

Chemical properties of different peat-moorsh soils from the Biebrza River Valley

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Abstract. The relationship between soil structure and the ability of soil to stabilize soils organic matter is a key element in soil C dynamics. In this investigation the chemical properties were determined for three different peat-moorsh soils – Czarna Wieś, Otoczne and Kwaterna 17 located in the Biebrza River Valley in Poland. Each considered soil, utilised as meadow, was sampled at two depths. The measured concentrations of total organic carbon in the considered soils ranged from 37.19% to 45.58%. Generally, a decrease of total organic carbon concentration with the depth of profiles was observed. The contents of dissolved organic carbon in the soils ranged from 5.34 to 19.39%. The quantities of dissolved organic carbon decreased simultaneously with E_4/E_6 values with the increasing depth of the soil profiles.

Key words: peat-moorsh soils, TOC, DOC, E_4/E_6

INTRODUCTION

Peat represents a mixture of organic compounds characterised by high molecular weight – humic and fulvic acids and their salts as well as cellulose, lignite, bitumines, peptides, enzymes and fats. Additionally, peat includes low molecular organic compounds like amino acids, alkaloids, purine and pyrimidine bases, carbohydrates, vitamins, sugars, phenols, antibiotics, steroids, triterpenoids, β -sitosterol etc. (Kondo, 1976; Bambalov et al., 2000; Szajdak, 2002). These substances establish colloidal behavior of peat and lead to loss of wetability caused by drying (Kwak et al., 1986). The structure, origin and fate of such molecular configurations are thus clearly linked to the water-retention properties of peat (Sokołowska et al., 2005).

The transformation of peat organic matter by chemical, biochemical and biological decay leads to the formation of a number of chemical substances. During the peat transformation the principal changes of the organic matter are the following: decrease of the total water content, increase of specific gravity, increase of compaction, decrease of pore space, increase of the degree of decomposition, colour changes towards dark brown and black and increase of the calorific value (Gotkiewicz & Kowalczyk, 1977; Lüttig, 1986; Lishtvan et al., 1989). The variations in peat organic matter arise from the variety of plants whose residues impact the peat formation and from the environmental conditions in which humification takes place (MacCarthy et al., 1990).

The long-term cultivation and agricultural use of peatland has an impact on the environment leading to decrease of ground water level, changes of aerobic conditions, changes in plant communities, and root exudates of cultivated plants as well as degradation and mineralization of peat (Grootjans et al., 1985, 1986; Lishtvan et al., 1989; Borys, 2002). Due to these factors peat may undergo a process of secondary transformation. In general, this process led to an increase of the total variable surface charge, which is manifested by the decrease of water holding capacity. Also, the progressive hydrophobic properties of moorsh are observed (Szajdak, 2002). Kalbitz et al., (1999) showed that the land use of peatlands has effects on fulvic acid (FAs) properties, which account for the major fraction of dissolved organic matter. The above mentioned authors suggested that long-term intensive land use (from 50 to above 200 years) resulted in a larger proportion of the aromatic structures and a larger degree of polycondensation of FAs. However it is unknown what changes in the units of the structure of FAs they cause. Leinweber et al., (2001) reported that in water-soluble FAs, which are the main component (about 60%) of dissolved organic matter, the proportion of carbohydrates and phenols together with lignin monomers increased with increasing intensity of soil tillage, aeration and peat degradation.

A great number of biochemical, chemical, and biological processes in peat require aqueous conditions. The drainage and agricultural use of peatlands result in intensive changes of biotic and abiotic properties, which lead to the degradation of the peat organic matter. Peat organic matter regulates long-term C storage and the availability of nutrients to plants and microbes. The content of water, dissolved organic matter (DOM), is closely associated with microbial activity, because this fraction of the organic carbon can be vulnerable to microbial degradation. The quantities of dissolved organic matter are sensitive to land management, especially agricultural use which reduces inputs to the soil's organic matter evolution through removal of plant biomass (Marscher & Noble, 2000; Marscher & Bredov, 2002). The mechanism of the DOM degradation depends on the aromaticity and complexity of dissolved organic matter molecules whereas carbohydrates and amino acids increase this process. DOM degradation results also in a relative enrichment of the lignin-derived parts, which affects the thermal behaviour of individual compounds classes and increases thermal stability of residual dissolved organic matter. Analysis of soil profile under a wide range of conditions is necessary to fully understand the nature and extent of processes and mechanisms in the agricultural use of organic soils. In spite of extensive studies of the organic matter of peat soils (Dragunov & Kartatstsi, 1960; Efrimov & Tsaresenko, 1992; Bambalov & Belenkaya, 1993, 1997) the transformation of organic matter upon drainage is not yet fully understood.

