

Marcin Becher\*, Krzysztof Pakuła\*, Joanna Pielech\*, Ewa Trzcińska\*

## Phosphorus resources and fractions in peat-muck soils

\* Department of Soil Science and Plant Nutrition, Siedlce University of Natural Sciences and Humanities;  
e-mail: marcin.becher@uph.edu.pl

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### Abstract

The goal of the research was to determine the resources and speciation (forms of occurrence) of phosphorus in organic soils of drained fens of the Wysoczyzna Siedlecka. Two profiles of muck soils were generated from different peats. Basic physical and chemical properties of the soils and the quantity, resources and fractions of phosphorus in the soil were determined.

The majority of the total resource of soil phosphorus was accumulated in the muck horizons of the analysed soils. The total content of phosphorus materially correlated with characteristically variable parameters in the moorshification process (voids free bulk density of the content of organic matter, C/N ratio and C/P ratio). Additionally, a material positive correlation of the content of phosphorus with the content of iron, manganese and aluminium was observed.

The moorshification process of the analysed soils entails the qualitative transformation of phosphorus compounds, mainly involving an increase in the share of more labile and easily available forms, forms released in reduction conditions and forms combined with metallic oxides, apatite, carbonate and labile organic forms.

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## 1. INTRODUCTION

Phosphorus is characterized by complex and dynamic transformation processes in the soil environment, including mineralisation and immobilisation, dissolution and precipitation, oxidation and reduction, sorption, chelation and others [Stępniewska et al. 2006, Kang et al. 2009, Sapek 2011, 2014]. As a result of a complex transformation, the soil phosphorus occurs in numerous mineral preparations (minerals containing phosphorus, precipitations of phosphates and ions) and organic preparations (phytin, nucleic acids and phospholipids) [Paul and Clark 2000, Kalembasa, Kalembasa 2015].

Transformation of phosphorus compounds is very important in the research relating to the transformation of organic soils. Phosphorus (and nitrogen) is one of the basic biophilic elements (food and fertiliser ingredient) regulating biological processes and limiting biomass production. A lot of the scientific research refers to the dynamic interaction of phosphorus with organic and mineral components of the soil and its influence on the eutrophication of the hydrosphere (Litaor et al. 2004, Jordan et al. 2007, Kang et al. 2009). The quantity and forms

of the soil phosphorus are regulated with soil-forming processes and fertilisation [Sapek 2014].

An excessive quantity of labile soil phosphorus compounds causes migration to water reservoirs where they can constitute a measure of eutrophication of water reservoirs for anthropogenic reasons [Pokojska, Bednarek 2012]. This phenomenon is extremely important in the case of organic soils in marshy areas. Such soils are the border zone of the hydrosphere and lithosphere, and they often demonstrate a great dynamics of oxidation and reduction conditions. As a result of the mineralisation of the peat mass, phosphorus transformation is possible in organic compounds to mineral compounds susceptible to the release in the event of a change in the redox potential. The re-wetting of dried peats can lead to the release of phosphorus in the soil [Jordan et al. 2007, Zak, Gelbrecht 2007]. Processes of accumulation and release of the soil phosphorus are very complex; amongst other things, they depend on reaction, quantity of labile organic matter and quantity and quality of compounds of iron, manganese and aluminium. Human impact on the environment including nitrogen management [Chojnicki, Czarnowska 1993, Sapek 2014].

Resources and forms of the soil phosphorus influence the flora diversity and environmental values of meadows [Kamiński, Chrzanowski 2009].

The key information about forms of occurrence of phosphorus and the role of the soil in the biogeochemistry of that element is provided by the research using the speciation analysis [Brogowski 1966, Schlichting et al. 2002, Oktaba, Czerwinski 2003, Litaor et al. 2004, Urbaniak, Sapek 2004, Jordan et al. 2007]. Data regarding the abundance and speciation of the soil phosphorus are used to evaluate the existing and potential risk for the natural environment and to determine the need for fertilization [Sapek 2003, 2007, 2008, Fotyma, Fotyma 2004]. The attainment of and control over the balance between the quantity of phosphorus in the environment appropriate for the maintenance of the agricultural production and its losses because of the excessive enrichment of soils are strategic goals of the sustainable agriculture [Grzywna 2014, Sapek 2014].

The goal of the research was to determine the resources and speciation (forms of occurrence) of phosphorus in organic soils of drained fens of the Wysoczyzna Siedlecka.

