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The influence of soil properties and land use on the phosphate level in soils from Lubelskie region

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Abstract. Phosphorus is an important life-supporting nutrient and therefore it is often applied in fertilizers. As a result, its pool in soil may increase due to the presence of various elements effectively binding P, making it unavailable to plants. Each soil exhibits many characteristics important in P cycling, with the aeration state (redox potential and moisture), pH, and the presence of N, Ca, and Fe being the most important. In addition, agricultural practices, e.g. fertilization, may strongly affect P pools in the soil. We studied 7 different, both cultivated and natural, soil types from Lubelskie region. We found that agricultural practices strongly affected the soil aeration state, pH, and moisture level reducing them significantly. As a result, phosphate concentrations increased significantly up to 10 mg kg^{-1} in comparison to ca. 2–4 mg kg^{-1} in non-cultivated soils. This was caused by changes in soil characteristics depending on the soil type (availability of N, Ca, and Fe). The levels of nitrates increased up to 50 mg kg^{-1}, favouring P immobilization. It could be concluded that the soil aeration state (related to the manner of soil use) is important in P cycling through the effect on other soil characteristics, which differ among soil types.

Key words: arable soils, phosphate availability, soil characteristics, land use

INTRODUCTION

Phosphorus is an essential life-supporting element and one of the key nutrients. Therefore, supplementation thereof to soil is important for enhancement of agricultural production. This issue has always been important and there are still many attempts to improve soil fertility and crop production worldwide. From the other hand, increased application of fertilizers and manures (including phosphate-enriched) caused significant changes in agriculturally exploited areas (arable soils, meadows, and pastures). As a result of elevated levels of P in soils, plants could not uptake the whole available P leading to its accumulation. This may have an unfavourable impact on many environments, e.g. eutrophication of lakes and rivers observed worldwide (Banach, 2010; Dao, Schwartz, 2011).

The ability of soil to accumulate P depends on the soil type, its physicochemical properties (structure, pH, aeration state, and the contents of mineral and organic compounds), and land use (Kalembasa, Becher, 2010; Jouany et al., 2011). In addition, changes in the soil aeration state (related to water regime) and pH affect the biogeochemical cycling of P (Banach, 2010; Sapek, 2014). Under aerobic conditions, most P is unavailable and accumulates in soil. With increasing soil moisture, oxygen inflow to soil organisms decreases due to low oxygen diffusion in water. As a result, reducing processes prevail, affecting nutrient availability. After nitrate (V) reduction, manganese and iron forms are reduced subsequently leading to lower redox potential and accumulation of reduced compounds. As some soil P-fractions are bound to Fe (hydr)oxides, this process may increase the pool of available P in the soil. Moreover, further soil reduction connected with sulphate reduction may strengthen this process as the produced sulphide further affects the Fe~P fraction by the reduction of Fe(III), leading to high P flux to soil water. This process also generates higher bicarbonate alkalinity, which all contributes to a high trophic level in soil water (Eq. 1, Banach, Stępniewska, 2011). This process is called internal eutrophication and occurs even without any external P sources (Banach, 2010; Smolders at al., 2006).

$$SO_4^{2-} + 2CH_2O \leftrightarrow HS^- + HCO_3^- + CO_2 + H_2O \qquad \text{[Eq. 1]}$$

During this process, the pH of soil becomes alkaline, which changes other P fractions as well. In general, under pH > 7, most P is bound to Ca minerals, whilst low pH causes dissolution of these minerals and only the Al~P fraction is stable (Jensen, 2010).

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The situation described above is common in more or less inundated areas. In Lubelskie region, there are many arable areas located close to the Vistula river. These lands were flooded in the past years, which caused elevated levels of phosphates in soil water leading to internal and external eutrophication (Banach, 2010). The application of fertilizers and manures as well as other agricultural activities may only strengthen eutrophication (Banach, 2010; Banach, Stępniewska, 2011).

All these problems are still important due to both intense agriculture and climate changes. This work, part of a bigger project, aims to study the levels of phosphates in different soils in Lubelskie region, which differ in the structure and manner of cultivation. We attempt to study the role of these two factors on the pool of P, potentially a source of eutrophication during flood events in East Poland in order to better predict P pools in different soils. We hypothesized that soils agriculturally exploited would have higher P pools depending on soil type.

