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PHOSPHORUS FORMS IN SOME GRASSLAND SOILS IN WIELKOPOLSKA REGION: CHARACTERISATION AND AVAILABILITY FOR PLANTS

FORMY FOSFORU W WYBRANYCH GLEBACH ŁĄKOWYCH WIELKOPOLSKI: CHARAKTERYSTYKA I PRZYSWAJALNOŚĆ PRZEZ ROŚLINY

Summary. Phosphorus is an essential element for plant growth. The evaluation of available forms of this nutrient in soils used in agricultural productivity is demanded. The study assesses the amounts of phosphorus in different forms in surface horizon of Gleysols and Histosols used as meadow and pastures. Soil samples were collected from eight profiles situated in the eastern part of Wielkopolska in the Kujawskie Lake region, central Poland. Phosphorus forms were sequentially extracted by Hedley et al. (1982) procedure modified by Ajiboye et al. (2004). Moreover, total and available contents of phosphorus were determined. On the basis of the obtained results it was stated that the content of both total and available phosphorus was comparable for Gleysols and Histosols and on average amounted from 0.885 to 0.908 g·kg^{-1} for phosphorus total and from 0.220 to 0.276 g·kg^{-1} for the available form. The predominant extractable fractions were residual (58% of P_{tot}) in Gleysols and organically bound (49% of P_{tot}) in Histosols. The percentage share of phosphorus in fraction I (0.7%), fraction II (from 19 to 25%) and fraction IV (from 1.1 to 1.3%) in total content of phosphorus was similar for Gleysols and Histosols. The correlation coefficients indicated that the content of organic matter, the amounts of total and available phosphorus strongly influenced water soluble phosphorus in the investigated soils.

Key words: phosphorus, Gleysols, Histosols, available forms, sequential extraction

Introduction

Phosphorus, besides nitrogen, potassium, sulphur and magnesium, is one of the macronutrients needed by all plants, because it is a component of nucleic acids, the phospholipids that compose cellular membranes, ATP and ADP molecules (Fuentes et al.,

2006). With reference to this, inputs of phosphorus are necessary to maintain profitable crop production. Soil phosphorus exists in various chemical forms, including inorganic and organic, which differ widely in their behaviour and fate in soils. Soils generally contain between 100 and 3000 mg P per 1 kg of soil and ca. 15-80% of which is present in organic forms (Chen et al., 2008). Majority of studies concerning soils include only total content of phosphorus without consideration of its availability for plants. However, the total content of this element does not provide information on its potential mobility in the environment (Jakubus, 2012). Much greater practical importance is attributed to the identification of chemical forms of elements in soils, facilitating an assessment of the degree of their solubility, and thus their bioavailability.

Phosphorus availability to plants is controlled by several factors connected with soil properties as soil reaction, sorption, precipitation with iron, aluminium and calcium (Addiscott and Thomas, 2000; Khan and Joergensen, 2009; Malik et al., 2012). Sequential extraction methods are frequently used to evaluation of various forms of inorganic and organic phosphorus based on their solubility (Tyler, 2002). According to Schlichting et al. (2002), knowledge of the phosphorus chemistry in soils is important to evaluate possible effects of management (e.g. effect of induced degradation on nutrient status and its availability for plants). So far, majority of investigations connected with phosphorus fractionation have been performed on arable fertilized soil. Therefore, the objectives of the presents study were: 1) to determine content of total and available phosphorus, as well as its speciation in surface horizons of grassland soils by the sequential extraction procedure according to Hedley et al. (1982) and 2) to investigate the influence of chosen soil factors on phosphorus forms.

Materials and methods

Soil samples and study area

The area of the investigations from which soil samples were collected was situated in the eastern part of Wielkopolska in the Kujawskie Lake region extending between 52°30′20″ and 52°30′02″ N latitude and 18°30′03″ and 18°32′28″ E longitude. Soils on the study area were classified according to WRB (World reference base..., 2006) as Gleysols and Histosols (Table 1) and were used as meadows and pastures. Soil samples (n = 3) were collected from surface horizons (from 15 to 30 cm) of eight soil profiles (Fig. 1). After drying at room temperature, soil samples were sieved through a 2 mm mesh sieve.

