Approaches to estimating humification indicators for peat

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SUMMARY

Degree of decomposition is an important property of the organic matter in soils and other deposits which contain fossil carbon. It describes the intensity of transformation, or the humification degree (*HD*), of the original living organic matter. In this article, approaches to the determination of *HD* are thoroughly described and ^{14}C dated peat columns extracted from several bogs in Latvia are investigated and compared. A new humification indicator is suggested, namely the quantity of humic substances as a fraction of the total amount of organic matter in the peat.

KEY WORDS: chemical analysis, peat, degree of decomposition, humification degree.

INTRODUCTION

Natural organic matter (NOM) is a major constituent of the organic substances in soil, sediment, peat and fossil fuel; and it comprises the largest pool of carbon on the Earth (Schimel *et al.* 1997). NOM consists of organic material in the following phases: a) partially degraded but still identifiable plant tissues; b) microbial biomass; c) organic coatings of mineral phases; d) identifiable organic substances of low molecular weight; and e) the refractory part of organic matter - humic substances (humic acid, fulvic acid, and humin) (Piccolo 2001). Historically, the term “humus” has been applied to the dark-coloured organic matter in soils, and the terms “humic acid”, “fulvic acid”, and “humin” have been used to designate different portions of humus. NOM is the product of the decay of living organic matter formed in the following types of degradation reactions: a) biotic (enzymatically catalysed) reactions; b) pyrolytic reactions; and c) abiotic reactions exclusive of pyrolytic reactions (Lu *et al.* 2000). Parallel synthetic reactions of low molecular weight decay products are also important. During the process of decay, the bulk of living organic matter is mineralised and no more than 20% of its original mass is transformed into refractory organic substances (Lukoshko *et al.* 1988). Both degradation and synthetic reactions in decaying organic matter are described as humification; in general, the term refers to the transformation of the numerous groups of substances and individual molecules present in living organic matter into substances with similar properties (humic substances) and, finally, into mineral carbon compounds. All of these processes are important for understanding the carbon cycle and the transformation of living matter (Perez *et al.* 2004). Understanding how organic matter is transformed during mineralisation, and especially the formation of humic substances (humification), is of key importance in elucidating the biogeochemical carbon cycle (Francioso *et al.* 2003). Furthermore, the character of organic matter transformations influences the structure and properties of the humic substances that are formed. Thus humification indices that link the rate of organic matter transformation to the development of humic substances by describing the properties of the products can be important indicators (Lu *et al.* 2001). Several such indices have been suggested for evaluating the maturity of the resulting compost (Jerzykiewicz *et al.* 1999, Domeizel *et al.* 2004) and for the study of soil formation processes (Zsolnay *et al.* 1999, Cavani *et al.* 2003, Ikeya & Watanabe 2003, Rosa *et al.* 2005, Corvasce *et al.* 2006). The humification process is usually evaluated by making indirect measurements that describe accompanying structural changes. Several methods have been suggested, such as measurement of the E_4/E_6 ratio, which takes account of condensed macromolecules and the amount of organic/aliphatic carbon estimated by ^{13}C CP MAS NMR. Also, the presence of free radicals, which is determined using EPR and the fluorescence properties of humic macromolecules, has been used as a descriptor of the humification process (Milori *et al.* 2002).

A significant amount of NOM can be found in peat (Fuchsman 1980). However, although mires and peatlands form one of the largest reservoirs of refractory organic matter, few studies on the humification process for peat have been conducted

(Schnitzer & Levesque 1979, Preston *et al.* 1989, Hargitai 1994, Baran 2002, Francioso *et al.* 2003).

This paper reports the results of a study of the peat humification process for peat and the links between peat age (degree of decomposition), main chemical properties and organic matter.

METHODS

Sample collection and preparation

Twenty-eight peat samples were collected from depths of 0 to 145 cm in the profiles of five industrially important raised bogs which developed under typical north European conditions in Latvia. The samples were dried in the laboratory at 105°C, then homogenised and passed through a 1 mm sieve prior to the various analyses. For the analyses, analytical quality reagents (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification.

Peat characterisation

Botanical composition was ascertained using a Carl Zeiss binocular microscope. The degree of decomposition (von Post 1924, Lishtvan & Korol 1975) was determined using standard methods. ^{14}C dating was conducted at the Institute of Geology of the Tallinn Technical University (Estonia). Elemental analysis (C, H, N, S, and O) was carried out using an Elemental Analyser Model EA-1108 (Carlo Erba Instruments). Ash content was measured after heating 50 mg of each peat sample at 750°C for eight hours. Metal (Na, Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, Cd, Pb) concentrations were measured by flame atomic absorption (Perkin-Elmer AAnalyst 200) after wet digestion with HNO_3 + $HClO_4$ (Tan 2005). UV/Vis spectra were measured on a Thermospectronic Helios γ UV (Thermoelectron Co) spectrophotometer using a 1 cm quartz cuvette. Absorbance was determined for a solution of 5 mg of the humic or fulvic acid in 10 ml of 0.05 M $NaHCO_3$ at 280, 340, 465 and 665 nm and the ratios E_2/E_6, E_2/E_3, E_3/E_4, E_4/E_6 (Chen *et al.* 1977) derived. The organic carbon concentrations of peat extracts were determined with Shimadzu TOC–VCSN. For carbohydrate analysis, each humic sample (10 mg) was suspended in 10 ml of 6 M HCl and heated at 100°C for 3 hours, then the concentration of carbohydrates in the hydrolysate was determined using phenol-sulphuric acid assay following the method described by Chaplin & Kennedy (1994). Cation exchange capacity (ammonium acetate method) and concentration of phosphates were determined using methods suggested for soil analysis, and pH was determined in distilled water extracts using a Hanna pH 213 pH meter (Tan 2005).

Humification indicators

To determine Humification Index (*HI*) (Cavani *et al*. 2003) for each sample, 2.0 g of peat was placed in a 250 ml flask and extracted by shaking with 100 ml of 0.1 M NaOH plus 0.1 M $Na_4P_2O_7$ under nitrogen for 48 hours at 65°C in a thermostated shaker (Biosan, Latvia). The samples were then centrifuged at 5,000 rpm for 15 minutes and the supernatants were filtered through a 1 µm filter. The filtered solution constituted the total extract (TE) and was fractionated into humified (humic acids HA, fulvic acids FA) and non-humified (NH) fractions. In short, 25 ml of TE was placed in a 50 ml centrifuge tube and acidified to pH <2 by adding 0.3–0.5 ml of 9 M H_2SO_4, then centrifuged at 5,000 rpm for 20 minutes. The precipitated fraction (HA, organic carbon concentration C_{HA}) was collected and stored, and the supernatant fed onto a small column packed with about 5 cm^3 of insoluble polyvinylpyrrolidone which had been previously equilibrated in 0.005 M H_2SO_4. The eluate (NH, organic carbon concentration C_{NH}) was collected in a 50 ml volumetric flask, then diluted to volume with 0.005 M H_2SO_4 and stored. The retained fraction (FA, organic carbon concentration C_{FA}) was eluted with 0.5 M NaOH solution and collected in the centrifuge tube containing the HA precipitate, which was re-dissolved. Total organic carbon (TOC) and humified carbon (HA, FA) were determined with Shimadzu TOC–VCSN. The humification index (*HI*) was calculated as follows:

