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Impact of long-term liming on sandy soil phosphorus sorption properties

Abstract: The static fertilisation experiment conducted in Skierniewice (Central Poland) since 1923 investigates the effect of mineral fertilisation with lime (CaNPK) or without lime (NPK) on the accumulation and release of phosphorus in reference to phosphorus sorption properties in the sandy soil profile. In the case of application of same doses of mineral fertilisers, the content of total phosphorus was higher in NPK than CaNPK soil. Parameters related to sorption capacity and bonding energy from Langmuir and Freundlich model of P sorption were significantly lower in CaNPK than NPK soil profile. This was particularly caused by a lower content of poorly crystallised hydro(oxide) aluminium and iron forms in CaNPK than NPK soil. Higher content of oxide-extractable and bioavailable phosphorus extracted with double lactate solution, dissolved reactive phosphorus in water solution as well as degree of phosphorus saturation in the CaNPK soil profile suggests higher mobility and possibility of occurrence of losses of phosphorus from the profile of limed soil than from acidified soil. Therefore, management of phosphate fertilizers on permanently limed sandy soils requires the optimisation of phosphorus doses to a greater degree corresponding to the actual take-off of the element with crop. An additional finding of the study was evidence of the possibility of re-estimating contents of bioavailable phosphorus and, as a consequence, the degree of phosphorus saturation with Mehlich3 method in strongly acid soil receiving P mineral fertilisers, which can make it difficult to use the test for fertiliser recommendation.

Keywords: liming, long-term experiment, phosphorus sorption, phosphorus saturation, Mehlich3

INTRODUCTION

Phosphorus is a component the bioavailability of which largely depends on soil pH (Barrow 2017). Agronomic soil phosphorus testing is often the only available information about the phosphorus soil status. Meanwhile, a change in soil pH can modify its sorption properties towards phosphorus, increasing or decreasing not only its bioavailability but also phosphorus release (Murphy and Sims 2012; Szara et al. 2017). An increase in soil pH causes the process of deprotonation, and leads to an increase in negatively charged surfaces in the soil, reducing the anion sorption properties including phosphates. On the other hand, an increase in the ionic strength of the soil solution and Ca concentration can counteract the unfavourable anion electrostatic effect resulting from liming (Curtin et al. 1993). High Ca soil content can increase the precipitation of Ca-P compounds, and decreases phosphorus solubility (Jokubauskaite et al. 2015). Liming reduces the content of Al and Fe ions, which in reaction with fertiliser phosphorus, are precipitated to sparingly soluble Fe-P and Al-P compounds. The precipitation of exchangeable Al³⁺ as polymeric hydroxy-Al cations may create new highly

active phosphate adsorbing surface in soils (Haynes 1982). Due to this, the effect of liming and change in soil pH on phosphorus sorption properties and release of soil P is ambiguous. Research to date on these relations has been conducted especially in the surface soil layer and more often in laboratory conditions (Anjos and Rowell 1987; Sato and Comerford 2005; Gichangi and Mnkeni 2009; Broggi et al. 2011) than field conditions (Jokubauskaite et al. 2015, Szara et al. 2017, Simonsson et al. 2018). Meanwhile, phenomena occurring in deeper soil layers define the direction and intensity of transformations of phosphorus introduced with fertilisers related to leaching of this element (Andersson et al. 2016). Due to easy-drainage properties and low capacity of phosphorus retention, transfer of phosphorus to deeper layers of the profile and further to drainage waters can occur in sandy soil (Andersson 2013). Therefore, our study was based on a long-term experiment conducted since 1923 with the application of mineral fertilisation with or without lime. The objective of the study was the assessment of the effect of liming on the accumulation and release of P in reference to phosphorus sorption properties in the sandy soil profile.

