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Phosphorus sorption properties of deposits from peat-muck soil profile in the Kuwasy object

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Abstract

Sorption capacity and the energy of phosphorus adsorption on muck and peat deposits were studied in peatmuck soil profile from a lowland peatland in the Kuwasy object. Soils of the area are characterised by a laminar structure which results in variable sorption properties of peat deposits of different origin, degree of humification (decomposition - R) and transformation of organic matter of upper muck layers (degree of mucking - Z). There was a relationship between the maximum phosphorus adsorption calculated from the Langmuir isotherm (b) and adsorption energy (k) and the type and degree of humification of peat and transformation of muck mass. Muck deposits of the maximum sorption capacity similar to that of peat deposits bind phosphorus less intensively than peats. One may expect that different sorption capacity and the strength of phosphorus binding will effect in different migration of inorganic and organic P compounds in soil profile and their transfer to ground waters.

Key words: *adsorption energy, Langmuir adsorption isotherm, peat-muck soil, phosphorus, soil profile, sorption capacity*

INTRODUCTION

Phosphorus is one of mineral components of organic soils which is used in fertilisation and has long been the subject of studies [GRIFFIN, JURINAK 1973; OKRUSZKO 1964]. The release and outwashing of phosphorus from peatlands and peat soils of various drainage and use to waters is important in view of the ability of this element to enhance eutrophication a process that poses a remarkable threat to water quality [JASZCZYŃSKI et al. 2006; NADANY, SAPEK 2003; SAPEK 2008; SAPEK et al. 2001; SAPEK, GOTKIEWICZ 1987; SAPEK et al. 2004; SAPEK et al. 2005]. Water pollution by P compounds may be particularly important in renaturisation of formerly drained peatlands. It was shown that under such conditions there is a risk of P release and outwashing to ground waters [LEIN-WEBER et al. 2001; MEISSNER et al. 2008; SAPEK et al. 2004].

A high chemical affinity of phosphorus for organic matter and its ability to be adsorbed by peat deposits on one hand and a possibility of forming mobile compounds with dissolved organic carbon (DOC) on the other requires continuous studies of phosphorus transfer to waters particularly at currently changing natural and economic conditions [JASZCZYŃSKI 2010; MEISSNER et al. 2008; MORRIS, HESTERBERG 2010; SAPEK 2008; SAPEK et al. 2006]. Binding of phosphorus, as of other mineral and organic compounds, by peat deposits is a complex process which is accompanied by physical, chemical and biological adsorption. To describe the combined effect of these processes a notion "sorption" is also used [LITAOR et al. 2005; OKRUSZKO 1964; SAPEK 1994; SAPEK, SA-PEK 1993]. The risk of increasing content of dissolved P compounds and their migration to ground water depends on the efficiency of this process, determined by sorption capacity of formations in the soil profile, soil pH and the strength of P binding [MORRIS, HES-



TERBERG 2010]. Results of studies on P sorption in peat-muck soil were described in a paper dealing with P content and its performance in soils of drained lowland peatland in the Biebrza River valley in relation to soil developmental stage (accumulation and decession of organic matter), to the advancement of soil forming process (bog forming versus muck forming) and to physical and chemical properties of these deposits [SAPEK 2011].

The aim of this study was to assess sorption capacity and the strength of P binding by muck and peat deposits in peat-muck soil profile of a drained peatland in the Kuwasy object based on the determination of Langmuir adsorption isotherm parameters. The effect of deposits present in soil profile and their sorption capacity was analysed in view of a possibility of P migration to ground water.

MATERIAL AND METHODS

Studies and determinations of P sorption by muck and peat deposits were made within the PRO-WATER project [1999-2003]. Samples were taken from peat-muck soil profile situated at the Experimental Farm Biebrza of the Institute for Land Reclamation and Grassland Farming (now the Institute of Technology and Life Sciences in Falenty). Soil profile was situated near automatic station UGT installed within the mention project. Samples from soil profile were taken and the profile was described in 2002. Peat-muck soil was defined acc. to OKRUSZKO [1994] as moderately sapric made of highly decomposed moss and osier peat (MtIIcc). According to FAO classification the soil is defined as Haplic Histosol. Studied profile represents a characteristic feature of soils from this object - their laminar structure whose consequence is specific sorption properties of peat deposits of different origin, degree of humification (decomposition - R) and transformation of organic matter (the degree of mucking - Z) [ILNICKI 2002; OK-RUSZKO 1976; 1994].

