

EXPERIMENTAL STUDY OF PEAT HUMIFICATION INDICATORS

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An important parameter of organic matter in soils, peat, and fossil-carbon-containing deposits is their decomposition degree, which describes their transformation intensity—the humification degree of original living organic matter. In this article approaches to the analysis of humification degree 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: the ratio of the total amount of organic matter in peat in respect to the amount of humic substances.

Key words: peat, humification degree, decomposition degree, chemical analysis.

INTRODUCTION

Natural organic matter (NOM) forms a major part of soil, sediment, peat, and fossil fuel organic matter and comprises the largest pool of carbon on the Earth (Schimel *et al.*, 1997). NOM consists (Piccolo, 2001) 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) still identifiable organic substances of low molecular weight; and e) the refractory part of organic matter—humic substances (humic acid, fulvic acid, and humin). 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. Natural organic matter 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). In line with these reactions, synthetic reactions in low molecular weight decay products are of definite importance. In the process of the decay, the bulk of living organic matter is mineralised and no more than 20% of its mass are transformed into refractory organic substances (Lukosko *et al.*, 1988). Both degradation and synthetic processes in living organic matter are described as humification; in general, the term refers to the transformation of numerous groups of substances and individual molecules present in living organic matter into groups of substances with similar properties (humic substances) and, finally, into mineral carbon compounds. All these processes are important for understanding the carbon cycle and transformation processes of living matter. In this respect, the estimation of the extent of the humification process is of definite interest (Perez *et al.*, 2004).

The understanding of the transformations of living organic matter down to their mineralisation, and especially the for-

mation of humic substances (humification), is of key importance in understanding the carbon biogeochemical cycle (Franciosi *et al.*, 2003). Furthermore, the character of transformations of living organic matter does have impact on the structure and properties of humic substances. To characterise humification process, the development of humification indexes that link the rate of transformation of living organic matter and the development of humic substances with parameters describing the properties of the formed materials can be an important indicator (Lu *et al.*, 2001).

Several humification indexes have been suggested to study the humification process during composting, in order to evaluate the 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 by making indirect measurements that describe structural changes, which occur during the humification process. Several methods have been suggested for description of humification, such as the measurement of E_4/E_6 ratio that indicates development 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 studies of fluorescence properties of humic macromolecules, has been used as a parameter of description of humification processes (Milori *et al.*, 2002).

A significant amount of organic matter is stored as the organic matter of peat (Fuchsman, 1980). However, few studies on humification processes of peat have been conducted (Schnitzer and Levesque, 1979; Preston *et al.*, 1989; Hargittai, 1994; Baran, 2002; Franciosi *et al.*, 2003), although bogs and wetlands form one of the largest sources of refractory organic matter.

The aim of this article is to study the humification process of peat and finding out the best indicators for the characteri-

sation of humification process, to identify links between peat age (its decomposition degree) and the basic properties of peat and the organic matter of peat.

MATERIALS AND METHODS

Sampling. 28 peat samples were collected from the profiles of five raised bogs of industrial importance in Latvia. The profiles were obtained in varying depths from 0 to 145 cm. The peat samples were dried in laboratory conditions at 105 °C. The samples were then homogenised and sieved through a 1 mm sieve.

Materials. Analytical quality reagents (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification.

Peat characterisation. The basic characteristics of the peat samples are displayed in Table 1.

The analysis of botanical composition was performed using a Carl-Zeiss binocular microscope. The decomposition degree (von Post, 1924; Lishtvan and Korol, 1975) was determined using known methods. The ^{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 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. Metals (Na, Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, Cd, Pb) were determined after wet digestion with $\text{HNO}_3 + \text{HClO}_4$ (Tan, 2005). Metal concentrations were measured by flame atomic absorption (Perkin-Elmer AAnalyst 200). UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co) spectrophotometer in a 1-cm quartz cuvette. The ratios E_2/E_6 , E_2/E_3 , E_3/E_4 , E_4/E_6 (Chen *et al.*, 1977): ratio of absorbance at 280, 340, 465 and 665 nm was determined for the solution of 5 mg of the humic or fulvic acid in 10 ml of 0.05 M NaHCO_3 . Organic carbon concentration of peat extracts was determined and Shimadzu TOC-VCSN. For carbohydrate analysis, humic samples (10 mg) were suspended in 10 ml of 6 M HCl and heated at 100 °C for 3 hours. In the hydrolysates, the concentration of carbohydrates was determined using phenol-sulphuric acid assay following the method described by Chaplin and Kennedy (1994). Cation exchange capacity (ammonium acetate method) and concentration of phosphates were determined using methods suggested for soil analysis (Tan, 2005). pH was determined in demineralised water extracts using a pH meter Hanna pH 213 (Tan, 2005).

