Impact of Drainage on Hydrophobicity of Fen Peat-Moorsh Soils

L. Szajdak¹, J. Szatyłowicz²

¹Research Centre for Agricultural and Forest Environment, Polish Academy of Sciences, ul. Bukowska 19, 60-809 Poznan, Poland

²Department of Environmental Improvement, Warsaw University of Life Sciences - SGGW, ul. Nowoursynowska 159, 02-776 Warsaw, Poland

Investigations of the chemical and physical properties of three different peat-moorsh soils located in the Biebrza River Valley, in the north-east part of Poland, were performed. All examined soils were used as meadows. Soil samples were taken at two depths: 5–10 cm (moorsh) and 50-80 cm (peat). Total organic carbon (TOC), dissolved organic carbon (DOC), and humic acids (HA) extracted from these samples were measured. Basic physical properties such as the ash content and bulk density were also measured. Wetting behavior of soils was quantified using water drop penetration time test and the values of the soil-water contact angle. Significant differences were observed in the concentration of TOC, DOC and properties of HA between the two investigated depths of peat and moorsh samples. The concentrations of TOC in the soils ranged from 37.2% to 45.6%. Generally, the deeper the profiles were taken, the smaller were the TOC concentrations. The concentrations of DOC in the soils ranged from 5.3% to 19.4%, and the deeper the profiles were taken, the smaller were the quantities of dissolved organic carbon and E_4/E_6 values. However, an increase of the depth was accompanied by a decrease in the degree of humification or an increase in the chemical maturity of HA of the investigated peat. It was shown that the examined soils can be classified as severely or strongly water-repellent because the contact angle in most cases exceeded 90 degrees. The highest correlation between WDPT (water drop penetration time) and soil properties was obtained for the relationship between WDPT and the ash content in the examined soils. Furthermore, significant correlations between bulk density and WDPT, TOC and WDPT time, organic matter and WDPT, humic acids and WDPT, absorbance E, and WDPT, pH and the contact angle were revealed.

Keywords: contact angle, peat-moorsh soils, water repellency, DOC, E_4/E_6 , TOC.

INTRODUCTION

Interest in water retention and dewatering in peat has evolved from primary areas of peat use to more recent recognition of the impact of peat properties on several factors including the chemical composition and molecular structure of peat, evolution of soil gases arising of moisture, and degradation of organic matter. Assessments of water retention and dewatering in peat indicate that agricultural activity on peat has left a negative impact on peat and peatlands (Schnitzer, 1986; Lishtvan et al., 1989; Szajdak, 2002). Wettability reveals the ability of a liquid to spread over and wet the soil. A principal feature of humic materials of peat is their ability to absorb and retain large quantities of water. High water retention in peat is attributed to structural voids (macro-pores) due to the partial degradation of the structure of peat-forming plants, and molecular absorption sites (micro-pores) associated with the formation of humic substances.

A soil is commonly classified as being water-repellent (hydrophobic) if a drop of water on the soil is not spontaneously absorbed by the soil. Water repellency of soil is caused by organic compounds derived from living or decomposing plants or microorganisms. The soil temperature and the effect of burning of the vegetation covering the soil surface are important non-biological factors influencing hydrophobicity of soil (Doerr et al., 2000). It was observed that water-repellent soils show several negative properties: reduced infiltration causing runoff, erosion, and impaired plant establishment and growth (Doerr et al., 2000), high variation of water content in soil, and irregular moisture patterns (Ritsema et al., 1993; Dekker and Ritsema, 1995; 1996). Thus, water repellency reveals important properties of peat soils (Berglund and Persson, 1996; Brandyk et al., 2002; Szatyłowicz, 2004).

Various methods have been proposed for the characterization and quantification of water repellency (Letey et al., 2000). One of the simplest and the most common methods for characterizing soil repellency is the empirical water drop penetration time (WDPT) test described by Watson and Letey (1970). In short, the WDPT method consists of placing a water drop on the surface of soil and recording the time necessary for water to penetrate the sample. Wetting behavior can also be quantified by measuring the contact angle, which is defined as the angle at the soil-liquid-vapour three-phase contact line (Bachmann et al., 2000b).

Peat is characterized by colloidal behavior and irreversible loss of wettability produced by drying. Long-term cultivation and agricultural use of peatlands and their exploitation have revealed a number of effects including lowering of the water table, increased aeration, changes in plant communities, and release of carbon content. These processes show the disturbance of the thermodynamic balance in peat. Decline in peat soil moisture content resulting from drainage leads to shrinkage of peat. Change of volume due to shrinkage is the result of several forces acting at micro-scale, and its mechanism and magnitude differ from that in mineral (clay) soils. It was showed that drainage in particular results in a sharp change of biotic and abiotic conversions and consequent degradation of peat organic matter (Grootjans et al., 1985, 1986; Kwak et al., 1986; Lüttig, 1986).