MATERIAL AND METHODS

Site description

The studied soils originated from Lubelskie region, south-eastern part of Poland. This region is represented by a great diversity of soil types and is one of the largest and most important agricultural areas in Poland where all dominant soil units are represented. The soil materials were selected on the basis of earlier work for the typological soil recognition performed in 1991 within the framework of the Bank of Soil Samples (BSS) belonging to the Institute of Agrophysics PAS in Lublin (Bieganowski et al., 2013).

The soil samples (0–20 cm layer) were collected during the spring season (24–26 April 2014). For the survey, 16 locations representing 7 soil types were selected (Table 1). Soils were sampled from non-ploughed places in order to avoid artefacts from ploughing perturbations (Wolińska et al., 2014). In each location, we selected both agriculturally exploited (coded R) and non-cultivated soils and non-forested sites (covering at least 1 hectare area), located in close proximity to basic soils and belonging to the same soil type (i.e. fallow lands or grasslands not cultivated for years) (coded K). Detailed characteristics of the locations are presented in Table 1.

Material sampling

In each site, a 10x10 m square characterized by the homogeneity of the vegetation cover was chosen. Within the square, ca. 50 random soil samples were taken from the top layer (0–20 cm) using a 2.5-cm-diameter auger. *Eutric Cambisols* and *Orthic Podzols* are dominating soil types in Poland, accounting for 82% of the country's area, thus their share in the study material was significant (Wolińska et al., 2014). *Eutric Cambisols* were represented by 6 soil samples and *Orthic Podzol* by 3 samples. *Mollic Gleysol* and *Rendzina Leptosol* had 2 representatives, respectively (Table 1).

Laboratory analyses

The soil material was immediately transported to the laboratory in plastic bags to avoid drying. Under laboratory conditions, each sample was passed through a 2.0-mm sieve, to remove large pieces of rocks and plant material, and stored at 4ºC prior to analysis (2-3 days).

The following characteristics were estimated in the fresh material: soil pH, redox potential (Eh), soil moisture, contents of total carbon (TC), soluble phosphorus (PO_4-P), nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_4-N), and total contents of Ca and Fe.

Soil pH and redox potential (Eh) were determined in a soil suspension in distilled water (1:2.5) using a multifunctional potential meter pIONneer 65 (Radiometer Analytical S.A., France) according to Gliński et al. (2002). Soil actual moisture was determined by the gravimetric method (24 h, 105°C), whilst the total carbon content in per cent (TC) using an automatic carbon analyser TOC-V_{CSH} SSM 5000A (Shimadzu, Japan). The concentrations of PO_4-P, NO_3-N, NO_2-N, and NH_4-N were determined colorimetrically using an Auto Analyser 3 System (Bran+Luebbe, Norderstedt, Germany) in water extracts (35 g soil, 100 ml distilled water, Banach et al., 2009) and expressed in mg per kg of fresh soil. Contents of Ca and Fe (mg kg^{-1}) were estimated by means of an atomic absorption spectrometer using flame atomization (FAAS method, Hitachi Z-2000, Japan) after sample destruction in a mixture of HF and HNO_3 (Ethos I, Milestone, Italy). Each of lab analysis was performed in triplicate.

The results obtained were analysed statistically using Statistica 9 PL (StatSoft, USA). The assumptions of parametric tests were checked with Shapiro-Wilk W statistics and, if assumptions were not met, ln(x+1) transformation was applied. To reveal the significant effects of the manner of soil use and its characteristics of P levels in the studied materials, MANOVA test with Tukey post hoc was used followed by analysis of regression (correlation coefficients).

RESULTS

Differences between soil types

The moisture level of the tested soils ranged between 7 and 28%. The highest moisture characterized *Haplic Phaezoem* followed by *Rendzina Leptosol*, *Eutric Cambisol*, and *Mollic Gleysol* (13.8–10.7%) ($p<0.0001$). This parameter in the other soil types was below 10% (Table 2). The pH of the soils was slightly acidic, mostly around 5–6. There were, however, some exceptions. In the case of *Haplic Phaezoem*, *Mollic Gleysol,* and *Rendzina Leptosol* we noted the highest pH, between 6.1–6.9. *Orthic Podzol*, *Eutric Histosol,* and *Eutric Fluvisol* had pH around 5. The

Table 1. Location of the studied soils with the crop type (cultivated) and description of controls (after Wolińska et al, 2014, modified).