Estimation of humification indicators. Humification index (HI) (Cavani *et al.*, 2003). 2.0 g of peat sample in a 250 ml flask was extracted under shaking with 100 ml of 0.1 M NaOH plus 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ for 48 h at 65 °C in a thermostated shaker (Biosan, Latvia) under N_2 atmosphere. After the extraction the samples were centrifuged at 5000 rpm for

Table 1

BASIC CHARACTERISTICS OF THE PEAT SAMPLES

Sample	Depth, cm	Peat type	Peat age, years	Decomposition, H	Decomposition, %
Ploce 0–30	0–30	Raised bog fuscum peat	1460	H5	24
Ploce 30–60	31–60	Raised bog fuscum peat	n.d.	H1	8
Ploce 60–85	61–85	Raised bog fuscum peat	1560	H2	14
Ploce 85–110	86–110	Raised bog fuscum peat	n.d.	H2	14
Ploce 110–130	111–130	Raised bog cotton-grass – sphagnum peat	1670	H2	11
Gāgu 0–20	0–20	Raised bog cotton-grass – sphagnum peat	n.d.	H6	29
Gāgu 20–40	21–40	Raised bog cotton-grass – sphagnum peat	n.d.	H6	32
Gāgu 40–60	41–60	Raised bog cotton-grass – sphagnum peat	n.d.	H6	31
Gāgu 60–80	61–80	Raised bog fuscum peat	n.d.	H2	20
Gāgu 80–100	81–100	Raised bog fuscum peat	n.d.	H2	13
Gāgu 100–120	101–120	Raised bog fuscum peat	n.d.	H2	13
Gāgu 120–140	121–140	Raised bog fuscum peat	1640	H2	11
Kaigu 0–25	0–25	Raised bog cotton-grass – sphagnum peat	810	H6	33
Kaigu 25–45	26–45	Raised bog fuscum peat	n.d.	H2	10
Kaigu 45–70	46–70	Raised bog fuscum peat	1590	H2	11
Kaigu 70–95	71–95	Raised bog narrow-leaf sphagnum peat	n.d.	H2	33
Kaigu 95–125	96–125	Raised bog narrow-leaf sphagnum peat	n.d.	H1	7
Kaigu 125–145	126–145	Raised bog fuscum peat	2260	H2	9
Dižais Veiķenieks 0–25	0–25	Raised bog fuscum peat	520	H2	12
Dižais Veiķenieks 25–52	26–52	Raised bog fuscum peat	n.d.	H2	12
Dižais Veiķenieks 52–75	53–75	Raised bog fuscum peat	980	H2	6
Dižais Veiķenieks 75–98	76–98	Raised bog fuscum peat	n.d.	H2	9
Dižais Veiķenieks 98–118	99–118	Raised bog fuscum peat	1350	H1	6
Mazais Veiķenieks 0–30	0–30	Raised bog fuscum peat	400	H2	8
Mazais Veiķenieks 30–60	31–60	Raised bog Magellan's sphagnum peat	n.d.	H3	14
Mazais Veiķenieks 60–90	61–90	Transition type tree – grass peat	n.d.	H5	27
Mazais Veiķenieks 90–125	91–125	Low type tree – grass peat	1180	H6	31

15 min and the supernatants were filtered through a 1 µm filter. This 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 put into a 50 ml centrifuge tube and acidified to pH < 2 by adding a small volume (0.3–0.5 ml) of 9 M H₂SO₄, then centrifuged at 5000g for 20 minutes. The precipitated fraction (HA) was collected and stored, and the supernatant solution fed onto a small column packed with about 5 cm³ of insoluble polyvinylpyrrolidone, previously equilibrated in 0.005 M H₂SO₄. The eluate (NH) was collected in a 50 ml volumetric flask, then diluted to volume with 0.005 M H₂SO₄ and stored. The retained fraction (FA) was eluted with 0.5 M NaOH solution and collected in the centrifuge tube containing the HA precipitate, which was redissolved. Total organic carbon (TOC) and humified carbon (HA, FA) were determined using a TOC analyser as described elsewhere. The humification index (HI) was calculated as follows:

$$HI = \frac{C_{NH}}{C_{HA} + C_{FA}}.$$

Pyrophosphate index (PyI) (Schnitzer and Levesque, 1979). 0.50 g of peat sample was shaken for 18 hrs with 50 ml of 0.025 M Na₄P₂O₇ at room temperature. The peat residue was separated by filtration, washed with distilled water, and the filtrates with washings were diluted to 250 ml with distilled water. The optical density of this solution was measured at 550 nm and absorbance multiplied by 100 was referred to as pyrophosphate index PyI.

$$PyI = D_{550} \times 100.$$

Humus quality K value (Hargitai 1994). 1.00 g of peat sample was shaken for 6 hrs with 50 ml of 1% NaF, filtered, and in the filtrate the adsorption at 410 nm (D_{H5NaF}) was determined. Another 1.00 g portion of the same peat sample was extracted shaking for 6 hrs with 50 ml of 0.5% NaOH, filtered, and in the filtrate adsorption at 410 nm (D_{H5NaOH}) was determined.

The humus quality value K was calculated as:

$$K = \frac{D_{H5NaF}}{D_{H5NaOH}} \times C,$$

where C is the percentage of carbon in the sample.

