

Specific surface area of Lublin Polesie mucks determined from water vapour and nitrogen adsorption data

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A b s t r a c t. Laboratory studies of nitrogen and water vapour adsorption on mucks originating from Lublin Polesie Region are presented. The Brunauer-Emmet and Teller (BET) equation was used to analyze the experimental results and to calculate the specific surface area from both nitrogen adsorption and water vapour sorption isotherms in relation to the degree of mucking (secondary transformation). The existence of relationship between surface area determined from water vapor desorption data and water holding capacity index W_1 which characterizes the state of the secondary transformation of peat was proved. The relationships between the specific surface areas determined from water vapour and nitrogen adsorption data, and some important physical properties, eg ash content, bulk density and total porosity of the mucks studied were found. Both classification schemes of the secondary transformation of the peaty-muck soils, that according to Okruszko and W_1 index according to Gawlik, should be used simultaneously. In order to characterize the state of muck transformation, simultaneous evaluation of specific surface area from adsorption of polar and non-polar adsorbates is advisable.

K e y w o r d s: specific surface area, mucks, adsorption of water vapour and nitrogen

INTRODUCTION

The Lublin Polesie Region covers an area of about 350 000 ha. The contribution of marsh in Lublin Polesie is 28% of the total area and it is lower than in the main part of the Polesie Region. This can be related to the peripheral location of this region. Moreover, the Lublin Polesie was drained when the melioration system called the Wieprz-Krzna Canal was built (1954-1961) and more of the peat lands have been subjected to agricultural use. While water conditions change, soil mass loses its sorption abilities and assumes a more hydrophobic character. After drainage, the peat undergoes transformation under aerobic conditions,

which leads to the formation of muck. The phenomenon of the above changes is called the secondary transformation. This transformation is a set of simultaneous complex processes among which mineralization and humification are of the greatest importance (Okruszko, 1993).

During transformation, changes in chemical and physical soil properties occur (Okruszko, 1993; Sapek and Sapek, 1987; Sokołowska *et al.*, 2004). The secondary transformation strongly influences their surface properties (Sokołowska *et al.*, 2000). The measurement of adsorption at the gas-solid interface is also an essential part of the most fundamental and applied research on the nature and behavior of solid surfaces. Nitrogen adsorption measurements are widely used in soil science for determining the specific surface area and the pore size distribution. Water vapour adsorption measurements provide information on several important surface properties, such as surface area, adsorption energy distribution, heat of immersion, as well as on the nature and amount of interfacial forces. The surface area of mineral soil determined from water vapour adsorption isotherms is simply related to soil granulometric and ionic composition, mineralogy and organic matter content. Water vapour sorption on organic soils has a more complicated character. The term 'adsorption', used in the physical chemistry for mineral adsorbents and soils, is not adequate for organic soils as molecules of water vapour penetrate into bulk phase of the organic soil. In this case the term 'sorption' is more realistic, as sorption involves both phenomena, adsorption and absorption.

The sorption behaviour of water vapour within a organic soil was studied by Chiou *et al.* (1990), Lin (1997), Pennell *et al.* (1995), Sapek and Sapek (1987), and

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Sokołowska *et al.* (2000, 2002). The water vapour sorption on mucks is not a reversible process. The sorption-desorption curves did not exhibit any hysteresis loop. In all cases a strong asymmetry between sorption and desorption rates for water vapour was observed. This work presents the laboratory studies of nitrogen and water vapour adsorption on mucks originating from the Lublin Polesie Region. The Brunauer-Emmet and Teller (BET) (1938) equation is used to analyze the experimental results and to calculate the specific surface area from both nitrogen adsorption and water vapour sorption isotherms in relation to the state of secondary transformation of mucks. Also, the correlations between surface area and some physico-chemical properties of mucks are investigated. In our opinion, for organic soils it is advisable to evaluate simultaneously specific surface area based on adsorption processes of polar and non-polar adsorbates.