Code	Type of soil (FAO)	Crop type	Village	Geographic coordinates	Control sites
OP	*Orthic Podzol*	oat	Dęba	22º10'17.7" 51º26'24.6"	30 year old meadow planted with fruit trees
		triticale	Pryszczowa Góra	22º27'10.3" 51º24'30.8"	20 year old woodlots with birches
		wheat	Niemce	22º36'51.8" 51º21'27.0"	50 year old meadow (mowed once a year)
EC	*Eutric Cambisol*	triticale	Klementowice	22º06'54.2" 51º21'52.2"	Unmowed meadow, wasteland
		oat	Łany	22º15'19.0" 51º23'00.9"	20 year old field-woodlots
		oat	Markuszów	22º15'55.5" 51º23'10.9"	20 year old field-woodlots
		field prepared for seeding	Rogalin	24º04'00.3" 50º51'15.8"	Meadow (mowed once a year)
		triticale	Sady	23º22'52.4" 50º51'14.8"	Unmowed meadow, wasteland
		strawberries	Chrząchówek	22º07'29.9" 51º25'50.5"	Unmowed meadow, wasteland
HP	*Haplic Phaezoem*	triticale	Hostynne	50º44'48.3" 23º42'56.6"	Meadow (mowed once a year)
MG	*Mollic Gleysol*	colza	Pożóg Nowy	22º06'18.8" 51º22'48.0"	30 year old pine woodlots
		wheat	Bałtów	22º01'25.5" 51º29'15.3"	70 year old meadow (mowed once a year)
EF	*Eutric Fluvisol*	oat	Kośmin	21º59'10.1" 51º33'47.7"	15 year old meadow (mowed once a year)
EH	*Eutric Histosol*	oat	Wólka Kątna	22º16'38.9" 51º25'27.3"	20 year old meadow (mowed once a year)
RL	*Rendzina Leptosol*	celeries	Siedliszcze	23º10'58.3" 51º12'22.3"	40 year old meadow (mowed once a year)
		oat	Brzeziny	23º11'43.9" 51º12'10.8"	Meadow (mowed once a year)

latter showed the lowest pH (4.9, $p<0.0001$, Table 2). All the studied soils were well aerated in the surface layer; the recorded Eh ranged between 438 and 545 mV. It can be stated that only *EC* soil has significantly lower Eh (438 mV) from the other sites ($p<0.0001$, Table 2).

The levels of carbon, nitrogen, and phosphorus compounds were also significantly different in the studied soils. The carbon contents in the samples were very low – 1.1–3.5%. *HP*, *EH*, and *RL* soils were the richest in carbon (2.4–3.5%). *MG*, *EC*, and *OP* had average TC of ca. 1.4–1.8%, and the lowest TC of 1.1% was recorded in *Eutric Fluvisol* soil ($p<0.0001$, Table 2). The nitrate concentration in the soil extracts ranged between 2.6 (*EF*) and 33.5 mg kg^{-1} (*RL*). In most soils, it was at a level of 12–13 mg kg^{-1}. However, only *Rendzina Leptosol* had a significantly higher NO_3-N level in comparison to the other soils ($p<0.0001$). The nitrite levels were all below 0.3 mg kg^{-1}; in *RL*, *HP*, and *EC*, the values of NO_2-N were above 0.2 mg kg^{-1}, which was significantly higher than in the other samples ($p=0.049$). The ammonium concentration was the highest in *Mollic Gleysol* (1.5 mg kg^{-1}) and *RL* (0.98 mg kg^{-1}) soil, while the other soils exhibited significantly lower values of 0.016 (*HP*) – 0.50 (*EC*) mg kg^{-1} ($p<0.0001$, Table 2). The studied soil contained different amounts of phosphate; the highest level was recorded in *EC* (7.3 mg kg^{-1}), followed by 4.6 mg kg^{-1} in *OP*. The other soils were characterized by values of 1.4–2.7 mg kg^{-1} ($p<0.0001$, Table 2, Fig. 1).