Peat humification index (PHI). 1.00 g of peat sample was shaken for 24 hrs with 50 ml of deionised water, filtered, and in the filtrate the total organic carbon of the aquatic extract (C_w) was determined. Another 1.00 g portion of the same peat sample was extracted shaking for 24 hrs with 50 ml of 0.1 M NaOH, filtered, and in the filtrate the total organic carbon of the alkaline extract (C_{NaOH}) was determined. The peat humification index was calculated as:

$$PHI = \frac{C_w}{C_{NaOH}} \times 100.$$

Humification degree (HD). 1.00 g of peat sample was shaken for 24 hrs with 50 ml of 1.0 M NaOH, filtered, and in the filtrate the total organic carbon of the alkaline extract, containing humic substances (C_{HS}), was determined (mg C/g). The peat humification degree was calculated as:

$$HD = \frac{C_{HS}}{C_{peat}} \times 100,$$

where C is the percentage of carbon in the sample (mg/g).

Data analysis. Principal component analysis (PCA) (rotation method: Varimax with Kaiser Normalization (rotation converged in eight iterations)) was conducted using SPSS 12.0 for Windows.

RESULTS

In this study peat from five raised bogs of industrial importance in Latvia was used. Samples from different depths were obtained, representing bogs which reflect bog development conditions in Northern Europe. The botanical composition of the deepest layer of peat was mostly raised bog cotton-grass-sphagnum peat and fuscum peat, while upper layer was raised bog fuscum peat. The age of the samples varied from 400 to 2260 years, and their decomposition degree (von Post scale) varied from H2 to H6 (Table 1). In all obtained peat samples their elemental composition has been determined (Table 2).

Table 2
ELEMENTAL COMPOSITION OF THE STUDIED PEAT SAMPLES

Sample	C, %	H, %	N, %	S, %	O, %
Ploce 0–30	50.78	5.18	1.38	0.69	37.78
Ploce 30–60	54.26	5.73	1.08	0.44	36.19
Ploce 60–85	48.46	5.34	0.65	0.79	43.72
Ploce 85–110	52.41	5.31	1.05	0.67	39.87
Ploce 110–130	52.18	5.16	0.79	0.63	40.70
Gāgu 0–20	48.54	5.54	1.15	0.84	40.79
Gāgu 20–40	49.09	5.67	0.93	1.34	43.06
Gāgu 40–60	48.82	5.60	0.75	0.58	43.86
Gāgu 60–80	48.41	5.62	0.68	0.52	44.62
Gāgu 80–100	49.45	5.52	0.83	0.92	43.28
Gāgu 100–120	49.68	5.49	0.73	0.67	43.23
Gāgu 120–140	50.78	5.60	0.85	1.01	42.09
Kaigu 0–25	48.26	5.76	1.15	0.69	41.57
Kaigu 25–45	49.31	5.76	0.85	1.01	43.39
Kaigu 45–70	49.56	5.71	0.80	0.77	43.16
Kaigu 70–95	48.53	5.83	0.86	0.81	43.97
Kaigu 95–125	48.54	5.59	0.78	0.72	44.44
Kaigu 125–145	41.75	4.96	0.70	0.67	51.73
Dīžais Veiķenieks 0–25	46.85	5.39	0.59	0.89	46.23
Dīžais Veiķenieks 25–52	48.19	5.53	0.66	0.58	44.88
Dīžais Veiķenieks 52–75	47.53	5.52	0.45	0.53	45.82
Dīžais Veiķenieks 75–98	46.96	5.40	0.41	0.58	46.52
Dīžais Veiķenieks 98–118	46.72	5.47	0.43	0.81	46.92
Mazais Veiķenieks 0–30	45.67	5.65	0.73	0.69	46.87
Mazais Veiķenieks 30–60	46.49	5.80	0.53	0.54	45.87
Mazais Veiķenieks 60–90	52.46	6.15	1.88	1.08	37.19
Mazais Veiķenieks 90–125	53.01	6.09	2.38	0.94	35.37

The age and decomposition degree of peat gradually increases with increasing depth (Fig. 1).

However, the basic parameters of peat do not display a similar increasing trend for all the studied samples (Table 2). Carbon and nitrogen content of peat samples from the bog Mazais Veikeneks increases with increasing age (the depth and decomposition degree), but the content of sulphur decreases with increasing age. However, for the other studied bogs, the variability of elemental composition is not so random and most probably depends on the botanical composition and the specific peat formation conditions (mostly, the hydrological regime in the bog).

Not only peat basic characterisation (elemental composition), but also study of changes of properties, reflecting character of humification process has been done (Table 3).

