

VARIABLE SURFACE CHARGE OF SELECTED PEAT MATERIALS AS DETERMINED FROM BACK TITRATION

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A b s t r a c t. The surface charge studies were conducted on peat materials at various states of the secondary transformation characterised by W_1 index. A back titration method for the determination of the variable surface charge was applied and distribution of the apparent surface dissociation constants for investigated soils were determined. In this method the peat suspensions were titrated with 0.1 N NaOH in 1N NaCl solution. For weakly and medium secondary peats positive correlation between quality of the surface charge and the W_1 index was found. The best correlation appeared between the surface charge and the summary content of fulvic and humic acids. However, for proper moorsh material two populations can be distinguished. For all samples very strongly acidic surface sites are dominant. Furthermore, the average apparent surface dissociation constant values were similar for all peat-moorsh soils.

K e y w o r d s: agrophysics, variable surface charge, apparent surface dissociation constants, peaty moorsh, proper moorsh, state of secondary transformation.

INTRODUCTION

The large sources of natural organic matter, which is an important component of soils and aquatic environments, are peat-moorsh soils. The organic matter in soil plays a significant role in formation of aggregates, nutrient cycling and pollutant detoxification. Furthermore, soil organic matter takes part in a number of processes coupled with acid-base properties, playing a major role in buffering both proton and metal cation concentrations in the soil solution. In general natural organic matter has a negative charge caused by the dissociation of its surface functional groups [10]. As a result of various character, kind and/or localization of these groups, soil organic matter is highly heterogeneous. The number and acidic strength (dissociation constants) of these groups constitute a primary characteristics of soil organic matter.

Among many methods of getting information on acidic groups properties is potentiometric titration which is thought as the easiest and the most convenient [3]. The chemical heterogeneity implies that a single dissociation constant value should be replaced by a so-called distribution function of surface dissociation constants, showing the relative amount of surface acidic groups and their strengths [6]. In a potentiometric titration the pH is measured as a function of the amount of base added to a sample. The total proton consumption, Q , which accompanies the rise of pH from its starting value, is a measure of the variable surface charge increase. If the initial surface charge is known the titration curves can be converted into absolute charge vs. pH curves. If additionally the surface potential vs. pH relationship is known, the intrinsic surface dissociation constants distribution function can be evaluated. However, usually both above values are difficult to establish thus one evaluates the apparent surface dissociation constants distributions.

The aim of the present work was to evaluate the variable surface charge and apparent surface dissociation constants distribution functions for 14 variously secondary transformed peat-moorsh soils basing on back titration curves.

MATERIALS AND METHODS

The present study was conducted on selected peat materials taken from 14 peat-moorsh soils in which various phases of moorshing process could have been easily visually assessed. The sites were located in the region of Polesie Lubelskie and in the Biebrza River valley. The studied materials represent peats of weakly, medium, strongly, very strongly and completely secondary transformed stages. The quantitative degree of the secondary transformation of the studied materials was expressed by W_1 index determined according to Gawlik [4,5] method. W_1 is the ratio of centrifuge moisture equivalent (at 1000 g) after predrying at 105 °C and one week rewetting to that of fresh sample. For weakly secondary transformed peat, the range of W_1 values is 0.41-0.5; for medium secondary transformed peats 0.51-0.6; for strongly secondary transformed 0.61-0.7; for very strongly secondary transformed 0.71-0.80 and for the degraded peats $W_1 > 0.80$. The studied peats belong to two general groups: peaty moorshes - Z_1 ($0.44 < W_1 < 0.61$) and proper moorshes Z_3 ($W_1 > 0.61$). Table 1 shows W_1 values for the studied materials together with the content of humic and fulvic acids determined in the investigated soils according to the method described by Bambilov *et al.* [1]. Other physico-chemical properties of these soils can be found in Gawlik and Harkot's papers [5].