In general, drainage of peat leads to progressive differentiation of hydrophobic peptides and total amino acid contents in organic matter. In proteins of peat, hydrophobic contacts exist between hydrophobic structural elements (between the side chains of the radicals of phenylalanine, leucine, isoleucine, valine, proline, methionine, and tryptophan). Hydrophobic forces stabilize the tertiary structure of proteins and determine the properties of lipids and biological membranes. The presence of amino acids, hydrocarbon chains, and other nonpolar fragments in their composition is related to the hydrophobic properties of humic substances (Sokołowska et al., 2005). Organic matter constitutes the major part of the soil phase of peat and moors and causes soil water repellency. Thus, it is important to study the influence of chemical properties of soil on its wettability. It was observed that significant changes of chemical properties of transformed organic matter of peat have a considerable influence on the sequential changes in physical and hydraulic properties initiated by drainage for agriculture. Due to marked shrinkage, changes in many other properties of peat related to humic components are observed (Van Dijk, 1971). Therefore, this paper compares the chemical composition of organic matter of peat-moorsh soils with the data on wettability of these soils.

The objectives of this study are: (i) to measure the chemical and hydrophobic properties of a range of peat-moorsh soils; (ii) to assess the relationship between hydrophobicity and properties of the investigated soils.

The investigation of peat soils using extraction of soluble soil organic matter fractions allows to establish (Ellerbrock et al., 1999b) links to vegetation (Quideau et al., 2001) and comparison of peat soils with moorsh-peat soils.

MATERIALS AND METHODS

Site Description

Samples of peat and moorsh soils were collected at three fen peatland sites located in the Middle Basin of the Biebrza River Valley in the north-east part of Poland (53°39'N; 22°36'E), between the towns of Grajewo and Rajgród. All sites are disturbed by the Kuwasy drainage-subirrigation system. These sites were selected in order to cover different types of peat-moorsh soil profiles, the intensity of land use, and the impact of drainage-subirrigation systems. The first site – Czarna Wieś – represents deep sedge-moss peat soil profiles (depth 4 m) with a very low degree of decomposition. The impact of the drainage system is minor, resulting in low advances of the moorshing process (moorsh layer 10 cm). The site is used as an extensive fertilized meadow (2 cuts). The second site - Otoczne - is used as a very extensive, non-fertilized meadow (1 cut). The soil profile represents sedge-reed peat (2 m deep) with a medium degree of decomposition. The soil is subject to intensive drainage, which results in 25 cm of moorsh layer. The operation of subirrigation system is limited at the site. The third site - Kwatera 17 - represents a shallow peat-moorsh soil profile (peat depth 1.2 m) developed from alder swamp forest peat with a medium degree of decomposition. The moorsh layer thickens and equals 25 cm. The site is located in a drainage-subirrigation system with managed groundwater level and used as

a fertilized intensive meadow (3 cuts). The soil samples were collected from all sites at two different depths: 5-10 cm, representing the moorsh layer, and 45-80 cm, revealing the peat layer (Table 1).

Code	Sampling place	Depth, cm	Ash content, % a. d. m.	Bulk density, g·cm ⁻³	Soil material and degree of decomposition by the von Post scale
CWM	Course W/is/	5-10	17.99	0.176	Moorsh (peaty)
CWP	Czarna wies	50-70	5.93	0.071	Sedge-moss peat (H_1)
OTM	0	5-10	20.47	0.330	Moorsh (grainy)
OTP	Otoczne	45-50	11.08	0.162	Sedge-reed peat (H ₅)
KWM	V . 17	5-10	17.96	0.294	Moorsh (grainy)
KWP	Kwatera 17	70-80	19.10	0.198	Alder peat (H ₆)

Table 1. The depth of sampling and basic physical properties of peat-moorsh soil samples

Basic Physical Properties

The ash content, degree of humification, and botanical composition of peat soils was determined in each sample. In two layers of the investigated soil profiles, undisturbed soil cores (volume 100 cm³, height 5 cm) in three replications were collected for measurements of soil bulk density. The ash content was determined by igniting dried peat in a muffle furnace at about 550 °C until constant weight. The humification degree (by the von Post scale) and botanical composition of peat were determined by a microscope (Maciak and Liwski, 1996). The bulk density of each sample was evaluated by dividing the oven-dried (105 °C) mass of soil with the volume of a core of an undisturbed saturated sample.

Chemical Characterization

For chemical characterization, soils were sampled in 10 replications for each layer at each site. Samples were air-dried and crushed to pass a 1 mm mesh sieve. The 10 replications collected for each layer were mixed in order to prepare a mean sample. This material was used for the potentiometric determination of pH (in H_2O and in 1 N KCl) and for the measurements of dissolved organic carbon (DOC) and total organic carbon (TOC).

Twice-distilled water in a silica glass equipment was used for the laboratory analysis. For the investigation of DOC, soil samples were heated in re-distilled water in the temperature of 100 °C by two hours under reflux condenser. Extracts were separated by using mean filter paper and analyzed with the aid

of TOC 5050A equipment produced by Shimadzu, Japan (Smolander and Kitunen, 2002).

Isolation of HA was achieved using the standard IHSS procedure (Swift, 1996). BECKMAN DU[®]-68 spectrophotometer with 1 cm thick layer was used for spectrophotometric measurements and, according to Chen et al. (1977), 3 mg of HA were dissolved in 10 ml of 0.05 M NaHCO₃. Absorbances at $\lambda = 464$ nm (E₄) and at $\lambda = 665$ nm (E₆) of HA in this solution were measured, and E₄/E₆ ratios were calculated from spectra in 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.

Wettability Measurements

Wettability of soils was assessed with the water drop penetration time (WDPT) method by Watson and Letey (1970) and the modified sessile drop method for determination of the initial soil-water contact angle proposed by Bachmann et al. (2000a, 2000b).

