Impact of Secondary Transformation of Peat-Moorsh Soils on the Process of Purification of Ground Water

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4.5 km-long transect of peatland located on secondary transformed organic soils (peatmoorsh soils) has been subjected to the purification of ground water. Such an element of landscape can be found in the Agroecological Landscape Park in Turew, 40 km south-west of Poznań, West Polish Lowland, along the Wyskoć ditch. pH, the contents of total and dissolved organic carbon (TOC and DOC), total nitrogen, N-NO3-, N-NH4+, and C/N ratios of peat from the peatland were determined. Dissolved total carbon and dissolved organic carbon were also measured in the water from the Wyskoć ditch and in the ground water. The investigation has shown the impact of the peatland located on secondary transformed peat-moorsh soils on the amount of total nitrogen, ammonium, nitrates, and dissolved organic carbon in ground water. Peatland efficiently decreases the concentration of the following compounds in ground water: nitrates - by 38.5%, N-organic - by 10%, N-total - by 24.5%, ammonium - by 38.7%, dissolved total carbon - by 33.1%, dissolved total inorganic carbon - by 10%, and dissolved organic carbon - by 57.5%. Additionally, a kinetic modeling study on the release of organic matter from secondary transformed peat soils was performed. It showed that the lowest values of TOC and DOC in peat from Zbechy were in agreement with the highest values of pseudo first-order reaction rate constants and the lowest values of half-time of organic matter release from peat. The highest values of TOC and DOC in peat from Mostek were connected with the lowest values of pseudo first-order reaction rate constants and the highest values of half-time of organic matter release.

Keywords: forms of organic carbon, secondary transformation of peat, $\rm N_{total},~\rm N-NO_3^-,~\rm N-NH_4^+.$

INTRODUCTION

Recent interest in utilizing land as a terminal place for waste disposal has focused on the potential non-point source contributions from such land application sites. Waste of animal, municipal, industrial, or agricultural origin are applied with an objective of either supplying plant nutrients to the growing crop at recommended rates or at higher rates for disposal purposes. Contamination of water by non-point source inputs is not a recent phenomenon, but the effects have been more marked due to more regulations and public and research awareness of this source of pollution. More recently, the impact of nitrogen, phosphorus, oxygen demand, microbial species, and other materials of non-point source pollution has drawn more attention than before. That coincides with the success in reducing point source inputs into receiving waters, resulting in greater evaluation and control of non-point sources. The control of non-point sources requires additional information on the phenomena.

Natural, compatible structures which are partly in control of matter cycles in an agricultural landscape are of great importance for the enhancement of a countryside resistant to degradation. Various plant cover types like peatlands, grasslands, stretches of meadows, hedges, shelterbelts, riparian vegetation strips are of special interest. However, the most important fact is that biogeochemical barriers decrease non-point pollution. Peatlands belong to a group of stable elements in the landscape which regulate water regime in soils, restrain soil erosion, improve the microclimate for agricultural production, and create refuge sites for wildlife. Peatlands show substantial ability to limit the spread of chemical elements among the ecosystems in an agricultural landscape (Fuchsman, 1986; Ilnicki, 2002; Szajdak, 2002). Mechanisms responsible for these processes are still elusive, but plant uptake and ion exchange capacities are generally assumed to be important. A better understanding of the impact of low moor peatland on the decrease of chemical compounds in ground water should permit us to find ways to improve the quality of ground water.

Peatland nitrogen, sulfur, phosphorus, and carbon cycles are controlled by the sharp gradient in dissolved oxygen concentration (Howard-Williams and Downes, 1993; Sokołowska et al., 2005). Nitrate, ammonium, and phosphate pollution caused by the usage of inorganic fertilizers creates a great threat to rural areas and leads to eutrophication of ground water. A number of physical, chemical, biochemical, and biological processes, which depend on the organic matter content and particularly on humic substances, control the dispersion of these chemical compounds in soils (Howard-Williams and Downes, 1993; Szajdak et al., 2002; Szajdak et al., 2003; Życzyńska-Bałoniak et al., 2005). Therefore, organic matter plays a pivotal role in several processes, conversions, and mechanisms in peatlands, including detoxication of anthropogenic chemicals, carbon sequestration, water retention, nutrient cycling, formation of soil structure, and energy supply to soil microorganisms (Belkevitch, 1962; Okruszko and Kozakiewicz, 1973). Humus in organic soils is affected by a great number of biological and chemical transformation mechanisms, including microbial processes and phytochemical degradation reactions, decomposition and loss of organic matter through biomineralization in the surface layer (Zeitz and Velty, 2002). Humics of different origins can differ significantly with respect to elemental composition, molecular weight, chemical structure, etc. These substances represent a class of biogenic, heterogeneous, and refractory organic compounds (Kondo, 1976; Hatcher et al., 1986; Lishtvan et al., 1989).

The goal of this study was to investigate the influence of peatland located in agricultural landscape on the transformation of inorganic and organic forms of nitrogen in soil, water of the ditch, and ground water in order to understand the role of peat as a biogeochemical barrier.

Additionally, the results obtained in the experiments should give a better insight into the changes in organic matter of secondary transformed peat-moorsh soils, water of the ditch, and ground water of peatland.

MATERIALS AND METHODS

The research site was a transect of a 4.5 km-long peatland located in the Agroecological Landscape Park in Turew (40 kilometers south-west of Poznań, West Polish Lowland) (Fig. 1, Table 1, 2).