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MATERIALS AND METHODS

The study has been carried out on a long-term fertilisation experiment (since 1923) at the Experimental Station of the Warsaw University of Life Sciences – SGGW in Skierniewice (Central Poland, 51°96'N, 20°16'E). The soil is a Planosol (IUSS Working Group WRB 2015) with content of clay particles (<0.002 mm) in the following diagnostic horizons: 8% in the upper layer (Ap), 7% in Et, and 16% in Bt. The average annual temperature and precipitation are 8° and 520 mm respectively. In the experiment, plants were cultivated in an arbitrary rotation. The research employed treatments (three repetitions) with a mineral fertilisation system with liming – CaNPK or without liming – NPK. The annual doses of mineral fertilisers equalled 90 kg N (as ammonium nitrate), 26 kg P (as superphosphate), and 91 kg K·ha⁻¹ (as potassium chloride). On CaNPK treatments, liming was applied every 4 years in a dose of 1.43 t Ca·ha⁻¹. The average phosphorus uptake by plants was 19 kg·ha⁻¹ under CaNPK and 17,5 kg·ha⁻¹ under NPK treatment.

Soil samples were collected in autumn after mustard (*Sinapis alba*) harvest in 2015 from the following diagnostic horizons: A_p (0–0.25 m), E_{et} (0.25–0.50 m), and B_t (0.50–0.75 m). Soil samples for chemical analysis were air-dried and sieved to 2 mm.

The following was determined in the soil samples: pH in 1M KCl (1:2.5), total organic carbon (TOC) by means of a TOC-analyser, total content of soil phosphorus (P_t) – after soil digestion in HNO₃/HClO₄, and content of inorganic phosphorus (P_i) after extraction in 0.5 M H₂SO₄. The content of soil organic phosphorus (P_o) was estimated as a difference between P_t and P_i (O'Halloran and Cade-Menun 2008). Bioavailable phosphorus content was determined by means of Eghner-Riehm's double lactate extraction (P_{DL}) (PN-R-04023 1996) and dissolved reactive P (DRP) after water soil extraction (1:5) following centrifugation and vacuum-filtration (<0.45 μm) (Sharpley et al. 2008).

The Mehlich3 method was applied to determine the content of Ca_{M3}, Mg_{M3}, Al_{M3}, Fe_{M3}, and P_{M3} (Ziadi and Sen Tran 2008). The content of amorphous (hydr)oxide form Al_{ox}, Fe_{ox}, and P_{ox} was determined by acid ammonium oxalate extraction (Schoumans 2000). The degree of phosphorus saturation (DSP) of soil was calculated as ratio (mmol·kg⁻¹): $DPS_{M3} = [P_{M3} / PSC_{M3}] \times 100\%$, where $PSC_{M3} = (Al_{M3} + Fe_{M3})$ (Khiari et al. 2000) and according to the Schoumans modification (2000) $DPS_{ox} = (P_{ox} / PSC_{ox}) \times 100\%$, where $PSC_{ox} = (Al_{ox} + Fe_{ox})$.

For the assessment of phosphorus sorption properties, soil samples were equilibrated with graded phosphorus concentration (0 to 20 mg P·dm⁻³ as KH₂PO₄) in 0.01 M CaCl₂ (1:10) for 24 hours. After centrifuging at 3000 rpm for 15 min, and filtering, the phosphorus concentration in the supernatant solution was measured (C, mg·dm⁻³). The amount of P sorbed (S, mg·kg⁻¹) 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 (Sharpley et al. 2008), and content of Fe, Al, Ca i Mg by means of atomic absorption spectrometry (AAS).

Sorption isotherms were examined by Langmuir equation: $C/S = 1/kS_{max} + C/S_{max}$, where S_{max} is the sorption maximum (mg·kg⁻¹), and k is constant related to bonding energy of soil for P (dm³·mg⁻¹). 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). Maximum buffering capacity (MBC) is derived as: $MBC = k S_{max}$ (Holford and Mattingly 1976).

The data were also fitted to the Freundlich equation: $S = a_F C^{b_F}$, where a_F is the extent of P adsorption (mg·kg⁻¹), and b_F a constant corresponding to the degree of linearity between the solution equilibrium concentration and absorption (mg·dm⁻³). 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 suitability of sorption equations was based on coefficient of determination (R²) values. One-way analysis of variance (ANOVA) at P<0.05 was used for comparison of means for each soil horizon of treatments separately, and mean total contents of parameters in soil profiles of treatments (SPSS IMAGO 23).