The WDPT measurements were done by placing three drops of distilled water from a standard medicine dropper on each soil surface samples which were used for determination of soil bulk density. For each drop, the WDPT value was measured with a stopwatch. The WDPT tests were conducted on air-dried soil samples whose volumetric moisture content did not exceed 7%.

Contact angle measurements were done on a thin layer of air-dried soil material (such that droplets could not infiltrate). Before the measurements, the soil material was crushed using soil mixer in order achieve very fine and homogeneous particles. A smooth microscope glass slide was covered with a double-sided adhesive tape and the soil was sprinkled on a 2 to 3 cm area. Particles were pressed to the tape with a 100 g weight for several seconds. The slide was then shaken carefully to remove non-adhering soil particles. This procedure was repeated twice for each sample.

Contact angles were determined at room temperature (20 °C) within 10 min after sample preparation using Contact Angle Meter – CAM 100 (KSV Instruments). The meter is a camera-based instrument which allows to capture an image of the shape of a water drop placed on a solid. A drop of deionized water (volume 1.7 ml) was placed on the soil sample using dropper, and shortly thereafter the drop image was recorded. The contact angles were evaluated by fitting a mathematical expression to the shape of the drop and then calculating the slope of the tangent to the drop at the liquid-solid-vapour interface line at the left and the right side of the drop was measured every 3 s during a period of 15 s. A decrease of the contact angle values on the sample surface during the short period immediately after the drop was placed was observed. The contact angle measurements were conducted trice for each investigated soil sample.

RESULTS AND DISCUSSION

Physical and Chemical Properties

The results represented in Table 1 show that the ash content and bulk density of moorsh layers are considerably higher than that of peat except the ash content of the Kwatera 17 profile (sample KWP), in which the ash content of peat is higher than that of moorsh due to a specific type of peat, i.e. alder, which contains wood residue resulting in a higher value of ash content. The bulk density of peat samples varies according to the botanical composition of the plant remains and the degree of decomposition of peat. The lowest values of bulk density were measured in undecomposed sedge-moss peat (sample CWP), while the highest values were recorded in decomposed alder peat (KWP).

Table 2. The values of pH and content of total organic carbon (TOC), dissolved organic carbon (DOC), organic matter (OM), and E_4/E_6 ratios of HA in the investigated soils

Code	рН		TOC,	DOC,	OM,	НА			
						Comtont	Absorbance at		
	H ₂ O	1 N KCl	%	%	%	%	$\lambda = 445 \text{ nm}$ (E_4)	$\lambda = 665 \text{ nm}$ (E_6)	E_4/E_6
CWM	5.54	5.19	37.19	12.81	64.34	18.97	0.892	0.128	6.968
CWP	5.66	5.16	44.02	5.80	76.16	24.01	0.868	0.139	6.244
OTM	6.02	5.46	38.10	10.80	65.19	19.43	1.350	0.196	6.887
OTP	6.10	5.63	45.58	7.55	78.85	24.85	1.215	0.214	5.677
KWM	5.05	4.70	38.20	19.39	66.09	19.78	1.152	0.165	6.981
KWP	5.88	5.39	40.23	5.34	69.60	22.75	1.753	0.308	5.691

See Table 1 for explanation of acronyms

The examined peat-moorsh soils with pH (in H_2O) ranging from 5.05 to 6.02 belong to medium acidic soils (Table 2). Among the investigated soils, the moorsh profile from Kwatera 17 (KWM) is characterized by highly acidic properties. We can see from the data presented in Table 2 that there was less TOC in moorsh layers than in underlying peat layers. In moorsh layers these concentrations are of a narrower range (from 37.19 to 38.20%) compared to the concentrations in peat layers (from 40.23 to 45.58%).

We discovered that in all investigated peat-moorsh soil samples, the concentrations of DOC, in contrast to concentrations of TOC, decreased with an increase in the depth of the soil profiles (Table 2). The amount of DOC measured at the depth of 5–10 cm ranged from 10.80 to 19.39%. The highest content of DOC equaled 19.39% in the moorsh sample collected at Kwatera 17, and the lowest equaled 10.8% in the sample taken at Otoczne. The samples collected from peat layers at a depth from 45 to 80 cm to contained lower contents of DOC than moorsh layers, ranging from 5.34 to 7.55%. The moorsh sample taken at Kwatera 17 at the depth of 5–10 cm was characterized by the

highest concentration, but the peat sample collected at the depth of 70-80 cm – by the lowest concentration of DOC.

The determined values of HA in moorsh layers (5–10 cm), with the exception of samples collected from Kwatera 17, are characterized by significantly higher optical density at 465 nm and higher E_4/E_6 ratios than the HA from the lower depths of peat (Table 2). This reflects a lower degree of condensation and polyconjugation in the molecules of HA from shallower moorsh compared to the deeper layers of peat.

The phenomenon of increasing absorbance as a result of an increase of TOC in the structure of humic substances is well known (Schnitzer and Khan, 1978). The performed investigations allowed to formulate linear relationships between the values of E_4/E_6 ratio and TOC and DOC concentrations. The correlation coefficients determined for these linear relationships are r = -0.777 and r = 0.793. The results show a proportional and inversely proportional correlation between these two forms of organic carbon and E_4/E_6 ratios.

