Journal of Elementology ISSN 1644-2296

Tokarz E., Urban D., Szafranek-Nakonieczna A., Stępniewska Z. 2015. *Selected chemical and physicochemical properties of sediments in Moszne Lake and mire (Polesie National Park).* J. Elem., 20(4): 1041-1052. DOI: 10.5601/jelem.2014.19.3.767

SELECTED CHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF SEDIMENTS IN MOSZNE LAKE AND MIRE (POLESIE NATIONAL PARK)

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Abstract

Properties of peat reflect the peat-forming environment, peat development processes and the types of peat-forming plant. They also enable peat classification and quality evalution. Investigation of the physicochemical properties of organic matter is the key to understanding the history, evolution and geology of bogs. The purpose of this study was to determine some physicochemical properties, such as pH, Eh, electrolytic conductivity, carbon forms in water extracts and dry peat samples (TOC, IC, TC), degree of decomposition, macrofossil plant analysis and ash content, in a whole stratigraphic profile of bog sediment located near Lake Moszne. The research comprised a 17.5 ha lake, which was described in the 1990s as a dystrophic one, and the adjacent mires. The open water surface of the lake is surrounded by a 30–150 m wide belt of floating mat, composed of peatmosses and sedges with the dominant *Sphagno-Caricetum rostratae* association, all representing vegetation typical for transitional mires. These communities are most often found in the Polesie Lubelskie Region, in old lakes, and usually on their floating mat. The research material was collected from such a site. The analysis demonstrated acidic pH (4.17 in profile I and 4.08 in profile II, respectively) in the layer of 0-0.65 m, whilst from the 1.50 m depth to the mineral bottom the pH increased to nearly neutral (pH = 6.62 ± 0.18 in profile I and pH = 6.45 ± 0.12 in profile II). Redox potential in the surface layer corresponds to good oxygenation of mineral soils: 577 mV and 490 mV for profile I and II, respectively. A nearly linear decrease of Eh was observed to about 118 mV at the depth of 2.50 m. Lower than that, down to the depth of 3.50 m, the Eh value was stabilized. The graphical presentation of the Eh-pH relationship shows that in both cases (profiles I and II) aerobiosis prevails to the depth of 0.45-0.65 m, confirming that oxygen continues to be the final electron acceptor.

Keywords: transitional mires, Lake Moszne, pH, redox potential.

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INTRODUCTION

According to literature, the research on physicochemical properties of peat dates back to the 18th century and focuses mainly on the potential use of this material. Early publications on peat properties includes J. H. Pegener's book: Teutschlands Neuentdeckte Golg-Grube, Torf (1731), which deals with peat utilization and properties. M. V. Lomonosov in Russia discussed peat properties and values in the Earth's surface. In the 1950s and later, I.I. Lishtvan and co-authors wrote: Basic Properties of Peat and Measuring Methods, Physical and Chemical Principles of Peat Production Technology, and Physical and Chemical Properties of Peat. With the development of science, civilization and technology, peat became an object of comprehensive research e.g. balneology, extraction, drainage, land conversion for agricultural production and restoration.

Peat properties are the main indicator in the classification of peat and evaluation of its quality. They reflect the peat-forming environment, development process and the types of peat forming plants. Changes in one physicochemical property of peat implies changes in many chemical, physical and biological processes in the soil. Understanding the transformations of living organic matter in a peatland environment is the key to understanding the carbon biogeochemical cycle. Simultaneously, living organic matter transformation is a very complex research subject, considering the high variability of the environmental conditions under which living organic matter decays, and the large number of chemical and structural differences. For example, soil's redox potential depends on pH, moisture, content of organic matter, soil respiration, diffusion of O_2 and CO_2 in soil, microbial activity and on changes in the system's biochemistry (Reddy et al. 1975, Callebaut et al. 1982, Bartlett et al. 1993). As redox potentials decline, electron acceptors are generally reduced in the following order: O_2/H_2O, NO_3^-/NO_2^-, Fe^{3+}/Fe^{2+} and Mn^{4+}/Mn^{2+} (Bohrerova et al. 2004).