Figure 1. The map of the investigated peatland

Peat-moorsh soils were described and classified according to the Polish Hydrogenic Soil Classification (Okruszko, 1976; Systematyka Gleb Polski, 1989) and World Reference Base Soil Notation (WRB, 1998). The investigated points were located along the Wyskoć ditch. Twice a month, during the vegetation season, the following material was obtained from four chosen sites marked as Zbechy, Mostek, Shelterbelt, and Hirudo (Tables 1–3):

- (i) samples of peat from the depth of 0-20 cm,
- (ii) samples of water from the ditch,
- (iii) samples of ground water from wells created especially for this investigation.

Table 1. Plant associations of the investigated places

Place of sampling	Plant associations
Zbęchy	Carex aculiformis, Phalaris arundinacea, Taraxacum officinale, Ranunculus repens, Polygonum amphibium, Holcus lanatus, Achillea millefolium, Galium mollugo, Cirsium arvense, Plantago lanceolata, Glechoma hederacea, Trifolium repens, Acorus calamus, Trifolium hybridum, Plantago major, Rumex crispus, Cerastium holosteoides, Mentha aquatica, Lythrumsalicaria, Lycopus europaeus, Bidens frondosa, Urtica dioica, Potentilla reptans, Phleum pretense, Lathyrus palustris, Conyza canadensis, Sonchus asper, Stachys palustris, Galium palustre, Epilobium hirsutum, Matricaria maritima, Galium uliginosum, Phragmites australis, Acorus calamus, Iris pseudoacorus, Lemna minor, Alnus glutinosa
Mostek	Cirsium oleraceum, Arrhenatherum elatior, Holcu lanatus, Rumex crispus, Carex gracilis, Deschampsia caespitosa, Lythrum salicaria, Achillea millefolia, Cirsium arvense, Ranunculus repens, Heracleum sphondyllum, Galium mollugo, Leucanthemum vulgare, Trifolium repens, Rumex acetosa, Plantago lanceolata, Glechoma hederaracea, Serratula tinctoria, Phragmites australis, Trifolium pretense, Lolium multiflorum, Urtica dioica, Carex acutifornis, Epilobium hirsutum, Plantago major, Agrostis canina, Lysimachia vulgaris, Taraxacum officinale, Rumex hydrolapathum, Solanum dulcamara, Salix alba, Salix cinerea, Typha angustifolia, Phragmites australis, Hydrocharis morsus-ranae, Lemna trisulca, Cerathophyllum demersum
Shelterbelt	Deschampsia caespitosa, Carem gracilis, Eupatorium cannabinum, Poa pratensis, Poa trivialis, Mentha aquatica, Plantago lanceolata, Achillea millefolium, Ranunculus repens, Cirsium oleraceum, Calystegia sepium, Holcus lanatus, Centaurea jacea, Taraxacum officinale, Galium album, Galium uliginosum, Cardaminopsis arenosa, Cerastium holosteoides, Phleum pratense, Daucus carota, Plantago major, Sonchus arvensis, Hypericum tetrapterum, Potentilla anserine, Lysimachia vulgaris, Dactylis glomerata, Cirsium arvense, Molinia caerulea, Solanum dulcamara, Festuca arundinacea, Rubus plicatus, Lycopus europaeus, Agrostis canina, Carex hirta, Betula pendula, Frangula alnus, Rhamnus catharticus, Salix cinerea, Viburnum opulus, Nymphaea alba, Sparganium ramosum, Typha latifolia
Hirudo	Plantago lanceolata, Achillea millefolium, Plantago major, Lolium multiflorum, Deschampsia casespitosa, Holcus lanatus, Phleum pratense, Ranunculus repens, Trifolium repens, Trifolium pratense, Rumex obtusifolius, Cerastium holosteoides, Galium mollugo, Stellaria media, Glechoma hederacea, Heracleum sphondylium, Echinochloa crus-gali, Rorippa palustris, Angelica silvestris, Polygonum persicaria, Filipendula ulmaria, Rumex acetosa, Lythrum salicaria, Mentha verticillata, Bellis perennis, Centaurea jacea, Eupatorium cannabinum, Dactylis glomerata, Sonchus arvensis, Vicia cracca, Polygonum amphibium, Caltha palustris, Lysimachia vulgaris, Lycopus europaeus, Humulus lupulus, Frangula alnus, Alnus glutinosa

1	2	3	4	5	6	7	8	9	10	11
Place of sampling	Properties of peat- moorsh soil	Stage of soil moorshi- fication, degree of de- composition	Type of moorsh forma- tion	pH in 1 M KCl	TOC, %	DOC, %	N-total, %	TOC/N	HA E ₄ /E ₆	Oscillation of ground water, cm
Zbęchy	Wooden-sedge moorsh soil with peat, weakly moorshified – MtI, deep soil developed with low <i>Carex-Phragmiteti</i> strongly decomposed (sapric) peat, 10 YR 2/1 black, amorphic- fibrous structure. The upper peat horizon has thin 1–2 mm mineral layers. Peaty muck horizon with subangular blocky structure with low fiber content. Moorsh horizon Mt 0–10 cm depth. Polish Hydrogenic Soil Classification (Okruszko, 1976): MtIcc. World Reference Base (WRB, 1998) Soil Notation: Sapri- Eutric Histosols.	MtIcc 0–20 cm, R3	Z_1	6.22- 6.97	22.54 16.73– 32.12	0.37 0.22– 0.51	2.01 <i>1.64–</i> <i>2.62</i>	12.33 8.81– 19.57	7.12	69– 109
Mostek	Alder, moorsh soil with peat, averagely moorshified – MtII, deep soil developed with low strongly decomposed (sapric) wood peat, 10 YR 2/1 black, angular blocky structure. Humic muck horizon with subangular blocky microstructure. Very strongly developed M1 moorsh sod subhorizon and subangular blocky M2 muck undersod subhorizon. Moorsh horizon Mt 0–20 cm depth. Polish Hydrogenic Soil Classification (Okruszko, 1976): MtIIcc. World Reference Base (WRB, 1998) Soil Notation: Sapri- Eutric Histosols.	MtIIcc 0–20 cm R3	Z ₂	6.00- 6.46	33.25 <i>30.18–</i> <i>36.37</i>	0.43 0.31- 0.49	2.14 <i>1.54–</i> <i>2.82</i>	16.25 <i>12.88–</i> <i>21.35</i>	6.19	68– 119

