{436}$  (Shirshova et al., 2006),  $A_{340}$  (Scotta et al., 2001) were calculated based on UV-Vis absorbance at 280, 254, 436 and 340 nm, where values were normalized per mol C with units  $L mol^{-1} cm^{-1}$  of organic matter in solution (Chin et al. 1994).

The value of  $\Delta \log K$  coefficient,  $\Delta \log K = \log A_{400} - \log A_{600}$ , was calculated to determine degree of humification (Fong et al., 2006).

## **Results and discussion**

For description of molecular properties of humic acids (HA) UV-Vis spectroscopy is widely used as simple and informative method (Shirshova et al., 2006). It is known that the UV-Vis spectra of humic acids are broad, featureless and monotonously decrease with increasing wavelength, but there are UV regions and absorbances of spectra that can be used to analyse HA (Uyguner and Bekbolet, 2005). Vieyra (Vieyra et al., 2009) suggests to describe UV absorption spectra by three Gaussian-like bands which are related to electronic transition of benzene-like molecules. Very intense band centred to 180 nm due to allowed  $\pi-\pi^*$  transition. Less intense benzenoid and electron transfer bands are centred to 205 nm and 250 nm and largely are affected by the presence of polar functional

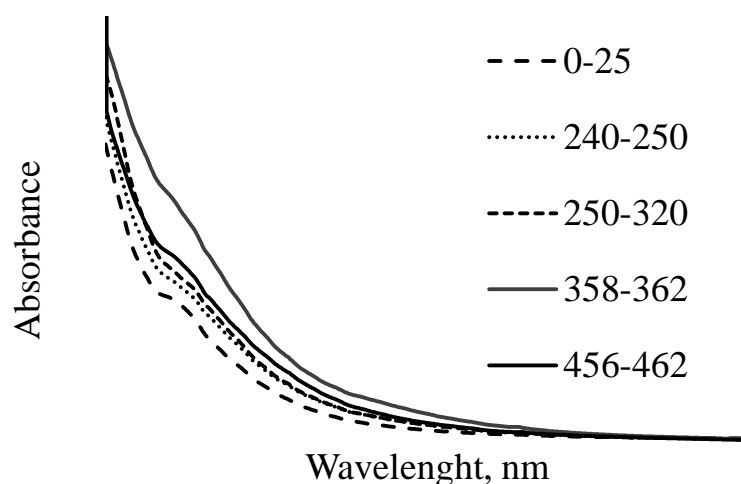
groups, such as hydroxyl, carbonyl, carboxyl, etc., whereas the benzenoid band is almost unaffected (Vieyra et al., 2009). The UV absorbance at 280 nm represents total aromaticity, because  $\pi-\pi^*$  electron transition occurs in this UV region (ca. 270-280 nm) common for phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings (Chin et al., 1994; Glatzel et al., 2003) and also specific absorbance  $A_{280}$  can be used to characterize humification of the peat (Chin et al. 1994). Many of these compounds are thought to be common structural subunits in humic matter and  $E_2/E_3$  as absorbance ratios measured at 250 and 365 nm corresponds to correlation of molecular size and aromaticity (Peuravuori et al., 1997). To describe aromaticity of humic acids with UV absorbance at 280 nm (Chin et al. 1994) also absorbance at 254 nm is used (Uyguner and Bekbolet, 2005). Studies of aquatic humic acid photocatalytic degradation shows that specific absorbance  $A_{254}$  decreases during photocatalytic degradation (Eggin et al., 1997) and may represent an alternative indicative parameter for research humic acids (Lipski et al., 1999; Kumke et al., 2001; Uyguner and Bekbolet, 2005).

