

Soil phosphorus sorption properties in different fertilization systems

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Citation: Szara E., Sosulski T., Szymańska M. (2019): Soil phosphorus sorption properties in different fertilization systems. *Plant Soil Environ.*, 65: 78–82.

Abstract: The study aimed at the evaluation of the accumulation and vertical distribution of different forms of phosphorus (P) in reference to phosphorus sorption properties subject to mineral (NPK), mineral-organic (NPK + M), and organic (M) fertilisation. It was carried out in a long-term experimental field in Skierniewice (Central Poland) conducted since 1923 under rye monoculture. Total P content in the M and NPK soil profile was similar and lower than in the NPK + M soil. The content of organic P in A_p and E_{et} horizons of both manured soils was similar and higher than in the NPK soil. The Langmuir P sorption maximum (S_{max}) in the studied soils ranged from 39.7 to 90 mg P/kg, while the Freundlich P sorption coefficient a_F ranged from 6.9 to 41.9 mg P/kg. Higher variability of parameters related to the binding energy from the Langmuir (k) and Freundlich (a_F) equations was determined between soil horizons than between the fertilisation systems. Nonetheless, in M and NPK + M soils, sorption parameters a_F and S_{max} and binding energy (k , b_F) were considerably lower than in the NPK soil. The content of water extracted P in manured soils was higher than in the NPK soil.

Keywords: macronutrient; *Secale cereale* L.; vertical variability of phosphorus; static experiment; soil-phosphorus

The accumulation and sorption of phosphorus (P) in the soil depends on the content of clay minerals, Al and Fe oxide and soil organic matter (Börling et al. 2001), soil acidity, and fertilisation (Hooda et al. 2001, Varinderpal-Singh et al. 2006, Szara et al. 2017). Fertilisation exceeding the nutritional needs of plants for phosphorus affects the total content of the elements to a higher degree than the content of a selected form of P in the soil (Szara et al. 2004). Nonetheless, the processes of sorption-desorption, precipitation-dissolution, and mineralisation-immobilisation lead to the development of soil phosphorus forms with variable availability for plants and mobility in the soil (Parham et al. 2002, Verma et al. 2005, Koopmans et al. 2007). Low content of phosphorus in sandy soil usually forces the application of high doses of mineral and organic fertilisers. The accumulation of phosphorus in the soil is also determined by the degree of uptake and use of the element by plants. Approximately twice higher use of phosphorus from mineral fertilisers than from manure (Szara et al. 2004) suggests that organic fertilisation favours the accumulation of phosphorus

in the soil to a greater degree than mineral fertilisation. Meanwhile, after 78 years of experimental fertilisation with similar doses of P, content of total phosphorus in manured soil was only 11% higher than in the soil fertilised with superphosphate (Szara et al. 2004). This result suggests substantial differences in the effect of mineral and organic fertilisation on the sorption soil properties towards phosphorus, and the chemical form in which P is accumulated in soils under different systems of fertilisation.

The objective of the study was the assessment of the effect of the fertilisation system (organic, mineral and mineral-organic) on the accumulation and vertical distribution of different forms of phosphorus in reference to phosphorus sorption properties in the sandy soil profile.

MATERIAL AND METHODS

The research was conducted in a long-term experiment (since 1923) with rye monoculture at the Experimental Station of the Warsaw University of

<https://doi.org/10.17221/696/2018-PSE>

Life Sciences – SGGW in Skierniewice (Central Poland, 51°96'N, 20°16'E). The soil is Luvisol (FAO 2006). The soil particle size was reported elsewhere (Sosulski et al. 2017). The mineral (NPK), mineral-organic (NPK + M) and organic (M) fertilization systems were studied in four repetitions with plot area of 36 m². The doses of fertilisers amounted to 90 kg N, 26 kg P and 91 kg K/ha. Manure was applied at the dose of 30 t/ha every 4 years and at 20 t/ha yearly in the NPK + M and M treatment, respectively. Consequently, the annual doses of phosphorus and nitrogen applied in M and NPK + M systems can be approximated as 21.9 kg P/ha, 100 kg N/ha and 33.7 kg P/ha, 127.5 kg N/ha, respectively. The average of grain rye yield obtained in the long-term experiment was higher under NPK + M than under NPK and M treatment (4.3 vs. 3.6 and 2.5 t/ha). Consequently, the P-accumulation by rye was higher under NPK + M (21.4 kg/ha) than under NPK (15.7 kg P/ha) and M treatment (11.2 kg P/ha). Liming (1.43 t Ca/ha) was applied every 4 years.

