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VARIABILITY OF CATION-EXCHANGE CAPACITY (CEC) OF FEN PEATS IN VERTICAL PROFILES FROM EASTERN AND CENTRAL POLAND IN RELATION TO FUNCTION OF PEATLANDS AS NATURAL GEOLOGICAL BARRIERS

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Abstract
An analysis of cation-exchange capacity (CEC) variability of peats is presented in vertical profiles from eastern and central Poland. CEC values were compared with ash content (Ac), pH and $CaCO_3$ content. Eight peatlands were selected for research in the following areas: Warsaw Plateau (2 objects), Siedlce Plateau (2 objects), Lubartów Plateau (2 objects), Nałęczów Tableland (1 object) and Dobrohusk Depression (1 object). The peatlands represented a fen peat type of similar botanic compositions of sediments, but they differed in the area, peat thickness and drainage conditions. Characteristic regularities in CEC variability were noted in the peatlands and there were three types of CEC variability in vertical profiles. Carbonate peats (types 1 and 2) had the highest pH and definitely the highest values of CEC. In vertical profiles, there was also a zonation, but the regularities similar to non-carbonate peats were not observed. Different distribution of physical and chemical parameters were established in vertical profiles in partly drained peatlands (with a muck layer on top) with non-carbonate peats (type 3) and there were three distinct zones in vertical profiles, with different Ac and CEC. Determination of the vertical CEC variability and other physical and chemical parameters in peatlands made it possible to distinguish zones with potentially most beneficial isolation conditions.

Key words: natural geological barrier, peat, fen, cation-exchange capacity

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INTRODUCTION

The term 'natural geological barrier' (soil layer that isolates a shallow groundwater from pollution) is used both in case of soil used as insulation of sealing landfills (Langer, 1998; Zhou and Li, 2001; Dorn and Tantiwanit, 2001; Łuczak-Wilamowska, 2013) and in a regional scale in case of natural *in situ* soil layers (Syrovetnik *et al.*, 2007; Falkowska, 2009; Rydelek, 2011). Apart from low permeability the geological barriers should indikcate a high natural retention capacity for hazardous substances, large thickness and high homogeneity (Dorn and Tantiwanit, 2001; Majer, 2007). These criteria are commonly fulfilled by organic soils within peatlands. Peats have high absorption capabilities (cf. Ho and McKay, 1999; Allen *et al.*, 2004; Ma and Tobin, 2004; Twardowska and Kyzioł, 1996; Twardowska *et al.*, 1999; Kyzioł, 2002; Borkowski *et al.*, 2013) and they are usually connected with high content of organic matter (indicating a low ash content). Depending on a composition of organic matter (humid acid content), a cation-exchange capacity of organic matters is 4 to 12 times higher than of clay minerals (Appelo and Postma, 1993). Peats are classified as soils with extraordinarily high variability of physical and chemical parameters: ash content (Ac), moisture content, density and porosity (Ingram, 1978; Hobbs, 1986). A hydraulic conductivity oscillates in a wide range between 10^{-10} and 10^{-3} m/s in fen peats (Boelter, 1965; Hobbs, 1986; Hoag and Price, 1995; Rizutti *et al.*, 2004; Beckwith *et al.*, 2003a, 2003b; Rydelek *et al.*, 2015). Variability of peat properties is an outcome of processes that run during deposition (process of sedentation) and post-depositional stages. Variability of different parameters is observed both in vertical profiles of peatlands (Rydelek 2005; Domińczak and Okupny 2010; Borówka *et al.*, 2015; Ścibior *et al.*, 2015; Kittel *et al.*, 2016; Pawłowski *et al.*, 2016) and in horizontal plane (Pawłowski *et al.*, 2014). Aim of this paper was to establish regularities in CEC variability of peats in vertical profiles of fens in eastern and central Poland (Fig. 1) against other varied physical and chemical parameters. Studied peatlands were similar in botanic composition of peats, but they were different in chemical and physical properties, thickness, area and drainage conditions.