The impact of peat development conditions on peat properties is also evident from the carbohydrate concentration,

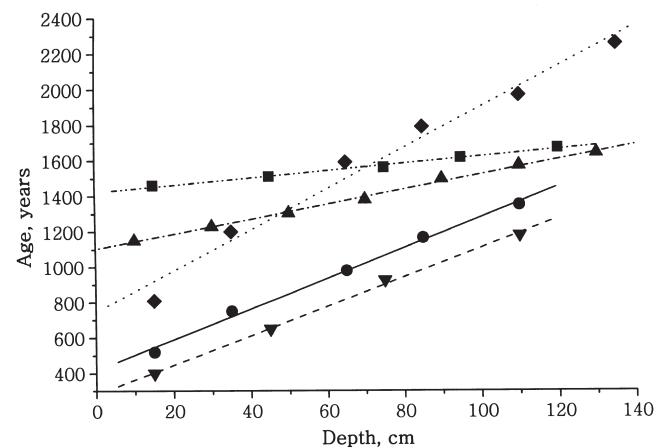


Fig. 1. Relationship between peat sample age and depth of their location.
 ● Dižais Veikeneks peat bog; ▲ Gāgu peat bog; ◆ Kaigu peat bog;
 ■ Ploce peat bog; ▽ Mazais Veikeneks peat bog.

Table 3

COMPOSITION OF THE STUDIED PEAT SAMPLES

Sample	pH	Ash, %	CEC, cmol(+)/kg	PO_4^{3-} , mg/kg	Carbo-hydrates, mg/g	Na, mg/kg	Mg, mg/kg	K, mg/kg	Ca, mg/kg	Mn, mg/kg	Fe, mg/kg	Ni, mg/kg	Cu, mg/kg	Zn, mg/kg	Cd, mg/kg	Pb, mg/kg
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
Ploce 30–60	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
Ploce 60–85	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
Ploce 85–110	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
Ploce 110–130	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
Gāgu 20–40	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
Gāgu 40–60	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
Gāgu 60–80	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
Gāgu 80–100	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
Gāgu 100–120	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
Gāgu 120–140	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
Kaigu 25–45	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
Kaigu 45–70	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
Kaigu 70–95	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
Kaigu 95–125	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
Kaigu 125–145	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 Veikeneks 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
Dižais Veikeneks 25–52	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
Dižais Veikeneks 52–75	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
Dižais Veikeneks 75–98	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
Dižais Veikeneks 98–118	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 Veikeneks 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
Mazais Veikeneks 30–60	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
Mazais Veikeneks 60–90	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
Mazais Veikeneks 90–125	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 5

LOADING STRUCTURE OF THE FIRST SIX COMPONENTS EXTRACTED BY PCA ANALYSIS OF THE DATA ON THE SELECTED PEAT PROPERTIES

Variable/acronym	Component					
	1	2	3	4	5	6
Type	PV1	0.006	0.393	0.761	-0.042	-0.255
Depth, cm	PV2	-0.453	0.008	0.129	-0.719	0.061
C, %	PV3	0.022	0.912	-0.132	-0.229	-0.107
H, %	PV4	0.057	0.406	0.394	0.197	-0.733
N, %	PV5	0.172	0.763	0.498	0.051	0.017
S, %	PV6	0.019	0.143	0.142	-0.010	-0.231
O, %	PV7	-0.233	-0.948	-0.051	0.057	0.011
Ash content, %	PV8	0.609	0.575	0.183	0.271	0.363
pH	PV9	-0.073	0.174	0.913	0.162	-0.047
CEC, mEq/kg	PV10	0.234	-0.079	-0.556	0.274	-0.109
PO ₄ ³⁻ , mg/kg	PV11	0.557	0.229	-0.675	0.125	0.311
Carbohydrates, mg/g	PV12	0.557	0.229	-0.675	0.125	0.311
Decomposition degree	PV13	0.587	0.401	0.307	0.344	0.106
Age, years	PV14	-0.055	-0.035	0.001	-0.860	0.228
Na, mg/kg	PV15	-0.112	-0.167	-0.890	0.133	-0.115
Mg, mg/kg	PV16	0.128	0.150	-0.080	-0.298	0.792
K, mg/kg	PV17	0.708	-0.086	-0.144	0.410	-0.039
Ca, mg/kg	PV18	0.136	0.668	0.261	0.258	0.502
Mn, mg/kg	PV19	0.768	0.153	0.133	0.320	0.228
Fe, mg/kg	PV20	0.132	0.659	0.608	0.233	-0.051
Ni, mg/kg	PV21	0.321	0.707	0.508	0.182	0.053
Cu, mg/kg	PV22	0.683	0.468	0.248	0.093	0.302
Zn, mg/kg	PV23	0.943	0.153	-0.125	0.065	0.058
Cd, mg/kg	PV24	0.936	0.085	-0.050	-0.130	-0.139
Pb, mg/kg	PV25	0.938	0.158	-0.090	0.088	-0.010

cation exchange capacity, and the metal concentration in the peat samples analysed (Table 3). The results of the extensive peat characterization have been used to study the impact of the peat formation conditions on the major peat properties and humification character of the peat organic matter.

DISCUSSION

Although knowledge of the transformation process of living organic matter (humification) is of importance in understanding of the carbon biogeochemical cycle, the number of studies dedicated to this topic is rather small (Jerzykiewicz *et al.*, 1999; Zsolnay *et al.*, 1999; Ikeya and Watanabe, 2003; Cavani *et al.*, 2003; Domeizel *et al.*, 2004; Rosa *et al.*, 2005; Corvasce *et al.*, 2006). Peat can be considered an especially appropriate subject of studies of humification because it is possible to establish links between the properties of peat and the decomposition degree of original organic matter. In addition, the studies of peat humification are of definite applied and theoretical interest.