$$HI = \frac{C_{NH}}{C_{HA} + C_{FA}} \qquad [1]$$

The method for determination of Pyrophosphate Index (*PyI*) followed Schnitzer & Levesque (1979). 0.50 g of peat was shaken with 50 ml of 0.025 M $Na_4P_2O_7$ for 18 hours at room temperature. The peat residue was separated by filtration, washed with distilled water, and the filtrate with washings diluted to 250 ml with distilled water. The optical density of this solution was measured at 550 nm and *PyI* derived from the absorbance (D_{550}) as

$$PyI = D_{550} \times 100 \qquad [2]$$

To derive the Humus Quality *K* Value (Hargitai 1994), 1.00 g of each peat sample was shaken with

50 ml of 1% NaF for six hours, filtered, and the adsorption of the filtrate at 410 nm (D_{HSNaF}) determined. Another 1.00 g portion of the same peat sample was extracted by shaking with 50 ml of 0.5% NaOH for six hours, filtering, and determining adsorption of the filtrate at 410 nm (D_{HSNaOH}). The humus quality value K was calculated as

$$K = \frac{D_{HSNaF}}{D_{HSNaOH}} \times C \qquad [3]$$

where C is the percentage of carbon in the sample by mass.

For Peat Humification Index (*PHI*), 1.00 g of each peat sample was shaken with 50 ml of distilled water for 24 hours, filtered, and the total organic carbon content (C_w) of the filtrate (water extract) determined. Another 1.00 g portion of the same peat sample was extracted by shaking with 50 ml of 0.1 M NaOH for 24 hours, filtering, and determining the total organic carbon content (C_{NaOH}) of the filtrate (alkaline extract). *PHI* was then calculated as

$$PHI = \frac{C_w}{C_{NaOH}} \times 100 \qquad [4]$$

To determine Humification Degree (*HD*), 1.00 g of peat sample was shaken with 50 ml of 1.0 M NaOH for 24 hours, filtered, and the total organic carbon content (C_{HS}) of the filtrate (alkaline extract containing humic substances) determined (mg C g^{-1}). *HD* was calculated as

$$HD = \frac{C_{HS}}{C_{peat}} \times 100 \qquad [5]$$

where C is the carbon content of the sample (mg g^{-1}).

Data analysis

Principal component analysis (PCA) (rotation method VARIMAX with Kaiser normalisation; rotation converged in 8 iterations) was conducted using SPSS 12.0 for Windows.

RESULTS

The basic characteristics and elemental composition of the peat samples are shown in Table 1, the results of the various analyses that were conducted in order to characterise the humification process in Table 2, and elemental ratios for the peat samples in Table 3.

The botanical composition of the deepest layer of peat was mostly cottongrass - *Sphagnum* and *S. fuscum* peat, while the upper layer was *S. fuscum* peat. The ages of the samples ranged from 400 to 2260 years, and their decomposition degree (von Post scale) from H2 to H6. The ages of the peat samples from each profile increased gradually with depth (Figure 1). However, the basic properties of the peat did not display similar increasing trends at all sites (Table 1). The carbon and nitrogen contents of peat samples from Mazais Veiķenieks varied with increasing age and depth, whilst the sulphur content actually declined. The variability of elemental composition was not so random for the other sites, however, and most probably reflected botanical composition and the specific conditions (mostly the hydrological regime) when the peat was formed. The impact of peat development conditions on peat properties is also evident from the carbohydrate concentration, cation exchange capacity, and metal concentration data (Table 2).

The results of the peat characterisation were used to study the impact of peat formation conditions on the major properties and humification characteristics of the peat. PCA was used to determine the main factors affecting peat composition. Six principal components were extracted and these accounted for 87% of the total variance of the data (Tables 4, 5). Component 1 is characterised by depth within the peat layer, ash content and the concentrations of phosphate ions, carbohydrates and potassium (Table 5). The concentrations of metals (mostly of anthropogenic origin, for example Cd and Pb) in the peat can be explained by this component. Component 2 is associated with degree of decomposition and the contents of ash, carbon and metals of mostly natural origin (Ca, Mg, Fe); it is also suggested that this factor describes peat genesis. Component 3 is associated with biogenic processes (presence of carbohydrates, which are abundant in living plants but rapidly consumed during the decay process), the presence of phosphate and nitrogen ions, and sodium. Component 4 is characterised by depth and age; Component 5 by magnesium and calcium concentration; and Component 6 by sulphur content and cation exchange capacity.

The peat humification process was examined using van Krevelen graphs, which are frequently employed in analyses relating to the biogeochemical carbon cycle and the genesis of fossil fuel (van Krevelen 1950). Figure 2 shows the relationship between the H/C and O/C atomic ratios for organic

Table 1. Basic characteristics and elemental composition of the peat samples (n.d. = not determined).

Site	Depth (cm)	Peat type	Age (years)	Decomposition		C %	H %	N %	S %	O %
				von Post	%					
Ploce	0−30	Raised bog *S. fuscum*	1460	H5	24	50.78	5.18	1.38	0.69	37.78
	31−60		n.d.	H1	8	54.26	5.73	1.08	0.44	36.19
	61−85		1560	H2	14	48.46	5.34	0.65	0.79	43.72
	86−110		n.d.	H2	14	52.41	5.31	1.05	0.67	39.87
	111−130	Raised bog cottongrass-*Sphagnum*	1670	H2	11	52.18	5.16	0.79	0.63	40.70
Gāgu	0−20	Raised bog cottongrass-*Sphagnum*	n.d.	H6	29	48.54	5.54	1.15	0.84	40.79
	21−40		n.d.	H6	32	49.09	5.67	0.93	1.34	43.06
	41−60		n.d.	H6	31	48.82	5.60	0.75	0.58	43.86
	61−80	Raised bog *S. fuscum*	n.d.	H2	20	48.41	5.62	0.68	0.52	44.62
	81−100		n.d.	H2	13	49.45	5.52	0.83	0.92	43.28
	101−120		n.d.	H2	13	49.68	5.49	0.73	0.67	43.23
	121−140		1640	H2	11	50.78	5.60	0.85	1.01	42.09
Kaigu	0−25	Raised bog cottongrass-*Sphagnum*	810	H6	33	48.26	5.76	1.15	0.69	41.57
	26−45	Raised bog *S. fuscum*	n.d.	H2	10	49.31	5.76	0.85	1.01	43.39
	46−70		1590	H2	11	49.56	5.71	0.80	0.77	43.16
	71−95	Raised bog narrow-leaf *Sphagnum*	n.d.	H2	33	48.53	5.83	0.86	0.81	43.97
	96−125		n.d.	H1	7	48.54	5.59	0.78	0.72	44.44
	126−145	Raised bog *S. fuscum*	2260	H2	9	41.75	4.96	0.70	0.67	51.73
Dižais Veiķenieks	0−25	Raised bog *S. fuscum*	520	H2	12	46.85	5.39	0.59	0.89	46.23
	26−52		n.d.	H2	12	48.19	5.53	0.66	0.58	44.88
	53−75		980	H2	6	47.53	5.52	0.45	0.53	45.82
	76−98		n.d.	H2	9	46.96	5.40	0.41	0.58	46.52
	99−118		1350	H1	6	46.72	5.47	0.43	0.81	46.92
Mazais Veiķenieks	0−30	Raised bog *S. fuscum*	400	H2	8	45.67	5.65	0.73	0.69	46.87
	31−60	Raised bog *S. magellanicum*	n.d.	H3	14	46.49	5.80	0.53	0.54	45.87
	61−90	Transition type tree-grass	n.d.	H5	27	52.46	6.15	1.88	1.08	37.19
	91−125	Fen type tree-grass	1180	H6	31	53.01	6.09	2.38	0.94	35.37