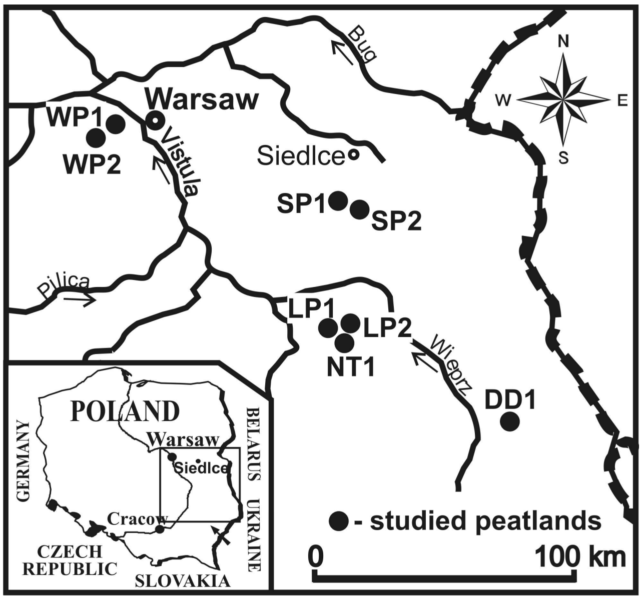

Fig. 1. Location of the studied peatlands. WP – Warsaw Plateau, SP – Siedlce Plateau, LP – Lubartów Plateau, NT – Nałęczów Tableland, DD – Dorohusk Depression.

MATERIALS AND METHODS

Eight peatlands were selected in the following areas: Warsaw Plateau (2 objects marked as WP1 and WP2), Siedlce Plateau (2 objects marked as SP1 and SP2), Lubartów Plateau (2 objects marked as LP1 and LP2), Nałęczów Tableland (1 object marked as NT1) and Dobrohusk Depression (1 object marked as DD1). Except for DD1 peatland at Pawłów, 20 km west of Chełm, all other peatlands represented the valley-bog type. Peatlands WP1 and WP2 were located in the valleys of Raszynka and Utrata rivers, SP1 and SP2 in the valley of the Bystrzyca River, LP1 and LP2 in the valley of the Kurówka River, while NT1 in the valley of the Struga-Kurów River (tributary of the Kurówka River).

In total, 16 vertical profiles were examined for the CEC variability. Two most representative profiles from every peatland were selected and marked with symbols "a" and "b" (e.g. LP1a and LP1b), so the widest spectrum of different types and features of peats could be considered.

Peat samples for e thlaboratory studies were collected at every noticed macroscopic change of botanic composition or degree of decomposition but not less often than every 30 cm. Peat type and degree of decomposition were determined for every sample using shortened three-step approach by Okruszko (1974): R1 – fibrous peats (poorly decomposed), R2 – pseudo-fibrous peats (moderately decomposed) and R3 – amorphous peats (highly decomposed).

Basic properties of peats (ash content A_C, pH, $CaCO_3$ content and CEC) were determined for all samples. Ash content was determined after ignition at 550 C (Andrejko *et al.*, 1983). The division of peats as to the ash content according to Okruszko (1994) was adopted: non-silty peats (ash content below 25%), slightly silty (25–50% of ash content) and strongly silty (50–80% of ash content). Degree of decomposition was specified for non-silted peats only (Borys, 1993). Acidity (pH) of peat was determined in suspension in a distilled water by using electometric method, while $CaCO_3$ content was determined by Scheibler's method (cf. Myślińska, 2010). Depending on $CaCO_3$ content, a classification of Okruszko (1976) was adopted: non-carbonate peats ($CaCO_3$<5%), poorly carbonate (5–20%), moderately carbonate (20–45%) and highly carbonate ($CaCO_3$>45%). Cation-exchange ca-

Table 1

Basic characteristics of studied peatlands and average values of physical and chemical parameters of peats (there are coefficient of variation given in parentheses)