The contents of calcium showed the highest values in *RL* and *HP* soils (1939 and 2897 mg kg^{-1}, respectively). The other samples contained much less Ca <1000 mg kg^{-1} ($p<0.0001$, Table 2). In the case of Fe, all soils were rich in this element, especially *EF*, *MG*, and *OP* (>4000 mg kg^{-1} in comparison to 3300–3700 mg kg^{-1} in the other soils, $p<0.0001$, Table 2).

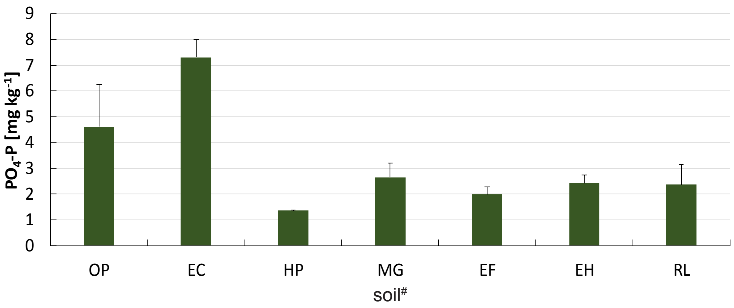
Effects of land use and its interactions with soil types

The manner of land use seemed to be a strong determinant of soil chemical features. As could be anticipated,

Table 2. Mean values of selected characteristics of the studied soil.

Soil#	n	%H_2O	pH	Eh [mV]	Ca	Fe	NO_3-N	NO_2-N	NH_4-N	PO_4-P
OP	18	9.55 a	5.37 ad	496.05 a	475.95 a	4213.93 b	13.52 a	0.1571 a	0.0395 a	4.612 ab
EC	36	11.08 ab	5.97 b	437.86 b	675.83 a	3765.79 a	12.25 a	0.2283 ab	0.4984 a	7.312 b
HP	6	27.70 c	6.93 c	545.28 a	2897.43 b	3296.60 a	17.83 a	0.2688 ab	0.0162 a	1.353 a
MG	12	10.70 ab	6.11 bc	507.42 a	724.83 a	4600.05 b	12.20 a	0.1204 a	1.5382 b	2.647 a
EF	6	6.95 a	4.91 a	548.25 a	437.45 a	4745.71 b	2.59 a	0.1175 a	0.2071 a	1.987 a
EH	6	7.80 a	5.06 a	521.70 a	310.04 a	3357.50 a	9.64 a	0.0877 a	0.0173 a	2.418 ab
RL	12	13.78 b	6.08 bcd	483.02 ab	1939.05 b	3323.47 a	33.52 b	0.2943 b	0.9837 ab	2.371 a

All concentrations except TC (which is in %) are in mg kg^{-1} fw
Means followed by the same letter do not differ at $p<0.05$
see Table 1



see Table 1

Fig. 1. Phosphate concentrations in the studied soil types (means+standard error of mean, SEM)

agricultural soil exploitation was the cause of the decrease in soil moisture, pH, TC, NO_2-N, and Ca. The water content was lower by 3–8% ($p<0.001$) in exploited soils, showing the strongest reduction for *HP*, *RL*, *EF*, and *EH* soils (Fig. 2A). The drop in pH resulted in more acidic conditions in the cultivated soils (4.2–4.9) than in controls, especially in *OP*, *EF* and *EH*. Only *EC*, *HP*, *MG,* and *RL*, which exhibited more natural pH, showed a shift to more neutral pH (5.6–6.6, $p<0.0001$, Fig. 2B). Soil cultivation reduced the pool of carbon by 20–70%, depending on soil type, which revealed an interactive effect of the soil type and the manner of land use (soil x land use, $p<0.0001$). The strongest reduction was observed in *Haplic Phaezoem* and *Rendzina Leptosol,* whilst in *OP*, *EF*, and *EH* it was only around 25% ($p<0.0001$, Fig. 2C). During soil cultivation, nitrite was depleted ($p<0.05$) in *OP*, *EC*, and *HP* soils, whilst we recoded one NO_2-N peak for *RL* revealing different responses of the studied soils (soil x land use, $p<0.0001$, Fig. 2F). The calcium content was lower in the cultivated soils ($p<0.0001$); moreover, the significant soil x land use interaction ($p<0.0001$) displayed responses dependent also on the soil type. The strongest reduction occurred again in HP and RL soils with no effect in the others (Fig. 2I).