Soil samples were collected after rye harvest in 2015 from the following soil horizons: A_p (0–25 cm); E_{et} (25–50 cm) and B_t (50–75 cm). The following was determined in the soil samples: pH in 1 mol/L KCl (ISO 10390, 2005), total organic carbon (TOC) by means of a TOC-analyser, total content of soil phosphorus (P_t) – after soil digestion in HNO₃ and HClO₄, and the content of inorganic phosphorus (P_i) after extraction in 0.5 mol/L H₂SO₄ (O'Halloran and Cade-Menun 2008) and dissolved reactive P (DRP) after water soil extraction following centrifugation and vacuum-filtration (< 0.45 μm) (Sharpley et al. 2008). The content of soil organic phosphorus (P_o) was estimated as a difference between P_t and P_i.

The Mehlich-3 method was applied to determine the content of Al_{M3}, Fe_{M3} (not presented), and P_{M3} (Ziadi and Sen Tran 2008). The degree of phosphorus saturation (DSP) of soil was calculated as molar (mmol/kg) ratio: $DPS_{M3} = [P_{M3}/PSC_{M3}] \times 100\%$, where $PSC_{M3} = (Al_{M3} + Fe_{M3})$ (Khiari et al. 2000).

For the assessment of phosphorus sorption properties, soil samples were equilibrated with graded phosphorus concentration 0–20 mg P/L (KH₂PO₄) in 0.01 mol/L CaCl₂ (1:10) for 24 h. After centrifuging at 3000 rpm for 15 min and filtering, the phosphorus concentration (C) in the supernatant solution was measured. The amount of P sorbed (S) by the soil was calculated as the difference between the amount of phosphorus in solution before and after equilibrium (Sharpley et al. 2008).

In all extracts, phosphorus concentration was determined by means of the molybdenum-blue ascorbic method, and the content of metals by means of the atomic absorption spectrometry (AAS).

Sorption isotherms were examined by the Langmuir equation:

$$C/S = 1/kS_{\max} + C/S_{\max}$$

Where: S_{max} – sorption maximum; k – constant related to bonding energy of soil for P. A plot of C/S versus C gives a straight line with the slope value equal to 1/S_{max} and 1/kS_{max} as the y-axis intercept (Sharpley et al. 2008).

The data were also fitted to the Freundlich equation:

$$S = a_F C^{b_F}$$

Where: a_F – extent of P adsorption; b_F – constants corresponding to the degree of linearity between the solution equilibrium concentration and absorption. A linear plot of log₁₀a_F versus log₁₀C yields a_F and b_F from the intercept and slope, respectively (Graetz and Nair 2000).

The equilibrium of phosphorus concentration in solution (EPC₀) is the value of C where S = 0 and it was determined from isotherm plots. Maximum buffering capacity (MBC) is derived as: $MBC = kS_{\max}$ (Holford and Mattingly 1976).

The suitability of sorption equations was based on R² values. One-way analysis of variance (ANOVA) at P < 0.05 was used for comparison of means for each soil horizon and treatments separately and mean total contents of parameters in soil profiles under treatments. The Spearman's correlation coefficients (r) were calculated at P < 0.01 and P < 0.05 (SPSS IMAGO 23, IBM, Chicago, USA).

RESULTS AND DISCUSSION

The content of soil TOC was the highest in the A_p horizon of the studied soils and decreased with soil depth. Depending on the soil horizon, TOC soil content on M treatment was 1.2–1.4 times higher than in NPK + M treatment and 1.5–2.1 times higher than in NPK treatment (Table 1).

The highest content of P_t was determined in the NPK + M soil profile. Content of P_t in the M and NPK soil profiles was similar (Table 1). The fertilisation system affected the vertical variability of P_t content more than its total content in the soil profile. Organic forms of phosphorus in manure are particularly orthophosphate monoesters and the contribution of diesters is low (Li et al. 2014). Rapid and strong adsorption on soil surface and formation of stable

Table 1. Properties of the soil profile

Fertilization system	Horizon	TOC (g/kg)	P (mg/kg)		
			P _t	P _i	P _o
NPK	A _p	7.2 ^a	297 ^b	210 ^b	87 ^a
	E _{et}	2.1 ^a	120 ^a	82 ^b	38 ^a
	B _t	1.7 ^a	182 ^a	132 ^b	50 ^a
	total	11.1 ^A	599 ^A	424 ^B	175 ^A
M	A _p	10.7 ^b	283 ^a	169 ^a	114 ^c
	E _{et}	4.4 ^c	146 ^b	87 ^a	59 ^b
	B _t	3.0 ^c	161 ^a	118 ^a	43 ^a
	total	18.0 ^C	590 ^A	374 ^A	216 ^B
NPK + M	A _p	9.3 ^b	275 ^a	174 ^a	101 ^b
	E _{et}	3.3 ^b	165 ^c	107 ^b	55 ^b
	B _t	2.3 ^b	202 ^c	137 ^b	65 ^b
	total	14.9 ^B	639 ^B	418 ^B	221 ^B