Soil analyses

Basic soil physico-chemical properties were determined using methods commonly applied in agro-chemical analytics. Soil reaction in 1 mol·dm^{-3} KCl measured potentiometrically and organic matter (OM) content by loss-on-ignition were determined (Jakubus, 2010). Oxidizable organic carbon (C_{tot}) was determined using Vario Max CNS.

Total phosphorus of soils (P_{tot}) was assessed colorimetrically using the molybdate--blue method (Murphy and Riley, 1962) after 1 g of samples was incinerated at 550°C

Table 1. Diagnostic horizons and nomenclature of soils according to World reference base... (2006)
Tabela 1. Poziomy diagnostyczne i nazewnictwo gleb według World reference base... (2006)

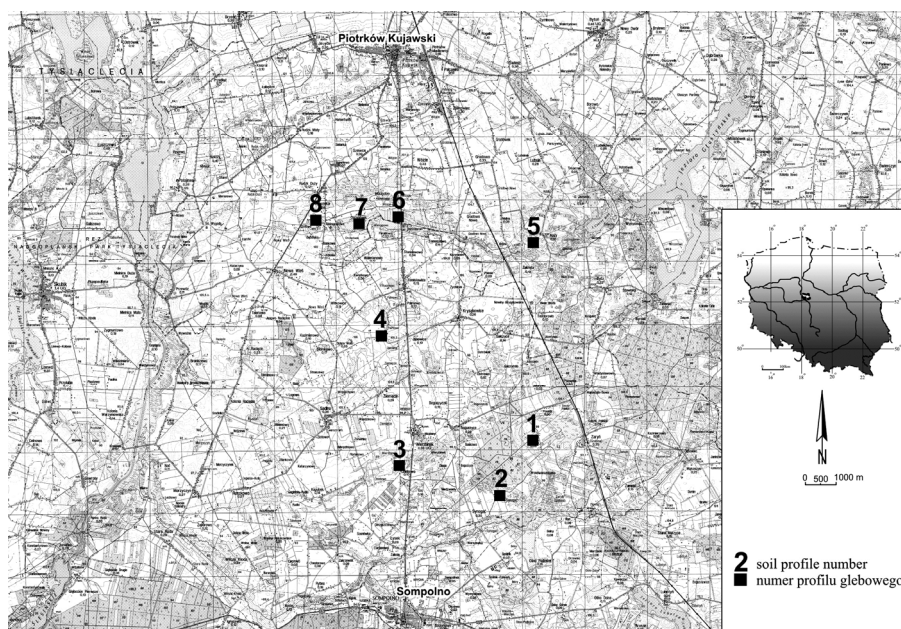| Profile number Numer profilu	Diagnostic horizon Poziom diagnostyczny	WRB
1-4	Mollic	Mollic Gleysol
5-8	Histic	Sapric Histosol

Fig. 1. Area of study
Rys. 1. Obszar badań

for 3 h. Then 5 cm^3 of concentrated HCl was added to the ash and the mixture was heated for 30 min at 180°C. The amounts of phosphorus available for plants (P$_a$) was obtained by procedure described by Sapek and Sapek (1997).

Soil samples were subjected to sequential phosphorus fractionation using a modified version of the Hedley et al. (1982) procedure as described by Ajiboye et al. (2004). Extraction was performed sequentially using deionized water (Fr. I), 0.5 mol·dm^{-3} NaHCO$_3$ (pH 8.5) (Fr. II), 0.1 mol·dm^{-3} NaOH (Fr. III) and 1 mol·dm^{-3} HCl (Fr. IV) (Table 2). A 0.5 g (on an oven-dry basis) sample of analysed soils were weighed into 30 cm^3 of extractant inside a 50 cm^3 centrifuge tubes and shaken for 5 h at room temperature. Then the samples were left overnight and next day were shaken for 3 h at room temperature. The suspensions were centrifuged for 10 min at 8000 rpm and filtered. A portion of NaHCO$_3$ and NaOH extracts was acidified to precipitate extracted