	Peatland							
	WP1	WP2	SP1	SP2	LP1	LP2	NT1	DD1
Area [ha]	65	51	275	91	180	25	43	38
Maximum thickness [m]	1.5	1.4	4.0	3.0	3.5	3.7	3.3	1.7
Peat type	reed peat/tall sedge peat	alder peat/ reed peat	tall sedge peat/reed peat	tall sedge peat/alder peat	alder peat/reed peat/tall sedge peat	reed peat/alder peat	tall sedge peat/alder peat	reed peat/tall sedge peat
Maximum thickness of muck [m]	0.3	0.4	0.3	0.4	0.5	0.4	0.4	0.2
Degree of decomposition	silted	silted	R2/R1	R2/R1	R2/R3	R2/R1	silted	R2
Ac %	42.4 (0.22)	51.6 (0.31)	20.7 (0.47)	37.1 (0.57)	32.4 (0.46)	47.9 (0.41)	55.1 (0.18)	26.2 (0.19)
$CaCO_3$ %	13.9 (0.84)	1.3 (0.37)	2.2 (0.47)	13.7 (1.16)	2.1 (0.49)	16.7 (1.06)	36.8 (0.36)	4.4 (1.26)
pH H_2O	6.7 (0.06)	5.6 (0.05)	6.0 (0.06)	7.0 (0.03)	5.7 (0.06)	6.4 (0.06)	7.2 (0.03)	6.4 (0.05)
CEC cmol/kg	123 (0.12)	96 (0.14)	117 (0.08)	132 (0.11)	107 (0.14)	120 (0.14)	143 (0.04)	120 (0.12)

Ac – ash content, CaCO3 – calcium carbonate content, CEC – cation-exchange capacity. WP – Warsaw Plateau, SP – Siedlce Plateau, LP – Lubartów Plateau, NT – Nałęczów Tableland, DD – Dorohusk Depression.