MATERIALS AND METHODS

The study was conducted on muck samples taken from upper layers of 7 differently transformed peat-muck profiles located on grasslands in the Lublin Polesie Region. The samples studied were taken from depths of 5 to 10, 5 to 15 and 5 to 25 cm, depending on the mucking stage. All the samples originated from soils utilized for grassland. The samples were classified as peaty-mucks – Z_1 and proper (granulated) mucks – Z_3 (Okruszko, 1993). The state of secondary transformation was expressed by the W_1 index determined according to Gawlik's approach (1992). Gawlik (2000) divided the muck formation with differentiated content of mineral parts into classes according to the advancement of their secondary transformation as determined by the numerical values of the water capacity index W_1 . This division comprises five different classes in all the groups of muck formations. The W_1 index expresses the ratio of water capacity of a sample that has been previously dried at 105°C to water capacity of the sample in its natural state. Water capacity of muck was determined by the centrifugal method with the rate of centrifugation equal to the acceleration of 1000 g. Values of $W_1 < 0.36$ distinguish non-transformed peat fraction. Values of the index W_1 in the range of 0.36 to 0.75 are characteristic for weakly and medium transformed peat-mucks. Peat-mucks with the index W_1 higher than 0.76 and lower than 0.90 are strongly transformed. Mucks with the index of above 0.90 are degraded (Gawlik, 2000).

Physical properties of the soils under investigation were determined by the methods used at the Institute for Land Reclamation of Grassland Farming (Zawadzki, 1973), whereas all the remaining properties were evaluated according to Myślińska (2001).

The composition of humic substances in the soils investigated was determined according to the method described by Bambilov *et al.* (1998).

The sorption isotherms of water vapor were measured by the gravimetric method using a vacuum chamber. This procedure is in accordance with the Polish standard PN-Z-19010-1 for soil surface area determination. A soil sample of the weight of approximately 3 g was put into a glass vessel and placed over sulphuric acid solution. The sample was then equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample with adsorbed water and that of dry sample (dried in an oven at 105°C). The relative water pressures were obtained from the density of sulphuric acid solutions. The sorption measurements were repeated three times, keeping the temperature constant at $T=20^\circ\text{C}$.

The adsorption-desorption isotherms of nitrogen gas at liquid nitrogen were obtained with Sorptomatic 1999 (Fisons) apparatus. Before adsorption measurements, the samples were dried at 105°C and outgassed overnight at 105 C under vacuum. The surface area of the investigated mucks was then evaluated. The first step in the application of the BET method is to determine the monolayer capacity (N_m) from the BET plot. The second step is to calculate the surface area from the dependence: $S=N_m L \omega$, where: L is the Avogadro number and ω is the molecular cross-section area ($10.8 \cdot 10^{-20} \text{ m}^2$ for water and $16.2 \cdot 10^{-20} \text{ m}^2$ for nitrogen molecule).

RESULTS AND DISCUSSION

The selected properties of the investigated soil samples, along with the content of humic (HA) and fulvic (FA) acids, are shown in Table 1.

All of the samples have low (< 25%) ash content. The soils greatly differ by bulk densities, which is undoubtedly related to the degree of mucking and of the soil mass. The lowest density ($0.21\text{-}0.28 \text{ g cm}^{-3}$) has been observed for peaty mucks (Z_1), which also has the lowest water holding capacity index ($0.41 < W_1 < 0.61$). For the proper mucks (Z_3), the bulk density is higher (from 0.29 to 0.34 g cm^{-3}), and the values of W_1 range from 0.60 to 0.74. According to Gawlik (2000), these samples belong to the medium transformed peat soils. Most of the soils are acidic (samples 1, 3-5, 7), one is slightly acidic (sample 6), and one – very acidic (sample 2).