Table 2. Sequential extraction procedure
Tabela 2. Metoda ekstrakcji sekwencyjnej

Fraction of phosphorus Frakcja fosforu	Reagent Odczynnik	Extraction conditions Warunki ekstrakcji	
		time czas (h)	temperature temperatura (°C)
I – water soluble phosphorus fosfor wodnorozpuszczalny	H_2O	5.3	20-25
II – phosphorus associated with Al and Fe oxides fosfor połączony z tlenkami Al i Fe	$0.5\ mol \cdot dm^{-3}$ $NaHCO_3$ (pH 8.2)	5.3	20-25
III – phosphorus associated with organic matter fosfor połączony z materią organiczną	$0.1\ mol \cdot dm^{-3}$ NaOH	5.3	20-25
IV – phosphorus associated with Ca fosfor połączony z Ca	$1\ mol \cdot dm^{-3}$ HCl	5.3	60-70
V – residual phosphorus fosfor pozostałościowy	–	–	–

organic matter and supernatant analysed for inorganic phosphorus (P_i). A portion of $NaHCO_3$ and NaOH extracts was analysed for total phosphorus fraction. For this purpose 10 cm^3 of extractants were digested with 30% H_2O_2 at 80°C for 2-3 h and then the whole was evaporated until dryness. A residue was dissolved in 3 $mol \cdot dm^{-3}$ HCl. The amount of organic phosphorus (P_o) in fractions II and III was calculated by subtracting the value of P_i from P_{tot}. The phosphorus concentration in all extracts was determined colorimetrically using the molybdate-blue method (Murphy and Riley, 1962) on spectrophotometer at a wavelength of 720 nm.

The phosphorus in residual fraction of soils was calculated by subtracting the sum of all the phosphorus fractions from the total content of the phosphorus.

Analyses of soil samples were carried out in three replicates and the presented data are the mean. The obtained data were subjected to statistical analysis employing the correlation coefficients.

Results and discussion

Selected properties of the investigated soils are presented in Table 3. Irrespective of the investigated soil, the soil reaction was alkali. The samples of Histosols contained on average more C_{tot} (mean 228.16 $g \cdot kg^{-1}$) and OM (mean 515.25 $g \cdot kg^{-1}$) than the soils of Gleysols (mean for C_{tot} – 94.92 $g \cdot kg^{-1}$ and for OM – 228.08 $g \cdot kg^{-1}$) (Table 3). This is explained by a higher degree of organic substance humification in Gleysols. Table 3 shows that mean values of total phosphorus ranged from 0.650 $g \cdot kg^{-1}$ (profile No. 7) to 1.190 $g \cdot kg^{-1}$ (profile No. 5) and the quantitative difference between these data was 2.0-fold. It is worth noticing that the amounts of total phosphorus in surface horizon of the investigated soils were representative for Polish conditions, what is consistent with the

Table 3. Soil reaction, organic matter content, total carbon, total and available phosphorus ($g \cdot kg^{-1}$)
Tabela 3. Odczyn gleby, zawartość materii organicznej, węgiel ogólny, fosfor ogólny i przyswajalny ($g \cdot kg^{-1}$)

Profile number Numer profilu	pH	OM – MO	C_{tot} – C_{og}	P_{tot} – P_{og}	P_a – P_p
Gleysols					
1	7.3	244.33	49.59	0.92	0.33
2	7.6	206.00	83.77	0.98	0.34
3	7.5	194.00	82.86	0.79	0.03
4	7.3	268.00	163.47	0.85	0.17
SD	–	34.19	48.39	0.08	0.14
Mean – Średnio	–	228.08	94.92	0.88	0.22
Histosols					
5	7.7	345.00	120.70	1.19	0.11
6	7.2	713.00	328.36	1.10	0.32
7	7.3	400.00	183.88	0.65	0.37
8	6.5	584.00	279.69	0.69	0.30
SD	–	163.29	93.46	0.27	0.11
Mean – Średnio	–	515.25	228.16	0.91	0.28