## 2. MATERIALS AND RESEARCH METHODS

Soil science research was conducted in marsh areas of the upper Liwiec (left tributary of Bug), in the most important moors of Wysoczyzna Siedlecka [Dembek 2000, Dembek et al. 2000, Becher 2013]. The appearance of vastest peats is related to the occurrence of post-glacial basins of the Warta stadial, amongst other things, in the upper Liwiec where they occupy ca. 1,400 ha [Dembek et al. 2000]. Marshes in the area were meliorated in the 1960s and are currently intensely used for agricultural purposes and subject to intense secondary transformations in the moorshification process [Grzyb 1964, Becher 2013].

The research covered 2 profiles of muck soils [Systematyka Gleb Polski 2011]:

- Organic hemic-muck soil (Hemic Sapric Histosol, Drainic – WRB) generated out of moderately decomposed reed peat (*hemic*) – profile 1;
- Organic sapric-muck soil (Sapric Histosol, Drainic – WRB) generated out of strongly decomposed alder peat (*sapric*) – profile 2.

Samples were collected in a natural state in the course of the field work (to cylinders,  $d = 100 \text{ cm}^3$ ) in order to determine the bulk density [Bednarek et al. 2004]. Soil samples collected for the study of chemical properties were dried (at the temperature of  $40^\circ\text{C}$ ) and passed through a sieve (diameter  $\varnothing = 2.0 \text{ mm}$ ). The representative part of the collective sample was ground in an agate mortar (up to  $\varnothing < 0.25 \text{ mm}$ ) and subjected to chemical analyses (three repetitions). Test results were compared with the absolutely dry weight (determined by weight after the drying of prepared samples at the temperature of  $105^\circ\text{C}$ ).

The following chemical analyses were conducted [Sapek, Sapek 1997, Bednarek et al. 2004]:

- pH measurement (potentiometric; in soil suspension in 1M KCl);
- the total content of carbon (TC) and total content of nitrogen (TN) were determined in an auto-analyser for elemental analysis CHNS (thermal conductivity detector, acetanilide as the benchmarking material);
- the content of phosphorus ( $P_T$ ) and elements potentially important in soil phosphorus binding processes (Fe, Mn, Al, Ca) was determined using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) after mineralisation in aqua regia.

In the muck horizons, the enrichment index of phosphorus was calculated as the ratio of the content in muck horizons (M) to its average content in peat horizons (O) of the studied soils.

On the basis of the TC (in  $\text{g}\cdot\text{kg}^{-1}$ ), the content of the soil organic matter (SOM) was calculated:  $\text{SOM} [\text{g}\cdot\text{kg}^{-1}] = \text{TC}\cdot 1.724$ .

The content of phosphorus was expressed in m/m ( $\text{g}\cdot\text{kg}^{-1}$ ) and m/v ( $\text{g}\cdot\text{dm}^{-3}$ ). Resources of soil phosphorus were calculated ( $P_{ZAS}$  in  $\text{kg}\cdot\text{m}^{-2}$ ) using the following formula:

$$P_{ZAS} = \sum_{i=1}^n \sum_{j=1}^n (h_i \cdot D_j \cdot P_{Tij}) + (h_1 \cdot D_1 \cdot P_{T1}) + (h_2 \cdot D_2 \cdot P_{T2}) + (h_n \cdot D_n \cdot P_{Tn})$$

where  $i$  is the number of the genetic horizon of the soil;  $h$  is the thickness of the genetic horizon [m];  $D$  is the volumetric density of the dry soil of the genetic horizon [ $\text{g}\cdot\text{cm}^{-3}$ ]; and  $P_T$  is the phosphorus content in the genetic horizon [ $\text{g}\cdot\text{kg}^{-1}$ ].