Table 2. Some properties of peat-moorsh soil

1	2	3	4	5	6	7	8	9	10	11
Shelterbelt	Sedge-rushes, moorsh soil with peat, strongly moorshified – MtIII, deep soil developed with low <i>Carex</i> wood decomposed (sapric) peat, 10 YR 3/1 very dark gray, angular-fibrous blocky structure. Moorsh horizon strongly dried, subangular blocky microstructure. Well- developed subhorizons M1, M2. Degraded moorsh M3 subhorizon has an easily identifiable structure. Moorsh horizon Mt 0–32 cm depth. Polish Hydrogenic Soil Classification (Okruszko, 1976): MtIIIcc. World Reference Base (WRB, 1998) Soil Notation: Sapri-Eutric Histosols.	MtIIIcc 0–20 cm R3	Z ₂ Z ₃	7.05– 7.56	30.23 27.53– 33.23	0.49 0.42– 0.56	2.01 <i>1.55–</i> <i>2.62</i>	14.37 9.70– 20.32	7.02	51- 111
Hirudo	Alder, moorsh soil with peat, averagely moorshified – MtII, deep soil developed with low wood decomposed (sapric) peat, 10 YR 2/2 very dark brown, angular blocky structure. Moorsh horizon strongly dried, subangular blocky macro- and microstructure. Well- developed sod and undersod subhorizons M1 and M2. Moorsh horizon Mt 0–20 cm depth. Polish Hydrogenic Soil Classification (Okruszko, 1976): MtIIcc. World Reference Base (WRB, 1998) Soil Notation: Sapri-Eutric Histosols.	MtIIcc 0–20 cm R3	Z ₂	5.82– 6.41	26.4 7 <i>14.67–</i> <i>35.9</i>	0.40 0.33– 0.48	2.19 <i>1.55–</i> <i>2.54</i>	11.92 6.58– 14.14	6.64	90– 148

Mt – stage of soil moorshification, MtI – weakly moorshified, MtII – averagely moorshified, MtIII – strongly moorshified; a – according to classification WRB 1998-Sapri-Eutric Histosols, Z_1 – grain moorsh, Z_2 – peaty moorsh, Z_3 – humic moorsh, bold – mean, italic – range, E_4/E_6 – ratio of absorbances measured at 464 nm (E_4) and at 665 nm (E_6) of HA

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Place of sampling	pH in 1 N KCl	N-NO ₃ , mg/l	N-total, mg/l	N-NH _{4,} , mg/l	N-org, Mg/l	DTC, mg/l	DOC, mg/l		
Wyskoć ditch									
Zbęchy	7.11–7.47	0.83 0.13–2.41	6.99 1.12–12.88	1.80 0.84-2.80	5.19 0.28–10.08	51.82 <i>44.71–71.1</i>	16.34 11.31–19.71		
Mostek	7.19–7.70	0.51 0.19–1.04	4.82 1.12–9.52	2.28 1.12–3.36	2.54 0.00-7.84	53.1 7 <i>46.25–65.0</i>	17.17 14.89–19.85		
Shelterbelt	7.21–7.72	0.41 <i>0.16–1.24</i>	7 .19 1.68–16.24	2.44 1.12–3.92	4.75 0.56–14.00	66.86 46.25–65.0	20. 44 <i>15.73–24.73</i>		
Hirudo	7.11–7.80	0.56 0.14–1.87	5.60 1.96–10.64	2.28 1.68–2.80	3.32 0.28-8.40	58.50 45.94–81.86	15.48 <i>12.76–18.21</i>		
Ground wate	Ground water								
Zbęchy	6.51-7.06	0.52 0.50-0.55	11.39 8.40–14.56	5.76 5.60–5.88	5.60 2.80-8.68	169. 73 <i>159.00–183.50</i>	82.75 <i>81.25–84.59</i>		
Mostek	6.78-7.52	0.44 0.30–0.63	11.01 8.96–13.44	6.25 5.88–6.16	4.76 3.08–6.72	178.43 171.00–189.50	64.90 <i>60.70–68.50</i>		
Shelterbelt	6.40-7.46	0.46 0.35-0.64	10.08 8.96–11.76	3. 74 <i>3.36–4.48</i>	7 .34 4.48–11.37	137.47 135.70–139.70	32.9 7 31.00–36.00		
Hirudo	6.98-7.44	0.32 0.25-0.35	8.59 7.00–10.08	3.55 1.68–7.28	5.04 2.80-7.00	113.53 108.10–121.90	35.1 7 <i>30.14–38.09</i>		

Table 3. Contents of chemical compounds in the water from the Wyskoć ditch and ground water

DTC – dissolved total carbon, DOC – dissolved organic carbon, bold – mean, italic – range.