C_{tot} – total carbon, OM – organic matter, P_{tot} – total phosphorus, P_a – available phosphorus.
C_{og} – węgiel ogólny, MO – materia organiczna, P_{og} – fosfor ogólny, P_p – fosfor przyswajalny.

results of other authors (Gotkiewicz et al., 2006; Sammel and Niedźwiecki, 2006). Schlichting et al. (2002) found that top layer of Histosols is richer in total and available phosphorus than Gleysols. Neither total nor available content of nutrient were confirmed by the statement during the study. Moreover, the data presented at Table 3 testified that samples of Gleysols characterised on average the comparable level of P_{tot} (0.908 $g \cdot kg^{-1}$) and P_a (0.276 $g \cdot kg^{-1}$) as samples of Histosols (0.885 and 0.220 $g \cdot kg^{-1}$ for P_{tot} and P_a, respectively). Regardless of this, significance difference (12 times) between minimum value (0.032 $g \cdot kg^{-1}$ in profile No. 3) and maximum (0.368 $g \cdot kg^{-1}$ in profile No. 7) values of available phosphorus was revealed (Table 3). Pawluczuk and Alberski (2011) investigated surface horizon of Histosols used as a grassland soil and they found similar amounts of available phosphorus as in the presented study. However, Gotkiewicz et al. (2006) assessed a higher level of P_a in the examined Histosols in comparison to the author's own studies where the contents of available form of nutrient in the analysed Histosols ranged between 0.114 and 0.368 $g \cdot kg^{-1}$ (Table 3).

Also Sammel and Niedźwiecki (2006) observed a considerable fluctuation of available phosphorus in soils of similar genesis. Ilnicki (2002) and Sapek (2011) maintained that quantity differentiation of nutrients depends on presence of organic matter and soil

reaction. According to class abundance for available phosphorus prepared for organic soils (Sapek and Sapek, 1997) top layers of the investigated soils characterised medium and very low content of available forms of nutrient. Low and medium abundance of phosphorus available for plants in Gleysols and Histosols was also reported by Sammel and Niedźwiecki (2006) and Pietrzak (2012).

On the basis of the results it can be assumed that such soils should show phosphorus deficiency, thus a greater phosphorus turnover in soil depends on many different processes, such as e.g. precipitation, sorption, mineralization and leaching. Taking into account these factors identification of phosphorus in soils is a fundamental prerequisite to understanding nutrient dynamics in soil systems and the mechanisms responsible for the rate of release of potentially available forms of phosphorus for plants (Fuentes et al., 2006). Moreover, Szara and Sosulski (2012) stressed that it is necessary to monitor agricultural soils in terms of their susceptibility to phosphorus losses. The monitoring should focus on the level of available and active nutrient.

In the present study, four fractions (the fifth one is residual) of soils were separated using the modified Hedley's method. According to this method the pool of soil phosphorus is partitioned into soluble, aluminium/iron bound, organic bound, calcium bound and residual forms. Table 4 presents results referred to phosphorus quantitative changes in sequentially separated fractions. Phosphorus quantities in obtained fractions increased in the following succession: I < IV < II < III < V for surface diagnostic horizon of Gleysols. On the other hand, Histosols were characterised by an increase of the nutrient in the following sequence of fractions: I < IV < V < II < III (Table 4). Irrespective of the analysed soils, the highest concentrations of the inorganic phosphorus were found in the residual (V) fraction (147.34-698.09 mg·kg^{-1}), whereas the lowest contents of P_i were obtained in soluble fraction (I) (3.95-8.45 mg·kg^{-1}) and calcium bound fraction (IV) (3.77-20.34 mg·kg^{-1}). The difference between minimum and maximum values of phosphorus content in mentioned fractions were 2.0 (fr. I) and 5.0 fold (fr. IV and V). The surface horizons from Gleysols contained higher proportions of residual phosphorus, however surface horizons of Histosols were richer in phosphorus of fractions II, III and IV. This kind of tendency was confirmed by literature (Schlichting et al., 2002).