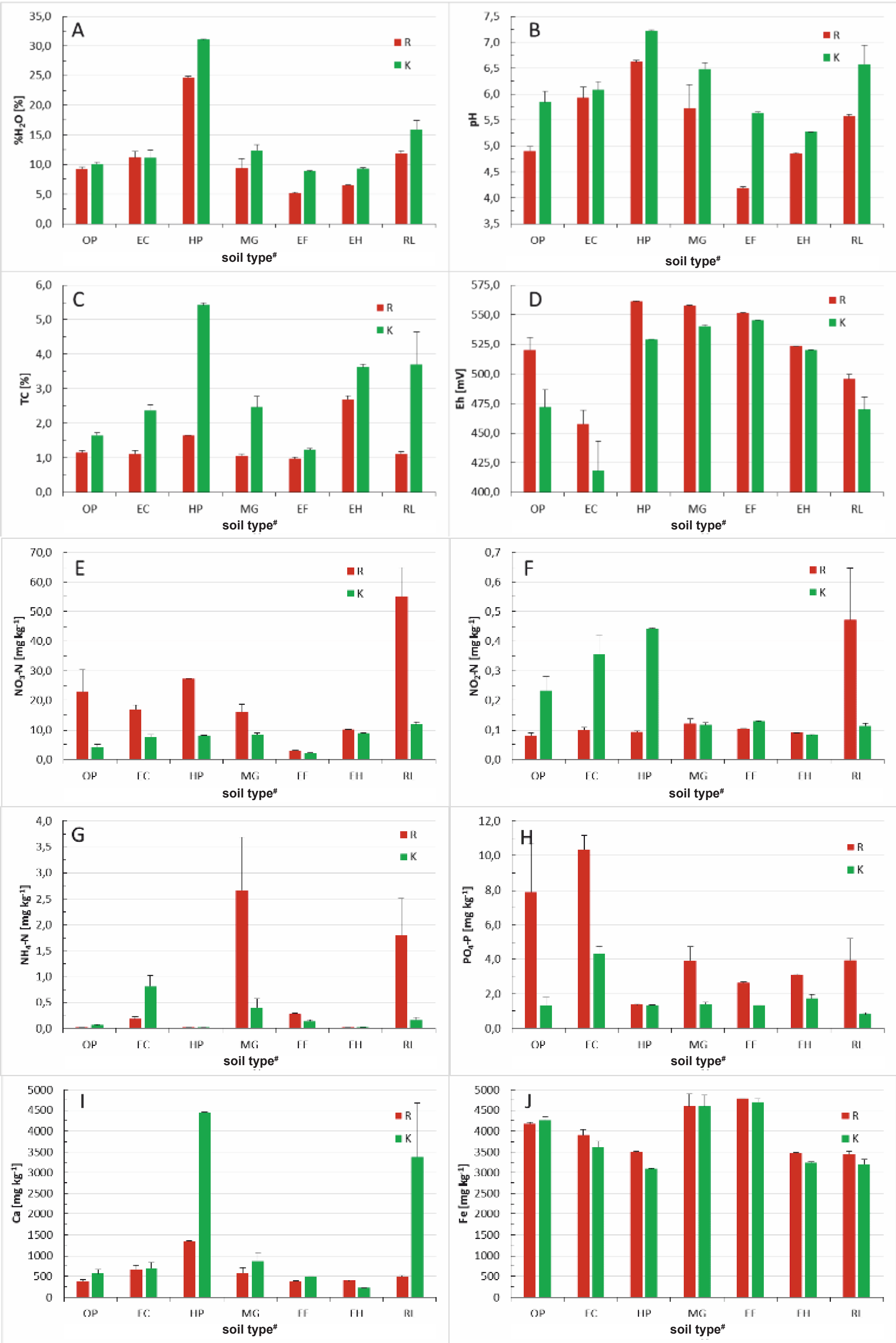
Among the investigated factors, Eh, NO_3-N, and PO_4-P displayed higher values in the cultivated (R) than in the control (K) soils. The increase in Eh in the cultivated soils ($p<0.0001$, Fig. 2D) resulted from the fact that agricultural practices, i.e. ploughing, improve the oxygen status in the surface part of soils, whereas the growth of NO_3-N and PO_4-P may be caused by systematic fertilization practices in arable soils. The strongest changes in Eh were noted in *OP*, *EC*, and *HP* soils (Fig. 2D). In the case of nitrates, there was soil-dependent response (soil x land use $p<0.0001$). The highest concentration of NO_3-N was recorded in *RL* soil (55 mg kg^{-1}, Fig. 2E). The other soils showed an increase in the range of 10–20 mg kg^{-1}, whilst *EF* and *EH* displayed a very small change in the nitrate level. The phosphate levels showed very high peaks in the cultivated areas and the concentrations ranged between 1.3 and 10.3 mg kg^{-1} in comparison to the values of 0.8–4.3 mg kg^{-1} in the controls. The most drastic changes were noted in *OP* and *EC* soils: the PO_4-P levels were 2–6 times higher in arable areas ($p<0.001$, Fig. 2H).