To study the humification process, principal component analysis was used to determine the main factors affecting peat composition (Table 4, 5). Six principal components were extracted explaining 87% of the total variance of data (Table 4, 5). The six components define the main peat property factors: component 1 is characterised by depth of the peat layer, ash content, as well as the concentration of phosphate ions, carbohydrates and potassium (Table 5). Concentration of metals (mostly of anthropogenic origin, for example, Cd, Pb) in peat can be explained by this very component. Component 2 is associated with peat decomposition degree, ash content, carbon content, and also metals of, most likely, natural origin (Ca, Mg, Fe); it can also be suggested that this factor describes peat genesis. Component 3 is associated with biogenic processes (presence of carbohydrates—abundant in living plants, but rapidly consumed during the decay process), presence of phosphate ions and nitrogen, and sodium. Component 4 is characterised by peat layer depth and age, component 5—by magnesium and calcium concentration and component 6—by sulphur content in peat and cation exchange capacity.

Table 4
SUMMARY STATISTICS OF PCA OF THE DATA ON THE SELECTED PEAT PROPERTIES*

Component	Variance	% of explained variance	Cumulative % of variance
1	6.064	24.254	24.254
2	5.020	20.081	44.335
3	4.841	19.365	63.699
4	2.248	8.991	72.690
5	2.138	8.552	81.242
6	1.362	5.449	86.691

* VARIMAX rotation and Kaiser's normalisation were used on the initial component structure

The peat humification process was examined using van Krevelen graphs frequently applied for the analysis of carbon biogeochemical cycle and genesis of fossil fuel (Van Krevelen, 1950). Table 6 shows the elemental ratios of the studied peat samples. According to Steelink (1985), the atomic ratios O/C, H/C, and N/C indices are useful in the identification of structural changes and the degree of maturity of peat in different depositional environments. The graph of H/C atomic ratio versus O/C atomic ratio reveals changes in the properties associated with coalification reactions.

Figure 2 shows the relation between H/C atomic ratio and O/C atomic ratio of organic material of a differing decomposition degree—beginning with bog plants up to brown coal, lignite, and coal. The graph in Fig. 2 could be considered as a graphical statistical representation of 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 continuing up to coal. These changes are especially evident when atomic ratios of peat-forming plants are compared to the atomic ratio of organic matter of a high decomposition degree (low moor peat,

Table 6

ELEMENTAL RATIOS AND HUMIFICATION COEFFICIENTS OF PEAT

Sample	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
Ploce 30–60	1.258	0.017	0.501	22.000	2.600	2.056	4.115	27.507	0.155	0.515	18.2	0.942
Ploce 60–85	1.312	0.011	0.677	15.875	2.000	2.082	3.813	35.362	0.140	0.636	16.6	1.055
Ploce 85–110	1.207	0.017	0.571	17.833	2.000	2.058	4.333	31.742	0.134	0.290	13.8	0.994
Ploce 110–130	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
Gāgu 20–40	1.376	0.016	0.658	15.778	2.167	1.986	3.667	52.431	0.150	0.424	16.8	1.107
Gāgu 40–60	1.368	0.013	0.674	12.313	1.875	1.931	3.400	66.310	0.171	0.400	39.1	1.124
Gāgu 60–80	1.383	0.012	0.692	12.071	1.929	1.920	3.259	63.467	0.195	0.609	39.0	1.214
Gāgu 80–100	1.330	0.014	0.657	13.222	2.056	1.935	3.324	48.207	0.171	0.474	21.7	1.168
Gāgu 100–120	1.317	0.013	0.653	15.955	2.273	2.006	3.500	39.179	0.191	0.305	19.7	1.048
Gāgu 120–140	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
Kaigu 25–45	1.391	0.015	0.661	10.526	1.842	1.923	2.971	12.334	0.122	0.271	12.1	1.106
Kaigu 45–70	1.373	0.014	0.654	16.250	2.125	1.970	3.882	7.992	0.083	0.188	14.7	1.113
Kaigu 70–95	1.431	0.015	0.680	24.091	2.727	2.008	4.400	7.228	0.068	0.191	11.5	1.187
Kaigu 95–125	1.372	0.014	0.687	16.571	2.000	2.035	4.071	6.442	0.072	0.209	9.1	1.187
Kaigu 125–145	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
Dižais Veiķenieks 25–52	1.368	0.012	0.699	11.947	1.737	2.009	3.424	69.336	0.404	0.721	24.1	1.123
Dižais Veiķenieks 52–75	1.383	0.008	0.724	13.308	2.000	2.012	3.308	89.385	0.298	0.843	24.7	1.144
Dižais Veiķenieks 75–98	1.369	0.008	0.744	12.083	1.833	1.986	3.318	199.601	0.406	1.277	27.7	1.157
Dižais Veiķenieks 98–118	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
Mazais Veiķenieks 30–60	1.488	0.010	0.741	12.667	1.500	2.000	4.222	10.220	0.077	0.610	17.6	1.237
Mazais Veiķenieks 60–90	1.398	0.031	0.532	26.333	2.667	2.079	4.750	2.984	0.069	0.326	39.1	1.055
Mazais Veiķenieks 90–125	1.369	0.038	0.501	23.182	2.727	2.056	4.133	2.485	0.071	0.545	36.6	1.035