a – within each horizon, means followed by the same small letter are not significantly different ($P < 0.05$); A – within each treatment, means of the total content in profiles by the same capital letter are not significantly different ($P < 0.05$). TOC – total organic carbon; P_t – total phosphorus; P_i – inorganic phosphorus; P_o – organic phosphorus

inner-sphere complexes with humic substances protect monoesters from mineralisation. Orthophosphate diesters are considerably weakly sorbed onto soil particles, more mobile and susceptible to mineralisation in the soil (Turner et al. 2003). As a consequence,

phosphate monoesters are the main organic P forms in the upper layer of soils (Dou et al. 2009, Dodd and Sharpley 2015), and their content may increase after manure application (Koopmans et al. 2007). This explains considerably higher content of P_o in A_p and E_{et} horizon of M and NPK + M soil in comparison to NPK soil. In spite of considerably higher content of farmyard manure (FYM) introduced in M soil than in NPK + M soil, the combined content of P_o in the profile of both soils was similar (216–221 mg/kg). The content of P_o in B_t horizon was determined in NPK + M treatment, and the lowest in M treatment. This is explained by results of Koopmans et al. (2007) who determined strong accumulation of orthophosphate monoesters in the upper layers of the long-term manure-treated soils, and downward movement of only orthophosphate.

The mobility and availability of P accumulated in the soil is determined by phosphorus sorption properties. In our research, the soil phosphorus sorption data for different fertilisation systems were well fitted to the Langmuir ($R^2 > 0.991$) and Freundlich ($R^2 > 0.960$) equation (Table 2). Considering all soil horizons and fertilisation systems, the Langmuir P sorption maximum (S_{max}) ranged from 39.7 to 90 mg P/kg, while the Freundlich P sorption coefficient a_F ranged from 6.9 to 41.9 mg P/kg, and both parameters were strongly mutually correlated ($r = 0.924$, $P < 0.01$). Unlike in the case of the indices of the number of sites of P sorption

Table 2. Phosphorus sorption parameters from the Langmuir and Freundlich equations

Fertilization system	Horizon	Langmuir		MBC (L/mg)	Freundlich	
		S _{max} (mg/kg)	k (L/mg)		a _F (mg/kg)	b _F (L/mg)
NPK	A _p	54.6 ^c	0.152 ^A	8.3 ^b	7.9 ^b	0.540 ^b
	E _{et}	44.4 ^b	0.363 ^c	16.1 ^b	19.7 ^b	0.265 ^a
	B _t	99.0 ^c	0.656 ^c	64.9 ^c	41.9 ^c	0.327 ^c
	total	198.0 ^B	–	89.3 ^C	70.9 ^C	–
M	A _p	39.7 ^a	0.130 ^a	5.1 ^a	6.9 ^a	0.496 ^a
	E _{et}	41.0 ^{ab}	0.188 ^a	7.7 ^a	9.8 ^a	0.460 ^c
	B _t	82.6 ^b	0.506 ^b	41.8 ^b	33.6 ^b	0.312 ^b
	total	163.3 ^A	–	54.7 ^B	50.5 ^B	–
NPK + M	A _p	49.3 ^b	0.147 ^b	7.2 ^b	9.2 ^c	0.488 ^a
	E _{et}	38.8 ^a	0.223 ^b	8.6 ^a	10.6 ^a	0.387 ^b
	B _t	75.2 ^a	0.335 ^a	25.1 ^a	24.6 ^a	0.365 ^d
	total	163.4 ^A	–	41.1 ^A	44.7 ^A	–

a – within each horizon, means followed by the same small letter are not significantly different ($P < 0.05$); A – within each treatment, means of the total content in profiles by the same capital letter are not significantly different ($P < 0.05$). MBC – maximum buffering capacity

<https://doi.org/10.17221/696/2018-PSE>

(S_{\max} and a_F), the parameters related to the bonding energy k from the Langmuir model and b_F from the Freundlich model were mutually negatively correlated ($r = -0.800$, $P < 0.01$).