Table 2. Properties and composition of the peat samples analysed.

Site	Depth (cm)	pH	Ash %	CEC cmol(+) kg^{-1}	PO_4^{3-} mg kg^{-1}	Carbohydrates mg g^{-1}	Na mg kg^{-1}	Mg mg kg^{-1}	K mg kg^{-1}	Ca mg kg^{-1}	Mn mg kg^{-1}	Fe mg kg^{-1}	Ni mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	Cd mg kg^{-1}	Pb mg kg^{-1}
Ploce	0−30	2.95	5.18	13.8	0.69	37.78	66	584	109	7483	6.51	659	1.16	2.42	8.94	0.07	4.76
	31−60	2.46	5.73	10.8	0.44	36.19	63	639	66	2590	2.74	534	0.97	2.12	16.67	0.30	15.86
	61−85	2.51	5.34	6.5	0.79	43.72	69	632	54	2628	2.92	279	0.55	1.17	11.38	0.07	5.61
	86−110	2.40	5.31	10.5	0.67	39.87	72	886	27	1434	0.91	146	0.31	0.60	2.02	0.01	0.69
	111−130	2.50	5.16	7.9	0.63	40.70	61	961	51	1984	5.06	168	0.32	2.00	2.42	0.04	0.79
Gāgu	0−20	2.50	5.54	11.5	0.84	40.79	60	502	165	1726	15.15	756	1.23	3.37	29.38	0.58	27.74
	21−40	2.47	5.67	9.3	1.34	43.06	81	389	67	813	6.44	185	0.33	0.64	8.51	0.06	3.88
	41−60	2.41	5.60	7.5	0.58	43.86	74	372	65	523	2.00	147	0.33	0.76	4.56	0.05	6.31
	61−80	2.36	5.62	6.8	0.52	44.62	82	437	68	522	2.55	141	0.27	0.77	3.94	0.03	0.70
	81−100	2.46	5.52	8.3	0.92	43.28	83	365	86	453	2.01	130	0.25	0.69	3.30	0.03	0.96
	101−120	2.42	5.49	7.3	0.67	43.23	77	363	79	425	0.73	106	0.23	0.78	2.19	0.02	0.59
	121−140	2.45	5.60	8.5	1.01	42.09	80	373	72	506	1.72	113	0.33	1.24	2.20	0.03	1.18
Kaigu	0−25	3.02	5.76	11.5	0.69	41.57	64	558	202	1786	17.31	566	1.08	2.00	13.39	0.18	10.78
	26−45	3.07	5.76	8.5	1.01	43.39	51	250	80	443	0.86	113	0.23	0.49	2.09	0.03	0.42
	46−70	3.11	5.71	8.0	0.77	43.16	54	333	74	503	1.73	128	0.28	0.90	3.71	0.03	0.98
	71−95	3.15	5.83	8.6	0.81	43.97	62	313	83	476	1.22	109	0.29	0.63	3.25	0.27	0.84
	96−125	3.26	5.59	7.8	0.72	44.44	47	359	63	424	1.03	83	0.20	0.55	2.46	0.01	0.40
	126−145	3.31	4.96	7.0	0.67	51.73	34	665	54	782	2.70	127	0.19	0.71	2.26	0.01	0.33
Dižais Veiķenieks	0−25	2.94	5.39	5.9	0.89	46.23	81	507	94	704	6.98	115	0.35	0.59	5.84	0.05	5.53
	26−52	2.90	5.53	6.6	0.58	44.88	80	312	90	329	1.05	95	0.18	0.44	2.67	0.02	3.04
	53−75	2.28	5.52	4.5	0.53	45.82	115	336	99	414	0.77	120	0.08	0.53	2.48	0.01	0.55
	76−98	2.29	5.40	4.1	0.58	46.52	102	333	81	537	0.98	157	0.12	0.31	2.57	0.02	0.23
	99−118	2.35	5.47	4.3	0.81	46.92	90	465	69	973	2.36	352	0.12	0.47	3.22	0.03	0.36
Mazais Veiķenieks	0−30	3.01	5.65	7.3	0.69	46.87	51	456	54	1058	1.55	398	0.17	1.14	3.45	0.02	2.43
	31−60	3.14	5.80	5.3	0.54	45.87	30	445	43	2191	2.00	665	0.51	2.11	2.68	0.01	2.63
	61−90	3.66	6.15	18.8	1.08	37.19	28	352	73	3051	5.58	1503	1.24	1.50	4.34	0.03	4.60
	91−125	4.17	6.09	23.8	0.94	35.37	26	387	51	4473	6.48	2464	2.88	2.02	2.84	0.02	1.02

Table 3. Elemental ratios and humification coefficients of the peat samples.