coal). From the point of view of chemistry, humification can be considered as a process in which more labile structures (carbohydrates, amino acids, etc.) are destroyed, but thermodynamically more stable aromatic and polycyclic structures emerge. It follows that the atomic ratios are associated with the processes transpiring during peat humification. As shown in Figure 2, H/C ratio decreases with increasing decomposition degree of the original living matter,

starting with peat-forming plants, cellulose, and proteins, and up to bituminous coal. Comparatively, the studied peats are at the start of the transformation process of living organic matter. The van Krevelen graph (Fig. 2) also indicates a decrease in O/C ratio, illustrating the decrease in the amount of oxygen-containing functional groups, such as methoxyl, carboxylic, and carbonyl functional groups, in the fossil material with increasing humification degree. In order to provide reliable and quantity information about the early diagenesis, we carried out further studies of the dependence of the elemental composition of the peat samples on their age (depth and decomposition degree) (Fig. 3).

H/C value showed a negative relation with peat depth; Kaigu and Mazais Veiķenieks peat bogs had the highest negative correlations. However, Dižais Veiķenieks bog showed a strong positive relation. This demonstrates that atomic ratio cannot be correctly used to study the humification process due to the significant impact of the original plant composition and peat formation conditions.

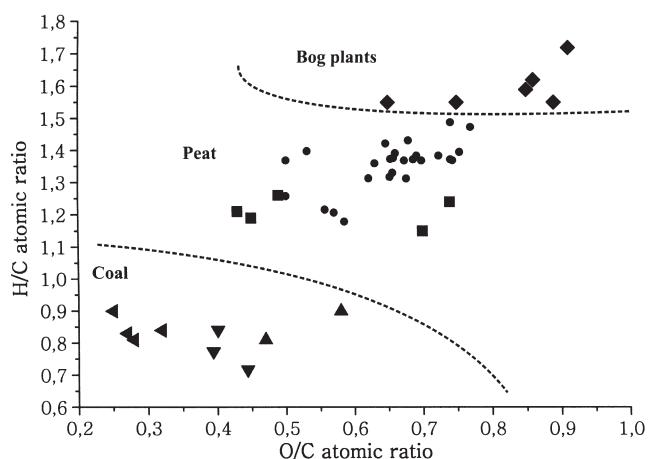


Fig. 2. Van Krevelen (H/C vs. O/C atomic ratio) graph of bog plants (◆) peat samples from studied bogs in Latvia (●), reference peat samples (IHSS) and peat samples from common peat bogs (■), brown coal (▲), coal (◀), lignite (▼).

Changes of carbohydrate concentration in peat correlate more strongly with peat depth and, evidently, peat age (Fig. 4). The carbohydrate concentration in peat decreased with depth of the studied peat layers (Fig. 4) clearly indicating that carbohydrate degradation is amongst the major processes describing peat formation and humification.

Table 7

SUMMARY STATISTICS OF PCA ANALYSIS OF THE DATA ON THE SELECTED PEAT PROPERTIES AND HUMIFICATION COEFFICIENTS

Component	Variance	% of explained variance	Cumulative % of variance
1	6.582	34.641	34.641
2	3.201	16.847	51.489
3	3.137	16.509	67.998
4	1.945	10.239	78.237
5	1.091	5.742	83.979

Table 8

LOADING STRUCTURE OF THE FIRST FIVE COMPONENTS EXTRACTED BY PCA ANALYSIS OF THE DATA ON THE SELECTED PEAT PROPERTIES AND HUMIFICATION COEFFICIENTS

Variable/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

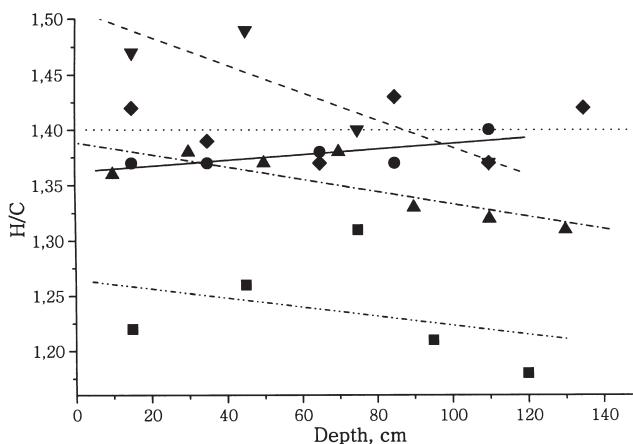


Fig. 3. Dependence of H/C value of peat depth in different peat bogs.