Samples of peat-moorsh soils were collected at the depth of 0-20 cm. Analyses of pH, total nitrogen, total organic carbon (TOC), dissolved organic carbon (DOC) were performed (Table 3).

Soils were sampled from 10 places at one site. Briefly, samples were air-dried and crushed to go through a 1 mm mesh sieve. These 10 sub-samples were mixed and a "mean sample" was comprised, which was used for the determination of pH (in 1 N KCl), dissolved organic carbon (DOC), total organic carbon (TOC), total nitrogen (N_{total}) , and N-NO₃⁻, as well as N-NH₄⁺.

pH, N_{total}, N-NO₃, N-NH₄⁺, DTC, and DOC were also measured in the water from the Wiskoć ditch. Twice-distilled water in silica glass equipment was used. For the investigation of DOC, soil samples were heated in redistilled water in 100 °C for two hours under reflux condenser. Extracts were separated by means of filter paper and analyzed on TOC 5050A facilities (Shimadzu, Japan) (Smolander and Kitunen, 2002). N_{total} was measured with the semimicro-Kjeldahl methods, ammonium and nitrate ions with the Sprurwaya method (Rowell, 1994; Szajdak and Matuszewska, 2000).

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

Satisfactory precision based on replicate analyses was \pm 0.01 for pH measurements, \pm 3.5% for TOC, \pm 3.4% for DOC, \pm 4.3% for N_{total}, \pm 3% for N-NO₃⁻, \pm 3% for N-NH₄⁺.

All the experiments were repeated 5 times, and the results averaged. All the chemicals used in this study were of analytical grade. A summary of the soil characteristics is presented in Table 2.

Kinetic Studies

7 grams of peat were filled to the fixed level equaled to 50 ml into a glass column (ID = 1 cm). Water as the mobile phase was pumped at the rate of 2 cm³ × min⁻¹ and developed a pressure of 2.5 MPa. Samples of 5 ml were collected at suitable time intervals. Absorbances of these samples were monitored at four wavelengths: $\lambda = 272$ nm, $\lambda = 320$ nm, $\lambda = 465$ nm, and $\lambda = 665$ nm. BECKMAN DU[®]-68 spectrophotometer with 1 cm thick layer was used for spectrometric measurements. Ostwald's equation was applied for the calculation of the reaction order of organic matter release. All kinetic experiments were performed trice, and the results averaged.

RESULTS AND DISCUSSION

Peatlands are areas which share ecosystem properties with both terrestrial and aquatic systems. Aquifers are vulnerable to contamination by agricultural, residential, and industrial pollutants. Sources of ground water contamination are numerous and include, among many others, agricultural activities, accidental spills, landfills, storage tanks and pipelines. Agriculture-related activities are well-known for causing non-point source pollution in small to large watersheds especially due to fertilizers and various substances found in pesticides (Reddy, 1980).

The investigated peatland represents a different kind of peat-moorsh soils (Table 2). Our earlier investigations have shown that organic soils of the transect represent a different stage of moorshification (Szajdak and Szczepański, 2006). Zbęchy sampling site located in the border area of the peatland is characterized by weakly moorshified soil. The farther the soils are located from the border area the more they are moorshified. The most moorshified is the soil of Shelterbelt

with peaty and humic moorsh. All the soils exhibit slightly acidic (No. 2 and 4) to neutral properties (No. 1 and 3). In peat moorsh soils the pH values ranged from 5.82 to 7.56 (Table 3) (Szajdak, 2002). The highest pH was recorded in peat from Shelterbelt, the lowest in Hirudo.

Dissolved organic matter may contribute significantly to the cycling of soil nutrients. It can play the role of a substrate for microbial growth, but its production is also partly mediated by microbes. This fraction is responsible for microbiological activity (Qualls and Haines, 1991; Puget et al., 1999; Smolander and Kitunen, 2002). The influence of water content and moist conditions on the behavior of soil organic matter was noted by several authors (Lyon and Rhodes, 1993; Altfelder et al., 1999). Gödde et al. (1996) reported an impact of moistening intervals on the release of carbon from the organic layer. Some authors have suggested that soil organic matter and dissolved organic matter should be described by their colloidal and gel properties which are caused by their interaction with water (Pignatello, 1989; Benedetti et al., 1996).

Swelling and shrinking, a high water uptake capacity, and hysteresis during water uptake and release are typical gel properties, which can also be found in soil organic matter. It is possible that diffusion in a gel phase is slower than in the liquid phase. Thus, many reactions in which soil organic matter participates should be diffusion-controlled, with control taking place in the gel phase. Electrolyte and moisture conditions are expected to influence the rigidity of the gel phase (Voyutsky, 1978). The data published by Voyutsky indicate that diffusion in the gel phase influences the rate of dissolution of soil organic matter.

The concentrations of TOC ranged from 14.67% to 36.37% in peat-moorsh soils. The highest yearly mean content of TOC was determined in Mostek and equaled 33.25%, while the lowest, 22.54%, was recorded in Zbęchy. The concentration of DOC ranged from 0.22 to 0.56%. The lowest yearly mean content of DOC was recorded in Zbęchy and equaled 0.37%. The highest concentration of DOC was determined in Shelterbelt and equaled 0.49%.

The yearly mean content of N_{total} ranged from 2.0l to 2.19%. The highest content of N_{total} was recorded in Hirudo and was connected to the high concentration of TOC. The ratios of TOC/ N_{total} ranged from 11.92 to 16.25. The highest ratio of TOC/ N_{total} was associated with the highest content of TOC and with high concentration of DOC and N_{total} . The increase of TOC/ N_{total} ratios was connected to the degree of distribution of the secondary transformed peat-moorsh soils (Szajdak and Szczepański, 2006).