Wettability

Table 3 presents the results of water drop penetration time (WDPT) and contact angle measurements in the examined peat-moorsh soils. The measured mean WDPT ranged from 63 to 1986 s in all these soils. Based on the time needed for the water drop to penetrate into the soil, Dekker and Jungerius (1990) proposed a classification of wettability. According to this classification, the following five classes of water repellence can be distinguished: (i) wettable or non-water-repellent (WDPT < 5 s), (ii) slightly (5–60 s), (iii) strongly (60–600 s), (iv) severely (600–3600 s), (v) extremely water-repellent (> 3600 s). According to this classification, all but one examined moorsh layers and two peat layers can be classified as strongly water-repellent; sedge-moss (sample CWP) is severely water-repellent. We can also see from the analysis of WDPT that standard deviation of the time is increasing with increasing mean WDPT value. The present results are consistent with findings of recent studies by Buczko and Bens (2006).

 Table 3. Mean and standard deviation (SD) values of water drop penetration time and contact angle in the studied soils

 Code
 Water drop penetration time (s)
 Contact angle (°)

Cada	Water drop pen	etration time (s)	Contact angle (°)		
Code	Mean	SD	Mean	SD	
CWM	105	41.5	107.3	2.15	
CWP	1986	2700.7	114.2	6.93	
ОТМ	63	10.7	81.4	3.14	
OTP	431	300.8	90.0	2.98	
KWM	392	198.4	114.3	3.76	
KWP	67	94.4	112.4	2.13	

See Table 1 for explanation of acronyms

Contact angle investigations were performed primarily to provide additional data for subsequent comparison with the WDPT method, as well as for further assessment of wettability of the investigated soil materials. The measured values of the contact angle in investigated soils ranged from 81.4 to 114.3 °, indicating high water repellency. The lowest values of the contact angle were obtained in the samples collected at Otoczne soil profile, while the highest at Kwatera 17. The reported values of the contact angle concerning the peat layers were comparable with the range of the values presented by Michel et al. (2001) concerning dry peat samples. The standard deviations of the measured contact angle values ranged from 2.13 to 6.93 ° were nearly identical to the data published in the literature concerning peat (Michel et al., 2001) and mineral soils (Woche et al., 2005; Buczko and Bens, 2006).

Wettability vs Soil Properties

To estimate the relations between soil parameters and wettability coefficients, a linear correlation (r) between water drop penetration time, the contact angle, and soil properties was calculated (Table 4). It was observed that WDPT positively correlated with TOC, organic matter and humic acid content, and negatively correlated with the ash content, soil bulk density, pH, and absorbance. The highest value of r (statistically significant) was obtained for the relation between WDPT and the ash content. This relation was more pronounced when data were fitted using power equation (Fig 1a).



Figure 1. Correlation between water drop penetration time and ash content (a), and contact angle and soil pH in H₂O (b)

The values of the correlation coefficient between the contact angle and soil properties were much lower in comparison with the relations between WDPT and soil properties, except pH. pH and the contact angle indicated a tendency that the contact angle increases with decreasing pH (Fig. 1b). The influence of pH on the contact angle values (a negative correlation) was also noticed by Woche et al. (2005). They explained this phenomenon by the decrease of soil

solution surface tension with decreasing pH due to increasing protonation of phenolic compounds in the solution of weak acids.

Table 4. Calculated values of the linear correlation coefficient between soil properties and indices of soil-water repellency

Soil properties	Water drop penetration time (s)	Contact angle (°)	
Ash content, %	-0.8964	-0.2116	
Bulk density, g·cm ⁻³)	-0.7047	0.1117	
Total organic carbon, %	0.5940	-0.0718	
Dissolved organic carbon, %	-0.3309	0.1117	
Organic matter, %	0.5898	-0.0712	
Humic acids, %	0.5314	0.0582	
Absorbance at $\lambda = 464 \text{ nm} - \text{E}_4$	-0.5533	-0.1660	
Absorbance at $\lambda = 464 \text{ nm} - \text{E}_6$	-0.4263	-0.0987	
pH in H ₂ O	-0.1199	-0.6962	
pH in 1 N KCl	-0.1912	-0.6878	

Physical and Chemical Properties

The results of the ash content and bulk density reported in Table 1 were comparable with previously published data (Okruszko, 1993; Brandyk et al., 2002) on drained fen peat soils used as meadows.

Soil organic matter is 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 characterized by various contents of C and N with molecular structure. A principal feature of organic matter is its ability to absorb and retain water molecules. Depletion of organic matter causes 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 of soil. Changes of land use or agricultural management lead to changes in soil organic matter content (Gotkiewicz and Kowalczyk, 1977; McCarthy et al., 1990; Ghani et al., 2003). It has been proven that drying of peat as a result of agricultural use leads to considerable shrinkage, activation of erosion, decrease of the nutrient content and biological and enzymatic activities. It was also suggested that shrinkage of peat is facilitated by increase of peat decomposition and humification degree. Therefore, shrinkage of peat is related to humic components of peat and the molecular structure of peat humic compounds (Van Dijk, 1971).

It was revealed that concentrations of DOC, in contrast to concentrations of TOC, decreased with the depth of the soil profiles (Table 2) in all investigated peat-moorsh soil samples. The amounts of DOC measured in moorsh samples ranged from 10.80% (OTM) to 19.39% (KWM). The samples collected from

peat layers revealed lower contents of DOC than samples from moorsh layers, which ranged from 5.34% (KWP) to 7.55% (OTP).