The ammonium levels showed different patterns depending on the soil type and the manner of land cultivation ($p<0.0001$). In the case of cultivated soils there was a clear increase in the NH_4-N levels in *MG* and *RL* and almost no changes in the other samples soils. In the case of *EC*, the ammonium levels were lower in the cultivated soil than in the control (Fig. 2G). The iron contents showed a similar pattern with no effect of the manner of land use ($p=0.127$), providing a stable pool for P binding (Fig. 2J).

Soil factors affecting P availability

The correlative study allowed determination of soil characteristics (different soil types) affecting P availability depending on soil use. These data are presented in Table 3.

In general, the phosphate levels were only moderately related to the nitrate levels ($r=0.4$*). When the data were split, we found more relations confirming the hypothesis that the soils differed in their characteristics and this was the cause of the variable P levels. It is worth noticing that NO_3-N was the main P level driver in almost all situations having



see Table 1

Fig. 2. Effect of land use (R – cultivated, K – non-cultivated and non-forested) on selected soil characteristics in different soil types (means+SEM).

Table 3. Correlation matrix between PO_4-P and soil characteristics.

	%H_2O	pH	Eh	TC	NO_3-N	NO_2-N	NH_4-N	Ca	Fe	n
					All data					
	-0.1940	-0.1646	-0.0774	-0.3311	**0.4167**	-0.0563	-0.0673	-0.2244	0.0525	96
					Soil usage#					
R	0.0195	0.0195	-0.2735	-0.1060	**0.2862**	0.0047	-0.1828	-0.2083	0.0053	48
K	-0.2135	-0.0871	**-0.3835**	-0.1769	**-0.3025**	0.2784	0.1252	-0.2510	-0.0646	48
					Soil type##					
OP	0.2455	-0.4078	0.3917	-0.2739	**0.9907**	-0.3969	-0.4031	0.0227	-0.0359	18
EC	-0.2753	-0.2340	**0.8269**	**-0.5810**	**0.3811**	**-0.3897**	**-0.4780**	-0.4069	0.2080	36
HP	-0.1063	-0.1923	0.1059	-0.1090	0.1100	-0.0996	0.0127	-0.1089	0.1639	6
MG	0.2063	0.2743	**0.5908**	-0.5451	-0.0898	**0.6531**	-0.2030	0.0248	0.4479	12
EF	**-0.9971**	**-0.9940**	**0.9968**	**-0.9037**	**0.9963**	**-0.9930**	**0.9071**	**-0.9988**	0.4725	6
EH	**-0.9482**	**-0.9373**	**0.9344**	**-0.8875**	**0.9457**	**0.8220**	-0.7733	**0.9450**	**0.9814**	6
RL	-0.5057	-0.3378	0.5160	-0.3920	**0.9575**	**0.9966**	**0.9993**	-0.3098	-0.0249	12

coefficients in bold are significant at $p<0.05$
n – number of samples
R – cultivated, K – non-cultivated and non-forested
see Table 1

a moderately strong positive impact on the PO_4-P levels in the studied soils (r=0.29–0.99*).