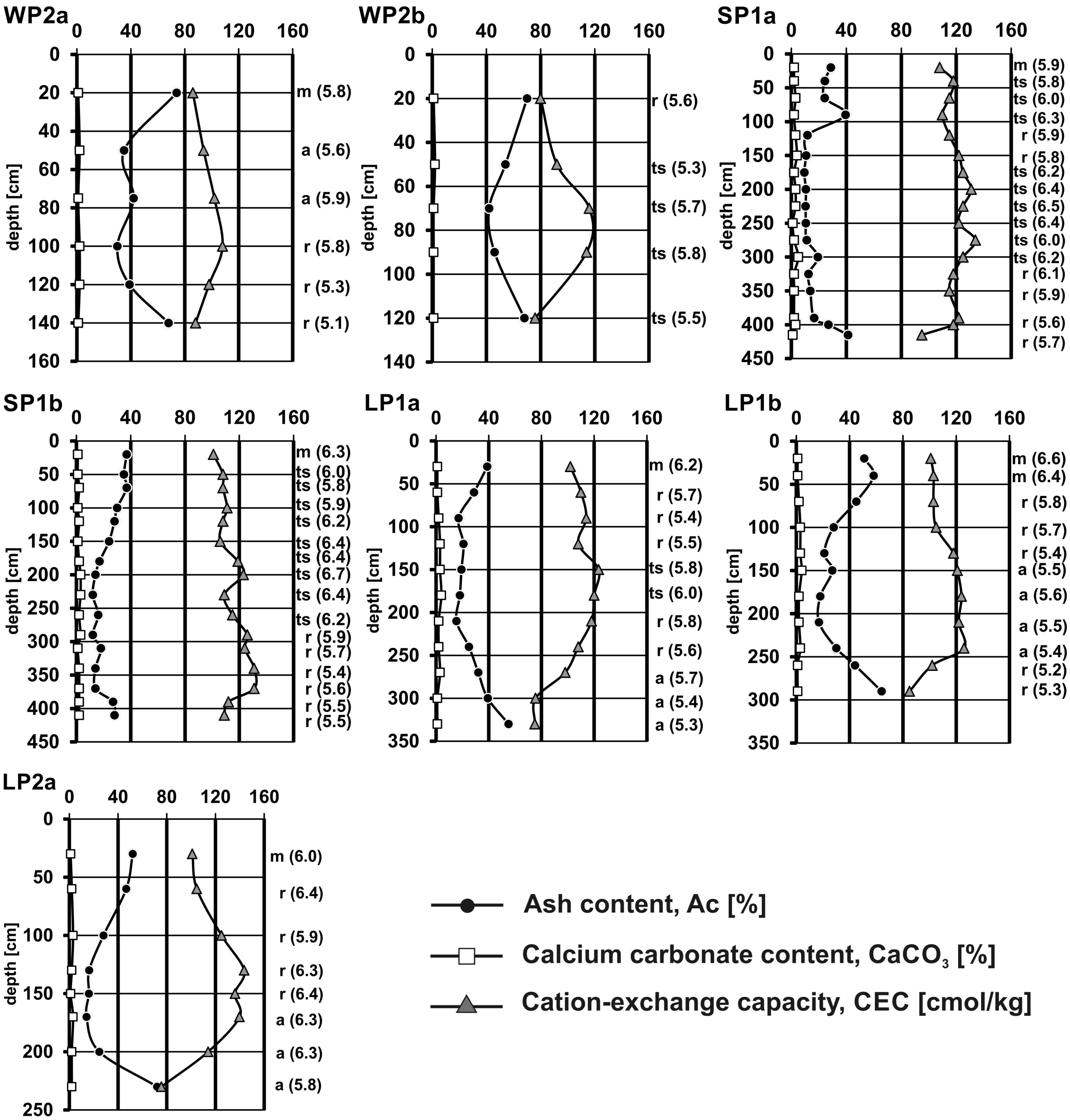

Fig. 2A. Variability of cation-exchange capacity (CEC) and ash content (Ac) in vertical profiles of non-carbonate peatlands, pH given in parentheses; m – muck, ts – tall sedge peat, r – reed peat, a – alder peat.

pacity was determined by the copper sorption method (Sapek, 1982). This method belongs to batch experiments and is based on measurement of copper ions concentration in a solution before and after a reaction with the soil.

RESULTS

Basic data of studied peatlands (16 profiles), CEC value and other physical and chemical parameters were presented (Table 1). The highest CEC values (>130 cmol/kg) were noted in peats at SP2 and NT1. Peats in those peatlands indicated a high content of $CaCO_3$ and slightly alkaline pH. The lowest values of CEC were observed in peats at WP2 and LP1 (96 and 107 cmol/kg). In those peatlands there were non-carbonate peats of pH < 6. CEC values in the remaining peatlands were similar and varied (117 and 123 cmol/kg).

Two types of profiles were compared considering the CEC variability: profiles with non-carbonate peats only (Fig. 2A) and profiles with highly carbonate peats (Fig. 2B).