Fertilisation leads to a decrease in soil P sorption capacity (Hooda et al. 2001, Lehmann et al. 2005, Jiao et al. 2007). In our research in manured soils (M and NPK + M), sorption parameters a_F and S_{\max} and binding energy (k , b_F) were significantly lower than in the NPK soil. Similar study results were obtained by Varinderpal-Singh et al. (2006) and Bhattacharyya et al. (2015). Organic acids released from FYM compete with orthophosphate for sorption sites, and replace the loosely adsorbed phosphate from the bonding sites, or may chelate Fe and Al oxide limiting the number of phosphate binding sites in the soil (Jiao et al. 2007, Yan et al. 2014). Organic P from FYM may also cause desorption of mineral forms of P (Berg and Joern 2006). Moreover, due to an increase in the net negative surface charge as a result of nonspecific sorption, organic acid may cause an increase in the electrostatic repulsion of phosphate in soil considerably reducing the binding energy of phosphate (Jiao et al. 2007). Whalen and Chang (2002) determined that 25 years of soil manuring reduced the binding energy (k) to a greater degree than the value of parameter S_{\max} . A higher variability of parameters related to the binding energy from the Langmuir (k) and Freundlich (a_F) between soil horizons than between fertilisation systems suggests different mechanisms of phosphorus sorption. High (more than 0.4) or higher than k value of b_F suggests a substantial contribution of precipitation in the sorption process (Castro and Torrent 1998, Hussain et al. 2006). It can be therefore presumed that systematic liming could favour the precipitation of Ca-P increasing the capacity for P retention. The importance of precipitation for P sorption, however, decreased with soil depth.

The maximum buffering capacity (MBC) value points to the capacity of the soil to maintain constant P concentration in the soil solution (Holford and Mattingly 1976). The MBC value in the A_p horizon of M and NPK + M soils showed relatively low fluctuations (5.1–7.2 L/mg). Fertilisation of soil with such a low MBC value can considerably increase the content of orthophosphorus in the soil solution. In deeper soil horizons, the variability of the values of the parameter was higher, and in soil B_t horizon it ranged from 25.1 to 41.8. This means that the properties of soils fertilised with manure can counteract the

transfer of 1.9–2.5 times smaller mass of phosphorus to drainage water than from the NPK soil.

The variability of soil P sorption properties was reflected in the vertical distribution of available phosphorus contents (P_{M3}) in the profiles of the studied soils (Table 3). The lowest variability of the P_{M3} content (78.7–112.0 mg/kg) concerned the A_p horizon of the studied soils. Due to the lowest buffer properties of deeper horizons in NPK + M soil profile, the P_{M3} content in the B_t horizon was 3.8 times higher than in the NPK soil. In M soil, the content of P_{M3} in the B_t horizon was 34.4 mg/kg and was considerably lower than in NPK + M soil.

Manured soils showed a considerable increase in the content of water extracted DRP in comparison to the NPK soil. Considerably higher content of DRP in the A_p horizon of M soil than NPK + M soil suggests that annual application of manure increases the risk of P losses with surface flow of water. Higher content of P can be leached from the NPK + M soil than from M soil.

The degree of P saturation (DSP) is also commonly used to predict the potential of soil to release P (Khiri et al. 2000). In both manured soils, the content of PSC_{M3} was only inconsiderably higher than in the NPK soil (Table 3). Due to the lack of higher variability of PSC_{M3} values between the studied soils, the DSP_{M3} value

Table 3. Content of P_{M3} extracted by Mehlich-3, P saturation degree (DSP_{M3}) and dissolved reactive P extracted with water (DRP)

Fertilization system	Horizon	PSC_{M3} (mmol/kg)	DSP_{M3} (%)	P_{M3} (mg/kg)	DRP
NPK	A_p	16.7 ^a	15.2 ^a	78.7 ^a	4.0 ^a
	E_{et}	15.0 ^a	6.7 ^a	30.7 ^a	1.9 ^a
	B_t	26.1 ^a	1.8 ^a	14.4 ^a	0.4 ^a
	total	57.2 ^A	–	123 ^A	6.4 ^B
M	A_p	16.4 ^a	22.1 ^c	112.4 ^c	8.9 ^c
	E_{et}	17.3 ^b	10.7 ^c	57.4 ^b	5.0 ^c
	B_t	26.9 ^{ab}	4.2 ^b	34.4 ^b	1.4 ^b
	total	60.1 ^B	–	191 ^B	12.5 ^B
NPK + M	A_p	15.5 ^a	18.6 ^b	90.0 ^b	6.8 ^b
	E_{et}	17.4 ^b	8.6 ^b	46.0 ^b	3.5 ^b
	B_t	27.2 ^b	6.5 ^c	54.8 ^c	2.1 ^c
	total	60.3 ^C	–	204 ^B	15.3 ^C

a – within each horizon, means followed by the same small letter are not significantly different ($P < 0.05$); A – within each treatment, means of the total content in profiles by the same capital letter are not significantly different ($P < 0.05$). PSC_{M3} – phosphorus sorption capacity

<https://doi.org/10.17221/696/2018-PSE>

depended exclusively on the P_{M3} content. Therefore, the highest value of DSP_{M3} was determined in the A_p horizon of M soil, and the lowest in the NPK soil.

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Received on October 24, 2018

Accepted on December 13, 2018

Published online on January 14, 2019