The mean percentage share of phosphorus in the obtained fractions in its total content was similar for Gleysols and Histosols in fractions I (0.7%), II (from 19 to 25%) and IV (from 1.1 to 1.3%) (Fig. 2). Taking into consideration that water soluble phosphorus (fr. I) is an easily available, nutrient for plants and at the same time may undergo different transformation, such a small portion is disadvantageous.

A significant difference was found for III and V fractions of the investigated soils. Histosols were characterised by a higher share of phosphorus in organic bound fraction (49%) and lower in residual one (24%) in comparison to the data assessed for Gleysols (21% and 58% for fractions III and V, respectively). Comparable levels of water soluble phosphorus and organically bound phosphorus in grassland soils were revealed by McDowell and Condron (2000).

It is evident from the data presented in Table 4 that the total, inorganic and organic phosphorus in fractions II and III oscillated in a wide range because the differences between extreme values were 3.0-18.0 fold. Gleysols samples were characterised by a lower mean value of P_{tot} in fractions II (168.47 mg·kg^{-1}) and III (165.59 mg·kg^{-1}), than Histosols (225.10 and 446.66 mg·kg^{-1} in fractions II and III, respectively). The quantitative

Table 4. Amounts of phosphorus in soil fractions (mg·kg^{-1})
Tabela 4. Ilości fosforu we frakcjach gleby (mg·kg^{-1})

Profile number Numer profilu	Fractions of phosphorus – Frakcje fosforu								
	I	II			III			IV	V
		$P_{tot} - P_{og}$	$P_i - P_n$	P_o	$P_{tot} - P_{og}$	$P_i - P_n$	P_o		
Gleysols									
1	8.31	151.88	67.85	84.03	175.14	77.20	97.94	3.77	580.89
2	8.45	77.18	29.57	47.61	181.94	37.52	144.42	14.33	698.09
3	4.49	155.71	43.98	111.73	131.85	35.42	96.44	6.97	490.97
4	3.95	289.11	101.34	187.77	173.41	52.10	121.3	13.16	370.37
SD	2.41	88.18	31.36	59.44	22.79	19.25	22.66	5.03	138.74
Mean Średnio	6.30	168.47	60.69	107.79	165.59	50.56	115.03	9.56	535.08
Histosols									
5	7.29	139.79	48.50	91.29	770.45	119.22	651.23	8.87	263.59
6	5.79	267.38	130.78	136.60	537.64	97.05	440.59	18.51	270.60
7	5.43	223.30	57.57	165.73	253.59	63.87	189.72	20.34	147.34
8	7.24	269.94	120.03	149.91	224.94	94.02	130.92	8.56	179.32
SD	0.97	60.77	42.18	32.02	257.91	22.75	239.12	6.22	61.38
Mean Średnio	6.44	225.10	89.22	135.88	446.66	93.54	353.12	14.07	215.21

I – water soluble phosphorus, II – phosphorus associated with Al and Fe oxides, III – phosphorus associated with organic matter, IV – phosphorus associated with Ca, V – residual phosphorus.

P_{tot} – total phosphorus, P_i – inorganic phosphorus, P_o – organic phosphorus.

I – fosfor wodnorozpuszczalny, II – fosfor połączony z tlenkami Al i Fe, III – fosfor połączony z materią organiczną, IV – fosfor połączony z Ca, V – fosfor pozostałościowy.

P_{og} – fosfor ogólny, P_n – fosfor nieorganiczny, P_o – fosfor organiczny.