Sorption properties of analysed deposits were determined with a modified method of static adsorption acc. to NAIR et al. [1984] in the year of sampling. KH₂PO₄ solutions of the concentrations of 0, 50, 100, 150, 200, 300, 400, 500, 600, 80, and 1000 µmol $P \cdot dm^{-3}$ in electrolyte solution of constant ionic strength equivalent to 30 mmol KCl were used to measure P sorption. Preweighed 0.5 g dry wt. soil samples at the soil to sorbate ratio 1:50 and 24-hour equilibration time were used. Phosphorus concentration in analysed solutions was determined with the molybdenum method using SKALAR Segment Flow Analyser. Maximum P adsorption by studied deposits and the energy of adsorption (the strength of P binding) was calculated from the Langmuir adsorption isotherm in its linear form [GRIFFIN et al. 1973].

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b}$$

where:

c – equilibrium P concentration, mmol·dm⁻³;

- x/m adsorbed phosphorus, mmol·kg⁻¹;
- b maximum P adsorption, mmol·kg⁻¹;
- k parameters describing the energy of adsorption, in dm³ (mmol)⁻¹.

Parameters b and k were estimated with the linear regression and the least square deviation method.

 pH_{KCl} of analysed deposits was determined in 1 M potassium chloride solution, the content of mineral components (ash) and the total content of P, Na, K, Mg, Ca, Fe after mineralization of soil samples in a mixture of nitric acid and perchloric acid were determined acc. to the method of chemical analyses of organic soils [SAPEK, SAPEK 1997].

RESULTS AND DISCUSSION

CHARACTERISTICS OF THE PEAT-MUCK SOIL PROFILE

The peat-muck soil profile selected for these studies had a muck layer of a thickness of 24 cm with distinct consecutive layers (M_1, M_2, M_3) (Tab. 1). The upmost layers (turf M_1 and sub-turf M_2) contained most ash particles and therefore – most mineral components. Transitory layer M_3 between 18 and 24 cm depth built of sedge peat in the initial stage of muck-ing contained much less mineral components, especially phosphorus, potassium and iron (Tab. 1).

Moderately to heavily decomposed (R_2/R_3) sedge peat beneath the muck layer and two underlying layers of strongly decomposed (R_3) osier peat were poorer in mineral components compared with the muck layer (Tab. 1). The next layer of largely decomposed (in 85%) osier peat at a depth of 76–84 cm was enriched in mineral components, mainly in phosphorus. Beneath, there were layers of poorly to moderately decomposed $(R_1/R_2 \text{ and } R_2)$ moss peat which contained less ash parts including less phosphorus, potassium, calcium and iron. Muck layers poorer in magnesium compared with peat layers of the profile indicate a great mobility of this components in the environment (Tab. 1).

PHOSPHORUS SORPTION CAPACITY OF MUCK AND PEAT DEPOSITS IN THE SOIL PROFILE

Empirical P adsorption isotherms present the amount of phosphorus (mmol $P \cdot kg^{-1}$) bound by consecutive diagnostic soil layers under adopted conditions of the static adsorption method. They were calculated from the difference of P concentration be-

Layer	Description of deposit	pН	Ash dry	Total content, $g \cdot kg^{-1} dry wt$.					Calculated parameters of Langmuir adsorption isotherm		
cm		-	wt. %	Р	Na	Na K Mg Ca	Fe	$b \\ mmol \cdot kg^{-1}$	k dm ³ ∙mmol ^{−1}		
1–4	M_1 – (sod layer), grey-black muck, visible plant residues	5.6	15.0	1.78	0.15	0.52	1.58	15.7	16.8	42.88	2.54
7-16	M2-(sub-sod layer), humic muck	5.9	15.2	1.60	0.09	0.40	1.53	16.9	16.4	41.29	3.44
18–24	M ₃ – (intermediate layer), tall sedge peat in the initial stage of muck-forming process	5.8	9.3	0.94	0.11	0.23	1.58	15.4	15.8	50.24	2.87
25–34	R_2/R_3 – tall sedge peat, dark brown, decomposed in H = 65%	5.9	9.7	0.73	0.10	0.19	2.01	14.8	17.6	17.6	4.63
36–60	R_3 – dark brown, strongly decom- posed osier peat (H = 75–80%) with parts of moss, sedge and alder	5.8	11.8	0.62	0.09	0.11	2.54	13.5	24.5	43.04	6.06
63–74	R_3 – dark brown, strongly decomposed osier peat (H = 80%), with a large contribution of reed	5.8	13.4	0.62	0.12	0.20	2.80	15.8	22.5	46.17	7.29
76–84	R_3 – dark graphite, strongly de- composed osier peat (H = 85%), visible residuals of reed and sedge	5.8	16.5	0.90	0.19	0.32	2.91	21.5	20.0	53.93	10.44
86–101	R_1/R_2 – brown moss peat (H = 40%) with residuals of osier and seeds of horse bean	6.0	10.6	0.22	0.16	0.25	2.51	13.2	13.2	37.74	7.52
102-111	R_2 – dark olive moss peat (H = 45%) with the traces of detritus	6.1	12.6	0.32	0.11	0.14	2.46	16.6	16.1	33.13	6.78