The relationship  $E_4/E_6$  (the ratio absorbances at 465 nm and 665 nm) is related to the aromaticity and to the degree of condensation of the chain of aromatic carbons of the humic acids, and could be used as a humification index (Kononova 1966; Stevenson and Schnitzer 1982). Low  $E_4/E_6$  ratio reflect a high degree of condensation of these structures while high ratios mean presence of large quantities of aliphatic structures and low quantities of condensed aromatic structures (Chin et al., 1997). This ratio also is inversely related to the degree of aromaticity, particle size, molecular weight, and acidity (Uyguner et al., 2004). Typically  $E_4/E_6$  is larger for non-humified material by presence of proteins and carbohydrates, which increase the absorbance at the UV region of the spectrum (Vieyra et al., 2009).

Coefficient  $E_{270/400}$  (the ratio absorbances at 270 and 400 nm) characterize the degradation of phenolic/quinoid core of HA to simpler carboxylic aromatic compounds (Uyguner and Bekbolet, 2005).

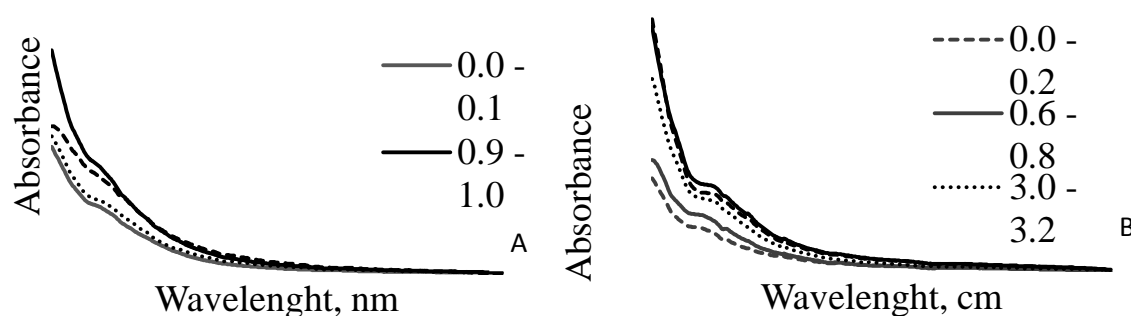
To analyze humification of organic matter commonly is used UV-Vis absorbance at 260-280 nm, due to lignin and quinone moieties (material at the very beginning of transformation). The absorbance at 460-480 nm reflects the organic material at the beginning of humification and the absorbance at 600-670 nm is indicative of strongly humified material with a high degree of aromatic, condensed groups (Albrecht, 2011). Therefore following absorbance ratios have been used to characterize aquatic humic material  $E_{280/472}$ ,  $E_{280/664}$ ,  $E_{472/664}$ . The  $E_{280/472}$  reflects the proportion between the lignins and other materials at the beginning of humification. The  $E_{280/664}$  denotes the relation between non-humified and strongly humified material.  $E_{472/664}$  ratio is used to indicate the degree of condensation and polymerization of the aromatic constituents. Low  $E_{280/664}$  or  $E_{472/664}$  ratios reflect a high degree of aromatic condensation and indicate a higher level of organic material humification (Albrecht, 2011).

The value of  $\Delta \log K$  coefficient can be used for describing degree of humification of organic matter, although this coefficient were not significant enough to use this parameter as indicator of humification degree of soil organic matter (Fong et al., 2006). On the basis of  $\Delta \log K$  coefficient, humic acids can be divided into 3 types: A – humic acids of high degree of humification for which the values of  $\Delta \log K$  coefficient is up to 0.6; type B – those of corresponding values between 0.6-0.8 and type C – where  $\Delta \log K$  within range 0.8-1.1 (Fong et al., 2006).



**Fig. 1.** UV-Vis spectra of peat humic acids from Eipurs bog depending on the sample location depth

The shape of UV-Vis spectra of humic acids revealed a monotonically decrease with increasing wavelength (Fig. 1, 2). Presence of shoulder between 240 and 290 nm are characteristic to aromatic or unsaturated compounds (conjugation of quinone and ketones) (C=C, C=O, N=N) (Chin et al., 1994). Absorption intensity increases with peat depth demonstrating nature of humification process in bogs – increasing aromaticity of isolated HAs. It depends not only on humification process, but also on peat forming biota. Bottom layers of the bog are composed of plants containing aromatic compounds (lignine) in their structure and thus UV-Vis spectra of HAs are affected.