- Dižais Veiķenieks peat bog ($Y = 1.362 + 2.543 \cdot X$; $R= 0.742$) $P > 0.05$
- ▲ Gāgu peat bog ($Y = 1.389 - 5.536 \cdot X$; $R= -0.195$) $P > 0.02$
- ◆ Kaigu peat bog ($Y = 1.400 - 4.892 \cdot X$; $R= -0.812$) $P > 0.05$
- Ploce peat bog ($Y = 1.265 - 4.118 \cdot X$; $R= -0.338$) $P > 0.05$
- ▼ Mazais Veiķenieks peat bog ($Y = 1.509 - 0.001 \cdot X$; $R= -0.889$) $P > 0.05$

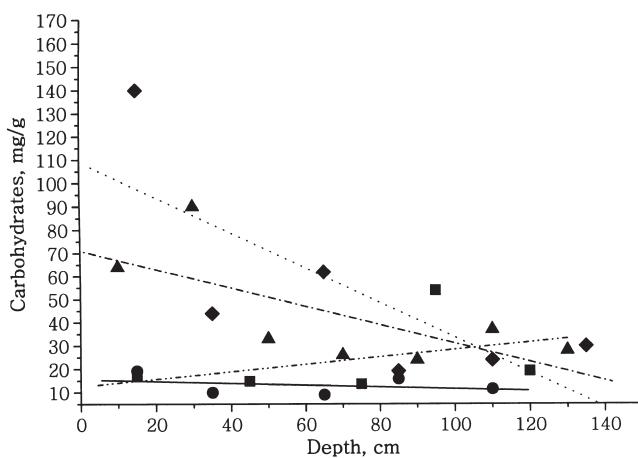


Fig. 4. Relationship between carbohydrate concentration and peat depth in different peat bogs.

- Dižais Veiķenieks peat bog ($Y = 15.599 - 0.041 \cdot X$; $R= -0.356$) $P > 0.05$
- ▲ Gāgu peat bog ($Y = 71.018 - 0.398 \cdot X$; $R= -0.697$) $P > 0.05$
- ◆ Kaigu peat bog ($Y = 108.944 - 0.752 \cdot X$; $R= -0.751$) $P > 0.05$
- Ploce peat bog ($Y = 12.521 + 0.159 \cdot X$; $R= -0.338$) $P > 0.05$

Variability of the 25 parameters, describing peat properties, their decomposition degree, age, and peat humification process were examined using principal component analysis. The first five components extracted explained 84% of the total variance (Table 7). The first component involved parameters describing the development of peat—its elemental composition (C, N and O) and correlated well with the suggested humification degree HD. The second component characterised the correlation between peat type, hydrogen,

and nitrogen; these parameters are correlated with peat humification index PHI. The third component characterised the humification processes, as it was associated with most of the humification coefficients used in our study. Association of peat age and type with the component was also suggested. It is supposed that all the used humification coefficients can be applied for analysis of peat humification process since each of them describes differing aspects of the humification process. The fourth component was characterised by a close relation between the extinction ratios of humic extracts; it rather described the properties of peat humic matter than the transformation degree of peat organic matter. However, the very simple parameter—extinction ratio E₄/E₆ is well correlated with the depth of the location of the peat samples and peat age; it can also be efficiently used to analyse the humification process. The fifth component can be designated as the “age component” since it is correlated with peat depth, age and humification indicators such as E₄/E₆, H/C, K, PyI, and HD. Therefore, these humification indicators can be recommended for characterisation of the peat humification process (Fig. 5, 6).