The values of pH ranged from 7.11 to 7.80 in the water from the Wyskoć ditch (Table 4). Low pH was recorded in Zbęchy and high pH in Shelterbelt and Hirudo. The farther the soils were located from the border area of the peatland, the higher the value of pH was. The content of N-NO₃⁻ ranged from 0.14 to 1.87 mg/l. The highest yearly mean content of N-NO₃⁻ equaled 0.83 mg/l and

was recorded in Zbęchy in the border area of the peatland. The farther the soils were located from the border area of the peatland, the lower the concentration of nitrates was. The decrease of the concentration of nitrates starting with the border area of peatland equaled 32.5%. The content of N_{total} ranged from 1.12 to 16.24 mg/l in the water from the Wyskoć ditch. The lowest yearly mean content of N_{total} was recorded in the water from Mostek (4.82 mg/l) and the highest was estimated in Shelterbelt (7.19 mg/l). The concentrations of N-NH₄⁺ ranged from 0.84 to 3.92 mg/l. The highest concentration of N-NH₄⁺ was determined in Shelterbelt and the lowest in Zbęchy. The highest N_{org} quantities in the water from the Wyskoć ditch equaled 5.19 mg/l at the beginning of the transect. The farther the soils were located from the border area of the peatland, the lower the content of N_{org} was. The decrease of N_{org} equaled 36% throughout the entire transect. Organic substances – humic and fulvic acids and dissolved organic compounds – were included in these measurements. Their chemical structures are well-known (Kondo, 1976; Hatcher et al., 1986; Bambalov et al., 2000).

The contents of DTC determined in the water from the Wyskoć ditch ranged from 44.71 to 81.86 mg/l and DOC from 11.31 to 24.73 mg/l. The concentration changes of DTC and DOC in the water from the Wiskoc ditch correlate to each other. The highest concentrations of DTC and DOC were noted in Shelterbelt and equaled 66.86 mg/l and 20.44 mg/l, respectively.

pH values of ground water from the wells created especially for this investigation ranged from 6.40 to 7.52 (Table 5). High values of pH were recorded in Hirudo and low in Zbęchy. The farther the soils were located from the border area of the peatland, the lower the content of N-NO₃⁻ was. The highest yearly mean content of N-NO₃⁻ was recorded at the beginning of the transect (0.52 mg/l) and the lowest was determined in Hirudo, which is located at the end of the transect (0.32 mg/l). The decrease in N-NO₃⁻ in the transect of the peatland equaled 38.5%.

The changes of N-NH₄⁺ concentrations were similar to those of N-NO₃⁻. The farther the soils were located from the border area of the peatland, the lower the content of N-NH₄⁺ was. The decrease in N-NH₄⁺ equaled 38.5% throughout the entire peatland.

In addition, the decrease in the concentration of N_{total} was noted. The highest content of N_{total} was determined in Zbęchy and equaled 11.39 mg/l. The farther the soils were located from the border area of the peatland, the lower the content of N_{total} was. Throughout the 4.5 km-long peatland, the decrease in N_{total} equaled 25%.

The farther the soils were located from the border area of the peatland, the lower the content of N_{org} was. The decrease in organic compounds containing nitrogen equaled 10%.

In addition, the content of the two forms of carbon decreased with the increase of the length of the transect. These forms are present in organic compounds, which may be bioavailable for plants and microorganisms. During the entire vegetation season, TOC concentration ranged from 108.1 to 189.5 mg/l. The yearly mean content of TOC was the highest in Zbęchy and the lowest in Hirudo and amounted to 169.73 mg/l and 113.53 mg/l, respectively. The decrease in the TOC amounted to 33.1%. The TOC concentrations increased approaching the peatland.

Ultimately, similar changes as in TOC were noted in DOC in the ground water from the wells dug for the investigation. The highest content of DOC was recorded at the beginning of the transect and equaled 82.75 mg/l. The results show that the lowest content of DOC was determined in ground water sampled from Hirudo and equaled 113.53 mg/l. The decrease of DOC equaled 57.5%. The farther from the peatland, the lower the amount of DOC was.

Several authors reported an influence of pH and electrolyte composition on the release of dissolved organic matter (Guggenberger, 1992; Guggenberger and Kaiser, 1998; Marschner, 1999). The influence of dissolved salts on the release of dissolved organic matter was proved by Reemtsma et al. (1999). It was also proved that the process of mineralization was more pronounced in fens than in raised bogs (Zeitz and Velty, 2002). This process affects leaching of dissolved organic matter and phosphate (Leinweber et al., 2001). Kalbitz et al. (1999) also reported that peatland management practices have an impact on the dissolved organic matter because the soil in the fen area is used differently. The study determined that land use affected fulvic acids which accounted for the major part of dissolved organic matter (Kalbitz et al., 2000a). Several investigations have provided evidence for the link between microbial activities and dissolved organic matter production either building on the relationship between microbial respiration and release of dissolved organic matter, or comparing the amount of dissolved organic matter produced as a result of the activity of selected microbial species (Brooks et al., 1999; Møller et al., 1999; Kalbitz et al., 2000b).