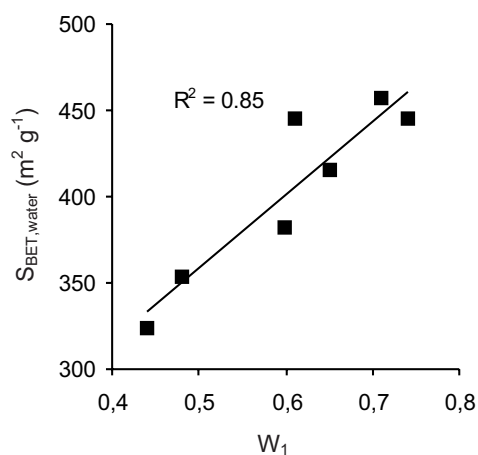
The specific surface area $S_{\text{BET,water}}$ estimated from the sorption isotherms of water vapour ranged from 324 (sample No. 1) to $457.7 \text{ m}^2 \text{ g}^{-1}$ (sample No. 6). The values of specific surface area evaluated from water vapour sorption data were estimated from desorption isotherms. For the surface area determined by the ethylene glycol method, Chiou *et al.* (1990) proposed the term 'apparent surface area' which is based on measurement by uptake of adsorbate that either changes the structure of the solid, dissolves in it, or both. On the other hand, Sokołowska *et al.* (2000, 2002) pointed out that surface area values of mucks obtained from desorption

Table 1. Some physical properties of the soil samples studied

No.	W_1	Kind of muck	FA	HA	Ash content (% d.m.)	Bulk density (g cm^{-3})	Total porosity (% vol.)	pH H_2O	pH KCl
1	0.44	Z ₁	8.84	29.82	22.69	0.21	88.5	5.13	4.54
2	0.48	Z ₁	8.71	31.12	20.54	0.28	84.7	4.72	4.23
3	0.61	Z ₁	11.49	14.40	15.14	0.24	85.2	5.84	5.33
4	0.60	Z ₃	10.18	31.98	21.24	0.34	81.4	5.44	4.97
5	0.65	Z ₃	9.60	26.84	18.94	0.31	80.9	5.45	4.97
6	0.71	Z ₃	11.67	24.55	22.70	0.30	83.6	6.15	5.75
7	0.74	Z ₃	12.33	21.95	21.47	0.29	84.1	5.78	5.33

isotherms are repeatable. Generally, those values of the specific surface area were higher than those obtained from 'adsorption' curves. The shape of all the sorption curves obtained were similar for all the samples and the isotherms belong to the same class according to the BET classification (Brunauer *et al.*, 1938). However, the detailed courses of curves and the amount of sorbed water in particular varied from sample to sample. It was the result of the different basic properties of the samples (Sokołowska *et al.*, 2000; 2004). Next, for the relative pressures range of $0.05 < p/p_0 < 0.35$, the experimental data were transformed, in accordance to the BET theory, to the linear form of the BET equation. The high values of the correlation coefficient R^2 (above 0.996) indicated that BET equation provides a good fit to the experimental data. It is now accepted to use the BET method to derive the specific surface area of organic material from physical adsorption data (Rutherford, 1992; Sikora *et al.*, 2002; Sokołowska and Matyka-Sarzyńska, 2002; Sokołowska *et al.* 2000; Stawiński *et al.*, 2000).

There exists a correlation between the specific surface area and the water holding capacity index W_1 (Fig. 1). Muck soils at different stages of mucking, as defined by the W_1 index, contain different amounts of polar functional groups,

**Fig. 1.** Relation between the specific surface area, $S_{\text{BET,water}}$, and water holding capacity index, W_1 .

eg OH, COOH (Sokołowska *et al.*, 2004; Sposito, 1989). These groups are the sorption sites for water molecules. Water molecules have high dipole moment and the ability to form hydrogen bonds, therefore they can adsorb in a highly specific manner, forming a quite complex adsorbed layer. This layer exhibits different properties depending on the kind of surface functional groups binding water molecules.

Nitrogen surface areas were also determined from the BET equation and they ranged from 3.21 to 5.55 $\text{m}^2 \text{g}^{-1}$. The surface area $S_{\text{BET,nitrogen}}$ of the samples studied increases in the following order: 5,4,3,2,6,1,7. Unfortunately, no dependence between the surface area and the W_1 index of the secondary transformation was found. In general, the values of the specific surface area obtained from water vapour isotherms are higher than the specific surface areas resulting from nitrogen adsorption. This indicates that water molecules exhibit much higher affinity with respect to organic soils.