The method of the sequential fractioning of phosphorus compounds was applied for the phosphorus speciation study – initially used in the research of bottom sediments and modified for the purpose of the research of organic sediments [Jordan et al. 2007]. Sequential extraction made it possible to define the following operational fractions (forms) of soil phosphorus: F1: (1 M  $\text{NH}_4\text{Cl}$ ), labile forms, loosely bound or absorbed, easily accessible; F2: (0.1 M  $\text{Na}_2\text{S}_2\text{O}_4\text{-NaHCO}_3$ ), forms bound on the surface of hydrated iron oxides (III) and hydrated manganese oxides (IV), released in reduction conditions; F3: (0.5 M HCl) forms bound by metal oxides (Fe, Al and Mn), phosphorus in apatite sand carbonates and labile forms of phosphorus in organic compounds; F4: (1 M NaOH), forms of phosphorus bound by humus substances and other polymorphic forms of phosphorus; F5: residual fraction, persistent organic and mineral phosphorus compounds. The content of phosphorus in distinguished forms was determined using an ICP-AES. The content of phosphorus in the residual fraction was calculated as follows:  $F5 = P_T - (F1 + F2 + F3 + F4)$ . Statistical calculations were carried out using the STATISTICA 10 PL statistical program (Statsoft, Tulsa, USA). Dependencies between selected characteristics were expressed in the form of a simple correlation coefficient ( $r$ ). In selected cases, the linear regression equation was determined.

**Table 1.** Some properties of tested soil.

Genetic horizon, depth (cm)	pH	D (g·cm <sup>-3</sup> )	SOM (g·kg <sup>-1</sup> )	TC/TN	TC/P <sub>T</sub>
Organic hemic-muck soil – profile 1					
M1, mursh, 0–10	6.20	0.404	620.6	11.3	109.5
M2, mursh, 10–25	6.17	0.380	670.6	12.2	127.7
Oe1, reed peat, 25–40	6.00	0.184	855.1	15.8	435.1
Oe2, reed peat, 40–70	5.81	0.155	899.9	16.2	998.1
Oe3, reed peat, 70–100	5.70	0.180	822.3	15.3	608.4
Organic sapric-muck soils – profile 2					
M1, mursh, 0–10	5.20	0.420	634.4	10.7	161.4
M2, mursh, 10–20	5.41	0.334	708.6	12.0	258.5
M3, mursh, 20–35	5.50	0.328	737.9	12.8	326.7
Oa1, alder peat, 35–50	5.99	0.193	796.5	16.8	822.1
Oa2, alder peat, 50–65	5.85	0.235	765.5	15.8	595.2

**Table 2.** The content, enrichment index and phosphorus recourses in tested soils.

Genetic horizon	P <sub>T</sub> (g·kg <sup>-1</sup> )	P <sub>T</sub> (g·dm <sup>-3</sup> )	P <sub>ZAS</sub> (kg·m <sup>-2</sup> )
Profile 1			
M1	3.29 (4.03)*	1.33 (9.23)*	0.405 (75.7:24.3)**
M2	3.05 (3.73)	1.16 (8.04)	
Oe1	1.14	0.210	
Oe2	0.523	0.081	
Oe3	0.784	0.141	
Profile 2			
M1	2.28 (3.49)	0.958 (6.75)	0.256 (83.4:16.6)**
M2	1.59 (2.43)	0.531 (3.74)	
M3	1.31 (2.00)	0.430 (3.03)	
Oa1	0.562	0.108	
Oa2	0.746	0.175	

\* Enrichment index of phosphorus to mean content in peat.

\*\* Percentage (%) of mucky and peaty horizons (M:O).

### 3. DESCRIPTION OF RESULTS

A very marked development of muck horizons was a characteristic feature of the structure of soils selected for the research (M1 and M2) with the persistent granular structure. In the sapric-muck soil profile (profile 2), there was the third muck horizon built of cracked organic

matter with the characteristics that were intermediate between surface muck horizons and the alder wood peat found deeper. Peats comprising source formations of the analysed soils demonstrated morphological characteristics of reed peats (profile 1) and alder wood peats (profile 2) [Systematyka Gleb Polski 2011].

The pH measurement demonstrated minor variations in that parameter in soil profiles (tab. 1). Lower acidification was found in the hemic-muck soil (profile 1). The obtained pH figures (5.20–6.20) in both profiles allow us to define them as moderately acidic [Okruszko 1993]. Such reaction is advantageous for the flora of mowed meadows [Pietrzak 2012]. The marked variability in morphological features of the analysed genetic horizons related to the intense moorshification was confirmed in the results of laboratory tests (Table 1). In particular, greater densities (higher bulk density figures) and lower contents of SOM were characteristic for muck horizons in comparison with peat horizons. More organic matter was found in reed peats. As a result of an intense aerobic decomposition of organic matter and carbon depletion, moorshification entails a clear reduction in the ratio of the content of carbon to nitrogen and carbon to phosphorus [Maciak 1995, Ilnicki 2002, Piaścik, Gotkiewicz 2004, Becher 2013, Ilnicki, Szajdak 2016]. These ratios were diminishing in the analysed soils in line with the degree of transformation of organic matter, that is, from the highest values in peat horizons to the clearly lower ones in muck horizons. Variability dynamics was much greater for the TC/P<sub>T</sub> figure. The TC/TN and TC/P<sub>T</sub> results obtained in muck horizons and slight acidification found in entire profiles are indicative of the eutrophics of the analysed soil environment, high biological activity and good conditions for organic matter mineralisation