Numerous publications describe the geochemistry of peat and mire formation, and their capacity to accumulate organic matter (Kewei et al. 2006, Malawska 2006, Wójcikowska-Kapusta, Urban 2008). However, analysis of the physicochemical properties (mainly Eh - redox potential) pertains only to the surface layer of peat (0-0.30 m). The aim of the current study has been to investigate selected physicochemical properties of peat in a whole profile (down to the mineral substrate) in transition mires surrounding Lake Moszne (Łęczna-Włodawa Lake District). Moreover, these parameters were confronted with the botanical composition and plant macrofossils. Since there are few published descriptions of the peat deposits in the Łęczna-Włodawa Lake District, this work makes a contribution to the existing knowledge of the global diversity of peatlands.

MATERIAL AND METHODS

The research was conducted on Lake Moszne and adjacent transitional mire, located in the north-western part of Polesie National Park. The basin of this lake and the surrounding peatbog, also called Moszne, was formed on the north-facing declivity of the vast knob of Wola Wereszczyńska, built of Cretaceous rock. The declivity is the fossil slope of a WE valley filled with fluvio-glacial deposits originating from Odranian Glaciation. To the west, the lake-peatbog basin borders with NS sandy esker dating back to the same glaciation period, on which a village called Jamniki lies (Dobrowolski et al. 2009) – Figure 1.

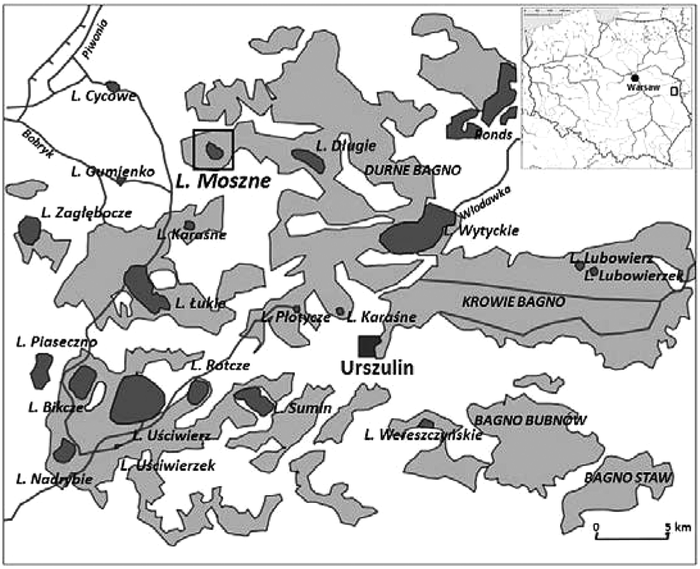

Fig. 1. Location of Lake Moszne and adjacent mires in Polesie National Park (modified after Dobrowolski et al. 2009)

Lithologic examinations were performed in transitional mires (so-called ‘floating islets’) surrounding Lake Moszne. Two bore-holes were drilled down to the mineral substrate, using an Instorf peat drill. Complete peat profiles (cores) were taken for laboratory analyses. The plant macrofossil analysis helped to identify the botanical composition of deposits. Samples of plant macrofossils (each 25 cm^3 in the volume) were taken from the core in correspondence with the differentiation of the deposits (approximately at every 10 cm from peat and at 25 cm from gyttja). The separation and identification of plant macrofossil were performed in accordance with the method developed by Lubliner-Mianowska (1951) and Tobolski (2000). The identification of plant macrofossils was made with the available keys and atlases (Dombrowskaja et al. 1969, Grosse-Brauckmann 1972, 1974, Grosse-Brauckmann, Stre-