**Fig. 2.** UV-Vis spectra of peat humic acids from Dzelve (A) and Dizpurvs (B) bog depending on the sample location depth

There are other UV spectra absorbances and absorbance ratios:  $A_{436}$ ,  $E_{254/436}$  suggested by Shirshova (Shirshova et al., 2006), representing that HAs with lower  $A_{436}$ ,  $E_{254/436}$ ,  $E_4/E_6$ ,  $A_{254}$  values contain more aliphatics, carbohydrates, aromatics and/or amides compared with HAs which are relatively rich in carboxylic and phenolic groups (Shirshova et al., 2006). The results of mean  $A_{340}$  indicated that the humic acid fraction had more colour per unit weight than the fulvic or the hydrophilic fractions, which means that HAs are more aromatic than FAs (Scotta et al., 2001).

Lower  $E_4/E_6$  ratios measured for humic acids from deeper bog layers accordingly to data in the literature (Zaccone et al., 2007) suggest a high degree of condensed aromatic systems and smaller particle sizes or molecular weights and acidity, whereas in upper layers large quantities of aliphatic structures, mainly polysaccharides probably are dominant. The  $E_4/E_6$  correlates with  $E_{472/664}$  ratio (Table 1, 2, 3) indicating the degree of condensation and polymerization of the aromatic constituents (Uyguner and Bekbolet, 2005). Typically for studied bogs lower degree of the aromatic constituents has been found for sphagnum, hypnum and sedge peat.

**Table 1** Calculated UV-Vis absorbance ratios, specific absorbance  $A_{280}$  and  $\Delta \log K$  of peat HAs isolated from Eipurs bog

Humic acid	$A_{280}$	$E_4/E_6$	$E_2/E_3$	$E_{280/472}$	$E_{280/664}$	$E_{472/664}$	$E_{270/400}$	$\Delta \log K$
Eipurs HA 0.0 - 0.25	19.99	5	3.4	10.05	47.75	4.75	5	0.81
Eipurs HA 0.25 - 0.50	18.96	7.2	3.46	10.56	71.8	6.8	5.14	0.88
Eipurs HA 0.50 - 0.70	20.16	5.86	3.34	9.67	53.86	5.57	4.8	0.85
Eipurs HA 0.70 - 1.20	18.67	6.28	3.1	8.73	51.14	5.86	4.38	0.83
Eipurs HA 1.20 - 1.35	16.74	6.86	2.96	7.62	49	6.43	4.08	0.78
Eipurs HA 1.35 - 1.70	28.22	6.23	2.84	6.97	40.77	5.85	3.81	0.79
Eipurs HA 1.70 - 1.87	28.64	6.58	2.86	7.03	40.54	5.77	3.88	0.78
Eipurs HA 1.87 - 2.20	25.16	5.92	2.83	7	39.08	5.58	3.78	0.77
Eipurs HA 2.20 - 2.30	26.20	6.36	2.86	7.38	44.27	6	3.85	0.80
Eipurs HA 2.30 - 2.40	25.35	6.4	2.92	7.59	46.3	6.1	4	0.81
Eipurs HA 2.40 - 2.50	24.17	6.77	2.94	7.62	49.11	6.44	4	0.81
Eipurs HA 2.50 - 3.20	24.23	6.2	3.09	8.12	47.1	5.8	4.18	0.80
Eipurs HA 3.20 - 3.58	29.48	8	3.09	7.45	55.9	7.5	4.14	0.82
Eipurs HA 3.58 - 3.62	36.18	6.69	2.96	6.51	41.125	6.31	3.86	0.77
Eipurs HA 3.62 - 4.10	29.95	7.22	3.05	8.77	59.44	6.78	4.31	0.86
Eipurs HA 4.10 - 4.56	28.22	6.55	3.08	9.27	56.67	6.11	4.34	0.85
Eipurs HA 4.56 - 4.62	24.45	7.2	2.76	7.55	50.6	6.7	3.78	0.88