For surface area $S_{\text{BET,nitrogen}}$, Chiou *et al.* (1990), Sokołowska *et al.* (1999) used the term 'free surface area'. This surface area corresponds to an interfacial area of a solid, which exists before the adsorption and is measured by an adsorbate that does not change the structure of the solid. Obviously, adsorption of nitrogen depends on the nature of organic soils. There exists a relationship between the surface area $S_{\text{BET,nitrogen}}$ and the ash content (Fig. 2).

In the adsorption process of nitrogen, the adsorption centers play a smaller role than the porous structure because nitrogen is an inert adsorbate. The total pore volume is often derived from the total amount of adsorbed nitrogen at a relative pressure close to unity, by assuming that pores are then filled with liquid adsorbate. The micropore volume is often obtained from the Dubinin-Radushkevich (DR) equation, applied to adsorption isothermal data over a limited range of relative pressures, p/p_0 (below the onset of capillary condensation). The estimated pore specific volume V_s values are given in Fig. 3 which shows the relationship between specific surface area $S_{\text{BET,nitrogen}}$ and the pore specific volume V_s . It is seen from Figs 2 and 3 that the mucks under investigation can be divided into two groups,

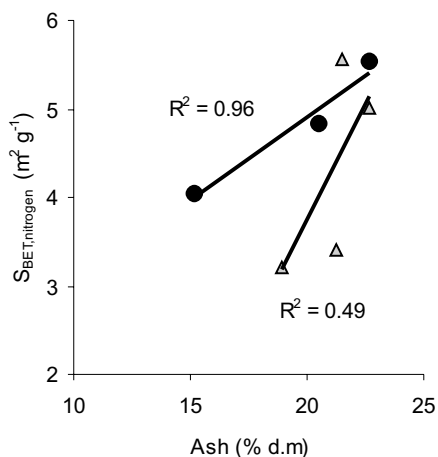


Fig. 2. Relation between the specific surface area, $S_{\text{BET,nitrogen}}$, and ash content (black circles - Z_1 mucks, triangles - Z_3 mucks).

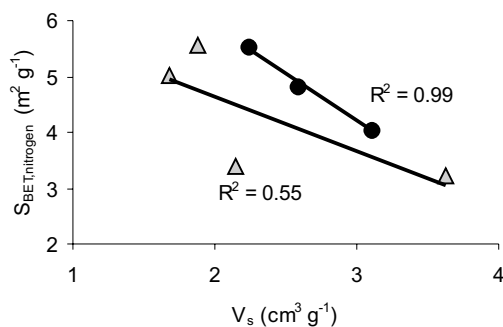


Fig. 3. Relation between the specific surface area, $S_{\text{BET,nitrogen}}$, and pore specific volume, V_s (black circles - Z_1 mucks, triangles - Z_3 mucks).