The object of this study was to characterize the chemical properties of the three different peat-moorsh soils from the Biebrza River Valley used as meadows.

MATERIALS AND METHODS

Peat-moorsh soils were sampled from Czarna Wieś, Otoczne and Kwaterna 17 sites located in the Middle Biebrza Basin (Poland). The sites can be characterised as follows:

- Czarna Wieś – peat-moorsh soil profile with a low degree of decomposition (sedge-moss peat) with a minor influence of a drainage system, and with significant surface level changes, used as an extensive meadow;

- Otoczne – peat-moorsh soil profile with medium degree of decomposition (sedge-reed peat) with only the influence of a drainage system, used as an extensive meadow;
- Kwatera 17 – peat-moorsh soil profile with medium degree of decomposition (alder peat) located in a drainage sub-irrigation system with managed groundwater level, used as an intensive meadow.

Samples were collected at two different depths: the first, 5–10 cm and the second in the range of 45–80 cm (Table 1). Soils were sampled in 10 replications for each layer at each site. Samples were air-dried and crushed to pass through a 1 mm-mesh sieve. These 10 replications collected for each layer were mixed in order to prepare a “mean sample”, which then was used for the potentiometric determination of pH (in H₂O and in 1M KCl) and for the measurements of dissolved organic carbon (DOC) as well as total organic carbon (TOC).

Twice-distilled water from silica glass equipment was used for the laboratory analysis. For the investigation of DOC, soil samples were heated in redistilled water at a temperature of 100°C for two hours under a reflux condenser. Extracts were separated by using the mean filter paper and analysed on TOC 5050A equipment produced by Shimadzu, Japan (Smolander & Kitunen, 2002).

Table 1. The depth of sampling and basic characteristics of peat-moorsh soils.

Place of sampling	Sampling depth [cm]	Soil type	Degree of decomposition [von Post scale]
Czarna Wieś	5–10	moorsh	–
	50–70	sedge-moss peat	H ₁
Otoczne	5–10	moorsh	–
	45–50	sedge-reed peat	H ₅
Kwatera 17	5–10	moorsh	–
	70–80	alder peat	H ₆

Isolation of HA was achieved using standard IHSS procedure (Swift, 1996). A BECKMAN DU®-68 spectrophotometer with 1 cm thickness of layer was used for spectrophotometric measurements and according to Chen et al. (1977), 3 mg of HA was dissolved in 10 ml of 0.05 M NaHCO₃. Absorbances at 445 nm (E₄) and at 665 nm (E₆) of HA in this solution were measured and E₄/E₆ ratios calculated from spectrums in the visible region.

All the measurements were run in triplicate, and the results were averaged. All the chemicals used in this study were of analytical grade.

RESULTS AND DISCUSSION

The chemical, biochemical, physical and biological processes in peat represent its catalytic character. Thus, these processes and their mechanisms occurring in peat-forming plants are significantly dependent on the properties of the environment. The examined peat-moorsh soils with pH (in H₂O) ranging from 5.05 to 6.02 belong to middle acidic range. However, the samples taken from the upper layer (5–10 cm) of the Kwatera 17 soil profile represent highly acidic properties, the most acidic among investigated soil layers (Table 2).

Table 2. The values of pH and the concentrations of total (TOC) and dissolved organic carbon (DOC) of investigated soils.

Place of sampling	Sampling depth [cm]	pH		TOC	Δ TOC*	DOC	Δ DOC*
		H ₂ O	1 N KCl				
Czarna Wieś	5–10	5.54	5.19	37.19 ±1.7 [#]	6.83	12.81 ±0.4	7.01
	50–70	5.66	5.16	44.02 ±1.9		5.80 ±0.2	
Otoczne	5–10	6.02	5.46	38.10 ±1.7	7.48	10.80 ±0.4	3.25
	45–50	6.10	5.63	45.58 ±1.7		7.55 ±0.3	
Kwaterna 17	5–10	5.05	4.70	38.20 ±1.3	2.03	19.39 ±0.7	14.05
	70–80	5.88	5.39	40.23 ±1.4		5.34 ±0.2	

* – Δ TOC and Δ DOC are the differences between concentrations in upper and lower soil layers of the soil profiles, [#] – mean concentration and ±95% confidence interval of TOC or DOC