Site	Depth (cm)	H/C	N/C	O/C	E_2/E_6	E_4/E_6	E_2/E_3	E_3/E_4	*PHI*	*HI*	*K*	*PyI*	*HD*
Ploce	0−30	1.216	0.023	0.558	24.100	2.700	2.060	4.333	18.139	0.113	0.534	31.6	1.014
	31−60	1.258	0.017	0.501	22.000	2.600	2.056	4.115	27.507	0.155	0.515	18.2	0.942
	61−85	1.312	0.011	0.677	15.875	2.000	2.082	3.813	35.362	0.140	0.636	16.6	1.055
	86−110	1.207	0.017	0.571	17.833	2.000	2.058	4.333	31.742	0.134	0.290	13.8	0.994
	111−130	1.179	0.013	0.586	18.600	2.760	1.938	3.478	39.033	0.139	0.307	15.3	1.102
Gāgu	0−20	1.359	0.020	0.631	10.438	1.813	1.942	2.966	27.007	0.142	0.971	16.2	1.029
	21−40	1.376	0.016	0.658	15.778	2.167	1.986	3.667	52.431	0.150	0.424	16.8	1.107
	41−60	1.368	0.013	0.674	12.313	1.875	1.931	3.400	66.310	0.171	0.400	39.1	1.124
	61−80	1.383	0.012	0.692	12.071	1.929	1.920	3.259	63.467	0.195	0.609	39.0	1.214
	81−100	1.330	0.014	0.657	13.222	2.056	1.935	3.324	48.207	0.171	0.474	21.7	1.168
	101−120	1.317	0.013	0.653	15.955	2.273	2.006	3.500	39.179	0.191	0.305	19.7	1.048
	121−140	1.313	0.014	0.622	19.095	2.476	1.985	3.885	33.268	0.125	0.307	15.8	1.059
Kaigu	0−25	1.421	0.020	0.647	11.444	1.889	1.943	3.118	7.042	0.070	0.946	21.9	1.182
	26−45	1.391	0.015	0.661	10.526	1.842	1.923	2.971	12.334	0.122	0.271	12.1	1.106
	46−70	1.373	0.014	0.654	16.250	2.125	1.970	3.882	7.992	0.083	0.188	14.7	1.113
	71−95	1.431	0.015	0.680	24.091	2.727	2.008	4.400	7.228	0.068	0.191	11.5	1.187
	96−125	1.372	0.014	0.687	16.571	2.000	2.035	4.071	6.442	0.072	0.209	9.1	1.187
	126−145	1.417	0.014	0.930	29.500	2.700	1.916	5.704	1.670	0.067	0.323	10.8	1.348
Dižais Veiķenieks	0−25	1.372	0.011	0.741	24.300	2.650	1.876	4.887	27.909	0.314	0.804	45.5	1.170
	26−52	1.368	0.012	0.699	11.947	1.737	2.009	3.424	69.336	0.404	0.721	24.1	1.123
	53−75	1.383	0.008	0.724	13.308	2.000	2.012	3.308	89.385	0.298	0.843	24.7	1.144
	76−98	1.369	0.008	0.744	12.083	1.833	1.986	3.318	199.601	0.406	1.277	27.7	1.157
	99−118	1.395	0.008	0.754	17.750	2.375	2.014	3.711	126.397	0.349	1.177	22.7	1.206
Mazais Veiķenieks	0−30	1.473	0.014	0.770	16.167	1.667	2.021	4.800	23.807	0.087	0.814	19.2	1.184
	31−60	1.488	0.010	0.741	12.667	1.500	2.000	4.222	10.220	0.077	0.610	17.6	1.237
	61−90	1.398	0.031	0.532	26.333	2.667	2.079	4.750	2.984	0.069	0.326	39.1	1.055
	91−125	1.369	0.038	0.501	23.182	2.727	2.056	4.133	2.485	0.071	0.545	36.6	1.035

Table 4. Summary statistics generated by principal components analysis (PCA) of selected peat properties data. VARIMAX rotation and Kaiser normalisation were used on the initial component structure.

components	variance	% of variance explained	cumulative % of variance explained
1. depth of the peat layer sampled, ash content, phosphates, carbohydrates, potassium	6.064	24.254	24.254
2. peat genesis	5.020	20.081	44.335
3. biogenic processes	4.841	19.365	63.699
4. depth and age	2.248	8.991	72.690
5. magnesium and calcium concentration	2.138	8.552	81.242
6. sulphur content of peat and cation exchange capacity	1.362	5.449	86.691

Table 5. Loading structure of the first six components extracted by principal components analysis (PCA) of selected peat properties data.

variable	units	acronym	component					
			1	2	3	4	5	6
type	-	PV1	0.006	0.393	0.761	-0.042	-0.255	0.084
depth	cm	PV2	-0.453	0.008	0.129	-0.719	0.061	0.001
C	%	PV3	0.022	0.912	-0.132	-0.229	-0.107	0.082
H	%	PV4	0.057	0.406	0.394	0.197	-0.733	0.116
N	%	PV5	0.172	0.763	0.498	0.051	0.017	0.256
S	%	PV6	0.019	0.143	0.142	-0.010	-0.231	0.826
O	%	PV7	-0.233	-0.948	-0.051	0.057	0.011	-0.095
ash content	%	PV8	0.609	0.575	0.183	0.271	0.363	-0.004
pH	-	PV9	-0.073	0.174	0.913	0.162	-0.047	0.146
CEC	cmol(+) kg^{-1}	PV10	0.234	-0.079	-0.556	0.274	-0.109	-0.465
PO_4^{3-}	mg kg^{-1}	PV11	0.557	0.229	-0.675	0.125	0.311	0.026
carbohydrates	mg g^{-1}	PV12	0.557	0.229	-0.675	0.125	0.311	0.026
decomposition (*DD*)	-	PV13	0.587	0.401	0.307	0.344	0.106	0.294
Age	years	PV14	-0.055	-0.035	0.001	-0.860	0.228	0.068
Na	mg kg^{-1}	PV15	-0.112	-0.167	-0.890	0.133	-0.115	-0.042
Mg	mg kg^{-1}	PV16	0.128	0.150	-0.080	-0.298	0.792	-0.134
K	mg kg^{-1}	PV17	0.708	-0.086	-0.144	0.410	-0.039	0.240
Ca	mg kg^{-1}	PV18	0.136	0.668	0.261	0.258	0.502	-0.105
Mn	mg kg^{-1}	PV19	0.768	0.153	0.133	0.320	0.228	0.324
Fe	mg kg^{-1}	PV20	0.132	0.659	0.608	0.233	-0.051	-0.022
Ni	mg kg^{-1}	PV21	0.321	0.707	0.508	0.182	0.053	0.039
Cu	mg kg^{-1}	PV22	0.683	0.468	0.248	0.093	0.302	-0.143
Zn	mg kg^{-1}	PV23	0.943	0.153	-0.125	0.065	0.058	-0.059
Cd	mg kg^{-1}	PV24	0.936	0.085	-0.050	-0.130	-0.139	-0.115
Pb	mg kg^{-1}	PV25	0.938	0.158	-0.090	0.088	-0.010	-0.124