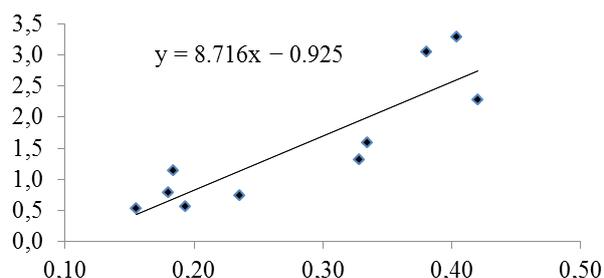
**Table 3.** Correlation of the total phosphorus content with soil properties.

Parameter	pH <sub>KCl</sub>	D	TC/TN	SOM	Content				
					Fe	Mn	Al	Ca	Mg
P <sub>T</sub>	0.205	0.880	-0.849	-0.859	0.950	0.891	0.713	-0.295	-0.482

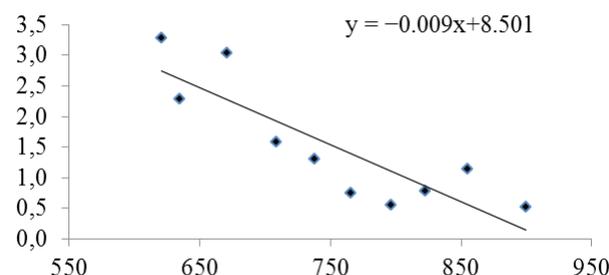
Value of critical (n = 10): 0.632 (α = 0.05); 0.765 (α = 0.01)

processes [Lucas 1982, Okruszko 1993, Kalisz et al. 2010, Becher et al. 2013]. The value of the TC/P<sub>T</sub> parameter below 300 in muck horizons of analysed soils can be indicative of advantageous conditions for the mineralisation of organic compounds of phosphorus and probably good supply of phosphorus for the meadow flora as well as the advanced process of secondary accumulation of that element [Becher 2013]. The obtained research results characterising analysed soils are typical and correspond to the source literature describing the moorshification process and peat-muck soils [Lucas 1982, Okruszko 1993, Kalisz et al. 2010, Mocek 2015, Ilnicki, Szajdak 2016]. Phosphorus quantity varying in individual profiles was found in analysed soils (Table 2). The highest content of that element was characteristic for surface horizons (M1) constituting the main part of the rhizosphere of analysed soils. Significant accumulation of phosphorus in muck horizons and the rapid (multifold) drop in its content in peat horizons were characteristic for both profiles. This observation is confirmed in the enrichment coefficient (especially calculated based on the phosphorus content expressed in g·dm<sup>-3</sup>). The research confirmed data reported by other authors who demonstrate that phosphorus distribution in organic soils is related to the depth of sample collection and the type and degree of decomposition of a peat formation. As a rule, most phosphorus is found in surface muck horizons as a result of the moorshification, collection of plant residues from the current plant formation and mineral fertilisation [Urbaniak, Sapek 2004, Kalembsa, Becher 2010]. The research confirmed the high natural status of organic soils as regards phosphorus accumulation. The great majority of total soil phosphorus resources found in the analysed soils was accumulated in muck horizons. The positive influence of the moorshification on phosphorus accumulation is confirmed by correlation coefficient values (Table 3).