The chemical composition of peat-forming plants is evidently decisive for the peat composition. Thus, soil organic matter refers to a critical component of the soil – plant ecosystem: it constitutes the major part of organic carbon. There are different classes of biogenic, heterogeneous, dynamic and refractory organic compounds, characterising various contents of C and N having molecular structure. A principal feature of organic matter is its ability to absorb and retain water molecules. Depletion of organic matter cause a loss of water-holding capacity, poor aggregation, acceleration of soil erosion, poor retention of applied nutrients as well as reduced biological and enzymatic activities in the soil. Changes in land use or agricultural management lead to changes in the organic matter content (Ghani et al., 2003) of soils. Among the factors accelerating the decomposition of organic matter are the high content of cellulose and the total concentrations of hexoses, nitrogen compounds, and active mineral elements (P₂O₅, and CaO). However the following factors restrict the decomposition: the content of antiseptics (phenols and phenolcarbonic acids) and biochemically stable components (lignin, wax, cork tissues, etc.) (Inisheva & Dementeva, 2000). The drying of peat as a result of agricultural use leads to considerable shrinkage, activation of erosion, decrease of the nutrient content as well as a decrease of the biological and enzymatic activities. Shrinkage of peat increases with the increase of the degree of peat decomposition and humification. Thus, shrinkage of peat is related to its humic components (Van Dijk, 1971).

The biodegradation of organic carbon drives biogeochemical cycles. The data presented in Table 2 indicate that no significant concentrations of TOC were detected in the investigated moorsh soil samples collected from the 5–10 cm layer. These concentrations ranged from 37.19% to 38.20%. The highest amount of TOC equal to 38.20% was measured for the sample from Kwaterna 17; the lowest content, 37.17%, was determined for soil from Czarna Wieś. The results showed that all samples collected from the peat layers located at 45 to 80 cm depth were characterised by higher contents of TOC in comparison with moorsh samples taken from the 5 to 10 cm layer. The concentration of TOC for the depth 45–60 cm ranged from 40.23% to

45.58%. The highest amount of TOC, 45.58%, was determined for the sample collected from Otoczne and the lowest value, 40.23%, from Kwara 17. Generally, the sample collected from Kwara 17 from the moorsh layer (5–10 cm) manifested the highest content and the peat sample collected from 70–80 cm for the same profile represented the lowest concentration of TOC from all investigated samples.

Several products of the hydrolysis of peat humic substances were studied for their relevance to molecular structure and to changes occurring during humification. Primary polysaccharides, representing un-decomposed plant carbohydrates, can be converted to levulinic acid on prolonged hydrolysis. However, humic substances yield higher levels of levulinic acid than those obtainable by conventional methods of carbohydrate hydrolysis. This excess is attributed to altered carbohydrates, presumably attached to the central core of humic acid molecular structure. The primary polysaccharides in pyrolysis studies are associated with dianhydromonosaccharide fragments, whereas secondary polysaccharides yield furan fragments. The fen peat showed a steady increase of nonpolypeptide nitrogen with increasing depth. The loss of some phenolic compounds and fulvic acid components by natural drainage of the bog waters may account for the apparent changes in organic matter content with advanced humification (Anderson & Hepburn, 1986). Dissolved organic matter can contribute significantly to the cycling of soil nutrients. It can be a substrate for microbial growth, but its production is also partly mediated by microbes. This fraction is responsible for the microbiological activity (Puget et al., 1999). Fischer (1993) showed the relationship between the content of dissolved organic carbon and the amount of CO₂ evolution from soils to the atmosphere. This fraction of organic carbon is also connected with the movement of xenobiotics in soils. Therefore it seems to be most important to know the actual quantity of this fraction in soils.

It was shown for all investigated peat–moorsh soil samples that the concentrations of DOC, in contrast to TOC contents, decreased with the increase of the depth of the soil profiles (Table 2). The amounts of DOC measured for 0–10 cm depths ranged from 10.80% to 19.39%. The highest content of DOC, equal to 19.39%, was determined for the moorsh sample collected from Kwara 17, and the lowest, equal to 10.8% , for the sample collected from Otoczne. The samples collected from peat layers located at depths from 45 to 80 cm revealed lower contents of DOC than in moorsh layers, which ranged from 5.34% to 7.55%. Contrary to TOC measurements the moorsh sample from Kwara 17 representing depth 0–10 cm was characterised by the highest concentration of DOC; the peat sample collected from depth 70–80 cm showed the lowest content.

Spectrophotometry UV–VIS is a well known and commonly used method for the investigation of the structure of humic substances of soils. The light absorption of humic substances appears to increase with an increase in the degree of condensation of the aromatic rings that these substances contain, and in the ratio of C in aromatic ring to C in aliphatic side chains and total C content as well as molecular weight.