ITZ 1992, TOBOLSKI 2000) and by using comparative specimens prepared from contemporary vegetation. The names of vascular plants are given after MIREK et al. (2002), and those of mosses – after OCHYRA et al. (2003). The peat decomposition degree was classified on a scale from H1 (peat undecomposed and fibrous) to H10 (fully decomposed, humified peat) on the basis of the von Post index (GLATZEL et al. 2004). In each sample of sediments, the following were determined: pH, Eh, electrolytic conductivity (EC) by the electrochemical method (meter pIONeer 65; resolution 0.1 mV; accuracy ±1012 Ohm; electrodes – Radiometer Analytical AS), and the ash content through the incineration of samples in a muffle furnace at 550°C (SAPEK, SAPEK 1997). Eh was measured with a voltmeter and a combined Pt/Calomel electrode. A platinum electrode conducts electrons from the soil solution to the wire while a reference calomel electrode provides a standard redox reaction that will accept or discard electrons to the soil solution. Redox potential was calibrated to the standard H_2 electrode by adding 239 mV (the correction factor for a calomel reference electrode at 20°C) to the observed instrument reading. Organic carbon was determined in water extracts (dissolved organic carbon – DOC) and dry peat samples (total organic carbon – TOC) by combustion and the analysis of evolved CO_2 was achieved by means of TOC-VCSH with a SSM-5000A module (Shimadzu, Japan).

RESULTS AND DISCUSSION

Lithology and plant macrofossils in studied cores

In the Łęczna-Włodawa Lake District, transitional mires cover a relatively small area (< 2 %) and usually occur near dystrophic lakes or on the marginal parts of peat bogs. They are overgrown by turf and moss sedge plants, which also form floating blankets of vegetation, called ‘floating iselets’. The peat deposits submitted to this study were composed of moss (e.g. *Sphagnum magellanicum, S.* section *Cuspidata, S. rubellum*), sedge (e.g. *Carexrostrata)*, sedge-moss peat and vascular plants (e.g. *Oxycoccus palustris, Menyanthes trifoliata, Equisetum fluviatile, Phragmites australis)* – Table 1*a*, 1*b*). The peat decomposition degree fell within a wide range of variation, being closely related to the depositional environment of peat, the types of peat-forming plants as well as other peat properties.

The paleoecological record is a set of natural, long-term ecological observations. It is a means of ‘coaxing history to conduct experiments’ because in many environmental sciences ‘when time is needed, there is no better substitute for history’ (TOBOLSKI 2004). Fossil pollen, seeds, animal remains and plant macrofossil in lake or bog sediments are used to reconstruct the ecology of past flora, fauna, populations, communities, landscapes, and environments of the last 100-100 000 years. Table 1 presents data from macrofossil plant analysis of transition mires surrounding Lake Moszne.