On the basis of the results obtained with different forms of nitrogen and carbon in ground water, it was discovered that secondary transformed peat soils influence the release of organic matter into ground water. Kinetic modeling studies of organic matter release from peat were performed. The absorbances of organic matter release were characterized by an exponential equation (1) as a function of time (Figure 2).

$$A = A_0 e^{-kt} \tag{1}$$

Its transformations lead to linear relationship in agreement with the firstorder reaction model (2) (Figure 3) (Frost and Pearson, 1961; Lasaga et al., 1981; Connors, 1990):

$$\ln A = \ln A_o - kt \,, \tag{2}$$

where A is the value of absorbance, A_0 – absorbance at the time 0, k – pseudo first-order reaction rate constant, t – time.



Figure 2. Typical changes of absorbance at $\lambda = 272$ nm of organic mater released from Zbęchy in accordance with the eq. (1)



Figure 3. Semilogarithmic plots $\ln A = \ln A_0 - kt$ for first-order reaction of organic matter release from Zbęchy, Mostek, Shelterbelt, and Hirudo measured at $\lambda = 272$ nm in accordance with eq. (2)

The absorbances of organic matter release were measured at four wavelengths as a function of time in accordance with the equation (1), and their graphical illustration revealed a linear curve. On the basis of the results obtained with the equation (2), the correlation coefficients ranged from -0.897 to -0.989. However, they yield linear relationships according to equation (1) (Table 4). Thus, the slopes of the equation describe the rates of the release process. It appeared that the rates of organic matter elution in all samples of peat significantly differed depending on the wavelengths: $\lambda = 272$ nm, $\lambda = 320$ nm, $\lambda = 465$ nm, and $\lambda = 665$ nm. It was observed that the rates increased at wavelengths between $\lambda = 272$ nm and $\lambda = 320$ nm and decreased at wavelengths between $\lambda = 465$ nm and $\lambda = 665$ nm. The lowest values of the pseudo first-order rate constants measured at $\lambda = 665$ nm in all samples of peat ranged from 1.9524 10⁻⁴ s⁻¹ to 2.7361 10⁻⁴ s⁻¹. The highest values of t_{0.5} ranged from 42.2 to 59.2 min in all samples from Zbęchy, Shelterbelt, Mostek, and Hirudo (Table 4).

Table 4. Pseudo first-order reaction rate constants (k x 10^{-4} s⁻¹), half-times (t_{0.5}, min),and correlation coefficients (r) for the reaction of the release of organic matterfrom peat

Wavelength,	Place of sampling								
nm	Zbęchy	Mostek	Shelterbelt	Hirudo					
$\lambda = 272$	k = 2.8549	k = 2.6534	k = 2.6832	k = 2.7641					
	$t_{0.5} = 40.5$	$t_{0.5} = 43.5$	$t_{0.5} = 43.1$	$t_{0.5} = 41.8$					
	r = -0.989	r = -0.986	r = -0.967	r = -0.986					
$\lambda = 320$	k = 2.8855	k = 2.7339	k = 2.6394	k = 2.8976					
	$t_{0.5} = 40.0$	$t_{0.5} = 42.3$	$t_{0.5} = 43.8$	$t_{0.5} = 39.9$					
	r = -0.987	r = -0.971	r = -0.969	r = -0.975					
$\lambda = 465$	k = 2.9089	k = 2.4593	k = 2.3045	k = 2.7526					
	$t_{0.5} = 39.7$	$t_{0.5} = 47.0$	$t_{0.5} = 44.4$	$t_{0.5} = 42.0$					
	r = -0.989	r = -0.985	r = -0.986	r = -0.989					
$\lambda = 665$	k = 2.7361	k = 1.9524	k = 2.3394	k = 2.2492					
	$t_{0.5} = 42.2$	$t_{0.5} = 59.2$	$t_{0.5} = 49.4$	$t_{0.5} = 51.4$					
	r = -0.944	r = -0.925	r = -0.897	r = -0.920					

HA – humic acids, k – first-order reaction rate constant, $t_{0.5}$ – half-time

A correlation between the values of the pseudo first-order constant and E_4/E_6 values was found (Table 4). The highest values of E_4/E_6 in peat from Zbęchy were associated with the highest pseudo first-order reaction rate constants. High value of E_4/E_6 reflects a lower degree of condensation and polyconjugation in the molecules of HA from Zbęchy than from other places (Orlov, 1990; Kumada, 1987). A linear relationship between $t_{0.5}$ and wavelengths of peat from four investigated sites was revealed (Figure 4). Peat representing higher values of E_4/E_6 and lower degrees of condensation and polyconjugation in the molecules of HA showed lower slopes (0.0046 and 0.0176). However, peat with lower

values of E_4/E_6 was characterized by higher slopes, 0.263 and 0.0420, respectively. Therefore, we can point out that the different mechanisms of the pathways of organic matter release were related to the values of E_4/E_6 (Figure 4).



Figure 4. Correlation of $t_{0.5}$ and the wavelengths, E_4/E_6 – ratio of absorbances measured at 464 nm (E_4) and at 665 nm (E_6) of HA

Kalbitz et al. (2000a, 2000b) suggested that the properties of dissolved organic matter determine its biodegradation. In turn, biodegradation changes the properties of the remaining dissolved organic matter, which may be decisive for the formation of stable organic carbon in soil. Increasing UV absorption and humification indices as well as portions of aromatic H indicated the enrichment of aromatic compounds during biodegradation. The enrichment significantly correlated with the amount of mineralized dissolved organic carbon, suggesting that aromatic compounds were relatively stable and mineralized slowly. The data published by these authors indicate that the partial degradation of higher-molecular lignin-derived dissolved organic matter compounds was accompanied by relative increases in the proportions of lower-molecular degradation products and microbial metabolites, carbohydrates, especially when some microbial production of carbohydrates and peptides during dissolved organic matter occurred. The authors concluded that biodegradation of dissolved organic matter seems to result in organic matter properties being preconditions for the formation of stable carbon. These structural changes induced by biodegradation of dissolved organic matter should also result in stronger sorption of dissolved organic matter into the soil matrix, additionally affecting stabilization of dissolved organic matter.