Measured values of HA for moorsh layers (5–10 cm), with the exception of samples collected from Kwara 17, are characterised by significantly higher optical density at 465 nm and higher E₄/E₆ ratios than the HA from lower depths representing peat (Table 3). The results of this study suggest a lower degree of condensation and polyconjugation in the molecules of HA from the upper depth (moorsh) compared to those from deeper layers (peat).

Table 3. The values of E_4/E_6 ratios for HA of investigated peat-moorsh soils.

Place of sampling	Sampling depth [cm]	Absorbance at		E_4/E_6	$\Delta E_4/E_6^*$
		$\lambda = 465 \text{ nm } (E_4)$	$\lambda = 665 \text{ nm } (E_6)$		
Czarna Wieś	5–10	0.892	0.128	6.968 $\pm 0.25^\#$	0.724
	50–70	0.868	0.139	6.244 ± 0.21	
Otoczne	5–10	1.350	0.196	6.887 ± 0.23	1.210
	45–50	1.215	0.214	5.677 ± 0.19	
Kwaterna 17	5–10	1.152	0.165	6.981 ± 0.25	1.290
	70–80	1.753	0.308	5.691 ± 0.21	

* – $\Delta E_4/E_6$ are the differences between the ratios in upper and lower layers of the soil profiles, $^\#$ – mean concentration and $\pm 95\%$ confidence interval of E_4/E_6

The measured values for HA of the investigated samples showed a decrease of E_4/E_6 ratio with the increase of the soil depth, indicating the increase in the degree of polyconjugation in their molecules (Chen et al., 1977). Lower E_4/E_6 ratios for measured HA values for peat samples collected from higher depths are due to an increase in the absorption at 625–665 nm, which can be explained by the presence of Pg-fraction (green fraction of HA) in these samples (Kumada, 1967; Orlov, 1985).

In addition, some trends for chemical properties of humic acids and the contents of the forms of organic carbon have been observed. The humic acids isolated in this study support the previous suggestions that these compounds collected from deeper peat layers of the soil profiles represent less secondary transformed structure than those collected from the upper layers, representing moorsh (Maryganova & Szajdak, 2000).

Natural, un-decomposed peat deposits are characterised by a relatively low degree of humification (Malterer et al., 1992). Consequently much of the humin fraction forming the peat organic matter may consist of unchanged substances originally present in the living plants. In some cases a decrease in humic acid content appears despite an apparent increase in humification, as indicated by the actual humin content. The decrease of humic acids may be attributed to loss of the humic acid fragments by selective oxidation and solution as well as by water removal during the natural bog drainage (Hatcher et al., 1986).

The phenomenon of increasing absorbance as result of an increase of total organic carbon in the structure of humic substances is known (Schnitzer & Khan, 1978). The performed investigations allowed the formulation of the linear relationship between the values of E_4/E_6 ratio and total and dissolved organic carbon concentrations. The correlation coefficients calculated for these linear relationships are equal to $r = -0.777$ and $r = 0.793$ (Fig. 1 and 2). The evaluation of the regression line shows proportional and inversely proportional correlation between these two forms of organic carbon and E_4/E_6 ratios. Hence, we expect that changes in the contents of organic carbon forms are reflected in temporal changes of HA properties.

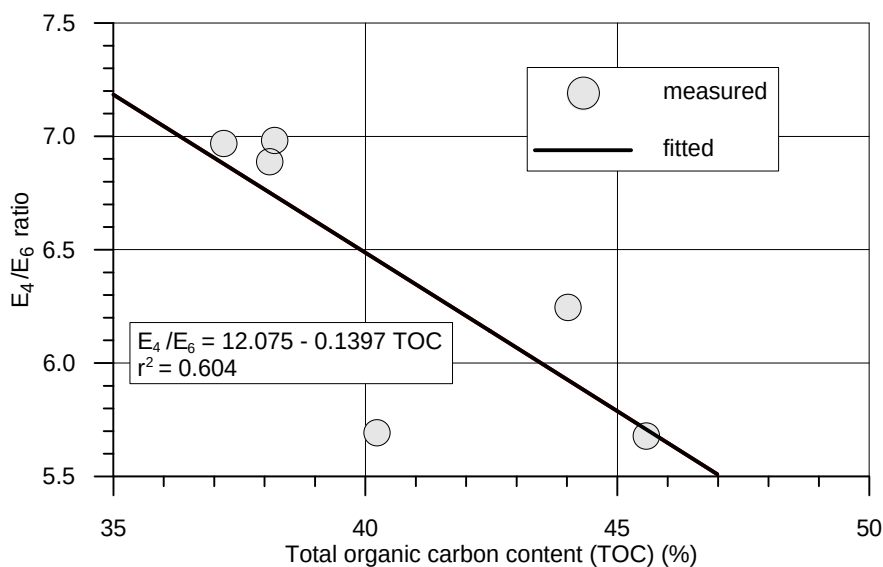


Fig. 1. The relationship between E_4/E_6 ratio and total organic carbon content for investigated peat-moorsh soils.