Table 1*a*

Basic properties of peat in profiles: *a* – I and *b* – II

Depth (m)	Ash content (%)	Degree of decomposition	Macrofossil plant composition
0.10-0.30	6.31	H1	raised bog *Sphagnum* peat *Ombro-Sphagnioni*, *Cuspidato-Sphagneti* (*Sphagnum* section *Cuspidata* 35%, *Sphagnum magellanicum* 10%, *Sphagnum* sp. 30%, *Oxycoccus palustris* 20%, *Eriophorum* sp. 3%)
0.30-0.60	7.43	H1	raised bog *Sphagnum* peat, *Ombro-Sphagnioni*, *Cuspidato-Sphagneti* (*Sphagnum* section *Cuspidata* 34%, *Sphagnum magellanicum* 10%, *Sphagnum* sp. 25%, *Bryales* 2%, *Oxycoccus palustris* 20%, *Eriophorum* sp. 3%, *Menyanthes trifoliata* 4%, *Scheuchzeria palustris* 2%)
0.60-0.80	10.81	H3	transition *Sphagnum* peat, *Minero-Sphagnioni* and *Sphagno-Scheuchzerietii* peat (*Sphagnum* section *Cuspidata* 40%, *Sphagnum magellanicum* 5%, *Sphagnum apiculatum* 2%, *Sphagnum* sp. 15%, *Bryales* 3%, *Polytrichum strictum* 1%, *Oxycoccus palustris* 25%, *Scheuchzeria palustris* 2%, *Menyanthes trifoliata* 4%, indeterminate 3%)
0.80-1.30	17.56	-	water with organic-detrital gyttja
1.30-4.00	16.21	-	organic gyttja (*Nymphaea* sp., *Chara* sp. – oospors, *Schoenoplectus lacustris*, *Phragmites australis*, *Equisetum* fluviatile, Carex sp., *Carex rostrata*, *Menyanthes trifoliata*, *Scheuchzeria palustris*, *Typha* sp., *Eriophorum angustifolium*, *Bryales*, *Sphagnum* sp., *Sphagnum cuspidatum*, *Pinus sylvestris*– bark)
4.00-4.25	38.39	-	clay-organic gyttja (*Carex* sp., *Calla palustris*, *Menyanthes trifoliata*, *Comarum palustre*, *Sphagnum* section *Cuspidata*)
4.25-5.25	20.70	-	organic-detrital gyttja (*Schoenoplectus lacustris*, *Phragmites australis*, *Equisetum fluviatile*, *Carex* sp., *Menyanthes trifoliata*, *Bryales*, *Sphagnum* sectio *Cuspidata*, *Alnus glutinosa*- bark)
5.25-6.78	41.64	-	clay-organic gyttja (*Schoenoplectus lacustris*, *Typha* sp., *Stratiotes aloides*, *Equisetum fluviatile*, *Menyanthes trifoliata*, *Comarum palustre*, *Carex* sp., *Eriophorum angustifolium*, *Bryales*, *Drepanocladus* sp., *Meesia* sp., *Sphagnum* sectio *Cuspidata*, *Pinus sylvestris* - bark)
6.70-6.80	58.11	H4	fen peat *Bryalo-Parvocaricioni, Bryaleti* with gyttja (*Nymphaea* sp. 2%, *Carex sp.* 10%, *Carex rostrata* 5%, *Equisetum fluviatile* 9%, *Phragmites australis* 10%, *Menyanthes trifoliata* 3%, *Bryales* 40%, *Sphagnum* sekcja *cuspidata* 1%, *Alnus glutinosae* – bark, indeterminate 10%)
6.80-6.95	75.63	-	clay sapropel
6.95-7.00	90.47	-	sand

Table 1*b*

Depth (m)	Ash content (%)	Degree of decomposition	Macrofossil plant composition
0.10-0.30	4.41	H1	raised bog peat *Ombro-Sphagnioni*, *Cuspidato-Sphagneti* (*Sphagnum* section *Cuspidata* 35%, *Sphagnum magellanicum* 10%, *Sphagnum rubellum* 5%, *Sphagnum* sp. 10%, *Bryales* 2%, *Oxycoccus palustris* 30%, *Andromeda polifolia* 1%, *Equisetum fluviatile* 2%, *Menyanthes trifoliata*3%, *Eriophorum* sp. 2%)
0.30-0.60	6.96	H3	Transition *Sphagnum* peat *Minero-Sphagnioni*, *Scheuchzeria* peat *Sphagno-Scheuchzerietii* (*Sphagnum* section *Cuspidata* 40%, *Sphagnum magellanicum* 5%, *Sphagnum apiculatum* 2%, *Sphagnum* sp. 15%, *Bryales* 3%, *Polytrichum strictum* 1%, *Oxycoccus palustris* 25%, *Scheuchzeria palustris* 2%, *Menyanthes trifoliata* 4%, indetermine 3%)
0.60-1.50	24.17	-	water with gyttja
1.50-2.00	48.59	-	organic-detrital gyttja (*Chara* sp. – oospors, *Typha* sp., *Equisetum fluviatile*, *Carex* sp., *Carex rostrata, Menyanthes trifoliata, Eriophorfum angustifolium*, *Fontinalis* sp., *Calliergon* sp., *Sphagnum* section *Cuspidata*, *Pinus sylvestris* - bark)
2.00-3.45	57,30	-	organic-detrital gyttja (*Najas* sp., *Schoenoplectus lacustris*, *Typha* sp., *Equisetum fluviatile*, *Carex* sp., *Carex rostratae*, *Calla palustris*, *Menyanthes trifoliate*, *Sphagnum* section *Cuspidata*, *Calliergon stramineum*)
3.45-3.50	89.77	-	sand