**Table 2** Calculated UV-Vis absorbance ratios, specific absorbance  $A_{280}$  and  $\Delta \log K$  of peat HAs isolated from Dzelve bog

Humic acid	$A_{280}$	$E_4/E_6$	$E_2/E_3$	$E_{280/472}$	$E_{280/664}$	$E_{472/664}$	$E_{270/400}$	$\Delta \log K$
Dzelve HA 0.0 - 0.10	10.68	10	3.31	10	100	10	4.91	0.87
Dzelve HA 0.10 - 0.20	14.52	12	3.36	10.36	114	11	4.77	0.94
Dzelve HA 0.20 - 0.30	16.62	8	3.08	8.53	64	7.5	4.28	0.81
Dzelve HA 0.30 - 0.40	20.87	10	3.39	9.63	73.83	7.67	4.81	0.92
Dzelve HA 0.40 - 0.50	15.76	4	2.76	6.21	50	3.8	3.57	0.64
Dzelve HA 0.50 - 0.60	20.22	8.5	3.35	9.875	79	8	4.75	0.95
Dzelve HA 0.60 - 0.70	15.47	14	3.39	9.85	128	13	4.79	0.99
Dzelve HA 0.70 - 0.80	17.23	7	3.35	9.77	63.5	6.5	4.72	0.86
Dzelve HA 0.80 - 0.90	19.03	8	3.43	9.6	72	7.5	4.73	0.82
Dzelve HA 0.90 - 1.00	21.20	6.3	3.42	8.78	39.5	4.5	4.65	0.79
Dzelve HA 1.00 - 1.10	21.78	7.3	3.22	7.95	55.67	7	4.18	0.86
Dzelve HA 1.10 - 1.20	19.16	4.5	3.38	8.35	35.5	4.25	4.22	0.79
Dzelve HA 1.20 - 1.30	19.84	5	3.17	7.74	36.75	4.75	4.21	0.73
Dzelve HA 1.30 - 1.40	19.81	6.3	3.2	8.11	48.67	6	4.24	0.79
Dzelve HA 1.40 - 1.50	21.42	4.2	3.12	7.74	29.4	3.8	4.07	0.75
Dzelve HA 1.50 - 1.60	15.00	12	3.21	9.36	103	11	4.44	1.10
Dzelve HA 1.60 - 1.70	13.56	10	3.39	10.44	94	9	4.81	1.02
Dzelve HA 1.70 - 1.80	12.25	8	3.5	12.57	88	7	5	0.98
Dzelve HA 1.80 - 1.90	14.01	10	3.32	10.56	95	9	4.63	1.04
Dzelve HA 1.90 - 2.00	12.49	9	3.31	11.125	89	8	4.8	1.00
Dzelve HA 2.00 - 2.10	13.84	6	3.22	9.18	50.5	5.5	4.54	0.78
Dzelve HA 2.10 - 2.20	14.48	11	3.38	10.4	104	10	4.66	1.08
Dzelve HA 2.20 - 2.30	13.27	9	3.63	11.875	95	8	5.2	1.00
Dzelve HA 2.30 - 2.40	15.29	11	3.48	10.9	109	10	4.87	0.90
Dzelve HA 2.40 - 2.50	15.51	4.67	3.1	8.46	36.67	4.33	4.21	0.75
Dzelve HA 2.50 - 2.60	14.21	6	3.24	9.27	51	5.5	4.58	0.78
Dzelve HA 2.60 - 2.70	12.82	5.5	3.3	9.3	46.5	5	4.54	0.74
Dzelve HA 2.70 - 2.80	12.26	5.5	3.25	8.8	44	5	4.57	0.85
Dzelve HA 2.80 - 2.90	24.87	4.2	3.05	7.87	30.17	3.83	4.06	0.78
Dzelve HA 2.90 - 3.00	22.74	4	2.98	7.5	27.5	3.67	4.02	0.74
Dzelve HA 3.00 - 3.10	23.16	3	2.95	6.72	18.67	2.78	3.83	0.59