The relevance of several products of hydrolysis of peat humic substances to molecular structure and changes occurring during humification were studied. Primary polysaccharides representing undecomposed plant carbohydrates can be converted to levulinic acid with the aid of prolonged hydrolysis. However, humic substances yield higher levels of levulinic acid than those that can be obtained by conventional methods of carbohydrate hydrolysis. This excess is attributed to altered carbohydrates, presumably attached to the molecular structure of humic acids. Primary polysaccharides in pyrolysis studies are associated with dianhydromonosacharide fragments, whereas secondary polysaccharides yield furan fragments. 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 and Hepburn, 1986).

DOC can contribute significantly to cycling of soil nutrients. It can be a substrate for microbial growth, but its production also is partly mediated by microbes. This fraction is responsible for microbiological activity (Puget et al., 1999). Fischer (1993) showed the relationship between the content of DOC and the amount of CO_2 evolution from soils into the atmosphere. This fraction of organic carbon is also connected with the movement of xenobiotics in soils, and, therefore, it is suggested that degradation of DOC may be a much more important source of CO_2 than generally assumed (Marscher and Bredov, 2002).

UV-VIS spectrophotometry is a commonly used method for the investigation of the structure of soil humic substances. The light absorption capacity of humic substances appears to increase with an increase in the degree of the condensation of the aromatic rings that these substances contain, and the ratio of C in an aromatic ring to C in aliphatic side chains and the total C content, as well as molecular weight. The measured values of E_4/E_6 ratio in HA of the investigated samples showed a decrease of E_4/E_6 ratio with an increase of the depth of the soil, which in turn indicated an increase in the degree of polyconjugation in their molecules (Chen et al., 1977). It means that the maturity of the structure of HA from lower layers is higher than that of the upper layers. Lower E_4/E_6 ratios for measured HA values in peat samples collected from higher depths are due to have an increase in absorption at $\lambda = 625-665$ nm, which can be explained by the presence of the Pg-fraction (the green fraction of HA) in these samples (Kumada and Hurst, 1967; Orlov, 1985).

Some trends of the chemical properties of HA and the contents of the forms of organic carbon were noted in this study. The HA isolated in this study confirm the previous suggestions that the compounds collected from deeper peat layers of the soil profiles represent less secondary transformed structure than those collected from the upper levels of moorsh.

Natural, undecomoposed peat deposits are characterized 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 same cases, a decrease in HA content appears despite an apparent increase in humification, as indicated by the actual humin content. The decrease of HA can be attributed to the loss of HA fragments by selective oxidation and solution, as well as by water removal during natural bog drainage (Hatcher et al., 1986).

The performed investigation revealed that organic matter in the investigated peat-moorsh soils ranged from 64.2 to 78.7% (Table 2). These results suggest a significant proportion of humus in the total amounts of peat organic matter with dominating HA and FA (Maryganova and Szajdak, 1999; Bambalov et al., 2000; Maryganova, 2000).

The results have also revealed that the values of HA from both depths of peatmoorsh soil at Kwatera 17 were characterized by the smallest difference of TOC values – 2.03%, and the biggest difference of DOC values – 14.5%, as well as the smallest difference in E_4/E_6 ratio – 1.29 (Table 2). These results suggest the impact of environmental factors on the content of the forms of organic carbon in peat-moorsh soils, and reveal the relationship between the chemical properties of organic matter of peat-moorsh soils and the maturity of isolated HA.

Water retention of peat can be usefully viewed as an important factor in geological transformation. The alternation 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 the substances and aggregates most likely to retain water. Knowledge on these structures can provide a rationale for treatments intended to remove, or render less water-retentive, the most hydrophilic fraction. The substances of the greatest immediate interest are HA, peptides, proteins, amino acids, and carbohydrates (Fuchsman, 1986; Kalbitz et at., 1999; Leinweber et al., 2001).

Humic substances are known to be macromolecular polydisperse biphyllic systems containing both hydrophobic and hydrophilic groups, i.e. of an amphiphilic character. The amphiphilic properties of humic substances are responsible for their wettability, solubility, conformation, surfactant-like character, and a variety of physicochemical properties of considerable practical significance (Sposito, 1989; Carpiel et al., 1995; Garnier-Sillam et al., 1999). These properties depend on the chemical and physical properties of organic matter created from decomposed plant materials and from different land-use practices. Additionally, the changes of water table, the content of oxygen, and the redox potential may modify very efficiently the chemical structures of humic substances (Quideau et al., 2001; Poulenard et al., 2004; Woche et al., 2005).

Wettability

The results of previously conducted research on soil water repellency clearly show that water repellency of peat and moorsh soils evaluated with the WDPT test depends very much on the moisture content of soil (Szatyłowicz, 2004). Because this data was obtained for air-dried soils, care should be taken when applying these data to other moisture contents.

Comparison of the measured contact angle with water drop penetration time data reveals a roughly positive linear relationship with correlation coefficient (r) equal to 0.3818. Such poor relationship between the analysed results is consistent with previous findings reported in the literature. For samples displaying the contact angle of about 90°, Buczko and Bens (2006) reported corresponding WDPT values ranging from 100 s to 1 h. Also, Woche et al. (2005), based on the comparison of the contact angle and WDPT, found restricted resolution of WDPT.