Variation of pH-EH

Transition mire is an intermediate type of peat in which neither precipitation nor surface/groundwater dominates in the water balance. This property is reflected in the distribution of pH and Eh in the upper layer of peat. Many redox processes which are connected with electron transfer occur in soil. Organic matter is the source of electrons in the soil, and their acceptors are, among others, oxidized inorganic compounds. The rate of the decrease in the Eh value and the minimum value depend on many factors, including the amount of easily degradable organic substrate (GLIŃSKI, STĘPNIEWSKI 1985).

Figures 2*a* and 2*b* show the distribution of acidity and Eh in peat I and II profiles. In the upper layer of the peat deposits (0-0.65 m), the pH was strongly acidic (on average 4.17 and 4.08 in profiles I and II, respectively). It is well known that in soils which have been made from transitional peat, pH decreases below 4 because of strong humic acids that are formed in this environment. According to MACIAK (1995), vulnerability to acidification of peat moorsh soils is a result of organic compound mineralization, release of nitrogen and creation of nitrate forms of this compound. Under low pH,

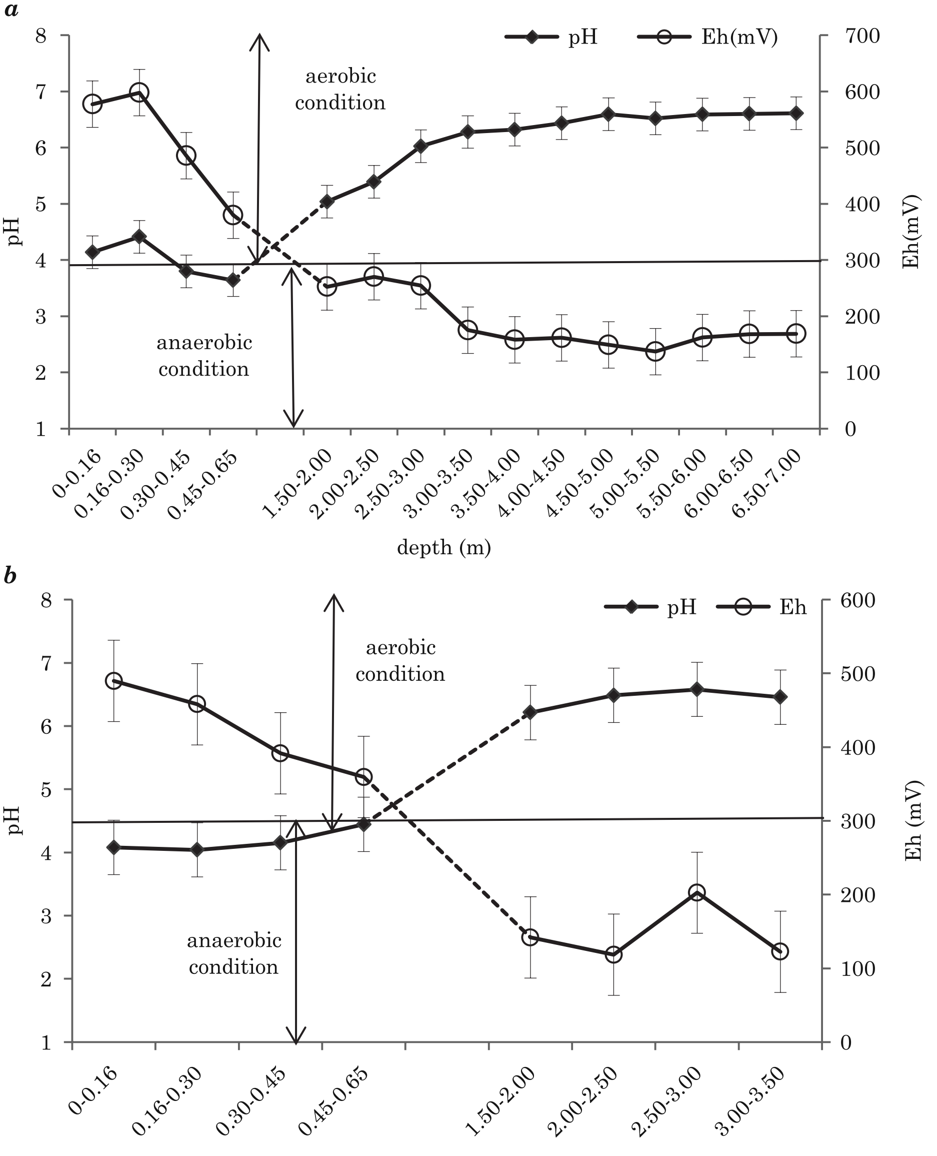

Fig. 2. Distribution of redox potential and pH in depth: *a* – point I, *b* – point II

much of phosphorus enters into insoluble compounds with Fe and Al, which immobilizes this component. In their recent study, Bielińska and co-authors (2003) noticed the minimum content of available P in transition mires near Lake Moszne. The largest variation in pH was recorded at the depth below 0.65 m, where pH rapidly increased down to the depth of to 1.50 m to weakly acidic reaction and remained on this level down to the mineral bottom (pH = 6.61 ± 0.18 in profile I and pH = 6.45 ± 0.11 in profile II).