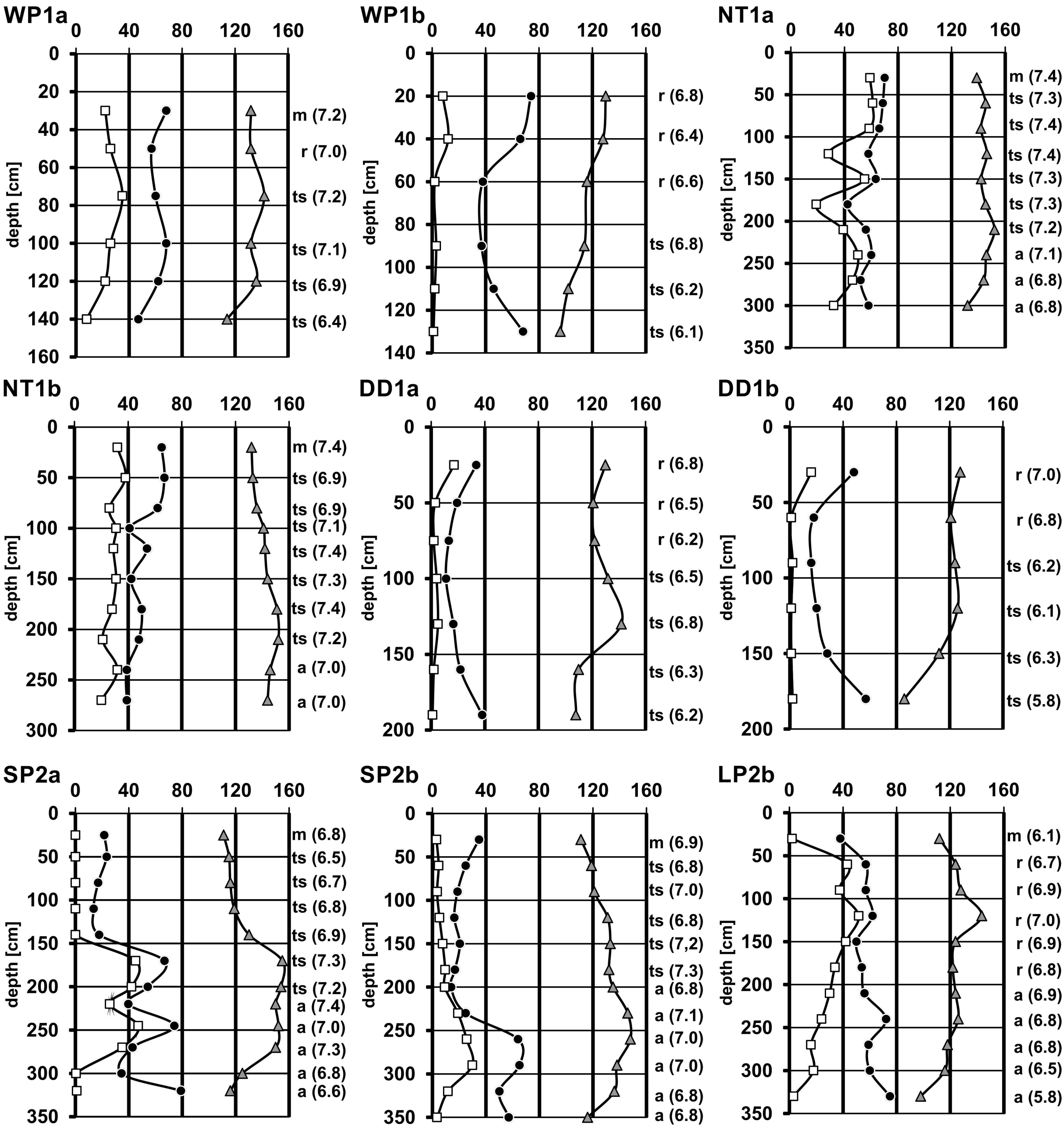

Fig. 2B. Variability of cation-exchange capacity (CEC) and ash content (Ac) in vertical profiles of carbonate peatlands, pH given in parentheses; m – muck, ts – tall sedge peat, r – reed peat, a – alder peat.

DISCUSSION

The analysis of CEC values variability in 16 vertical profiles (Fig. 2A, B) enabled to distinguished three types of vertical profiles.

The type 1 including WP1a, NT1a and NT1b profiles indicated high CEC values with low variability in the whole peat thickness (except for a single sample, all CEC values were <130 cmol/kg). In vertical profiles there were mainly carbonate peats (moderate and highly carbonate) with high pH and high ash content (41 to 70%) linked mainly to $CaCO_3$ content. Calcium carbonate occurred in the peats as of idiomorphic microcrystals, that indicated crystallization within a peat and autogenesis (Rydelek, 2013). High CEC values in profiles of the type 1 were established independent from peat type and independent from drainage conditions. In the muck layer that occurred in profiles of the studied peatlands, the high CEC levels were observed (134 cmol/kg). In peats that were a part of the type 1 profiles there was no meaningful relation between CEC and ash content (Fig. 3).

The type 2, which includes profiles DD1a, DD1b, LP2b, WP1b, SP2a and SP2b, had also the samples with high CEC