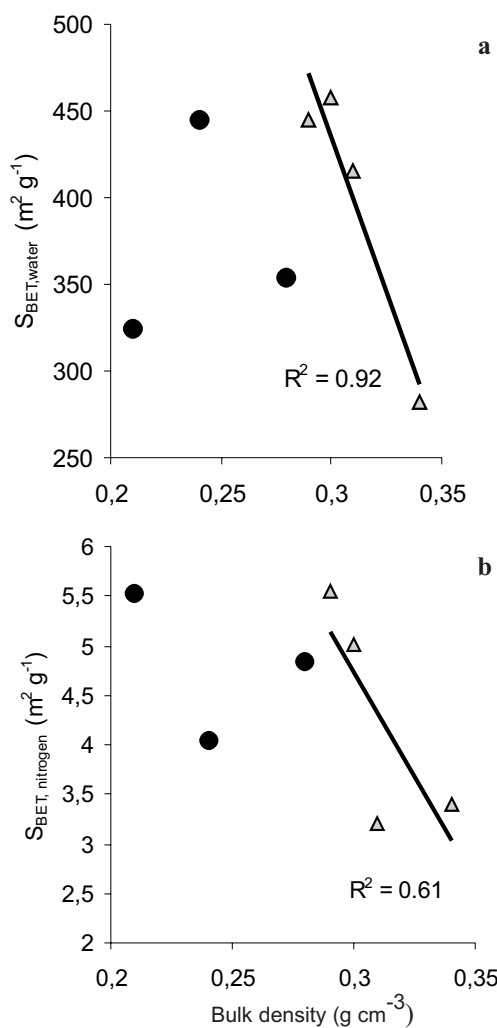


Fig. 4. Relation between the specific surface areas, $S_{\text{BET,water}}$ (a); $S_{\text{BET,nitrogen}}$ (b) and bulk density (black circles - Z_1 mucks, triangles - Z_3 mucks).

for which individual linear regression lines can be plotted. The first group (marked with black circles in all the figures) consists of peaty-muck formations (Z_1). The second one (triangles) contains proper mucks (Z_3). The correlation coefficients, R^2 , for the first group described above were high and equal to 0.96 and 0.99, respectively.

An attempt to find some relationships between the specific surface area resulting from water vapour and nitrogen isotherms and other soil parameters and characteristics was undertaken. Similarly as previously, there are two populations of the investigated mucks. In the case of soils Nos 4, 5, 6 and 7 (Z_3), an increase of the bulk density diminishes the surface area determined from water vapour as well as from nitrogen adsorption data (Fig. 4a, b). An opposite relationship is observed between the surface area determined from nitrogen adsorption data (Fig. 5) and the total porosity, TP. It should be also noted that this

tendency was found for both groups of mucks - Z_1 and Z_3 . The linear correlation coefficient for the data described above for both muck groups was 0.99 and 0.61, respectively.

In the mucks studied, the organic matter composition is a consequence of the state of secondary transformation. In general, surface area evaluated from water sorption curves decreases with the humic to fulvic acid ratio (Fig. 6a). An inverse relationship would rather be expected, because fulvic acids have lower molecular weight and contain more hydrophilic carboxylic groups per unit mass. The appearance of this tendency seems to indicate that more secondarily transformed mucks are characterized by higher relative contents of humic acids. So, it can be stated that the muck formation process enriches the soils investigated with humic acids: low molecular weight organic substances could be leached out from the soils during the transformation process. Humic acids did not remain intact through the secondary

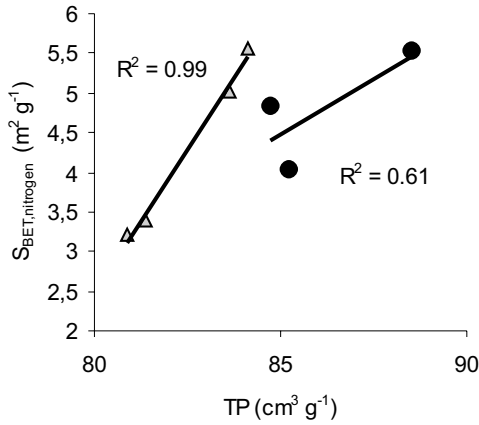


Fig. 5. Relation between the specific surface area, $S_{BET,nitrogen}$, and total porosity, TP (black circles - Z_1 mucks, triangles - Z_3 mucks).