The positive values of redox potential observed in the topsoil (0-0.30 m) were typical to aerated soils: 577 mV and 490 mV for profile I and II, respectively (BENADA 1995, PONNAMPERUMA 1972). These conditions do not inhibit plant growth (VOLK 1993). The redox state in the topsoil was affected by the processes which control oxygen exchange between the atmosphere and the soil. Precipitation is the main source of water and plays an important role in the supply of dissolved oxygen to soil. The redox potential in our study was lower in the subsoil (below 0.30 m) than in the topsoil, and decreased with the depth to about 158 mV at 3.50 m in profile I and to 118 mV at 2.50 m in profile II. Afterwards, the redox potential stabilized on that level down to the mineral bottom. The respiration of roots, the activity of microorganisms and the lower depth decrease the oxygen content of the soil, which is affected by the soil's aeration state (MARSHALL, HOLMES 1988), and therefore a significant positive correlation ($P < 0.01$) between redox potential and pH was found in the whole profile. Diluted gyttja, which was detected at the depth of 0.65 m, completely cut off the supply of oxygen, hence strongly reducing conditions below. Due to the consumption of protons during the reduction of electron acceptors, the pH gradually increased as the Eh value decreased (PONNAMPERUMA 1972). GLIŃSKI and STĘPNIEWSKI (1985) reported that the reduction processes in soil were accompanied by a change in pH to neutral, e.g. the pH of acidic soils increases. They explained that oxygen absorbed hydrogen ions primarily in redox reactions occurring in soil.