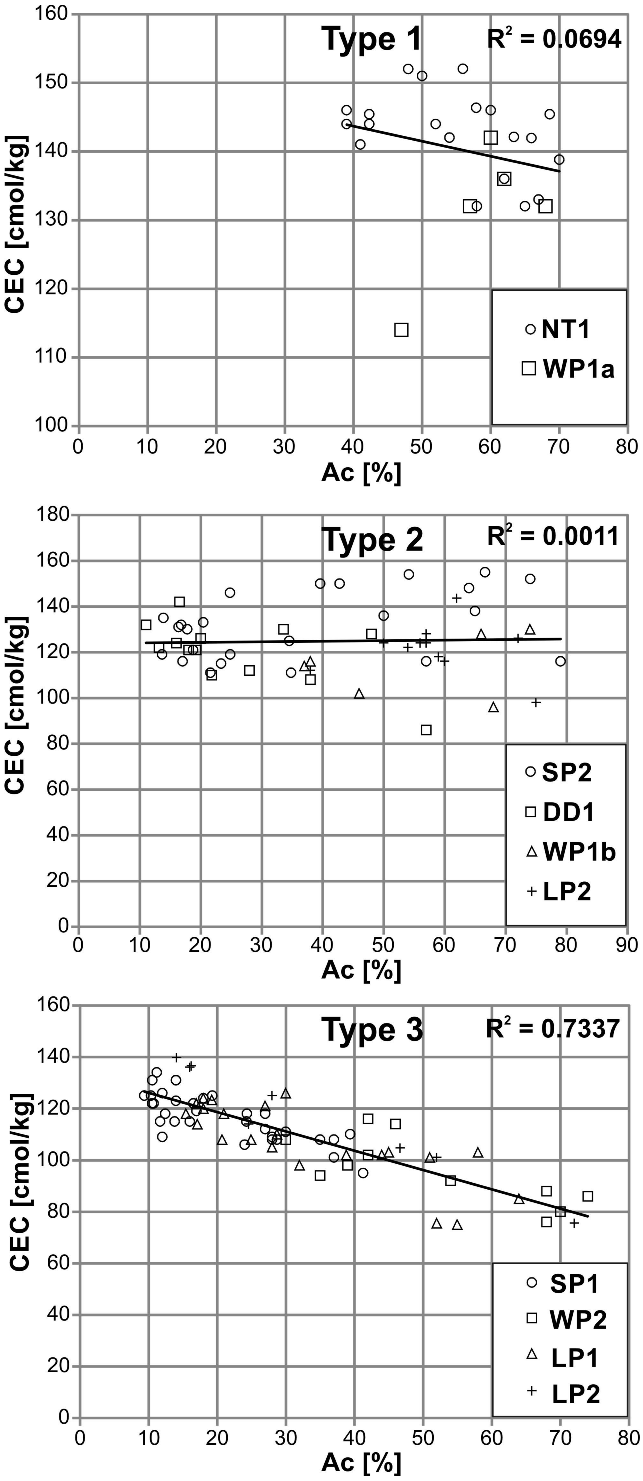

Fig. 3. Relationship between cation-exchange capacity (CEC) and ash content (Ac) in the studied peatlands.

(>100 cmol/kg) but with highly varied. In single profiles, there were peats with high variability of pH, ash content and $CaCO_3$ content. The highest values of CEC in the type 2 profiles were observed in samples with the highest $CaCO_3$ content and the highest pH. At the same time in thr profiles of partly drained peatlands in a muck layer in a top of a peatland (profiles LP2b, SP2a and SP2b), the lower values of CEC were noted if compared with the lower layers of a peat. Just as with a peat of the type 1, a dependency between CEC and Ac was described by the very low value of R^2 = 0,0011.

The type 3 comprised a peat with the lowest CEC (rarely >120 cmol/kg). This type occurred in the remaining profiles (SP1a, SP1b, LP1a, LP1b, LP2a, WP2a, WP2b), predominated by non-carbonate and poorly-carbonate peats with the lowest pH and with a top layer of muck. of CEC values in the profiles of the type 3 indicated clear connection with the ash content (R^2=0.7337) (Fig. 3).

The highest values of CEC, as well as the lowest ash content occurred in the middle part of the profiles, regardless the type of peat. High ash content and subsequently lower CEC value in the top part of the profiles was connected with muck occurrence.

Lower values of organic matter and subsequently lower CEC values in the bottom parts represented the first deposition phase. A sedentation started directly on a mineral subsoil, thus in a bottom part the peat was enriched in mineral constituents.

CEC values of the studied peat did not differ significantly from other peats in the Polish Lowland (e.g. Falkowska, 2002; Kyzioł, 2002) and were much higher than in mineral soils (Falkowska, 2009).

CONCLUSIONS

Apart from different in characteristics of peats in the studied peatlands, there were also varied parameters (including CEC) within single peatlands. It allowed distinguishing the zones of similar physical and chemical properties within the studied peatlands.

Among the described three types, the lowest CEC values were observed in the type 3, in which non-carbonate peat with low ash content and low pH occurred in the whole peat. The most influential parameter for CEC was a content of organic matter (expressed by ash content).

The highest values of CEC were noted in a carbonate peat with the highest pH (type 1), regardless of ash content and type of peat. The research proved that carbonate peatlands can be the most effective geological barrier due to their CEC values. Next to the content of the organic matter, the content of $CaCO_3$ influenced the pH and was a decisive factor for the CEC value.

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