RESULTS

Fertilisation applied for more than 90 years led to strong acidification of the soil with NPK treatment, where pH decreased with depth from 4.5 to 3.9. Also on CaNPK, treatment soil pH decreased with soil depth, although permanent liming permitted the maintenance of weakly acidic reaction throughout the profile (pH 6.7–6.3) (Table 1).

Content of Ca_{M3} in CaNPK soil (3235 mg·kg⁻¹) significantly higher than in NPK soil (2186 mg·kg⁻¹) was a natural effect of the introduction of the component from lime. An increase in the content of Ca_{M3} in

soil decreased with soil depth. Although no fertilisation with magnesium was applied in any of the treatments, content of Mg_{M3} was significantly higher in A_p ($57 \text{ mg}\cdot\text{kg}^{-1}$) and B_t ($131 \text{ mg}\cdot\text{kg}^{-1}$) horizons of the CaNPK soil profile than in the analogical NPK soil horizons (15 and $78 \text{ mg}\cdot\text{kg}^{-1}$, respectively).

In comparison to NPK treatment ($8.50 \text{ g}\cdot\text{kg}^{-1}$), lime did not change the total content of TOC in CaNPK treatment ($8.48 \text{ g}\cdot\text{kg}^{-1}$), but changed its distribution in the soil profile. In CaNPK soil, higher accumulation of TOC occurred in horizons A_p and E_{et} , and in NPK soil it's greater transfer to layer B_t occurred.

Content of P_t decreased with depth in both soils, but in spite of the application of the same dose of P fertiliser, content of P_t was significantly higher in the NPK ($661 \text{ mg}\cdot\text{kg}^{-1}$) than in the CaNPK soil profile ($634 \text{ mg}\cdot\text{kg}^{-1}$) (Table 1). Higher differences in P_t content were determined in analogical soil horizons of both soils. In the surface layer of NPK soil, content of P_t ($349 \text{ mg}\cdot\text{kg}^{-1}$) was 43% higher in comparison to the layer of CaNPK treatment ($244 \text{ mg}\cdot\text{kg}^{-1}$). In the layer of E_{et} soil, content of P_t was 54% higher in CaNPK than in NPK treatment. Because the contribution of P_i in P_t in the surface soil layer of NPK treatment equalled 71%, it can be presumed that the accumulation of unused by plants fertiliser phosphorus occurred in this particular horizon. A considerable reduction of the contribution of P_i in P_t with depth to 38% in E_{et} and 20% in B_t horizon suggests higher mobility of P_o than P_i in NPK soil profile. The contribution of P_i in P_t decreased with soil depth also on CaNPK treatment, although it was more even throughout the soil profile (54–40%).

Irrespective of the applied study method, the content of bioavailable P decreased with depth in both soils (Table 2). The content of P_{DL} on CaNPK treatment varied from 55 to $6 \text{ mg}\cdot\text{kg}^{-1}$, and was significantly higher than the content in each diagnostic horizon of the NPK treatment profile (from 41 to $2 \text{ mg}\cdot\text{kg}^{-1}$).

Content of P_{M3} (from 94 to $17 \text{ mg}\cdot\text{kg}^{-1}$ in CaNPK, and from 133 to $14 \text{ mg}\cdot\text{kg}^{-1}$ in the NPK soil profile) was higher than P_{DL} . In contrast to E_{et} and B_t horizons,

TABLE 1. Basic agrochemical properties of the soil profile

Treatment	Horizon	pH_{KCl}	TOC	Ca_{MB}	Mg_{MB}	P_t	P_i	P_o
			$\text{g}\cdot\text{kg}^{-1}$			$\text{mg}\cdot\text{kg}^{-1}$		
CaNPK	A	6.7a	5.28a	865b	57b	244a	131a	113a
	E	6.4a	1.52a	669b	31a	220b	104b	117a
	B	6.3a	1.67a	170b	131b	170a	68b	102a
	total		8.48A	3235B	218B	634A	302A	332A
NPK	A	4.5b	5.20a	406a	15a	349b	248b	102a
	E	4.2b	1.42a	261a	25a	143a	55a	88a
	B	3.9b	1.87b	1518a	78a	169a	34a	135b
	total		8.50A	2186A	118A	661B	336B	336A