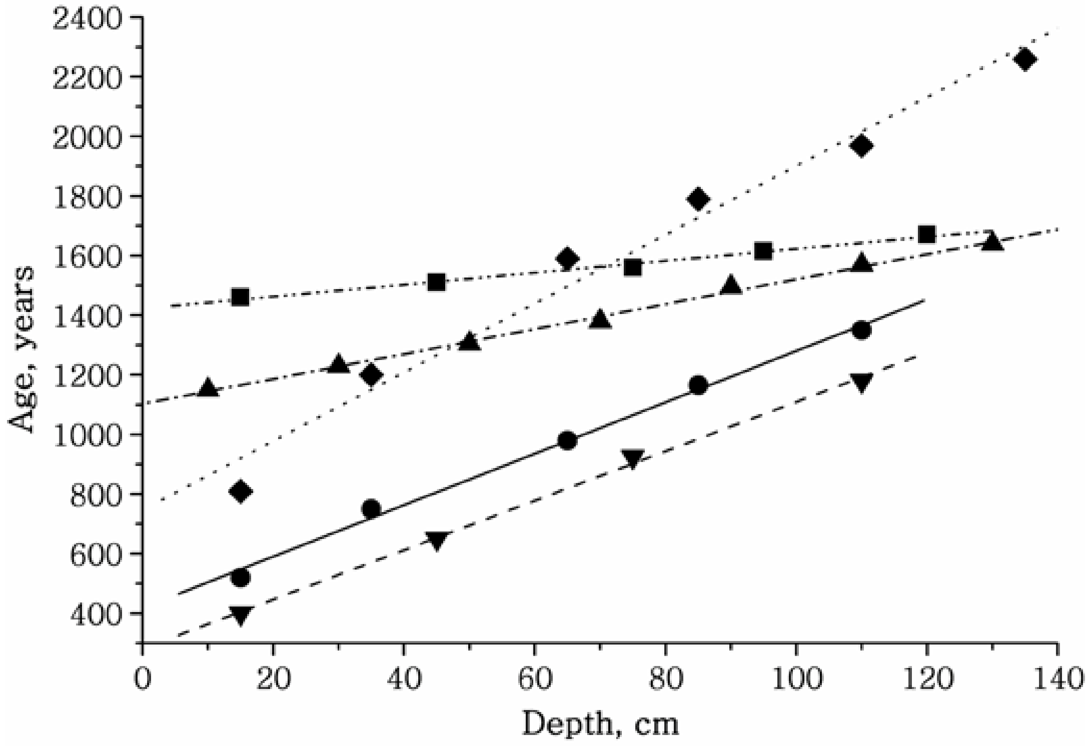

Figure 1. Relationship between depth and age of the peat samples from each site: ● Dižais Veiķenieks; ▲ Gāgu; ◆ Kaigu; ■ Ploce; and ▼ Mazais Veiķenieks.

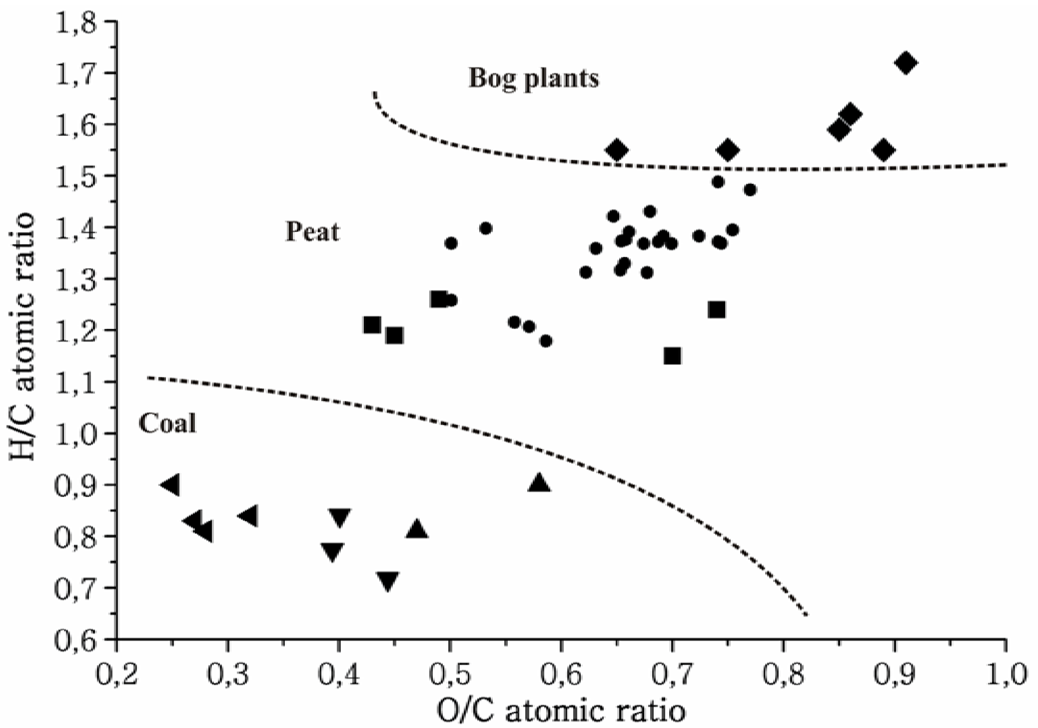

Figure 2. Van Krevelen graph (H/C *vs*. O/C atomic ratio) for bog plants (◆), the peat samples from the Latvian bogs studied here (●), reference peat samples (International Humic Substances Society) and peat samples from other bog sites (■), brown coal (▲), coal (◀) and lignite (▼).

material with different degrees of decomposition, from bog plants to brown coal, lignite and coal. The H/C ratio is highest for peat-forming plants, cellulose and proteins, it declines with increasing decomposition of the original living matter, and the lowest values are for bituminous coal. The O/C ratio also declines with increasing humification, reflecting the lower quantities of oxygen-containing functional groups such as methoxyl, carboxylic and carbonyl groups in the fossil material.

In this context, the peat samples studied here were at an early stage of transformation. In order to provide reliable quantitative information about early diagenesis, we investigated further the dependence of elemental composition on peat age (depth and decomposition degree) (Figure 3). In general, the H/C ratio was negatively correlated with depth; and Kaigu and Mazais Veiķenieks had the highest negative correlations. However, Dižais Veiķenieks showed a strong positive correlation. This analysis demonstrates that atomic ratio cannot be used reliably to study the humification process, due to the significant impact of the original vegetation composition and peat formation conditions.