 Table 1. Characteristics of layers in the peat-muck soil profile from permanent meadow near the automatic survey station UGT6; soil sampled on 09.04.2002

Explanations: b – maximum P adsorption, mmol·kg⁻¹, k – the energy of P adsorption (bonding strength), dm³·mmol⁻¹. Source: own study.

tween the solution used for adsorption and in the equilibrium state (μ mol·dm⁻³) (Fig. 1).

Maximum P sorption capacity (b) of deposit samples in peat-muck soil profile and adsorption energy (k) that describes the strength of P binding were calculated from Langmuir isotherms (Tab. 1). Obtained results showed a significant effect of peat type, the degree of its decomposition, the advancement of mucking process and transformation of muck mass in upper soil layers. Most transformed organic material in the upper soil layers - muck and moderately decomposed peat - showed relatively smaller sorption capacity (40.7–42.9 mmol P·kg⁻¹). From among peat deposits, the lowest maximum sorption capacity $(31.3-37.7 \text{ mmol } P \cdot kg^{-1})$ was found for poorly to moderately decomposed moss peat. However, it bound phosphorus much stronger than muck, whose binding strength was smallest compared with other deposits (k = 2.54 - 3.44). Maximum sorption capacity of peat in the initial stage of mucking (transitory layer of mucking peat M₃) and of highly decomposed peat (R₃) was highest (50.2–53.9 mmol $P \cdot kg^{-1}$). These deposits differed, however, in the strength of P binding. Mucking peat, as muck, bound P much weaker (k =2.87) than peats, especially osier peat deposited at a depth between 76 and 84 cm, which showed the greatest strength of P binding (k = 10.44) (Tab. 1). A greater strength of P binding by moss peats resulted





probably from the admixture of osier in peat at a depth of 86–101 cm and from the trace amounts of detritus gyttja in deeper layer (Tab. 1).

In view of presented results, one may conclude that the selected diagnostic soil layer does not directly affect P adsorption. The latter depends, however, on the type of deposit and its P sorption capacity which in turn is associated with the degree of organic matter transformation (Fig. 2). This study did not include the effect of water conditions in the soil profile and of changes in the ground water level (being at a depth of 55 cm during sampling) on P performance in the studied soil profile.



Fig. 2. Maximum phosphorus adsorption capacity of organic deposits in the peat-muck soil profile; description of deposits as in Table 1; source: own study

The effect of muck transformation and of the type and decomposition of peat on the total P content in similar peat-muck soil profile MtIIcb was demonstrated by URBANIAK and SAPEK [2004] in their studies on P fractionation. The authors showed also the relationship between the proportion of particular P fractions and ground water table depth. Most labile and variable with respect to ground water depth were the fractions of dihydrophosphate and phosphorus adsorbed by soil colloids.

The greatest share of organic P fraction and an increase of this share with the degree of mucking and humification of organic matter is an effect of increased content of dissolved organic carbon (DOC) [JASZCZYŃSKI 2010]. The energy of P adsorption calculated from the Langmuir adsorption isotherm increased with the advancement of organic matter transformation in muck and with the degree of peat humification. Similar relationship was demonstrated earlier in the study on copper adsorption by peat-muck soils in the Biebrza River valley [SAPEK 1980]. A high affinity of copper and phosphorus for organic matter and the formation of complexes with humic substances ("specific" sorption) allows for comparing the performance of the two elements in similar soil conditions.