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

content of P_{M3} in the surface layer of NPK soil was considerably higher ($133 \text{ mg}\cdot\text{kg}^{-1}$) than in CaNPK soil ($94 \text{ mg}\cdot\text{kg}^{-1}$).

Content of dissolved reactive phosphorus extracted with water solution (DRP) was the lowest of all of the determined bioavailable forms of phosphorus, and similarly as P_{DL} it was usually higher in horizons of the CaNPK soil profile ($5.72\text{--}0.48 \text{ mg}\cdot\text{kg}^{-1}$) than in NPK soil ($5.35\text{--}0.37 \text{ mg}\cdot\text{kg}^{-1}$).

Content of P_{ox} was significantly higher in the CaNPK soil profile ($479 \text{ mg}\cdot\text{kg}^{-1}$) than in NPK soil ($373 \text{ mg}\cdot\text{kg}^{-1}$), and depending on treatments it was 2–3 times higher than content of P_{M3} , and 6–7 times higher than content of P_{DL} . In CaNPK soil, P_{ox} content in A_p horizon constituted 86% of P_t , and in B_t horizon 51%. The contribution of P_{ox} in P_t in the analogical NPK soil horizons was considerably lower and equalled 63% and 31% respectively. This suggests that with depth in both of the studied treatments, the contribution of well-crystalline forms of phosphorus increased and was higher than in the NPK soil profile.

Sorption parameters for phosphorus determined based on Langmuir ($R^2 > 0.989$) and Freundlich

TABLE 2. Content of phosphorus and the degree of P saturation in soil profile

Treatment	Horizon	P_{ox}	P_{MB}	P_{DL}	DRP	DPS^{ox}	DPS_{MB}
			$\text{mg}\cdot\text{kg}^{-1}$			%	
CaNPK	A	210a	94a	55b	5.72b	24.8b	16.4a
	E	184b	41b	22b	1.81b	22.6b	7.2b
	B	86b	17a	6b	0.48b	7.5b	2.1b
	total	479B	151A	84B	8.01B		
NPK	A	209a	133b	41a	5.35a	22.6a	19.6b
	E	111a	21a	13a	1.44a	12.1a	3.6a
	B	52a	14a	2a	0.37a	4.0a	1.5a
	total	373A	168B	56A	7.16A		

a, b, A, B-as in table 1

TABLE 3. Phosphorus sorption parameters in soil profile

Treatment	Horizon	Langmuir		MBC	Freundlich	
		S_{\max} mg·kg ⁻¹	k dm ³ ·mg ⁻¹	dm ³ ·mg ⁻¹	a_F mg·kg ⁻¹	b_F dm ³ ·mg ⁻¹
CaNPK	A	38a	0.281a	11a	14a	0.313a
	E	59a	0.418a	25a	25a	0.290a
	B	122a	0.755a	92a	51a	0.351a
	total	219A	1.455A	127A	90A	0.954A
NPK	A	49b	0.392b	20b	20b	0.312a
	E	76b	0.539b	41b	32b	0.284a
	B	148b	1.091b	161b	73b	0.372a
	total	273B	2.022B	223B	125B	0.968A

a, b, A, B – as in table 1

sorption equations ($R^2 > 0.975$) are presented in Table 3. The maximum P sorption capacity (S_{\max}) assumed by the Langmuir sorption model increased with depth in both soils (respectively in CaNPK: 38–122 mg P·kg⁻¹ and M: 49–148 mg P·kg⁻¹). Total S_{\max} in the CaNPK soil profile (219 mg·kg⁻¹) however was considerably lower than in the NPK (273 mg·kg⁻¹). Similar patterns were determined in reference to the a_F parameter corresponding to the number of sorption sites for phosphorus in the Freundlich sorption model.