Well-documented solvent systems for isolation of organic components from soils were presented by Hayes (2006). The author shows the properties of organic and inorganic solvent systems, separation of organic matter components in aqueous media, and isolation of organic matter in organic solvents. The author postulates that application of combinations of aqueous and organic solvents for isolation of the components of organic matter that have special growth promotion or inhibition effects on plants could help resolve the debate regarding whether dissolved organic matter components can or cannot influence plant growth with the help of hormones or enhanced uptake of nutrients.

Our investigations revealed that peatland seems to be a very effective element of landscape for removal of dissolved organic carbon and nitrogen compounds from percolating waters when nitrogen is in the form of nitrate rather than ammonium nitrate or dissolved organic nitrate. This element of the landscape, representing the soil-plant system, has a significant function of purification of ground water.

CONCLUSIONS

Our research has revealed the impact of the peatland located on secondary transformed peat-moorsh soils on the changes of the total amount of nitrogen, ammonium, nitrates, as well as total and dissolved organic carbon in ground water. Peatland located on secondary transformed peat-moorsh soils acts as a reducer of nitrogen and carbon compounds in ground water. Peatland reduces the concentration of the following compounds in ground water: nitrates - by 38.5%, N-organic - by 10%, N-total - by 24.5%, ammonium - by 38.7%, dissolved total carbon - by 33.1%, dissolved total inorganic carbon - by 10%, and dissolved organic carbon - by 57.5%. The transformation of different forms of nitrogen and carbon in ground water is strongly related to the humification processes in peat. The lowest values of TOC and DOC in peat from Zbechy were in agreement with the highest values of pseudo first-order reaction rate constants and the lowest values of half-time of organic matter release. The highest values of TOC and DOC in peat from Mostek were connected to the lowest values of first-order reaction rate constants and the highest values of half-time of organic matter release.

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REFERENCES

- Altfelder S., Streck T., Richter J. (1999) Effect of air-drying on sorption kinetics of the herbicide chlortoluron in soil. J. Environ. Qual., 28, 1154–1161.
- 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.
- Belkevitch P. I. (1962) *Chimia i genesis torfa i sapropel* (Chemistry and Genesis of Peat and Sapropel). Publishing of the Academy of Sciences of Belarus, Minsk, pp. 3–319 (in Russian).
- Benedetti M. F., van Riemsdijk E. H., Koopal L. K. (1996) Humic substances considered as a heterogeneous Donnan gel phase. *Environ. Sci. Technol.*, 30, 1805–1813.
- Brooks P. D., McKnight D. M., Bencala F. E. (1999) The relationship between soil heterotrophic activity, soil dissolved organic carbon (DOC) leachate, and catchmentscale DOC export in headwater catchments. *Water Resour. Res.*, 35, 1895–1902.
- Chen Y., Senesi N., Schnitzer M. (1977) Information provided on humic substances by E₄/E₆ ratios. *Soil Sci. Soc. Am. J.*, 41, 352–358.
- Connors K. A. (1990) *Chemical kinetics. The study of reaction rates in solution.* VCH Publishers Inc., pp. 17–309.
- Frost A. A., Pearson R. G. (1961) Kinetics and mechanisms. A study of homogeneous chemical reactions. John Wiley & Sons Inc., pp. 8–405
- Fuchsman C. H. (1986) The peat-water problem: reflection, perspective, recommendations. In: McLaren A. D., Skujins J. (Eds.) *Soil Biochemistry* II, New York: Marcel Dekker, pp. 331–360.
- Gödde M., David M. B., Christ M. J., Kaupenjohann M., Vance G. (1996) Carbon mobilization from the forest floor under red spruce in the Northeastern U.S.A. *Soil Biol. Biochem.*, 28 (9), 1181–1189.
- Guggenberger G. (1992) Eigenschaften und Dynamik gelöster organischer Substanzen (DOM) auf unterschiedlich imissionsbelasteten Fichtenstandorten. Bayreuther Bodenkundl. Ber. 26, 164–175.
- Guggenberger G., Kaiser K. (1998) Significance of DOM in the translocation of cations and acidity in acid forest soils. Z. Pflanzenernähr. Bodenkd., 161, 95–99.
- Hatcher P. G., Spiker E., Orem W. H. (1986) Organic geochemical studies of the peat humification process in low-moor peat. In: McLaren A. D., Skujins J. (Eds.) Soil Biochemistry II. New York: Marcel Dekker, pp. 195–213.
- Hayes M. H. G. (2006) Solvent systems for the isolation of organic components from soils. Soil Sci. Soc. Am. J., 70, 986–994.
- Howard-Williams C., Downes M. T. (1993) Nitrogen cycling in wetlands. In: Burt T. P., Heathwaite A. L., Trudgi S. T. (Eds.) *Nitrate, Patterns, and Management* II, John Wiley & Sons, pp. 141–167.
- Ilnicki P. (2002) *Peatlands and Peat.* Wydawnictwo Akademii Rolniczej im A Cieszkowskiego w Poznaniu, 606 (in Polish).
- Kalbitz K., Geyer S., Geyer W. (1999) Spectroscopic properties of dissolved humic substances a reflection of land use history in a fen area. *Biogeochemistry*, 47, 219–238.