In both analyzed profiles, organic carbon dominated, while inorganic carbon was observed only in the bottom. The content of total organic carbon (TOC) in profile I was within a wide range of 578.89-50.84 g kg^{-1}, being only slightly higher than in profile II (544.18-442.61 g kg^{-1}). The surface layer in both profiles was characterized by the highest organic carbon, while the bottom sediment in profile I contained only 50.84 g kg^{-1} of organic carbon and 12.62 g kg^{-1} of inorganic carbon. The dominant carbon form in the solution was organic carbon, in which it resembled solid samples. The content of dissolved organic carbon in the analyzed profiles was lower in the bottom (I profile $TOC_{diss.}$ = 0.28 g kg^{-1} d.m.). The content of total dissolved organic carbon in profile I was in a range of 0.28-2.81 g kg^{-1} d.m. and in profile II varied from 0.96 to 18.08 g kg^{-1} d.m. The characteristics of carbon forms (from solid samples and solution) in both profiles are summarized in Table 2. Mires are a major storage of carbon in organic matter, which is the soil ecosystem's component mostly prone to to reduction. It is also the largest source of electrons derived from the organic matter decomposition process and therefore it can be seen as an electron pump supplying parts of soil characterised by better aeration (CHADWICK, CHOROVER 2001). An increase in the content of soil organic matter causes a decrease in the oxidation-reduction potential in soil rich in easily degradable organic matter, whose degradation requires high oxygen levels. As well as having a substantial impact on soil Eh, organic matter (its quality and quantity) demonstrates buffering properties like Eh and pH. At high pH values noted in mires and bogs, organic matter par-

Table. 2

The content of carbon forms

Depth (m)	TC dissolved (g kg^{-1} d.m.)	TOC dissolved (g kg^{-1} d.m.)	IC dissolved (g kg^{-1} d.m.)	TC (g kg^{-1})	TOC (g kg^{-1})	IC (g kg^{-1})
I profile						
0.10-0.30	1.35	1.16	0.19	530.50	530.50	0.00
0.30-0.60	1.25	1.14	0.11	579.00	578.89	0.12
1.30-4.00	4.57	2.81	1.76	499.53	498.62	0.91
4.00-4.25	3.34	2.13	1.20	467.87	462.13	5.73
4.25-5.25	3.20	1.27	1.93	442.77	442.77	0.00
5.25-6.78	1.48	0.92	0.56	354.10	354.10	0.00
6.70-6.80	1.40	0.85	0.56	298.50	298.50	0.00
6.80-6.95	1.06	0.49	0.58	121.97	93.25	28.71
6.95-7.00	0.72	0.28	0.43	63.46	50.84	12.62
II profile						
0.10-0.30	1.29	1.18	0.11	544.20	544.18	0.02
0.30-0.60	1.15	0.96	0.19	534.62	534.62	0.00
1.50-2.00	18.21	18.08	0.13	480.87	480.35	0.81
2.00-3.45	6.62	3.66	2.96	452.65	451.03	1.62
3.45-3.50	5.96	3.04	2.91	443.97	442.61	1.36

ticipates in acidification through the formation of soluble complexes with such cations as Ca^{2+} or Mg^{2+}, thereby eliminating alkaline cations from soil (Brady, Weil 2010). The soil oxidation-reduction potential and pH are the main factors that influence the rate and intensity of humification, which proceeds more slowly under anaerobic conditions. The soil redox potential and pH determine soil carbon persistence, particularly in organic soil, hence as long as organic matter is underwater, carbon undergoes sequestratation in sediments. Natural and anthropogenic disturbances (e.g. drainage, peat extraction, natural fire, increase of temperature) cause the release of carbon from peatlands. As a result, organic carbon that is normally underwater becomes suddenly exposed to air, where it decomposes and emits carbon dioxide (CO_2) – Figure 3.