Dzelve HA 3.10 - 3.20	22.96	3.43	2.94	7.32	23	3.14	3.91	0.69
Dzelve HA 3.20 - 3.30	15.84	5	3.17	8.62	37.33	4.33	4.25	0.75
Dzelve HA 3.30 - 3.40	16.72	5	3.13	8.5	39.67	4.67	4.34	0.76
Dzelve HA 3.40 - 3.50	21.71	5.75	2.97	6.64	36.5	5.5	3.83	0.71

Ratios  $E_{270/400}$ ,  $E_{280/472}$  and  $E_2/E_3$  (Table 1, 2, 3) strongly correlates and shows degradation of phenolic/quinoid core of HA (Uyguner and Bekbolet, 2005) as well as proportion between the lignins and other materials at the beginning of humification (Albrecht, 2011) in peat profiles. Also these ratios corresponds to detected humification index ( $D_{540}$ ) and peat decomposition degree and confirm the same results as other ratios ( $E_4/E_6$ ,  $E_{472/664}$ ) calculated from UV-Vis spectra - a high degree of aromatic condensation indicating a higher level of organic material humification in deeper layers of bog and higher proportion of material at the beginning of humification in upper layers of the bog.

Specific absorbance  $A_{280}$  indicates aromaticity of HAs and is reversely related with ratio  $E_{280/664}$  which denotes the relation between non-humified and strongly humified material, but aren't directly associated with other ratios indicated aromaticity ( $E_2/E_3$ ,  $E_4/E_6$ ,  $E_{270/400}$ ), although on average level correlates with peat decomposition degree and humification index.

**Table 3** Calculated UV-Vis absorbance ratios, specific absorbance  $A_{280}$  and  $\Delta \log K$  of peat HAs isolated from Dizpurvs bog

Humic acid	$A_{280}$	$E_4/E_6$	$E_2/E_3$	$E_{280/472}$	$E_{280/664}$	$E_{472/664}$	$E_{270/400}$	$\Delta \log K$
Dizpurvs HA 0.0 - 0.20	9.05	3	3.26	8	21.33	2.67	4.38	0.60
Dizpurvs HA 0.20 - 0.40	11.63	6	2.97	8.09	44.5	5.5	4.13	0.76
Dizpurvs HA 0.60 - 0.80	11.79	4.5	3.38	10.625	42.5	4	4.84	0.80
Dizpurvs HA 0.80 - 1.00	17.34	5	2.96	6.89	32.75	4.75	4.03	0.64
Dizpurvs HA 1.00 - 1.20	17.10	4.75	2.96	7.06	31.75	4.5	4.00	0.69
Dizpurvs HA 1.20 - 1.40	19.39	4.6	2.72	6.23	27.4	4.4	3.51	0.66
Dizpurvs HA 1.40 - 1.60	21.69	4.5	2.75	6.2	25.83	4.17	3.54	0.66
Dizpurvs HA 1.60 - 1.80	19.54	6.33	2.98	7.56	45.33	6	4.03	0.71
Dizpurvs HA 1.80 - 2.00	21.40	10	3.04	7.89	75	9.5	4.21	0.80
Dizpurvs HA 2.00 - 2.20	19.78	4	2.74	5.96	22.83	3.83	3.43	0.62
Dizpurvs HA 2.20 - 2.40	20.72	3.86	2.67	5.8	20.71	3.57	3.40	0.57
Dizpurvs HA 2.40 - 2.60	19.20	3.25	2.63	5.48	17.13	3.125	3.35	0.55
Dizpurvs HA 2.60 - 2.80	19.52	3.28	2.78	6.05	19	3.14	3.56	0.59
Dizpurvs HA 2.80 - 3.00	17.24	7	3.31	9.15	59.5	6.5	4.50	0.75
Dizpurvs HA 3.00 - 3.20	17.59	5	3.17	8.5	39.67	4.67	4.39	0.75
Dizpurvs HA 3.20 - 3.40	16.99	4.33	3.23	9.5	38	4	4.42	0.72
Dizpurvs HA 3.40 - 3.60	15.98	4.33	3.05	9	36	4	4.19	0.72
Dizpurvs HA 3.60 - 3.80	18.88	3.14	2.92	6.6	18.86	2.86	3.72	0.56
Dizpurvs HA 3.80 - 4.00	21.76	3.28	2.96	6.9	20.71	3	3.79	0.59
Dizpurvs HA 4.00 - 4.30	19.61	3.12	2.77	5.87	16.875	2.875	3.41	0.57