- Kalbitz K., Geyer S., Geyer W. (2000a) A comparative characterization of dissolved organic matter by means of original aqueous samples and isolated humic substances. *Chemosphere*, 40, 1305–1312.
- Kalbitz K., Solinger S., Park J. H., Michalzik E. (2000b) Controls on dynamics of dissolved organic matter in soils: a review. *Soil Sci.*, 165, 277–304.
- Kondo R. (1976) Humus composition of peat and plant remains. *Soil Sci. Plant Nutr.*, 20, 17–31.
- Kumada K. (1987) Chemistry of soil organic matter. Amsterdam: Elsevier, 241 p.
- Lasaga A. C., Berner R. A., Fisher G. W., Anderson D. E., Kirkpatrick J. R. (1981) Kinetics of geochemical processes. In: Lasaga A. C., Kirkpatrick R. J. (Eds.) *Review in Mineralogy*. Mineralogy Society of America, pp. 1–68.
- 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.
- Lishtvan I. I., Bazin E. T., Gajunow N. I., Terentiew A. A. (1989) *Fizika and chimia torfa*. Moskwa: Nedra, 304 p. (in Russian).
- Lyon W. G., Rhodes D. E. (1993) Molecular size exclusion by soil organic materials estimated from their swelling in organic solvents. *Environ. Toxicol. Chem.*, 12, 1405–1412.
- Marschner B. (1999) Sorption von polyzyklischen aromatischen Kohlenwasserstoffen (PAK) und Polychlorienten Biphenylen im Boden. *J. Plant Nutr. Soil. Sci.*, 162, 1–14.
- Møller J., Miller M., Kjøller A. (1999) Fungal-bacterial interaction on beech leaves: influence on decomposition and dissolved organic carbon quality. *Soil Biol. Bioch.*, 31, 367–374.
- Okruszko H., Kozakiewicz A. (1973) Humification and mineralization as basic elements of the moorsh forming process of peat soils. *Zesz. Probl. Post. Nauk Roln.*, 146, 63–76 (in Polish).
- Okruszko H. (1976) The principles of the identification and classification of hydrogenic soils according to the need of reclamation. *Bibl. Wiad. IMUZ*. 52, 7–53 (in Polish).
- Orlov D. S. (1990) *Humus acids of soils and general humification theory*. Lomonosov Moscow State University, 326 p. (in Russian).
- Pignatello J. J. (1989) Sorption dynamics of organic compounds in soils and sediments. Reaction and movement of organic chemicals in soils. SSSA Special Publication, 22, 46–80.
- 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.
- Qualls R. G., Haines B. L. (1991) Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. *Ecology* 72/1, 254–266.
- Reddy K. R. (1980) Land areas receiving organic wastes: transformations and transport in relation to nonpoint source pollution. In: Overcash M. R., Davidson J. M. (Eds.) *Environmental impact of nonpoint source pollution*, pp. 243–274.
- Reemtsma T., Bredov A., Gehring M. (1999) The nature and kinetics of organic matter release from soil by salt solutions. *Eur. J. Soil Sci.*, 50, 53–64.
- Rowell D. L. (1994) Soil Science: Methods and Applications. Essex, England: Addison Wesley Longman Limited, pp. 1–150.

- Smolander A., Kitunen V. (2002) Soil microbial activities 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.
- Swift R. S. (1996) Organic matter characterization. In: *Methods of Soil Analysis*, Part 3, Chemical Methods – SSSA Book Series No. 5, Madison, WI, 1011–1069.
- Systematyka Gleb Polski (1989) Rocz. Glebozn. 40/3-4, 1-150.
- Szajdak L. (2002) Chemical properties of peat. In: *Peatlands and Peat.* Ilnicki P. (Ed.) Poznań: Wydawnictwo Akademii Rolniczej im A Cieszkowskiego, pp. 432–450 (in Polish).
- Szajdak L., Matuszewska T. (2000) Reaction of woods in changes of nitrogen in two kinds of soil. *Pol. J. Soil Sci.*, 33, 9–17.
- Szajdak L., Maryganova V., Meysner T., Tychinskaja L. (2002) Effect of shelterbelt on two kinds of soils on the transformation of organic matter. *Environ. Inter.*, 28 (5), 383–392.
- Szajdak L., Życzyńska-Bałoniak I., Jaskulska R. (2003) Impact of afforestation on the limitation of the spread of the pollutions in ground water and in soils. *Pol. J. Environ. Stud.*, 12 (4), 453–459.
- Szajdak L., Szczepański M. (2006) Impact of secondary transformation on physicochemical properties of humic substances from organic soils of Dezydery Chłapowski Agroecological Landscape Park. In: Brandyk T., Szajdak L., Szatylowicz J. (Eds.) *Physic and Chemical Properties of Organic Soils*, SGGW, Warszawa, pp. 57–64 (in Polish).
- Voyutsky S. (1978) Colloid Chemistry. Moscow: MIR Publishers (in Russian).
- World Reference Base for Soil Resources. (1998) World Soil Resources Report 84, FAO: ISRIC-ISSS, Rome, pp. 1–88.
- Zeitz J., Velty S. (2002) Soil properties of drained and rewetted fen soils. *J. Plant Nutr. Soil Sci.*, 165, 618–626.
- Życzyńska-Bałoniak I., Szajdak L., Jaskulska R. (2005) Impact of biogeochemical barrier on the migration of chemical compounds with the water of agricultural landscape. *Polish J. Soil Sci.*, 14/5, 131–136.