The electrical conductivity (EC) of peat depends on both the fluid saturattion of the peat and the surface of the solid grains in contact with the fluid (Comas, Slater 2004). It is linearly correlated to the concentration of total dissolved solids in the pore water (Theimer et al. 1994). Conductivity is also strongly controlled by temperature and affected by other properties of peat, like cation exchange capacity (CEC), organic content, structure, pH and water content. Also a change of porosity has an influence on the conductivity of peat, as pore-throat diameters and pore geometry of water-saturated geo -materials contribute significantly to both in-phase and out-of-phase conduc-

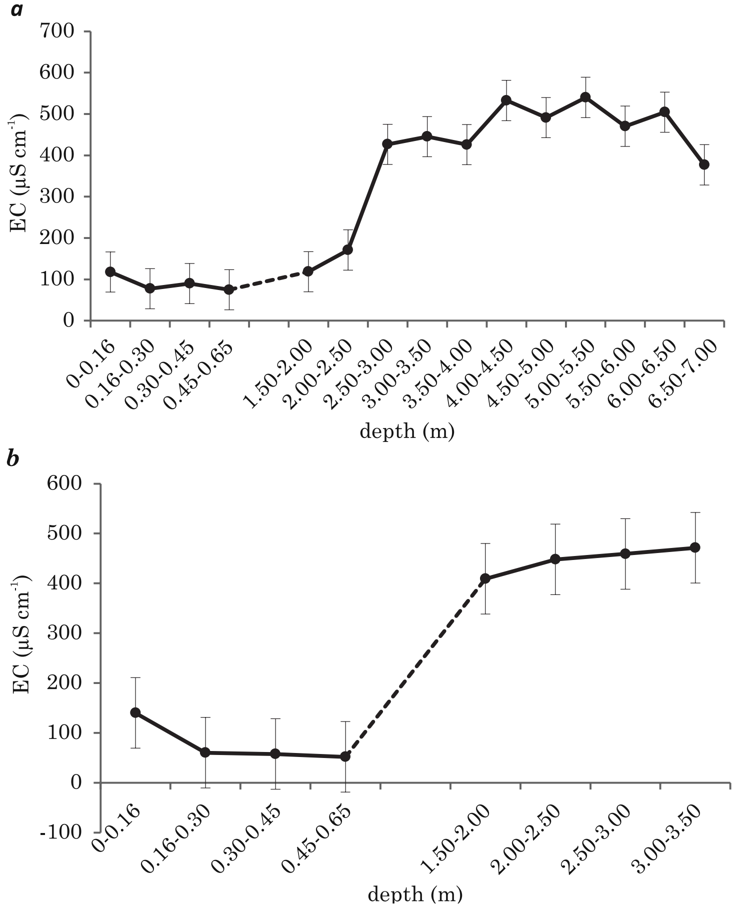

Fig. 3. Distribution of electrolitycal conductivity in peat profile: *a* – I and *b* – II

tion at low frequency (Ponziani et. al 2011). These results show that EC of highly decomposed peat was higher than that of very slightly decomposed peat. The EC of both highly- and very slightly-decomposed peat decreased as the organic content increased.

CONCLUSIONS

1. Differences in physicochemical parameters between vertical peat profiles show a multiphase process of biogenic accumulation, which respond to both the climate and anthropogenic change.

2. In the analyzed peat profiles, pH decreased while Eh was increased with depth. The depth below 0.65 m marks the boundary between oxic and

anoxic conditions. Above this threshold, there are good oxygenation conditions for plant growth (577 mV in profile I and 490 mV and in profile II).

3. Acidification of the upper part of the peat deposit is associated with a smaller supply of groundwater. The neutral and weakly acidic reaction on the bottom of the water body is connected with the neutralization of acidic products of plant decomposition, which is caused by peat groundwater supply, rich in mineral salts.

4. The electrical conductivity of highly decomposed peat was higher than that of very slightly decomposed peat. Furthermore, the results show that the content of organic matter and degree of decomposition strongly influenced EC.

5. The dominant form of carbon in the soil solution and solid samples was organic carbon, while inorganic carbon was observed only in the bottom.

6. The spatial diversity of organic matter in the studied biogenic sediments reflects the structure of the water body (Lake Moszne), which is steadily becoming more shallow.

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