Values k from the Langmuir model suggest that the bonding energy of phosphorus is considerably higher in each diagnostic horizon in NPK soil (0.392–1.091 dm³·mg⁻¹) than CaNPK (0.281–0.755 dm³·mg⁻¹), and in both soils the bonding affinity to soil particles increased with depth. Freundlich b_F coefficient also related to the bonding energy unlike to k did not show such substantial vertical variability in the profiles or between the analogical diagnostic horizons of the studied soils (0.313–0.351 for CaNPK and 0.312–0.372 dm³·mg⁻¹ for NPK).

The ability of soil to counteract changes in P concentration the in soil solution as a result of P fertilisation, measured by maximum buffering capacity (MBC), was considerably higher in NPK than in CaNPK soil, and varied from 20 dm³·mg⁻¹ in the surface layer to 161 dm³·mg⁻¹ in the B horizon of NPK treatment. In analogical horizons of CaNPK soil, MBC adopted values of 11 and 92 dm³·mg⁻¹ respectively.

The amount of (hydr)oxide aluminium extracted with Mehlich3 extract (Al_{M3}) was higher (1.1–1.4 times) than that determined in the oxalate solution (Al_{ox}), but their variability was similar. The amount of Al determined by means of both methods increased in the profile with soil depth, and in each horizon of NPK soil (15.7–28.7 mmol·kg⁻¹ for Al_{M3}

and 14.2–24.1 mmol·kg⁻¹ for Al_{ox}) it was significantly higher than in CaNPK soil (14.4–23.1 mmol·kg⁻¹ for Al_{M3} and 12.2–20.8 mmol·kg⁻¹ for Al_{ox}).

Unlike in the case of aluminium, content of Fe_{ox} was from 3.2 to 8.5 times higher than content of Fe_{M3} in different soil horizons. Content of Fe_{M3} decreased, and that of Fe_{ox} increased with soil depth. Total content of Fe_{M3} and Fe_{ox} in NPK soil (4.9–2.0 mmol·kg⁻¹ for Fe_{M3} and 15.7–17.5 mmol·kg⁻¹ for Fe_{ox}) was significantly higher than in

CaNPK soil (3.9–1.9 mmol·kg⁻¹ for Fe_{M3} and 15.0–16.2 mmol·kg⁻¹ for Fe_{ox}). The variability of contents of Fe_{M3} and Fe_{ox} between analogical horizons of both analysed treatments was lower than for Al_{ox} and Al_{M3} .

Total content of amorphous (hydr)oxide Al_{ox} and Fe_{ox} determined based on oxalate extraction (PSC_{ox}) was higher than in the case of Mehlich3 extraction (PSC_{M3}). Both parameters however constituting a measure of phosphorus sorption capacity, similarly as S_{\max} , were significantly higher in all horizons of NPK soil, and in both treatments they increased with depth.

The phosphorus saturation degree (DPS_{ox}) determined based on oxalate extraction adopted higher values in the CaNPK (7.5–24.8%) than NPK soil profile (4.0–22.6%) (table 2). This suggests a higher possibility of losses of phosphorus from limed soil. This is also confirmed by DSP_{M3} indices, but only in E_{et} and B_t horizons. Due to considerably higher content of P_{M3} , DPS_{M3} is also higher in the surface layer of NPK than CaNPK soil. Among the analysed indices of release of P from soil (MBC, DRP, k, S_{\max}), only the DSP_{M3} parameter points to higher susceptibility of NPK soil to losses of P from the surface layer of soil than CaNPK soil.