Factors Influencing Wettability of the Studied Soils

Soil organic matter is composed of a hydrophobic carbon backbone and functional groups (Ellerbrock et al., 1999a, 1999b, 2005; Clapp et al., 2001; McDonnel et al., 2001), which both affect soil wettability in a certain way (Clapp et al., 2001). In classes of pure chemical substances, the number of hydrophilic groups relative to that of hydrophobic groups determines the hydrophobic character of soil organic matter, and a larger carbon backbone allows for more complex three-dimensional arrangements of organic molecules. Under dry conditions, the hydrophilic groups within soil organic matter will approach each other (Ma'shum and Farmer, 1985) if the carbon backbone is large enough. It results in coiling molecules, which form a hydrophobic outside around a hydrophilic center (Sposito, 1989; Stevenson, 1994). Under moist conditions, the center of soil organic matter molecules becomes hydrophobic (Yates and von Wandruszka, 1999).

Maryganova et al. (2005, 2007) proved that the most chemically mature fraction of peat HA extracted with 0.1 M Na₄P₂O₇ at pH 7 was shown to contain the highest proportion of hydrophilic components (45–48%) and the lowest proportion of the most hydrophobic compounds (6–8%). In the less chemically mature fraction of peat HA extracted with 0.1 M NaOH, the content of hydrophilic components was 2 times lower (23–25%) and the proportion of the most hydrophobic components (18–24%). Peat FA were found to be nearly completely (95–96%) represented by the hydrophilic fraction. That suggested that the most hydrophilic components of peat HA are characterized by the highest content of carboxyl groups and the lowest proportion of saturated hydrocarbon chains, polypeptides, and carbohydrates. The most hydrophobic fractions of peat HA contain the largest number of hydrocarbon chains and the lowest proportion of carboxyl groups.

CONCLUSIONS

The analysis presented here demonstrates how the chemical and physical properties of peat organic matter can be studied by comparing measurements of wettability of drained peat. The study has shown the impact of the type and decomposition degree of peat on the chemical properties of organic matter and the chemical structure of HA and the wettability properties. The highest content of TOC was characteristic of sedge-reed peat with the decomposition degree H₅ and with the lowest value of pH. The investigated peat was characterized by an increase of TOC values and a decrease of DOC values with increasing depth of the soil profile. The results of the WDPT test and the soil water contact angle measurements performed on air-dried peat-moorsh soil showed that both methods render repellency levels to be high. The examined soils can be classified as severely or strongly water-repellent with the contact angle in most cases exceeding 90°. In examined soils the highest correlation between water drop penetration time and soil properties was showed in the relationship between WDPT and ash content. Increasing ash content caused a decreasing WDPT (soil water repellency). The soil water contact angle correlated less with peat-moorsh soil properties in comparison to WDPT, with the exception of pH. The correlation between pH and the contact angle indicates a tendency that the contact angle increases when pH decreases. Furthermore, significant correlations between bulk density and WDPT, TOC and WDPT, organic matter and WDPT, humic acids and WDPT, absorbance at E_4 and WDPT, pH in H_2O and the contact angle, as well as between pH in 1 N KCl and the contact angle were revealed.

ACKNOWLEDGEMENTS

This work was supported by the grant No. N N305 320436 of the Ministry of Education of Poland. Thanks to Mrs Teresa Stachecka for technical support.

REFERENCES

- Anderson H., Hepburn A. (1986) Variation of humic substances within peat profiles. In: *Soil Biochemistry*. 2nd ed. McLaren A. D., Skujins J. (Eds.) New York: Marcel Dekker, pp. 177–194.
- Bachmann J., Ellies A., Hartge K. H. (2000a) Development and application of a new sessile drop contact angle method to assess soil water repellency. J. Hydrol., 231–232, 66–75.
- Bachmann J., Horton R., Ploeg R. R., van der Woche S. (2000b) Modified sessile drop method for assessing initial soil-water contact angle of sandy soil. *Soil Sci. Soc. Am. J.*, 64, 564–567.
- Bambalov N., Smychnik T., Maryganova V., Strigutsky V., Dite M. (2000) Peculiarities of the chemical composition and the molecular structure of peat humic substances. *Acta Agroph.*, 26, 149–177.