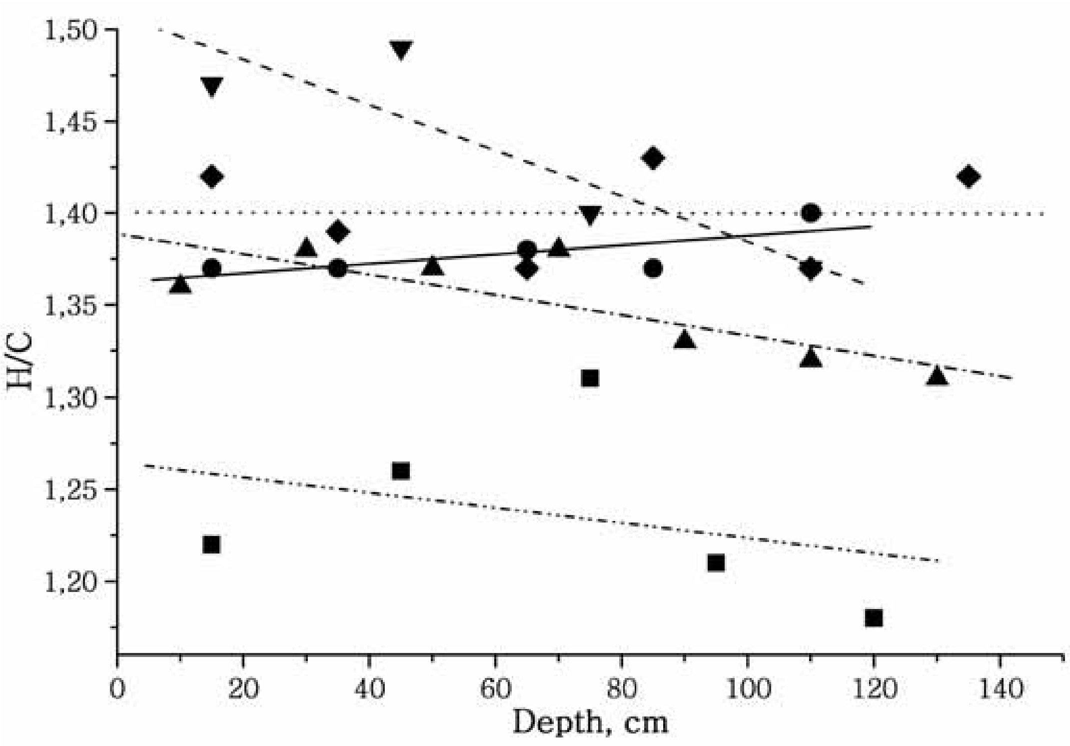

Figure. 3. Dependence of H/C on depth for each of the bogs sampled. Key:
● Dižais Veiķenieks (——— $Y = 1.362 + 2.543^{-4} \cdot X$; R= 0.742) $P > 0.05$;
▲ Gāgu (– · – · $Y = 1.389 - 5.536^{-4} \cdot X$; R= -0.195) $P > 0.02$;
◆ Kaigu (········· $Y = 1.400 - 4.892^{-6} \cdot X$; R= -0.812) $P > 0.05$;
■ Ploce (— · · $Y = 1.265 - 4.118^{-4} \cdot X$; R= -0.338) $P > 0.05$;
▼ Mazais Veiķenieks (– – – $Y = 1.509 - 0.001 \cdot X$; R= - 0.889) $P > 0.05$.

Carbohydrate concentration correlated more strongly with depth and thus, apparently, with age (Figure 4). The carbohydrate concentration decreased with depth, indicating clearly that carbohydrate degradation is amongst the major processes that characterise peat formation and humification.

The variability of the 25 peat properties was examined using principal component analysis. The first five components extracted explained 84% of the total variance (Table 6). The first component was related to the elemental composition (C, N and O) and thus to the development of peat, and correlated well with humification degree *HD*. The second component characterised the correlation between peat type, hydrogen and nitrogen, which are related to peat humification index *PHI*. The third component was associated with most of the humification coefficients used in our study, and thus apparently characterised the humification process;

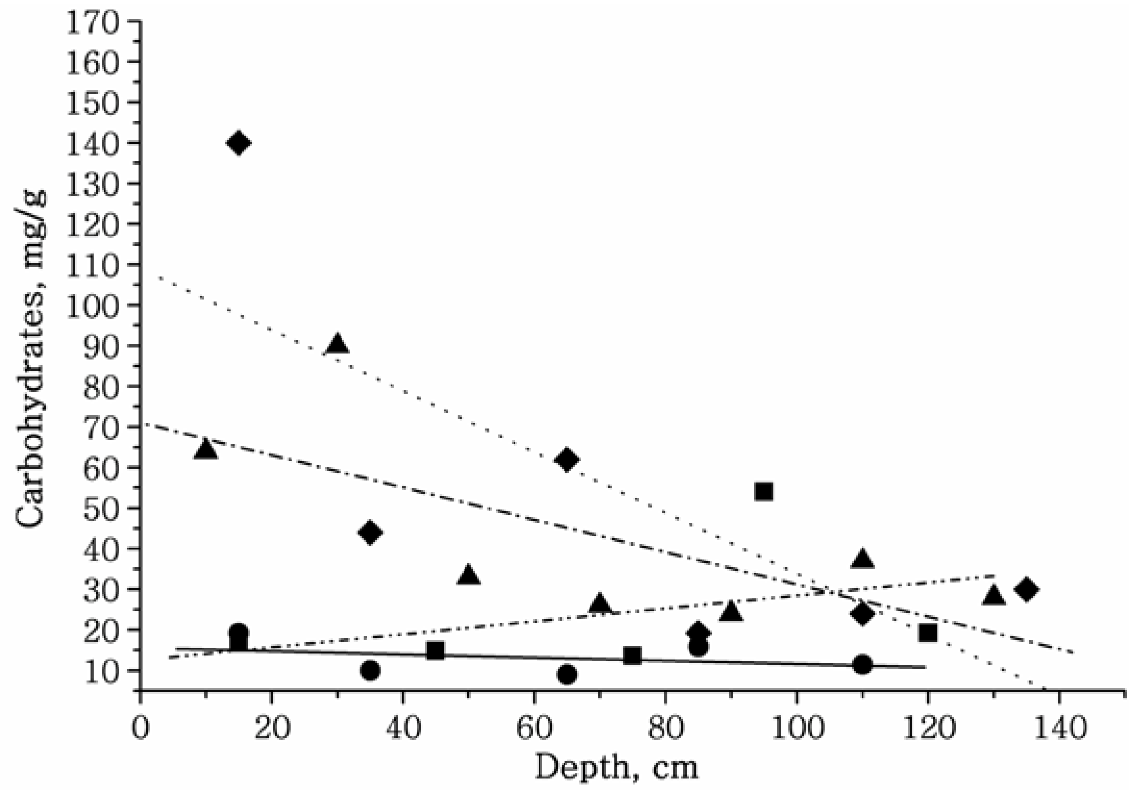

Figure 4. Relationship between carbohydrate concentration and peat depth at different sites. Key:
● Dižais Veiķenieks (——— Y = 15.599 - 0.041 · X; R= -0.356) $P > 0.05$;
▲ Gāgu (– · – · Y = 71.018 - 0.398 · X; R= - 0.697) $P > 0.05$;
◆ Kaigu (········ Y = 108.944 - 0.752 · X; R= - 0.751) $P > 0.05$;
■ Ploce (— · · Y = 12.521 + 0.159 · X; R= - 0.338) $P > 0.05$.