DISCUSSION

The results of plant yielding and phosphorus use efficiency from superphosphate not presented in this article can be found in other papers concerning experiments in Skierniewice (Mercik and Stepień 2012; Stepień et al. 2018). According to those, in the analysed experiment, the reduction of the yield size on NPK (14–31%) in comparison to CaNPK treatment depended on the plant species. Long-term P use efficiency from superphosphate averaged 31% on NPK and 37% on CaNPK soils. A smaller difference

TABLE 4. Content of Fe and Al extracted with oxalate (OX) and Mehlich-3 (M3)

Treatment	Horizon	Al _{ox}	Fe _{ox}	PSC _{ox} mmol kg ⁻¹	Al _{M3}	Fe _{M3}	PSC _{M3}
CaNPK	A	12.2a	15.0a	27.2a	14.4a	3.9a	18.4a
	E	11.2a	15.2a	26.2a	15.1a	2.8b	18.0a
	B	20.8a	16.2a	37.0a	23.1a	1.9a	25.0a
	total	44.0A	46.4A	91.0A	52.6A	8.7A	61.3A
NPK	A	14.2b	15.7b	29.9b	15.7b	4.9b	21.9b
	E	13.3b	15.7a	29.0b	16.6b	2.4a	18.6a
	B	24.1b	17.5b	41.6b	28.7b	2.0a	30.6b
	total	51.7B	48.9B	100.0B	62.3B	9.3B	71.3B

a, b, A, B – as in table 1

in P use efficiency than crop yields in the analysed experiments explains higher of P_i content in the CaNPK soil profile than NPK. Excess of mineral fertiliser phosphorus particularly accumulated in the surface layer of NPK soil, but in CaNPK soil, a considerable part of P_i was transferred to E_{et} horizon.

An increase in biological activity, mineralisation, returns of crop residue, and stability of mineral-organic aggregates are the main processes determining the effect of liming on the content of soil organic matter (Kołodziejczyk et al. 2017). The net effect of these processes on soil organic matter stock depending on the fertilisation soil and climatic conditions is ambiguous (Paradelo et al. 2015). In the presented study, a higher amount of harvest residue in CaNPK treatment did not considerably change the content of TOC and P_o . This suggests more intensive mineralisation of harvest residue than on NPK treatment. In the analysed soils, a considerably higher amount of Ca_{M3} and Mg_{M3} in CaNPK treatment could have reduced the mobility of organic compounds in comparison to NPK soil (Gao et al. 2014). As a result, content of TOC and P_o in B_t horizon of NPK was considerably higher than in CaNPK soil. The contribution of P_o in P_t in B_t horizon was as much as 80% in NPK and only 60% in CaNPK soil.

Values of parameters from sorption models can increase or decrease due to liming depending on soil conditions (Haynes 1982, Sato and Comerford 2005; Gichangi and Mnkeni 2009; Broggi et al. 2011). In our study, values of parameters related to the number of site, P sorption (S_{max}) and bonding energy (k) from Langmuir and a_F from Freundlich model were considerably higher throughout the NPK than CaNPK profile. This particularly resulted from considerably higher content of poorly crystallised (hydr)oxide Al and Fe obtained with oxalate and Mehlich3 method which are the main phosphate adsorbents in sandy soil (Lookman et al. 1995). Contrary to our study results, in multi-annual experiments in Sweden, liming caused no substantial changes in the content

of oxalate-extractable Al and Fe (Simonsson et al. 2018). Already after 23 months following the application of lime, Anjos et al. (1987) determined a reduction of the number of sites for P sorption as a result of crystallisation of Al (hydr)oxide in soil.

The observed decrease in bonding energy related to a decrease in the number of sorption sites in the soil is a pattern confirmed in the results of research by Sato and Comerford (2005). A decrease in the value of parameter k (by 28%) throughout the profile of CaNPK in comparison to NPK soil was higher than the decrease in the value of S_{max} (by 20%), PSC_{ox} (by 9.3%), and PSC_{M3} (by 14%). This can confirm the theory that an increase in soil pH attributed to competition of hydroxyl (OH^-) concentration with phosphate ions for specific sorption sites, and an increase in deprotonation intensifies electrostatic repulsion of P weakening the affinity to mineral surfaces (Curtin et al. 1993). Therefore, even in the case of an increase in phosphorus capacity as a result of liming, a decrease in bonding energy is observed (Broggi et al. 2011). According to Holford and Mattingly (1976) the cooperation of the number of sites (S_{max}) and their affinity to phosphorus (k) decides about the maximum buffering capacity (MBC) of soil. The MBC value suggests the ability of soil to retain constant P concentration in the soil solution both in the case of its exhaustion and application under the condition of maintaining constant value of S_{max} . Therefore, the MBC value is of environmental and agronomic importance, because it can be used for the assessment of the possibilities of supply and immobilisation of phosphorus in the soil. In our study, there is significantly lower MBC value in each CaNPK horizon than in NPK soil, making it more susceptible to phosphorus loss in the case of further application of phosphorus fertilisers. MBC values indicate that B_t soil horizon can counteract the transfer of 1.8 times smaller mass of phosphorus to drainage water from CaNPK than NPK soil. Therefore, particularly in limed soils, doses of phosphorus