level of mean values of P_o was higher than P_i in fractions II and III of investigated soils. Such a significant difference was found for fraction III of Histosols, where mean amount of P_o (353.12 mg·kg^{-1}) was almost 4.0 times higher than P_i (93.54 mg·kg^{-1}). The difference between mean contents of P_o and P_i in fraction III of Gleysols was 2.0 fold and values amounted 115.03 mg·kg^{-1} and 50.56 mg·kg^{-1}, respectively. The results of McDowell and Condron (2000) studies corroborate with the obtained data in the author's own experiments. Lower differences between P_o and P_i amounts were found also for fraction II of the investigated soils. The data presented in Table 4 testified that mean content of P_o was by 50% (Histosols) and 80% (Gleysols) higher than amounts of P_i in fraction II. Schlichting et al. (2002) investigated P forms in Histosols and Gleysols by Hedley's sequential extraction procedure. The above researchers confirmed predominating share of organic phosphorus in fractions II and III of the analysed soils. Moreover,
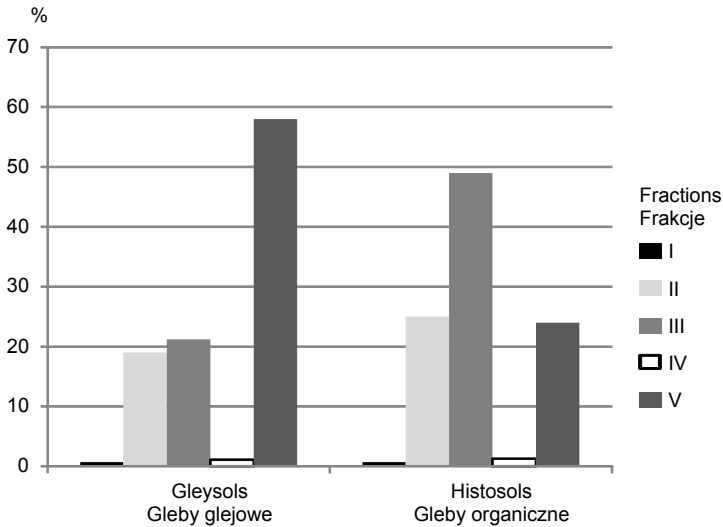
Fig. 2. Share of fractions of phosphorus in total phosphorus in Gleysols and Histosols
Rys. 2. Udział frakcji fosforu w fosforze ogólnym w glebach glejowych i organicznych

the cited studies confirmed that Histosols were more abundant in both organic and inorganic forms of nutrient in comparison to Gleysols.

According to literature data (McDowell and Condron, 2000; Schlichting et al., 2002) the amounts of phosphorus fractions are determined by the total phosphorus content and organic carbon in Gleysols and Histosols. This statement was only partly confirmed in the present study. The interdependencies between the amounts of phosphorus fractions and organic matter, total and available phosphorus were described by simple correlation coefficients in Table 5. The calculated correlation matrix was bigger for Histosols and, for the most part, the interdependencies were significant at the highest level of probability. It needs to be stressed that available phosphorus of Histosols had a strong influence on phosphorus fraction. Simultaneously such an interaction was not observed in Gleysols conditions. The organic matter content mainly affected the amounts of phosphorus fraction of Gleysols. The contents of inorganic and total forms of phosphorus fractions were mainly shaped by total content of nutrient in either Histosols or Gleysols. Regardless of the investigated soils, the influence of organic matter, phosphorus total and available on phosphorus level was observed only in the case of phosphorus fraction I. At the same time organic matter negatively affected the content of water soluble phosphorus and positively total and available phosphorus.

Table 5. Simple correlation coefficient values between analysed forms of phosphorus and chosen soil parameters
Tabela 5. Wartości współczynników korelacji prostej między analizowanymi formami fosforu a wybranymi parametrami gleby

Profile number Numer profilu	Fraction of phosphorus Frakcja fosforu	Soil parameters – Parametry gleby		
		$P_{tot} - P_{og}$	$P_a - P_p$	OM – MO
1-4	I	0.869**	0.867**	−0.617**
	II − $P_{tot} - P_{og}$	−0.560**	n.s.	0.973**
	II − $P_i - P_n$	n.s.	n.s.	0.894**
	II − P_o	−0.712**	−0.619**	0.800**
	III − $P_{tot} - P_{og}$	n.s.	n.s.	0.914**
	III − $P_i - P_n$	0.659**	n.s.	n.s.
	III − P_o	n.s.	n.s.	n.s.
	IV	n.s.	n.s.	n.s.
	V	0.680**	n.s.	−0.920**
5-8	I	0.976**	0.962**	−0.631**
	II − $P_{tot} - P_{og}$	n.s.	0.866**	0.911**
	II − $P_i - P_n$	−0.836**	0.928**	n.s.
	II − P_o	n.s.	0.528**	0.964**
	III − $P_{tot} - P_{og}$	0.917**	−0.828**	n.s.
	III − $P_i - P_n$	0.765**	−0.846**	n.s.
	III − P_o	0.912**	0.828**	n.s.
	IV	n.s.	0.651**	n.s.
	V	n.s.	n.s.	0.804**