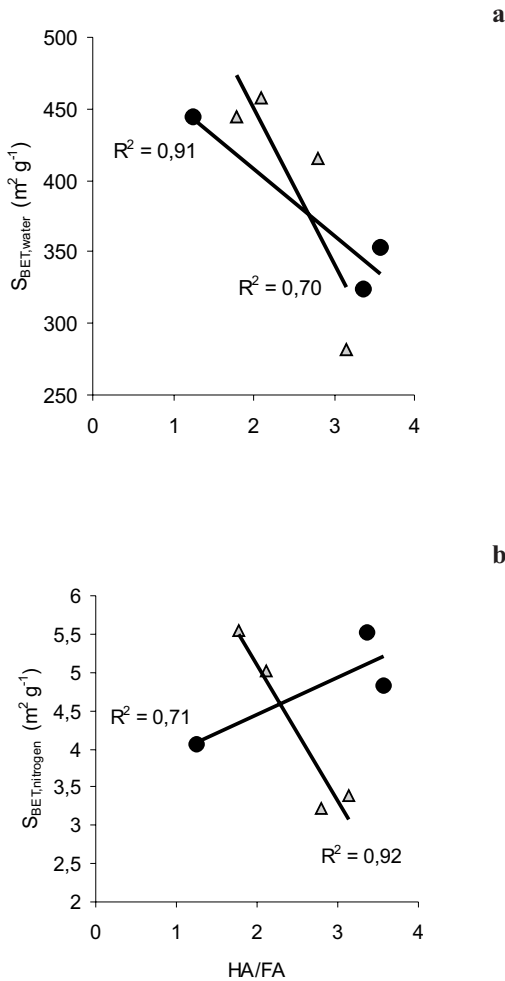


Fig. 6. Relation between the specific surface areas (a, b) and humic to fulvic acids ratio HA/HF (black circles - Z_1 mucks, triangles - Z_3 mucks).

transformation process. Their molecular mass was decreasing during intensive mineralization and oxidation. Lower molecular mass results in a decrease of specific surface area values. A similar tendency was observed in the group of proper-muck soils, for specific surface area determined from nitrogen adsorption process (Fig. 6b). In the case of the samples from the other population, the effect of the increase of HA/FA ratio on the specific area $S_{BET,water}$ is the opposite. This tendency can be connected with the structural changes occurring during the first stage of the humification process, where fulvic acids are predominant. Probably these three soils differ from the others in their content of lignin.

It has been found by numerous authors that for materials rich in organic matter, as forest litter, soil humus, sediments, peats and organic soils, the specific surface area determination frequently leads to several uncertainties. The main problem is high surface area measured by polar adsorbates such as water, ethylene glycol or ethyleneglycol monoethyl ether (Chiou *et al.*, 1990; De Jonge *et al.*, 1996; Pennell, 1995; Stawiński, 2000; Theng *et al.*, 1999) while that measured with nonpolar adsorbates (nitrogen) is extremely low (Chiou *et al.*, 1990; Stawiński, 2000). Such large differences may arise from differences in water and nitrogen molecules polarities: water is adsorbed on polar surfaces while nitrogen on non-polar ones. In organic matter, polar functional groups dominate (Sokołowska *et al.*, 2004). With this respect one should look for the reason for the differences mentioned either in complicated geometry of organic matter or in their heterogeneous energetic character (Sokołowska *et al.*, 1999). One of the reasons for the above phenomenon is sample pretreatment applied *eg* drying the sample before measurements that leads to irreversible sample structure changes. The next is volumetric sorption of polar adsorbates leading to uncontrolled structure expansion (Rutheford *et al.*, 1992).

CONCLUSIONS

1. The existence of a relationship between surface area determined from water vapour desorption data and water holding capacity index, W_1 , characterizing the state of secondary transformation of the peat, was proved. The mucking process leads to an increase of the total surface area determined from water sorption isotherms.
2. Both the classifications of the secondary transformation of the peaty-muck soils according to Okruszko and the W_1 index according to Gawlik should be used simultaneously. The differentiation of peaty and proper mucks with respect to the specific surface area seems to be the strongest. The above classification schemes are qualitative.
3. The relationships between the specific surface areas determined from water vapour and nitrogen adsorption data and some important physical properties (ash content, bulk density, total porosity) of the mucks studied were found.

4. It appears that the specific surface area of organic soils should be simultaneously evaluated on the basis of both adsorption processes using polar and non-polar adsorbates. Such a procedure leads to a better characterization of the surface properties of organic soils and of soil organic matter.

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