From the studied peats the suspensions containing such amount of the fresh homoionic hydrogen forms of peat materials which corresponded exactly to 0.02 g of

Table 1. W_1 index values and the content of fulvic and humic acids in studied soils (data are placed in sequence of W_1 increase)

No.	W_1	Kind of moorsh	Total content of fulvic and humic acids (%)		
			Fulvic acid, cf	Humic acid, ch	cf+ch
12	0.44	Z ₁	8.84	29.82	38.66
11	0.48	Z ₁	8.71	31.12	39.83
1	0.55	Z ₁	8.09	15.62	23.72
10	0.60	Z ₃	10.18	31.98	42.16
13	0.61	Z ₃	11.49	14.40	25.89
3	0.63	Z ₃	7.09	30.94	38.03
6	0.65	Z ₃	8.06	27.16	35.22
9	0.65	Z ₃	9.60	26.84	36.45
7	0.67	Z ₃	9.38	32.75	42.13
4	0.71	Z ₃	12.75	29.31	42.06
8	0.71	Z ₃	11.67	24.55	36.22
2	0.72	Z ₃	6.66	33.63	40.29
14	0.72	Z ₃	12.33	21.95	34.29
5	0.82	Z ₃	7.93	29.94	37.87

dry mass in 1N NaCl solutions were prepared, equilibrated for 24 h and then centrifuged. The supernatants were rejected and to the remaining sediments 1N NaCl was added to reach 1:1000 solid to liquid ratio and the pH of the suspensions were adjusted to 3.0 with concentrated HCl. The suspensions obtained were titrated with 0.1 N NaOH in 1N NaCl solutions using Radiometer Copenhagen autotitration unit equipped with Orion combined electrodes. The titration was performed at the lowest possible rate of the titrant addition (0.5 ml min⁻¹), according to the procedure described by Józefaciuk *et al.* [7]. The titration was stopped at pH 9.4. During the addition of the titrant, the suspensions were stirred vigorously. The pH

values during titration were automatically recorded for both the blank titration and the suspension curve with the step of 0.2 pH unit. Next, the titration curve of the solid phase was determined by subtraction the pH's curve of the equilibrium solution from the pH's curve of the suspension.

The amount (moles) of the base consumed in the titration by the suspension, N_{sus} , minus the amounts of the titer consumed in the blank titration, N_{sol} , from pH 3.0 to a given pH, was assumed to be equivalent to the negative surface charge increase, $\Delta SO^-(pH)$:

$$\Delta SO^-(pH) = SO^-(pH) - SO_{ini}^- N_{sus} - N_{sol} \tag{1}$$

where: $SO^-(pH)$ holds for the charge at a given pH value and SO_{ini}^- is the initial charge at the beginning of the titration. Assuming that the soil variable charge originates from the dissociation of surface acidic groups of kind i and the (intrinsic) dissociation constants K_i :

$$K_i = [SO_i^-][H_s^+] / [SOH_i] \tag{2}$$

where the brackets denote surface activities, the variable charge at a given pH, $SO^-(pH)$, may be written as:

$$SO^-(pH) = \sum_{i=1}^n N_i a_i(K_i, pH) \tag{3}$$

where $\alpha_i(K_i, \text{pH}) = (SO_i^-)/(SOH_i)$, is the degree of ionization of groups kind i and N_i is their amount. For any pH during the titration one has:

$$SO^-(\text{pH}) / N_t = a_t(\text{pH}) = \sum_{i=1}^n a_i(K_i, \text{pH}) N_i / N_t = \sum_{i=1}^n a_i(K_i, \text{pH}) f(K_i), \quad (4)$$

where N_t is the total amount of surface groups and $f(K_i) = N_i/N_t$ is the fraction of i -th groups. Using condensation approximation the $f(K)$ values are:

$$f(K) = 1 / N_t \Delta[\Delta DSO^-(\text{pH}) + SO_{ini}^-] / \Delta K; \quad K = [H_s^+], \quad (5)$$

in logarithmic scale:

$$f(\text{pK}) = 1 / N_t \Delta[DSO^-(\text{pH})] \Delta \text{pK}; \quad \text{pK} = \text{pH}_s \quad (6)$$