A consequence of much lower energy of P adsorption in muck (k = 2.5-3.3) than in peat (k = 10.4-6.8) is the weakest binding of P in the former which facilitates P outwashing from deeper soil layers (Tab. 2). The determined content of phosphorus in muck layers (1.60–1.78 g·kg⁻¹) is bigger than the calculated maximum capacity of these deposits (1.30 g P·kg⁻¹ dry wt.). Therefore, the excess of P bound in muck may be easily washed out to deeper soil layers and to ground waters. This process is limited by underlying highly decomposed osier peat whose binding energy is much higher than that of muck (k = 10.4). The smallest P sorption capacity (c. 1.10 g·kg⁻¹ dry wt.) in layers occupied by moss peat (86–111 cm) will, however, facilitate P release to ground waters. This was confirmed by a small content of P (0.22–0.32 g·kg⁻¹) in these layers (Tab. 2, Fig. 2).

Table 2. Total content of phosphorus, maximum P sorption capacity (b) and the adsorption energy index (k) in muck layer and in osier and moss peat

	Parameter b – Langmuir iso	Index k – calculated from			
Soil deposit	total content	maximum sorption (recalculated)	Langmuir iso- therm dm ³ ·mmol ⁻¹		
Muck layers	1.60-1.78	1.30	2.5-3.3		
Osier peat (R ₃ – 85%)	0.90	1.67	10.4		
Moss peat $(R_1/R_2 - 45\%)$	0.22-0.33	1.10	6.8		

Source: own study

SUMMARY

Peat-muck soils of studied, drained peatland are characterised by a laminar structure resulting in variable sorption properties of peat deposits of different origin, humification (decomposition - R) and transformation of organic matter in the upper soil layers (the degree of mucking – Z) [SAPEK 2011]. Maximum P sorption capacity (b) and the energy of P adsorption (k) (both calculated from the Langmuir isotherm) by an organic deposit in moderately mucking MtIIcc peat-muck soil depended on the type and advancement of peat humification and on the transformation of muck mass. The relationship was, however, not simply linear since muck, of similar maximum P sorption capacity, bound phosphorus less intensively than peat. Shown in other studies correlation between P release and ground water table depth puts the question if and how changes in the latter might affect the values of b and k in deposits of soil profile. This effect should be considered when predicting phosphorus release to ground waters.

Results of studies on P adsorption capacity and the energy of adsorption in differentiated deposits of peat-muck soil profile seen in view of possible P release to ground water lead to the following conclusions:

1. Due to different sorption capacity and the strength of P binding by soil deposits, the migration of inorganic and organic phosphorus in soil profile and its possible release to ground water is differentiated.

2. Maximum P sorption capacity bigger in muck than in peat and a weaker energy of P adsorption

would facilitate penetration of phosphorus compounds to deeper layers of soil profile.

3. Their further migration and a possibility of release to ground water depends on the type and the degree of decomposition of underlying peat deposits.

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Właściwości sorpcyjne w stosunku do fosforu utworów zalegających w profilu gleby torfowo-murszowej na obiekcie Kuwasy

STRESZCZENIE

Słowa kluczowe: energia adsorpcji, fosfor, gleba torfowo-murszowa, izoterma adsorpcji Langmuira, pojemność adsorpcyjna, profil gleby

Badano pojemność adsorpcyjną i energię adsorpcji murszu oraz utworów torfowych zalegających w profilu gleby torfowo-murszowej odwodnionego torfowiska niskiego na obiekcie Kuwasy względem fosforu. Gleby tego obszaru cechują się budową warstwową, z czego wynika zmienność właściwości sorpcyjnych zalegających w nich utworów torfowych różnego pochodzenia i stopnia humifikacji (rozkładu – R) oraz przeobrażenia masy organicznej wierzchnich warstw murszu (stopnia zmurszenia – Z). Wykazano zależność obliczonych z równania izotermy adsorpcji Langmuira wartości maksymalnej adsorpcji fosforu (*b*) i energii adsorpcji (*k*) od rodzaju i stopnia humifikacji torfu zalegającego w profilu gleby oraz stopnia przeobrażenia masy murszu. Mursze o podobnej do torfów maksymalnej pojemności sorpcyjnej wiążą fosfor z mniejszą siłą niż torfy. Można przewidywać, że skutkiem różnej pojemności sorpcyjnej utworów i siły wiązania fosforu będzie zróżnicowanie migracji jego związków nieorganicznych i organicznych w profilu gleby i przenikania do wody gruntowej.