Table 6. Summary statistics generated by principal components analysis (PCA) of selected peat properties and humification coefficients.

components	**variance**	**% of variance explained**	**cumulative % of variance explained**
1. elemental composition, *HD*	6.582	34.641	34.641
2. peat type, hydrogen, nitrogen, *PHI*	3.201	16.847	51.489
3. humification process	3.137	16.509	67.998
4. extinction ratios of humic extracts	1.945	10.239	78.237
5. “age component”	1.091	5.742	83.979

and an association of peat age and type with this component was also suggested. It is assumed that all of the derived humification coefficients can be applied in analysis of the peat humification process, since each coefficient describes different aspects of the humification process. The fourth component was closely related to the extinction ratios of humic extracts, and thus described the properties of humic matter rather than the degree of transformation of organic matter. However, the extinction ratio E_4/E_6 was well correlated with sample depth and peat age, and so also effectively reflected the humification process. The fifth component was designated the “age component” because it correlated with peat depth, age and humification indicators such as E_4/E_6, H/C, *K*, *PyI*, and *HD*. These humification indicators can, therefore, be recommended for characterisation of the peat humification process

(Figures 5, 6).

The peat age, depth and the suggested humification indicators are closely grouped within the three-dimensional space of the first three PCA components (Figure 7, Table 7). Other properties, such as H/C ratio and E_4/E_6 ratio, also group with peat age. These are the variables that reflect the formation conditions of peat.

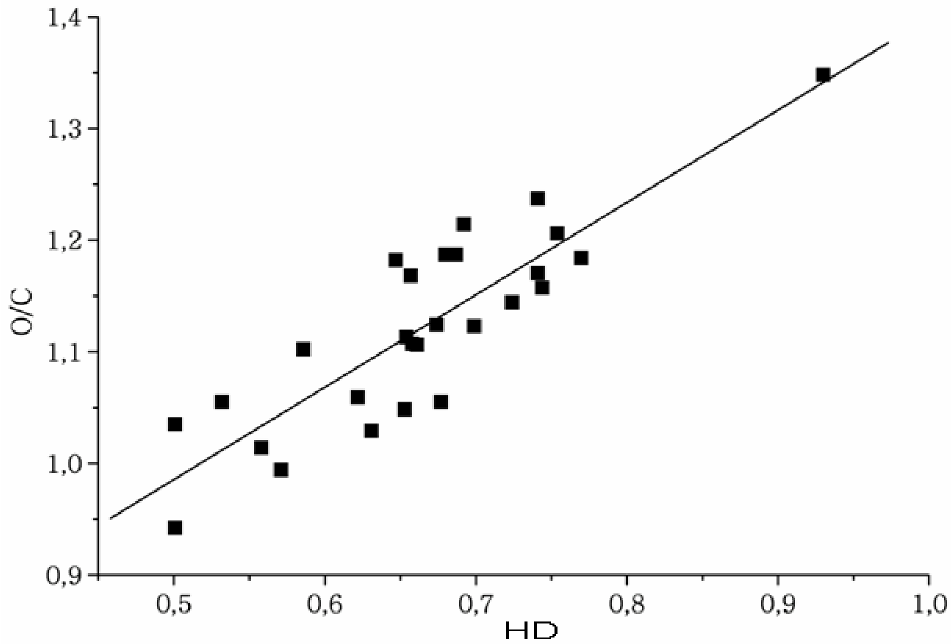

Figure 5. Dependence of O/C values on *HD* (Y = 0.572 + 0.828 · X; R= 0.863) ** *P* <0.0001.

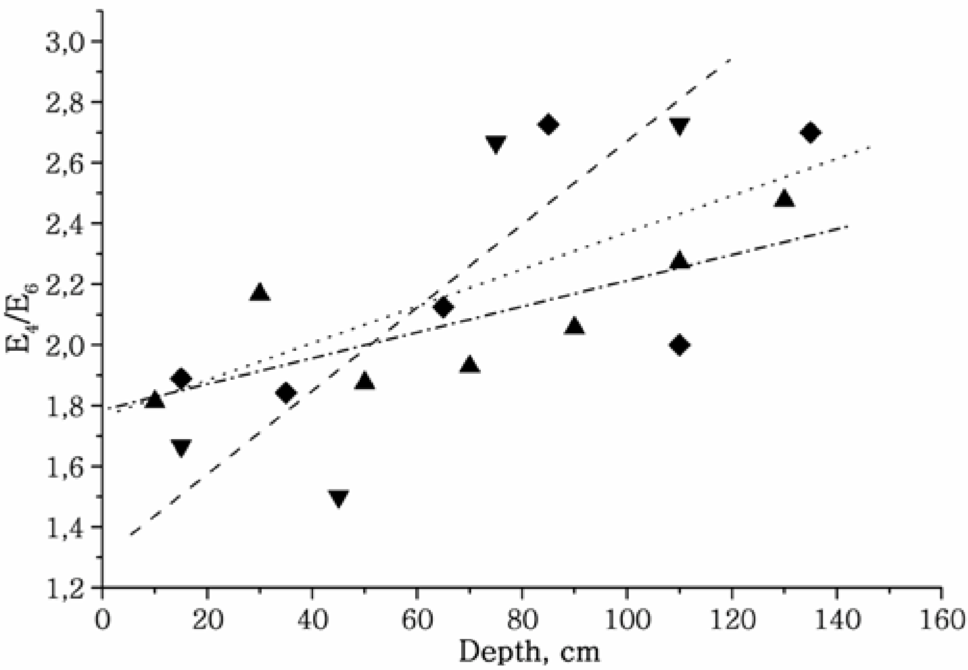

Figure 6. Dependence of E_4/E_6 values on depth at three sites:
▲ Gāgu peat bog (– · – · Y = 1.786 + 0.004 ·X; R= 0.774) *P* < 0.05;
◆ Kaigu peat bog (·········· Y = 1.763 + 0.006 X; R= 0.688) *P* > 0.05;
▼ Mazais Veiķenieks peat bog (– – – Y = 1.30 + 0.014 X; R= 0.863) *P* > 0.05.