The distribution function of surface dissociation constants can be calculated knowing both surface protons activity (pHs) and N_t values. As this was mentioned before these values are very difficult or impossible to be established for soil systems [11]. The easiest and most convenient way to overcome the above problem is to replace the proton activity on the surface by their activity in the solution, and assume $N_t = N_{max}$ = maximal experimental value of $(N_{susp} - N_{sol})$. Thus, instead of the intrinsic dissociation constants, the apparent surface dissociation constants, K_{app} , are determined [2]. The fraction of surface groups having given values of pK_{app} can be calculated from the formula:

$$f(\text{pK}_{app,i}) = 1 / N_{max} [\Delta SO^-(\text{pH}_{i+1}) - \Delta SO^-(\text{pH}_i)] / (\text{pK}_{app,i+1} - \text{pK}_{app,i}); \quad \text{pK}_{app} = \text{pH} \quad (7)$$

The average value of pK_{app} , $\text{pK}_{app,av}$ can be calculated as:

$$\text{pK}_{app,av} = \sum_{i=1}^n \text{pK}_{i,app} f_i(\text{pK}_{app}) \quad (8)$$

More details on the elaboration of titration data can be find in Józefaciuk *et al.* [7,8].

All the measurements were performed in triplicate with the deviation not exceeding 7 %.

RESULTS AND DISCUSSION

The exemplary titration curves of the solid phases of seven of the studied peat-moorsh soils plotted as the variable charge Q [mol g⁻¹] versus pH are shown in Fig. 1. The shapes of the titration curves obtained are similar, however the values of Q at the end of titration, i.e., the variable surface charge, N_{max} , is different. These values for all peats are shown in Table 2. These values range from

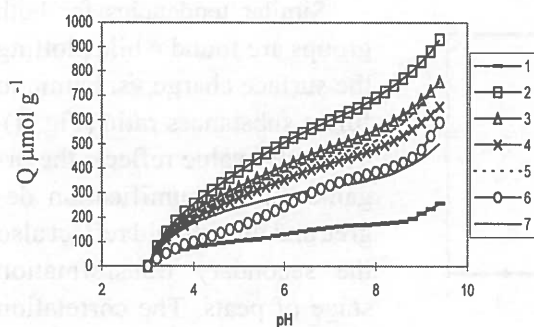


Fig. 1. Titration curves of soils Nos 1-7.

Table 2. The variable surface charge and average apparent surface dissociation constants for all studied soils (data are placed in sequence of W_1 increase)

No.	Variable surface charge, Q ($\mu\text{mol g}^{-1}$)	Average apparent surface dissociation constants, pK
12	375.3	5.75
11	425.6	5.77
1	257.2	6.20
10	637.9	6.01
13	482.5	5.56
3	757.8	6.00
6	590.5	6.65
9	618.0	5.98
7	504.4	5.90
4	654.8	6.01
8	639.0	5.72
2	930.7	6.03
14	466.7	6.21
5	761.1	6.22

257.2 [$\mu\text{mol g}^{-1}$] for the soil No. 1 (medium transformed peat of $W_1 = 0.55$) to 930.7 for the soil No. 2 (very strongly transformed peat, $W_1=0.72$).

An attempt to find some relationships between the variable charge and other important soil parameters was performed.

A positive correlation between the amount of surface charge and the degree of secondary transformation determined by W_1 index was found for weakly and medium transformed peats which is shown in Fig. 2. These peats group (marked with black dots in the figure) consists of peaty-moorsh formations of W_1 ranging from 0.44 to 0.61. The variable surface charge increases with the value of W_1 for these soils. The second (open circles in the figure) group contains soils of W_1 values above 0.63 (proper moorsh). No visible tendency of charge vs. W_1 for proper moorshes was observed. The correlation between the above described

data for both peat groups were about 0.98 and 0.13, respectively.

The variable surface charge plotted against the content of fulvic acid for all 14 soils is shown in Fig. 3. The results show that the surface charge increases with the amount of fulvic acid for peaty moorsh formations. The appearance of this tendency seems increasing obvious, because fulvic acid contains more carboxyl groups per unit mass than humic acid. However, the opposite tendency holds for the proper moorshes, indicating that the humic acid content and charge relationship can possibly differentiate both moorsh groups. The correlation between the above-described data for both peat groups was about 0.8.