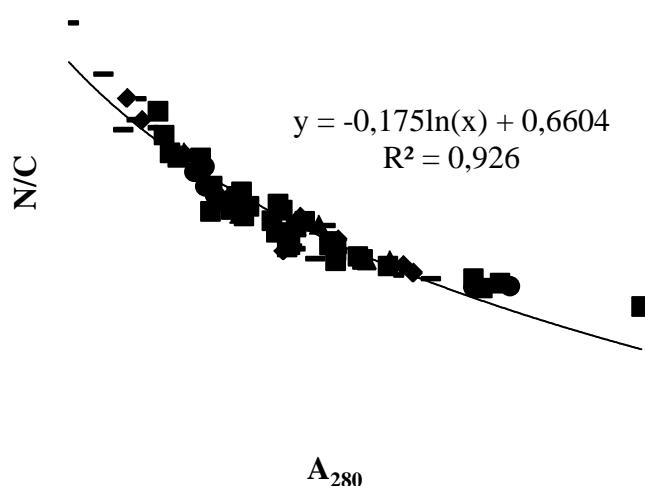
The value of  $\Delta \log K$  coefficient for peat humic acids range 0.55 – 1.09 describing them as less humified than soil humic acids (Fong et al., 2006). Value of  $\Delta \log K$  coefficient strongly correlates with other calculated UV absorbance ratios ( $E_4/E_6$ ,  $E_{472/664}$ ,  $E_{270/400}$ ,  $E_{280/472}$ ,  $E_2/E_3$ , and  $E_{280/664}$ ) except specific absorbance  $A_{280}$  (Table 4). If for soil humic acids this coefficient is not significant, then for peat humic acids with lower decomposition degree and quite wide range (10-60 %) of very well characterized humification parameters within peat profiles this coefficient might be used. Moreover,  $\Delta \log K$  on average level correlates with humification index –  $D_{540}$ .

**Table 4** Correlations between calculated UV absorbance ratios ( $E_4/E_6$ ,  $E_{472/664}$ ,  $E_{270/400}$ ,  $E_{280/472}$ ,  $E_2/E_3$ ,  $E_{280/664}$ , specific absorbance  $A_{280}$  and  $\Delta \log K$ ) and decomposition,  $D_{540}$ .

	$A_{280}$	$E_4/E_6$	$E_2/E_3$	$E_{280/472}$	$E_{280/664}$	$E_{472/664}$	$E_{270/400}$
<b>Decomposition, %</b>	0.38	0.01	0.3	0.29	0.08	-	
<b><math>D_{540}</math></b>	0.39	0.3	0.26	0.14	-	0.28	
<b><math>E_4/E_6</math></b>	0.03						
<b><math>E_2/E_3</math></b>	0.22	0.3					
<b><math>E_{280/472}</math></b>	0.25	0.39	<b>0.83</b>				
<b><math>E_{280/664}</math></b>	0.11	<b>0.91</b>	0.45	<b>0.59</b>			
<b><math>E_{472/664}</math></b>	0.03	<b>0.98</b>	0.26	0.36	<b>0.91</b>		
<b><math>E_{270/400}</math></b>	0.22	0.37	<b>0.92</b>	<b>0.91</b>	<b>0.53</b>	0.33	
<b><math>\Delta \log K</math></b>	0.03	<b>0.74</b>	0.46	<b>0.64</b>	<b>0.77</b>	<b>0.71</b>	<b>0.55</b>