Soil aeration state, being a combination of soil redox potential, moisture, and partially pH, is an important factor affecting P availability. In general, aerated conditions favour P immobilization on soil particles (negative correlations found); however, strong oxidation and low pH may together cause P release. This was the cause of P mobilization in the *EF* and *EH* cultivated soils characterized by acidic conditions, lower moisture, and high Eh (r=0.93–0.99*). In the controls (non-cultivated soils), Eh was responsible for lower availability of P (r=-0.38*). All *Eutric* soil types showed a negative impact of TC contents on the P levels (r=-0.6–0.9*).

There were other characteristics playing a significant role in phosphate availability, such as NO_2-N, NH_4-N, Ca, and Fe contents (Table 3). Besides nitrates, also their reduced forms were present in the studied soils. Their effects depended on the soil type – in *EC* and *EF* we noted negative effects (r=-0.39* and -0.99* for nitrites, -0.48* for ammonium in *EC*). *MG*, *EH*, and *RL* displayed moderately strong positive effects (r=0.65–0.99* for nitrites). The ammonium presence showed strong positive effects in *EF* and *RL* (r=0.9*). The effect of calcium on the PO_4-P levels was significant only in *Eutric Fluvisol* and *Eutric Histosol*. We observed opposite effects connected with the effect of agricultural activities on the Ca pool in these soils (see Fig. 2I). In the case of Fe, its significant positive effect was only revealed for the *EH* soil. This can be related to soil pH and its aeration state allowing catching P from the Ca~P fraction being available under acidic conditions.

DISCUSSION

The fact that soil agricultural practices affects chemical characteristics of many soils was reported previously, e.g. Girvan et al. (2003), Lopes et al. (2011), and Wolińska et al. (2014). The current study also confirms these observations (e.g. pH, Eh, TC, and P levels). Phosphate mobility in soil strongly depends on the way of binding thereof (different P fractions), soil moisture, and external sources (Banach, 2010; Domagalski, Johnson, 2012; Sapek, 2012). In Poland, many soils are agriculturally exploited and therefore P levels are expected to be elevated. Sapek (2014) presents P contents in many Polish soils – these data are similar to our results and, in some cases, we noticed even much higher P levels which may be connected to time of sampling. These values depend strongly on the soil type. It is important to remember that each soil has different origin (type of parent rock and formation process) resulting in various characteristics which play a key role in nutrient availability. In our work, we have shown that even non-cultivated soils may be loaded with phosphates e.g. due to biomass transfer (haymaking, manures) (Balemil, Negisho, 2012; Banach, 2010). Additional practices, including P fertilization may only increase the P pool, as plants cannot uptake all of it. Moreover, precipitation and surface runoff, or transport in the soil profile play a role (Banach, Stępniewska, 2011; Sapek, 2014).

Besides phosphorus, nitrogen is a crucial plant nutrient. Its cycling is also related to P. Depending on plant species, the composition these cycles may change (Jouany et al., 2011; Massey, 2012). Under oxygen deficiency, NO_3-N may serve as an electron acceptor, which may sustain the Fe~P fraction in soil. Accumulation of a reduced N-form and further soil reduction may lead to P mobilization in the soil solution for this fraction. This may result in higher P concentrations in the soil solution leading to internal eutrophication (Banach et al., 2009; Banach, Stępniewska, 2011; Smolders et al., 2006). However, if pH >5, the Ca~P fraction will still be present and P will be accumulated. Therefore, it is important to take into account different soil types and their characteristics.

CONCLUSIONS

1. The studied soils types differed for parameters important in P cycling.
2. The soil aeration state connected with moisture and pH was important in P mobilization.
3. Other important characteristics included nitrogen forms and Ca and Fe contents.
4. The manner of land use (cultivation) affected strongly the soil state (aeration, availability of nutrients) and P availability in the studied soils.
5. Changes in the soil aeration state may cause internal eutrophication, especially in highly P loaded cultivated soils.

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