- Berglund K., Persson L. (1996) Water repellence of cultivated organic soils. Acta Agric. Scand., B S-P. 46, 145–152.
- Brandyk T., Szatyłowicz J., Oleszczuk R., Gnatowski T. (2002) Water-related physical attributes of organic soils. In: Organic soils and peat materials for sustainable agriculture. Parent L.-E., Ilnicki P. (Eds.) Boca Raton, Florida: CRC Press and International Peat Society, pp. 33–66.
- Buczko U., Bens O. (2006) Assessing soil hydrophobicity and its variability through the soil profile using two different methods. *Soil Sci. Soc. Am. J.*, 70, 718–727.
- Carpiel P., Beck T., Borchert H., Gronholz J., Zachman G. (1995) Hydrophobicity of the organic matter in arable soils. *Soil Biol. Biochem.*, 27, 1453–1458.
- Chen Y., Senesi N., Schnitzer M. (1977) Information provided on humic substances by E₄/E₆ ratios. *Soil Sci. Soc. Am. J.*, 41, 352–358.
- Clapp C. E., Hayes M. H. B., Senesi N., Bloom P. R., Jardine P. M. (2001) Humic substances and chemical contaminants. Madison, WI: SSSA, pp. 142–230.
- Dekker L. W., Jungerius P. D. (1990) Water repellency in the dunes with special reference to the Netherlands. *Catena*, Suppl. 18, 173–183.
- Dekker L. W., Ritsema C. J. (1995) Fingerlike wetting patterns in two water-repellent loam soils. J. Environ. Qual., 24, 324–333.
- Dekker L. W., Ritsema C. J. (1996) Variation in water content and wetting patterns in Dutch water repellent peaty clay and clayey peat soils. *Catena*, 28, 89–105.
- Doerr S. H., Shakesby R. A., Walsh R. P. D. (2000) Soil water repellency: its causes, characteristics and hydro-geomorphological significance. *Earth-Sci. Rev.*, 51, 33–65.
- Ellerbrock R. H., Höhn A., Rogasik J. (1999a) Functional analysis of soil organic matter with respect to soil management. *Europ. J. Soil. Sci.*, 50, 65–71.
- Ellerbrock R. H., Höhn A., Gerke H. H. (1999b) Characterization of soil organic matter from a sandy soil in relation to management practice using FT-IR spectroscopy. *Plant Soil*, 213, 55–61.
- Ellerbrock R. H., Gerke H. H., Bachmann J., Goebel M. O. (2005) Composition of organic matter fractions for explaining wettability of three forest soils. *Soil Sci. Soc. Am. J.*, 69, 57–66.
- Fischer T. (1993) Einfluss von Winterweizen und Winterrogen in Fruchtfolgen mit unterschliedlichen Getreideanteil auf die mikrobiele Biomasse und jahreszeitliche Kohlenstoffdynamik des Bodens. Arch Acker Pflanzenbau Bodenkd., 37, 181–189.
- Fuchsman C. H. (1986) The pat-water problem: reflection, perspective, recommendations. In: *Soil Biochemistry*. 2nd ed. McLaren, A. D., Skujins J. (Eds.) New York: Marcel Dekker, pp. 331–360.
- Garnier-Sillam E., Hariyento S., Bourezgui Y. (1999) Humic substances in peats (Sumatra, Indonesia). *Analusis*, 27, 405–408.
- Ghani A., Dexter M., Perrott K. W. (2003) Hot-water extractable carbon in soils: a sensitive measurement for determining impacts of fertilization, grazing and cultivation. *Soil Biol. Biochem*, 35, 1231–1243.

- Gotkiewicz J., Kowalczyk Z. (1977) Biological processes in soils of different peatland habitats. *Zesz. Probl. Post. Nauk Roln.*, 186, 97–117 (in Polish).
- Grootjans A. P., Schipper P. C., van der Windt H. J. (1985) Influence of drainage on N-mineralization and vegetation response in wet meadows. I. *Calthion palustris* stands. *Oecol. Plant.*, 6, 403–417.
- Grootjans A. P., Schipper P. C., van der Windt H. J. (1986) Influence of drainage on N-mineralization and vegetation response in wet meadows. II. *Cirsio-Molinietum* stands. *Oecol. Plant.*, 7, 3–14.
- Hatcher P. G., Spiker E., Orem W. H. (1986) Organic geochemical studies of the peat humification process in low-moor peat. In: *Soil Biochemistry*. 2nd ed. McLaren A. D., Skujins J. (Eds.) New York: Marcel Dekker, pp. 195–213.
- Kalbitz K., Geyer W., Geyer S. (1999) Spectroscopic properties of dissolved humic substances – a reflection of land use history in a fen area. *Biogeochemistry* 47, 219–238.
- Kumada K., Hurst H. M. (1967) Green humic acid and its possible origin as a fungal metabolite. *Nature*, 214, 631–633.
- Kwak J. C., Ayub A. L., Shepard J. D. (1986) The role of colloid science in peat dewatering: principles and dewatering studies. In: *Peat and water. Aspects of water retention and dewatering in peat.* Fuchsman C. S. (Ed.) London: Elsevier Applied Science Publishers, pp. 95–118.
- Leinweber P., Schulten H.-R., Kalbitz K., Meissen R., Jancke H. (2001) Fulvic acid composition in degraded fenlands. J. Plant Nutr. Soil Sci., 164, 371–379.
- Letey J., Carrillo M. L. K., Pang X. P. (2000) Approaches to characterize the degree of water repellency. J. Hydrol., 231–232, 61–65.
- Lishtvan I. I., Bazin E. T., Gajunow N. I., Terentiew A. A. (1989) Physics and chemistry of peat. Moscow: Nedra.
- Lüttig G. (1986) Plants to peat. In: Peat and water. Aspects of water retention and dewatering in peat. Fuchsman C. H. (Ed.) London: Elsevier Applied Science Publishers, pp. 9–19.
- Ma'shum M., Farmer V. C. (1985) Origin and assessment of water repellency of a sandy South Australian soil. *Aust. J. Soil Res.*, 23, 623–626.
- Maciak F., Liwski S. (1996) *Practical guidelines for peatlands*. Warsaw Agricultural University Press, 6th ed., 159 p. (in Polish)
- Malterer T. J., Verry E. S., Erjaves J. (1992) Fiber content and degree of decomposition in peats: review of natural methods. *Soil Sci. Soc. Am. J.*, 56, 1200–1211.
- Marscher B., Bredov A. (2002) Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilized and biologically active soil samples. *Soil Biol. Biochem.*, 34, 459–466.
- Maryganova V. (2000) Impact of various genesis on chemical structure of peat humic substances. In: Sustaining our peatlands. Rochefort L., Daigle J.-Y. (Eds.) Proceedings of the 11th Inter. Peat Congress, Quebec, Vol. II, pp. 618–626.
- Maryganova V., Szajdak L. (1999) Fluorescence spectra of peat humic and fulvic acids. *Roczniki Akademii Rolniczej w Poznaniu*. CCCX, Melioracje i Inżynieria Środowiska, Cz. I, 355–366.