fertilisers should to a greater degree correspond with the actual take-off of P with crop.

The value of a_F less than 0.40 suggests that adsorption rather than precipitation is responsible for the retention of phosphorus in the soil of both analysed treatments (Castro and Torrent 1998). However, a higher value of parameter b_F ($0.313 \text{ dm}^3 \cdot \text{mg}^{-1}$) than parameter k ($0.281 \text{ dm}^3 \cdot \text{mg}^{-1}$) in the surface layer of CaNPK soil suggests that precipitation of P in this soil horizon largely contributes to the process of sorption of the component (Hussain et al. 2006). Considerable content of Ca_{M3} in this soil layer can contribute to the precipitation of Ca-P observed in limed soils (Jokubauskaitė et al. 2015).

One of the effects of an increase in soil pH as a result of liming is an increase in the bioavailability of P for crop production (Sato and Comerford 2005; Jokubauskaitė et al. 2015, Goulding 2016, Szara et al. 2017). Also in our study, in spite of identical doses of phosphorus, content of P_{ox} and P_{DL} was higher in CaNPK soil horizons than in NPK soil. Because oxalate solution extraction releases not only P absorbed on soil particles, but also a part of organic phosphorus, content of P_{ox} is usually more approximate to the total than bioavailable amount of this element (Guo and Yost 1999). Lower content of P_{ox} and its contribution in P_t suggests an increase in the content of well-crystalline form of P and lower risk of release of P in NPK than in CaNPK soil.

Contrary as for P_{DL} , considerably higher content of available P in the surface layer of NPK ($133 \text{ mg} \cdot \text{kg}^{-1}$) than CaNPK ($94 \text{ mg} \cdot \text{kg}^{-1}$) soil was obtained by means of the Mehlich3 method. A considerable effect of soil $\text{pH} < 5.5$ on the growth of phosphorus extracted with M3 solution (by 45–55%) was evidenced by Penn et al. (2018). According to the authors, the capacity of M3 solution to release P from hardly accessible bonds of Al-P in conditions of strong soil acidification is probably the effect of both a change in the form of P in soil and properties of the extractor itself. This particularly concerns the intensity of the deprotonation/protonation reaction and capacity of F^- to complex Al promoting dissolution of Al-P minerals (e.g. variscite, gibbsite). The specificity of Mehlich-3 solution in contrast to oxalate solution allows for extraction of only less stable forms of iron. Therefore according to Shang et al. (2013), in the case of application of those methods for risk assessment of soil, it is important to consider its mineralogical composition. Mineralogical composition was not the subject of our study, but perhaps it was the cause of

the fact that unlike in the case of A_p horizon, content of P_{M3} similarly as P_{DL} and P_{ox} in the E_{et} and B_t soil horizon was considerably higher in CaNPK than NPK soil.

Research by Shang et al. (2013) and Penn et al. (2018) also permits better understanding of the differences obtained in the content of Al_{ox} and Al_{M3} in different soil conditions. In the majority of soils, the ratio $\text{Al}_{M3}:\text{Al}_{ox}$ equals 0.8 (Sims et al. 2002, Pizzeghello et al. 2014). In our research, the content of Al_{M3} in all horizons was higher by approximately 10–20% in comparison to the content of Al_{ox} . Similar results were obtained by Penn et al. (2006) in the soils of Virginia.