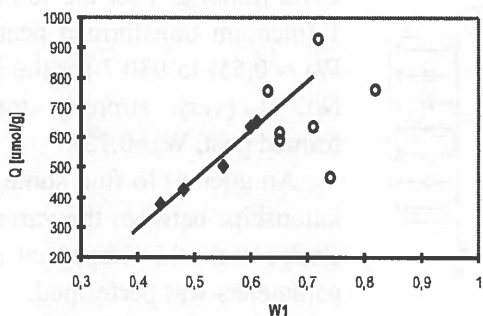


Fig. 2. The variable surface charge versus W_1 index. Open circles - proper moorsh, black dots - peaty moorsh.

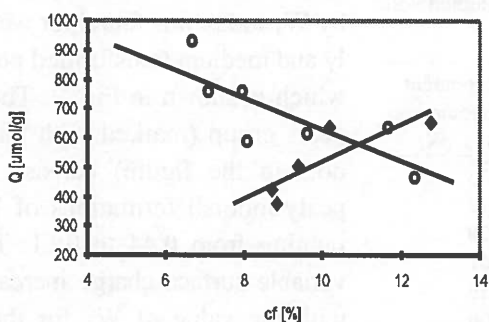


Fig. 3. The variable surface charge versus the content of fulvic acid. (cf) Open circles - proper moorsh, black dots - peaty moorsh.

One of these contains only two soils (Nos 4 and 7). Probably these two soils differ from the others by content of lignin.

In the investigated peat-moorsh soils two classes of the dominant acidic groups can be distinguished, what is seen from apparent surface dissociation constants distribution functions presented in Fig. 6, wherein the representative functions for the studied materials (soils Nos 5, 6 and 12) are depicted. In general, strongly acidic surface sites of low pK_{app} dominate in all moorshes studied. For sample No. 5 as well as for samples Nos 2-4 and 7 the number of very weakly acidic groups of pK_{app} values higher than about 8.0 increases with the further decrease of their acid strength. For sample No. 12 as well as for samples Nos 9-11 and 13-14 the number of very weakly acidic groups of pK_{app} higher than about 7.5 first increase and then decrease, forming a peak around $pK_{app} = 8.5$. For sample No. 6 as

Similar tendencies for both groups are found while plotting the surface charge vs. humic to fulvic substances ratio (Fig. 4). The latter value reflects the organic matter humification degree and thus should reflect also the secondary transformation stage of peats. The correlation between the above described data for both peat groups was 0.72 and -0.83, respectively.

The strongest correlation was found for the dependencies of surface charge on the total content of fulvic and humic substances, which are presented in Fig. 5. The differentiation of peaty and proper moorshes in respect to the above dependencies seems to be the strongest. The curves for both groups are straight lines and do not intersect. However, the proper moorsh group is hereby divided into two populations.

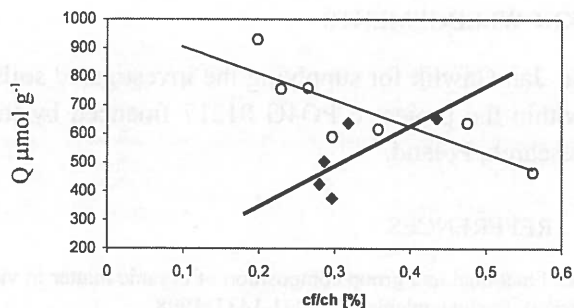


Fig. 4. The variable surface charge versus fulvic (cf) to humic (ch) acids ratio. Open circles - proper moorsh, black dots - peaty moorsh.

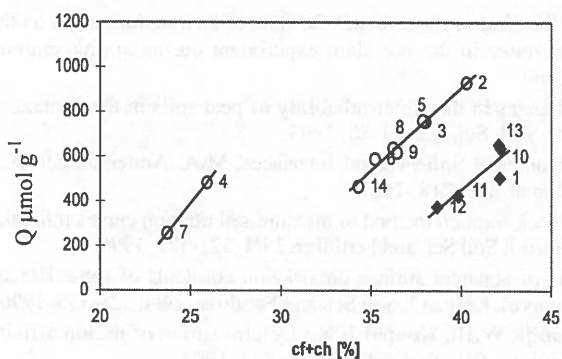


Fig. 5. The variable surface charge versus the total content of fulvic and humic acids. Open circles - proper moorsh, black dots - peaty moorsh.