Explanation of fractions of phosphorus – as under Table 4.
P_{tot} – total phosphorus, P_a – available phosphorus, OM – organic matter.
The statistically significant correlation coefficient values between chosen soil parameters and the content of phosphorus were designated by ** for $p < 0.01$; n.s. – not significant correlation.
Objaśnienie frakcji fosforu – jak pod tabelą 4.
P_{og} – fosfor ogólny, P_p – fosfor przyswajalny, MO – materia organiczna.
Statystycznie istotne wartości współczynników korelacji między wybranymi parametrami gleby i zawartością fosforu zostały oznaczone przez ** dla $p < 0,01$; n.s. – korelacja nieistotna.

Conclusions

1. The modified Hedley's fractionation appears to be a well suited and helpful method to study phosphorus in soils of different genesis.

2. The content of organic matter in Histosols was higher than in Gleysols; however, despite of this the amounts of total and available phosphorus were comparable.

3. The contents of available and water soluble phosphorus in the investigated soils were very low indicating on potential phosphorus deficiency.

4. The predominat portion of phosphorus in Gleysols was obtained in residual fraction, while in Histosols a significant share of phosphorus was recorded in the form bound with organic matter.

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FORMY FOSFORU W WYBRANYCH GLEBACH ŁĄKOWYCH WIELKOPOLSKI: CHARAKTERYSTYKA I PRZYSWAJALNOŚĆ PRZEZ ROŚLINY

Streszczenie. Fosfor jest niezbędnym dla roślin składnikiem pokarmowym. W glebach użytkowanych rolniczo w celach diagnostycznych określa się formy przyswajalne fosforu. W niniejszej pracy oznaczono ilości fosforu w różnych połączeniach z fazą stałą gleb klasyfikowanych jako Gleysols i Histosols, a użytkowanych jako łąki i pastwiska. Próbki glebowe do badań pobrano z wierzchniej warstwy ośmiu profili glebowych zlokalizowanych w centralnej Wielkopolsce na Pojezierzu Kujawskim. Formy fosforu określono, wykorzystując zmodyfikowaną metodę ekstrakcji sekwencyjnej według Hedleya i in. (1982). Ponadto w badanych glebach oznaczono ilości ogólne i przyswajalne fosforu. Na podstawie uzyskanych danych stwierdzono, że wierzchnia warstwa gleb organicznych (Histosols) i glejowych (Gleysols) charakteryzowała się zbliżonymi ilościami ogólnymi oraz przyswajalnymi fosforu. Zawartości ogólne fosforu wynosiły od 0,885 do 0,908 g·kg⁻¹, a fosforu przyswajalnego – od 0,220 do 0,276 g·kg⁻¹. Największy udział w stosunku do ogólnej ilości fosforu dotyczył składnika w związkach nieulegających ekstrakcji (58%) oraz w połączeniach organicznych (49%), co miało miejsce odpowiednio w odniesieniu do Gleysols i Histosols. Procentowy udział fosforu frakcji I (0,7%), frakcji II (od 19 do 25%) i frakcji IV (od 1,1 do 1,3%) w ogólnej ilości fosforu był podobny dla Gleysols i Histosols. Na podstawie współczynników korelacji prostej stwierdzono, że ilość materii organicznej, zawartość fosforu ogółem i fosforu przyswajalnego silnie wpływały na ilości fosforu wodnorozpuszczalnego.

Słowa kluczowe: fosfor, Gleysols, Histosols, formy przyswajalne, ekstrakcja sekwencyjna

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