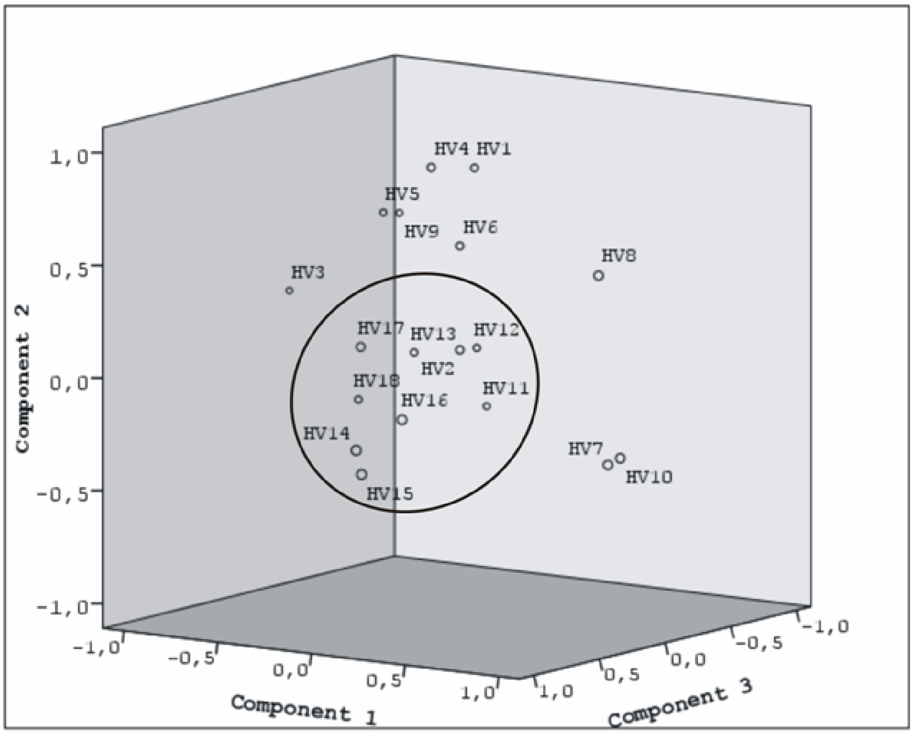

Figure 7. Ordination of variables representing selected peat properties and humification coefficients on the first three PCA axes. See Table 7 for key to acronyms.

Table 7. Loading structure of the first five components extracted by principal components analysis (PCA) of selected peat properties data and humification coefficients.

variable	units	acronym	component				
			1	2	3	4	5
type	-	HV1	-0.095	0.836	-0.268	0.093	0.031
depth	cm	HV2	0.069	0.095	0.077	0.159	0.913
C	%	HV3	-0.939	0.236	-0.063	0.010	0.105
H	%	HV4	-0.158	0.866	-0.028	-0.136	-0.255
N	%	HV5	-0.545	0.600	-0.217	0.433	-0.115
S	%	HV6	-0.061	0.516	-0.108	0.123	0.111
O	%	HV7	0.906	-0.322	0.143	-0.151	0.101
H/C	-	HV8	0.770	0.487	0.020	-0.125	-0.313
N/C	-	HV9	-0.482	0.600	-0.249	0.452	-0.138
O/C	-	HV10	0.937	-0.296	0.094	-0.043	0.041
Age	years	HV11	-0.069	-0.227	-0.325	0.139	0.816
E_2/E_6	-	HV12	-0.044	0.050	-0.214	0.853	0.271
E_4/E_6	-	HV13	-0.276	0.028	-0.067	0.803	0.394
HI	-	HV14	0.085	-0.232	0.889	-0.276	0.146
PHI	-	HV15	0.093	-0.343	0.860	-0.082	-0.078
K	-	HV16	0.197	-0.112	0.700	-0.086	-0.436
PyI	-	HV17	-0.143	0.152	0.530	0.462	-0.456
HD	-	HV18	-0.471	-0.180	0.079	-0.627	0.247

DISCUSSION

Although knowledge of the process of transformation of living organic matter (humification) is important in understanding the biogeochemical cycle of carbon, few studies have been dedicated to this topic (Jerzykiewicz *et al.* 1999, Domeizel *et al.* 2004, Zsolnay *et al.* 1999, Cavani *et al.* 2003, Ikeya & Watanabe 2003, Rosa *et al.* 2005, Corvasce *et al.* 2006). Peat is an especially appropriate focus for studies of humification because it is possible to establish links between the properties of peat and the decomposition degree of the original organic matter. In addition, studies of peat humification are of clear applied and theoretical interest.

According to Steelink (1985), the O/C, H/C and N/C atomic ratios are useful for identifying structural changes and the degree of maturity of peat in different depositional environments. A graph of H/C atomic ratio versus O/C atomic ratio reveals changes in the properties associated with coalification reactions. Thus Figure 2 can be regarded as a graphical statistical representation of 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 maturation culminating in the formation of coal. The changes are especially evident when the atomic ratios of peat-forming plants are compared with those of highly decomposed organic matter (e.g. fen peat and coal). Chemically, humification is a process in which more labile structures (carbohydrates, amino acids *etc.*) are destroyed, but thermodynamically more stable aromatic and polyaromatic structures emerge. It follows that the atomic ratios are associated with the processes occurring during peat humification.

The aim of most humification studies has been to analyse composting and soil formation processes. However, the humification process in peat differs from that in composts and soils, in that quite rapid decomposition of organic matter occurs during its early stages, whereas humification is very much retarded in the waterlogged, anaerobic and acidic environment experienced at later stages. Nevertheless, it is possible to follow the humification of peat for very long periods, and several thousand years is not the limit. The results obtained here demonstrate that it is possible to study the stage of humification of organic matter in peat according to its age, and to apply the suggested analysis methods in estimating the degree of humification using peat humification indices.

The first question to be resolved is the definition of the concepts "decomposition degree" and "humification degree". The decomposition degree describes the extent to which the original (living) organic matter has been transformed. Thus the decomposition process includes: a) transformation of living organisms and their tissues; b) degradation of the molecules of the living organisms; c) mineralisation (transformation of organic carbon compounds containing nitrogen, phosphorous and sulphur into their inorganic species); and d) formation of refractory organic substances, i.e. humic substances. Decomposition can also be described as the breakdown of plant material by micro-organisms that use decaying organic matter as a source of energy and building materials. Besides chemical decomposition, an important indicator of decomposition is mechanical friction. Decomposition degree is one of the key properties describing the utility of peat for agricultural purposes and several schemes for characterising decomposition have been suggested, such as the von Post scale, the r value and the International Peat Society (IPS) classification (Fuchsman 1980). Humification is the process of development of humus (humic substances). Estimation of the humification degree is often based on monitoring of humic substances (HS), humic acids (HA), and fulvic acids (FA) isolated by extraction in alkaline solution (Stevenson 1994). For the proposed indices of maturity, those that are most closely linked to ageing/maturation of the compost were selected, especially those that measure the production of humic acids (HA) relative to the fulvic fraction (FF) or fulvic acids (FA). To represent humification degree, we suggest use of the ratio of the amount of formed humic substances to the total amount of organic matter.

CONCLUSION

The degree of decomposition is an important factor which describes the transformation intensity of organic matter in soils and other deposits that contain fossil carbon, and at the same time characterises the humification degree of the originally living organic matter. By investigating and comparing different approaches to the analysis of humification degree in thoroughly described and ^{14}C dated peat columns extracted from several bogs in Latvia, we came to the conclusion that the concept of humification describes the transformation of organic matter to humus (humic substances). On this basis we propose that the degree of humification (*HD*) should be expressed in terms of the quantity of formed humic substances C_{HS} as a fraction of the total amount of organic matter C_{peat}, i.e.

$$HD = \frac{C_{HS}}{C_{peat}} \qquad [6]$$

This factor can also be used to study the process of transformation of organic matter because it correlates well with peat age and depth in the profile.

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