- Maryganova V. V., Bambalov N., Szajdak L., Parmon S. V. (2005) Fractionation of sapropel humic acids by hydrophobic interaction chromatography. *Prirodopolzovanie*, 11, 199–202 (in Russian).
- Maryganova V. V., Szajdak L., Tychinskaya L. Y. (2007) Fractionation of alkali-soluble peat organic matter by method of adsorption chromatography on hydrophobic resins. *Prirodopolzovanie*, 13, 170–176 (in Russian).
- McCarthy P., Clapp C. E., Malcolm R. L., Bloom P. R. (1990) *Humic substances in soil and crop sciences: selected readings.* Madison: American Society of Agronomy, 281. p.
- McDonnel R., Holden N. M., Ward S. M., Collins J. F., Farrel E. P., Hayes M. H. B. (2001) Characteristics of humic substances in peatland and forested peat soils of the Wicklow Mountains. *Biol. Environ.*, 101B, 187–197.
- Michel J. C., Riviere L. M., Bellon-Fontaine M. N. (2001) Measurement of the wettability of organic materials in relation to water content by the capillary rise method. *Europ. J. Soil* Sci., 52, 459–467.
- Okruszko H. (1993) Transformation of fen-peat soils under the impact of draining. Zesz. Prob. Post. Nauk Rol., 406, 3–73.
- Orlov D. S. (1985) *Humus Acids of Soils*. Rotterdam: A. A. Balkema.
- Poulenard J., Michel J. C., Bartoli F., Portal J. M., Podwojewski P. (2004) Water repellency of volcanic ash soils from Ecuadorian paramo: effect of water content and characteristics of hydrophobic organic matter. *Eur. J. Soil Sci.*, 55, 487–496.
- Puget P., Angers D. A., Chenu C. (1999) Nature of carbohydrates associated with waterstable aggregates of two cultivated soils. *Soil Biol. Biochem.*, 31, 55–63.
- Quideau S. A., Chadwick A., Benesi A., Graham P. C., Anderson M. A. (2001) A direct link between forest vegetation type and soil organic matter composition. *Geoderma*, 104, 41–60.
- Ritsema C. J., Dekker L. W., Hendrickx J. M. H., Hamminga W. (1993) Preferential flow mechanism in a water repellent sandy soil. *Water Resour. Res.*, 29, 2183–2193.
- Schnitzer M. (1986) Water retention by humic substances. In: *Peat and Water. Aspects of Water Retention and Dewatering in Peat.* Fuchsman C. H. (Ed.) Elsevier Applied Science Publishers Ltd., pp. 159–176.
- Schnitzer M., Khan S. U. (1978) Soil organic matter. Amsterdam: Elsevier.
- Smolander A., Kitunen V. (2002) Soil microbial activity and characteristics of dissolved organic C and N in relation to tree species. *Soil Biol. Biochem.*, 34, 651–660.
- Sokołowska Z., Szajdak L., Matyka-Sarzyńska D. (2005) Impact of the degree of secondary transformation on acid-base properties of organic compounds in mucks. *Geoderma*. 127, 80–90.
- Sposito G. (1989) The chemistry of soil. New York: Oxford University Press, pp. 24–98.
- Stevenson F. J. (1994) Humic chemistry, composition, reactions. New York: John Wiley & Sons, pp. 20–88.
- Swift R. S. (1996) Organic matter characterization. In: *Methods of Soil Analysis*. Part 3. Chemical Methods – SSSA Book Series No. 5. Madison, WI, pp. 1011–1069.

- Szajdak L. (2002) Chemical properties of peat. In: *Peat and Peatlands*. Ilnicki P. (Ed.) Poznań: Wydawnictwo Akademii Rolniczej im. A. Cieszkowskiego, pp. 432–450 (in Polish).
- Szatyłowicz J. (2004) The influence of peat-moorsh moisture content on water repellency. In: *Wise Use of Peatland*. Paivanen J. (Ed.) Proceedings of the 12th Inter. Peat Congress, 6–11 June 2004, Tampere: International Peat Society, 2, 1156–1161.
- Van Dijk H. (1971) Colloid chemical properties of humic matter. In: *Soil Biochemistry*. McLaren A. D., Skujins J. (Eds.) New York: Marcel Dekker, 21.
- Watson C. J., Letey J. (1970) Indices for characterizing soil water repellency based upon contact angle-surface tension relationships. *Soil Sci. Soc. Am. Proc.*, 34, 841–844.
- Woche S. K., Goebel M.-O., Kirkham M. B., Horton R., van der Ploeg R. R., Bachmann J. (2005) Contact angle of soils as affected by depth, texture, and land management. *Europ. J. Soil. Sci.*, 56, 239–251
- Yates L. M., von Wandruszka R. (1999) Effect of pH and metals on the surface tension of aqueous materials. *Soil Sci. Soc. Am. J.*, 63, 1645–1649.