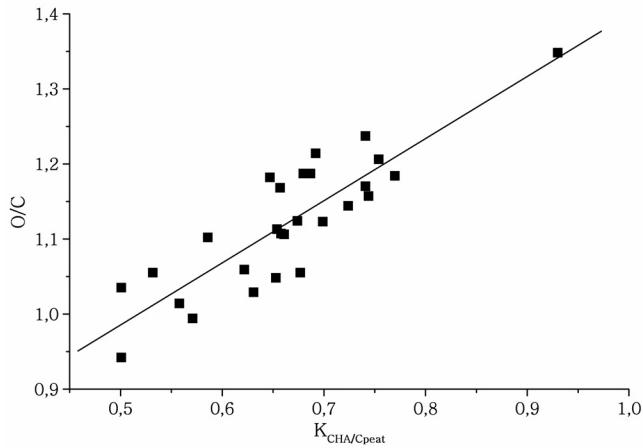


Fig. 5. Dependence of O/C values on $K_{\text{CHA}}/C_{\text{peat}}$

$$(Y = 0.572 + 0.828 \cdot X; R = 0.863) \quad ** P < 0.0001$$

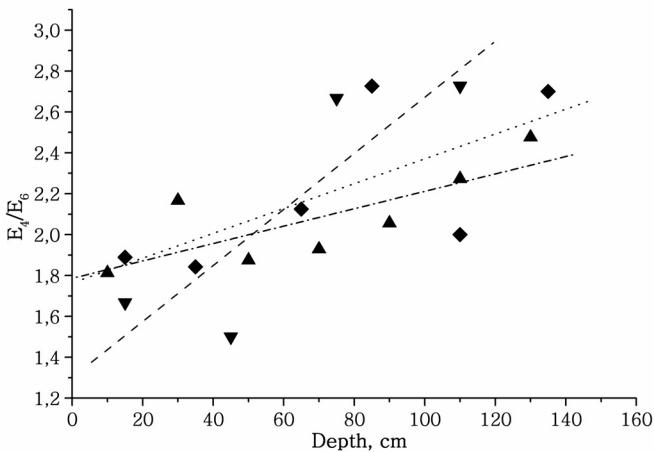


Fig. 6. Dependence of E_4/E_6 values on peat depth in different peat bogs

- ▲ 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) $P > 0.05$

The peat age, depth, and the suggested humification indicators are located closely in the 3D space of the first three components obtained using PCA analysis (Fig. 7). Other parameters, such as H/C ratio and E_4/E_6 ratio (Fig. 7), also group with peat age. These variabilities reflect the formation conditions of peat.

Humification has been mostly studied with the aim to analyse composting and soil formation processes. However, the humification process in peat very much differs from that in composts and soils in a quite rapid decomposition of organic matter in early humification stages. In water, under the impact of the anaerobic and acidic environment, the humification process of the saturated peat layers is very much retarded. Nevertheless, in peat it is possible to follow the humification for very long periods (several thousand years are not the limit). The obtained results demonstrate

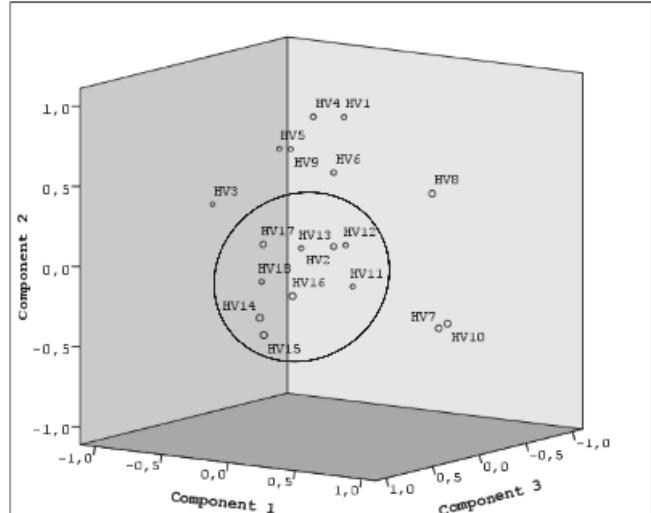


Fig. 7. Ordination of variables representing selected peat properties and humification coefficients on the first three PCA axes.

that it is possible to study the stage of humification of organic matter in peat according to its age and apply the suggested methods of analysis to the estimation of peat humification degree (peat humification indexes).

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 original (living) organic matter is transformed. The decomposition process thus includes: a) transformation processes of living organisms and their tissues; b) degradation of molecules forming a living organism; c) mineralisation (transformation of organic carbon compounds containing organic nitrogen, phosphorous, and sulphur compounds into their inorganic species); and d) formation of refractory organic substances—humic substances. Decomposition can also be described as the breakdown of plant material by microorganisms that use decaying organic matter as a source of energy and building material. Besides chemical decomposition, an important indicator of decomposition is mechanical friction. The decomposition degree is one of the key parameters describing the use of peat for agricultural purposes, several schemes for the characterisation of decomposition are suggested, such as von Post scale, r value, and the peat classification of International Peat Society (Fuchsman, 1980).

The estimation of the humification degree is often based on the monitoring of humic substances (HS), humic acids (HA), and fulvic acids (FA), isolated by extraction in alkaline solution (Stevenson, 1994). Among the proposed indexes of maturity, those most representative of the evolution of the maturity of the compost were presented, particularly indexes measuring the evolution of HA compared to fulvic fraction or FA. Humification is a narrower concept, describing the development of humus (humic substances). As humification degree we suggest to use the ratio

of the total amount of organic matter to the amount of formed humic substances:

$$HD = \frac{C_{HS}}{C_{peat}}.$$

As the results of our study show, this parameter corresponds well to the peat depth and age, so it can also be used to study the transformation processes of organic matter.

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KŪDRAS HUMIFIKĀCIJAS INDIKATORI: EKSPEIMENTĀLA ANALĪZE

Svarīgi augšņu, kūdras un fosilo oglekli saturošu nogulumu organiskās vielas raksturlielumi ir to sadalīšanās pakāpe, kas raksturo sākotnējās biomasas pārveidošanās intensitāti, un humifikācijas pakāpe, kas raksturo jaunu organisko vielu – humusvielu veidošanās tempu no sākotnējās dzīvās vielas. Šajā rakstā ir pētītas un salīdzinātas humifikācijas analizes metodes pilnīgi analizētām un datētām (^{14}C) kūdras kolonnām no vairākiem Latvijas purviem. Ieteikts humifikācijas pakāpi definēt kā kopējās organiskās vielas kūdrā un humifikācijas gaitā veidoto humusvielu attiecību.