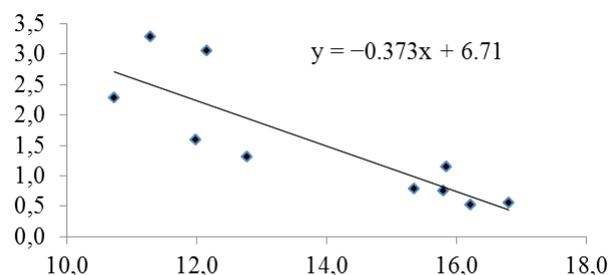
In the analysed population of genetic horizons, soil parameters representative for the moorshification process (bulk density, organic matter content, TC/TN value, and iron content) materially correlate with phosphorus content. Additionally, the calculated coefficient confirms the materiality of iron and manganese compounds for phosphorus accumulation in soils of marshy areas with dynamic oxidation and reduction conditions [Kalembsa, Becher 2010]. In the analysed soils, material correlation was also found as regards the content of phosphorus and aluminium. No material dependencies were found as regards the accumulation of the said element on



**Figure 1.** Relationship between soil bulk density and total phosphorus content in tested soils.



**Figure 2.** Relationship between soil organic matter content and total phosphorus content in tested soils.



**Figure 3.** Relationship between TC/TN ratio and total phosphorus content in tested soils.

magnesium and calcium. Selected and most characteristic dependencies of the described features were presented in a graphic form (Figs. 1–4).

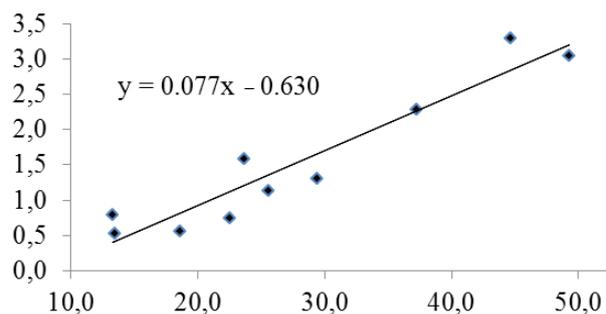
Presented fractions of phosphorus in the form of the share in the total content of that element (% P<sub>T</sub>) indicate the

**Table 4.** Percentage contribution of phosphorus fraction (F1–F5) in total content in tested soils.

Genetic horizon	Phosphorus fraction				
	F1	F2	F3	F4	F5
Profile 1					
M1	0.370	6.22	31.5	41.1	20.8
M2	0.150	5.07	22.1	50.0	22.7
Oe1	0.140	5.31	13.1	51.9	29.6
Oe2	0.090	3.04	3.00	52.2	41.7
Oe3	0.080	1.46	8.23	60.0	30.2
Profile 2					
M1	0.390	8.06	22.0	44.8	24.8
M2	0.250	5.46	12.5	54.4	27.4
M3	0.210	3.97	9.12	53.0	33.7
Oa1	0.160	3.21	7.40	55.9	33.3
Oa2	0.110	1.67	10.0	53.9	34.3
Mean for murshic horizons (M)	0.274	5.76	19.4	48.7	25.9
Mean for peat horizons (O)	0.116	2.94	8.35	54.8	33.8

variety of forms of occurrence of phosphorus, amongst other things, between genetic horizons of analysed soils (Table 4). The form that prevailed in both soils was phosphorus bound by humus substances and its other polymorphic forms (F4).

Jordan and co-authors [2007] obtained similar results. In general, the share of phosphorus fractions in individual genetic horizons can be ranked, as follows: F4 > F5 > F3 > F2 > F1. Surface muck horizons intensely overgrown with plant roots (M1) were somewhat different than other horizons. They had a greater share of most labile and easily accessible forms (F1), released in reduction

**Figure 4.** Relationship between iron content and phosphorus content in tested soils.

conditions (bonded on the surface, hydrated  $Al_2O_3$  and  $MnO_2$  – F2) and forms bound with metal oxides (Fe, Al and Mn), apatite, carbonate and organic, labile ones (F3). In the light of the share of distinguished phosphorus fractions in analysed soils, one can assume that a quality transformation of phosphorus compounds probably takes place in the moorshification process, mainly to increase the share of the first three fractions (F1, F2 and F3) and reduction in the most persistent forms of phosphorus (F4 and F5). As a consequence, the share of most accessible and labile forms of phosphorus was diminishing with the depth of the profile of analysed soils.

#### 4. CONCLUSIONS

1. A great majority of total soil phosphorus resources was accumulated in muck horizons of analysed soils.
2. The total content of phosphorus materially correlated with characteristically variable parameters in the process of moorshification of analysed soils.
3. The moorshification of analysed soils entails the quality transformation of phosphorus compounds, mainly to increase the share of most labile and easily accessible forms, forms released in reduction conditions and forms bound with metal oxides, apatite, carbonate and labile organic ones.

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