Significance level  $p=0.05$ 

There are small variability of UV-Vis ratios in Dzelve and Dizpurvs peat profiles indicating other factors influencing structure of HAs without humification of organic material. In Dzelve bog peat profile from 1.5 to 2.5 m have higher  $E_4/E_6$ ,  $E_{280/472}$ ,  $E_{472/664}$  and  $E_{280/664}$  ratios, and  $\Delta \log K$ , but lower specific absorbance  $A_{280}$  (Table 2). In this depth of bog lower decomposition degree of peat and therefore lower aromaticity and higher concentration of phenol groups are observed, but lower concentration of carboxylic groups is detected, which typically increases with depth of peat profile. Decrease of carboxylic group concentration in Dzelve bog and lower decomposition degree of peat are probably due to very intense peat growth rate in past (about 4-5 mm/year). In Dizpurvs peat profile from 2.0 to 2.8 m lower  $E_4/E_6$ ,  $E_2/E_3$ ,  $E_{270/400}$ ,  $E_{280/472}$ ,  $E_{472/664}$ ,  $E_{280/664}$  ratios and  $\Delta \log K$  was observed, but without significant changes of specific absorbance  $A_{280}$  (Table 3). Higher amount of carboxylic groups correlates with decomposition degree of peat. It could be expected incense of specific absorbance  $A_{280}$ , and loss of phenolic groups, but due to low aromaticity depending on botanical composition of peat – Sphagnum mosses are void of aromatic substances, but no major changes in this parameter was observed.

**Fig. 3.** Correlation between specific absorbance  $A_{280}$  and N/C relation of studied bogs

All three groups of associated ratios (1 -  $E_4/E_6$ ,  $E_{472/664}$ ; 2 -  $E_{270/400}$ ,  $E_{280/472}$  and  $E_2/E_3$ ; 3 - specific absorbance  $A_{280}$ ,  $E_{280/664}$ ) and  $\Delta \log K$  shows that aromaticity, acidity as well as degradation of phenolic structures increases with depth of peat profile and only partly have influenced from peat forming biota (Table 4). Moreover, these calculated ratios have not directly related to amount of aromatic carbon detected with  $^{13}\text{C}$  NMR spectroscopy. These findings corresponds to investigations in literature (Chen et al., 1977; Chen et al., 2002), where was found that  $E_4/E_6$  ratio not directly related to the relative concentration of condensed aromatic rings ratio, but have mainly governed by the particle size (or particle or molecular weight), correlated with the free radical concentration, contents of O, C, COOH and total acidity.

Most significant relation from calculated ratios have specific absorbance  $A_{280}$  and N/C ratio (Fig. 3) and corresponds to results from literature (Kalbitz et al., 1999; Kalbitz et al., 2000) and provides an initial estimate of the degree of humification because peat decomposition and humification tend to result in the decay of carbon structures and thus the relative enrichment of nitrogen.

### Conclusion

Different UV ratios can be successfully used as complex parameter for describing humification of organic matter. Calculated UV ratios and specific absorbance shows that aromaticity, acidity as well as degradation of phenols increase with depth of peat profile and only partly have influenced by peat forming biota. Peat humic acids (HA) are formed in a process in which more labile structures (carbohydrates, amino acids, etc.) are destroyed, but thermodynamically more stable aromatic and polyaromatic structures emerge.

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