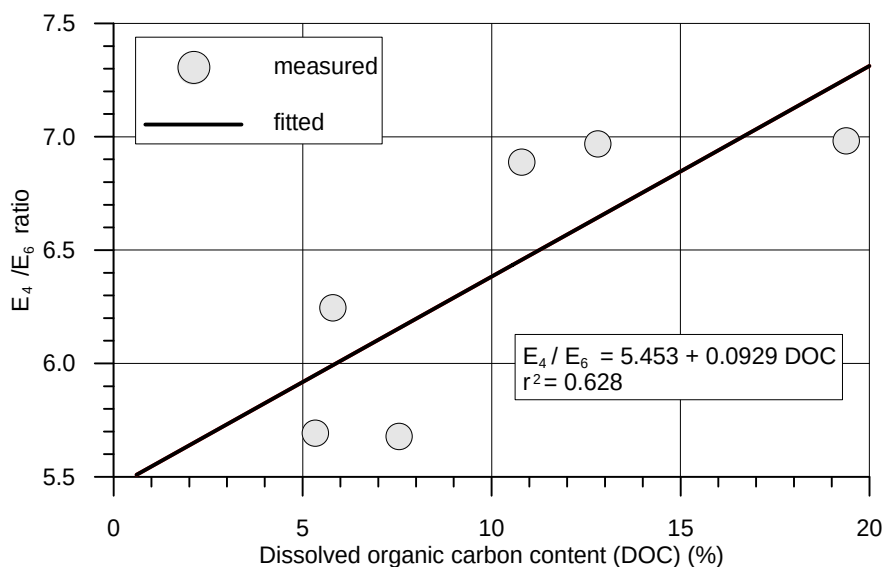


Fig. 2. The relationship between E_4/E_6 ratio and dissolved organic carbon content for investigated peat-moorsh soils.

The investigations revealed that organic matter of the investigated peat-moorsh soils ranged from 64.2% to 78.7% of the total amount (Table 2). These results suggest significant participation of humus in total amounts of peat organic matter in which

humic and fulvic acids predominate (Maryganova & Szajdak, 1999; Maryganova, 2000).

These results have shown that the measured values of HA from peat-moorsh soil from both depths of Kwaterna 17 characterised the lowest difference of TOC, measured value equal to 2.03%, and the highest difference of the measured DOC values equal to 14.5% (Table 2) as well as the lowest differences in of E_4/E_6 ratio values equal to 1.29 (Table 3). Our results suggest the impact of environmental factors on the content of the forms of organic carbon in peat-moorsh soils as well as revealing the relationships between the chemical properties of organic matter of peat-moorsh soils and the maturity of isolated humic and fulvic acids. The chemical and physical conditions in the soil profile suggest that the development of the structures of humic acid was driven by anaerobic conditions, which caused (a) continued reduction of pH, (b) accumulation of TOC, (c) decrease of DOC. These three factors would be expected to accumulate and to limit degradation of HA.

Moreover, it is useful to view the water retention by peat from another vantage point: It can be seen as an important factor in geological transformation. The alteration of peat's affinity for water by chemical treatment has been extensively studied. Considerable attention has been paid to the chemical composition and molecular structure of peat, identifying the molecular properties of substances and aggregates most likely to hold water strongly. Knowledge of these structures can provide a rationale for treatments intended to remove, or render less water-retentive, the most hydrophilic fraction. The substances of greatest immediate interest are humic acids, peptides and carbohydrates (Fuchsman, 1986).

CONCLUSIONS

The study showed the significant influence of agricultural use of peatlands on the content of different forms of carbon and chemical properties of humic acids:

1. The investigation has shown the impact of the peat type and the decomposition degree on the chemical properties of organic matter and the chemical structure of HA.
2. The highest content of TOC characterised reed-sedge moorsh with the decomposition degree of H_5 .
3. Investigated peats are characterised by the increase of TOC values and by the decrease of DOC values with the increasing depths in the soil profile.
4. For the investigated peat range it was found that the increase of depth of sampling in the soil profile is connected with an increase of the degree of condensation, aromatic polyconjugation, with the decrease of TOC and with an increase of DOC values.
5. For the investigated range of peat soils, the decrease of the depth is accompanied by the decrease in chemical maturity of HA.

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