Doubts resulting from the interpretation of study results due to higher content of P_{M3} and value of DPS_{M3} in the surface layer of NPK than CaNPK soil are largely eliminated by the observed values of DRP. Water used for its extraction does not interact with unavailable forms of P. Therefore DRP is not only a measure of readily available P, but also a good predictor of the potential loss of P from soil which usually shows a strong correlation with DSP_{M3} and DSP_{ox} (Sims et al. 2002, Penn et al. 2006, Szara et al. 2018). The content of DRP confirmed higher susceptibility of CaNPK soil in all profiles to release of P than NPK soil, as suggested by content P_{DL} and P_{ox} , and DSP_{ox} .

CONCLUSIONS

Liming applied in combination with mineral fertilisers reduces sorption capacity throughout the sandy soil profile particularly as a result of fixation of amorphous of (hydr)oxide Al and Fe to more crystalline forms. This leads to higher mobility of the balance surplus in the soil profile, causing an increase in the content of oxide-extractable P, bioavailable P and dissolved reactive phosphorus in water promoting release of P. Therefore management of the phosphate fertilisers on permanently limed sandy soil requires the optimisation of P doses to a greater degree corresponding to the actual take off of the component with yield to minimise the risk of losses of soil phosphorus.

An additional study finding is also the determination of the possibility to re-estimate contents of bioavailable phosphorus, and as a consequence, the degree of phosphorus saturation with Mehlich-3 test in strongly acid soil receiving P mineral fertilisers, which can make it difficult to use the test for fertiliser recommendation.

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- Received: December 6, 2018*
Accepted: March 6, 2019
Association editor: B. Rutkowska

Wpływ wieloletniego wapnowania na sorpcję fosforu w glebie lekkiej

Streszczenie: Celem badań była ocena wpływu systematycznego wapnowania na akumulację i mobilność fosforu w odniesieniu do właściwości sorpcyjnych wobec fosforu w profilu gleby lekkiej. Badania przeprowadzono w oparciu o kombinację z mineralnym nawożeniem stosowanym z wapnowaniem (CaNPK) lub z jego pominięciem (NPK) w wieloletnim doświadczeniu nawozowym prowadzonym od 1923 roku w Skierniewicach (Centralna Polska). Przy stosowaniu jednakowych dawek nawozów mineralnych zawartość fosforu ogólnego w profilu gleby niewapnowanej (NPK) była większa niż w profilu gleby wapnowanej (CaNPK). Wskaźniki oceny pojemności sorpcyjnej oraz siły wiązania fosforu wyznaczone opierając się o model Langmuira i Freundlicha były istotnie mniejsze w profilu gleby CaNPK niż NPK. Było to spowodowane przede wszystkim mniejszą zawartością słabo skryształizowanych form tlenków i hydroksytlenków glinu i żelaza w profilu gleby CaNPK niż NPK. Większa zawartość form słabo skryształizowanych oraz fosforu biodostępnego oznaczanego metodą Egnera-Riehma (DL) oraz fosforu rozpuszczalnego w wodzie wskazuje na większą mobilność i możliwość wystąpienia strat fosforu z profilu gleby wapnowanej niż z gleby zakwaszonej. Dlatego szczególnie na glebach systematycznie wapnowanych konieczna jest ścisła kontrola dawek nawozów fosforowych na podstawie faktycznego wynoszenia tego składnika z plonem. Dodatkowym efektem przeprowadzonych badań było wykazanie możliwości przeszacowania zawartości fosforu dostępnego, a w konsekwencji również stopnia wysycenia fosforem przy użyciu metody Mehlich3 w glebie silnie zakwaszonej w wyniku stosowania nawożenia mineralnego. Fakt ten może utrudniać używanie tego testu do celów agronomicznych i środowiskowych.

Słowa kluczowe: wapnowanie, wieloletnie doświadczenie nawozowe, sorpcja fosforu, wysycenie gleby fosforem, Mehlich3