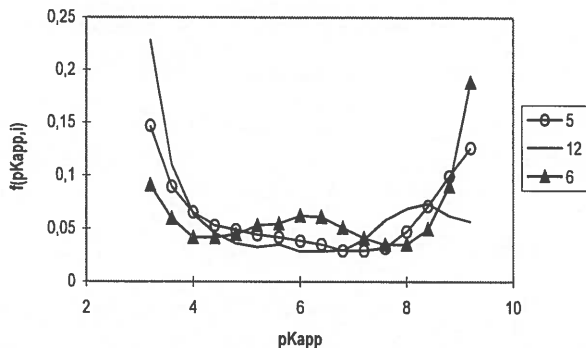


Fig. 6. Exemplary apparent surface dissociation constants distribution functions for soils Nos 5,6,12.

well for Nos 1 and 14 the number of very weakly acidic sites is higher than very strongly acidic. A peak around $pK_{app} = 6$ is noticeable. As this is seen, samples of both Z_1 and Z_3 peat groups can have different shapes of the distribution functions, in contrary to what we expected. Also, the average apparent surface dissociation constant values were similar, which are shown in Table 2. The $pK_{app,av}$ values range from 5.72 to 6.65 for all materials studied. No significant correlation between average dissociation constants and the state of secondary transformation was observed as well.

CONCLUSION

The application of back titration method to estimate the degree of secondary transformation of peats may be useful but with further investigation. More detailed studies on various fractions of soil humus extracted from investigated peat-moorsh soils should be useful in this respect.

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REFERENCES

1. **Bambalov N.N., Belen'kaya T.Ya.:** Fractional and group composition of organic matter in virgin and reclaimed peat soils (in Russian). *Pochvovedenie*. 12: 1431-1437, 1998.
2. **De Wit J.C.M., Van Riemsdijk W.H., Nederlof M.M., Kinniburgh D.G., Koopal L.K.:** Analysis of ion binding on humic substances and the determination of intrinsic affinity distribution. *Analytica Chimica Acta*. 232: 189-207, 1990.
3. **Duquette M., Hendershot W.:** Soil surface charge evaluation by back titration. *Soil Sci. Soc. Am. J.* 57: 1222-1234, 1993.
4. **Gawlik J., Harkot W.:** Influence of the kind of moorsh and the state of its transformation on the germination and growth of *Lolium perenne* in the pot plant experiment during spring-summer cycle. *Acta Agrophysica*, 26, 25-40, 2000.
5. **Gawlik J.:** An attempt to evaluate changes in the water reliability of peat soils in the context of their advancing degradation. *Polish J. Soil Sci.*, 25: 81-86, 1993.
6. **Huang C.P.:** In: *Adsorption of Inorganics at Solid-Liquid Interfaces*. M.A. Anderson and A.J. Rubin, Eds. Ann Arbor Science, Michigan. 183-218, 1981.
7. **Józefaciuk G., Shin J.S.:** A modified back-titration method to measure soil titration curves minimizing soil acidity and dilution effects. *Korean J. Soil Sci. and Fertilizer*. 29/4: 321-327, 1996.
8. **Józefaciuk G., Shin J.S.:** Distribution of apparent surface dissociation constants of some Korean soils as determined from back titration curves. *Korean J. Soil Sci. and Fertilizer*. 29/4: 328-335, 1996.
9. **Nederlof M.M., De Wit J.C., Riemsdijk W.H., Koopal L.K.:** Determination of proton affinity distributions for humic substances. *Environ. Sci. Technol.* 27: 846-854, 1993.
10. **Sposito G.:** *The Chemistry of Soils: Soil Organic matter*. NY, Oxford, Oxford University Press. 42-65, 1989.
11. **Van Riemsdijk W.H., Koopal L.K., De Wit J.C.M.:** Heterogeneity and electrolyte adsorption: intrinsic and electrostatic effects. *Neth. J. Soil Sci.* 35: 241-257, 1987.