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Phosphorous adsorption in soils after 20 years of organic (cattle slurry) and mineral (NPK) fertilization

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Abstract

The objective of this research work was the evaluation of the phosphorus (P) sorption capacity of soils fertilized for 20 years either with cattle slurry (CS) at application at rates of 25, 50, 100 and 200 m^3 ha^{-1} or mineral fertilizers (NPK) at rates of 25, 50, 100 and 200 P_2O_5 kg ha^{-1}. The microplot experiment was conducted on the experimental field of the Institute of Soil Science and Plant Cultivation (IUNG) in Pulawy, Poland ($51^025´N$, $21^058´E$). P adsorption was evaluated on the basis of maximal adsorption parameters (a_{max}, a_{max1} and a_{max2}) and energy bonding term values (b, b_1 and b_2), derived from Langmuir one-site and two-site isotherme equations, respectively. Additional evaluation was undertaken, based on P partition coefficients (K_d) calculated from Freundlich isotherme equations. It was found that cattle slurry by controlling the level of soil organic matter increased maximum P adsorption values (a_{max}). In the case of soils receiving mineral fertilizers only (NPK) maximum P adsorption was influenced by the occurrence of amorphous aluminium hydroxides. Both, maximal P adsorption (a_{max}) and partition coefficient (K_d) increased with fertilizer rates. Values of a_{max} correlated significantly with a_{max1} which is referred to as specific adsorption. About 50-66 % of the maximum adsorption can be considered as specifically retained P, irrespective of the type of applied fertilizers. From this it is concluded that the applied fertilizer rates did not saturate all available sorption sites.

Key words: adsorption, Freundlich isothermes, Langmuir isothermes, organic fertilization, phosphorous

Zusammenfassung

Phopsphatadsorption in Böden nach 20 Jahren organischer (Rindergülle) und mineralischer Düngung (NPK)

Ziel der vorliegenden Arbeit war es, den Einfluss organischer und mineralischer Düngung auf die Phosphat (P) Adsorption zu differenzieren. Der Kleinparzellenversuch wurde auf einem P armen sauren Boden des Versuchsfeldes des Institutes für Bodenkunde und Pflanzenbau (IUNG) in Pulawy, Poland (51^0 $25´N$, 21^0 $58´E$) durchgeführt. Rindergülle wurde in Aufwandmengen von 25, 50, 100 und 200 m^3 ha^{-1}, Mineraldünger (NPK) in Raten von 25, 50, 100 and 200 P_2O_5 kg ha^{-1}verabreicht. Die P Adsorption wurde auf der Basis maximaler Adsorption (a_{max}, a_{max1} und a_{max2}) und Bindungsenergie (b, b_1 und b_2) an Hand von Langmuir-Isothermen bestimmt. Zusätzlich wurden die Koeffizienten (K_d) der Freundlich-Isothermen ermittelt. Im Ergebnis war festzustellen, dass die Gülledüngung über Einfluss auf den Gehalt des Bodens an organischer Substanz die maximale P-Adsorption (a_{max}) erhöhte. Im Falle ausschliesslicher Mineraldüngung wurde die maximale P-Adsorption durch die Anwesenheit amorpher Aluminiumhydroxide kontrolliert. Beide Kennwerte der P-Adsorption (a_{max} und K_d) nahmen mit der Höhe der Düngung zu. Die Tatsache, dass a_{max} signifikant mit a_{max1} korrelierte, lässt dabei auf eine spezifische Adsorption schliessen. Der Anteil spezifischer P-Adsorption wird dabei auf 50-66 % geschätzt, wobei die Art der Düngung (organisch/mineralisch) auf diesen Wert keinen Einfluss hatte. Die Ergebnisse zeigen, dass in diesem Fall auch in der höchsten Düngungsstufe die Adsorptionskapazität des Bodens für P nicht erschöpft wurde.

Schlüsselwörter: Adsorptionsisothermen, Freundlich-Isotherme, Langmuir-Isotherme, organische Düngung, Phosphor

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1 Introduction

In arable soils, the phosphorus (P) concentration in the soil solution is controlled by plants (uptake) and additionally by two groups of processes i.e. dissolution/precipitation and adsorption/desorption (Sanyal and De Datta, 1991; Sharma et al., 1995; Nash and Halliwell, 1999).

In investigations dealing with P chemistry in soils, differentiating between sorption and precipitation processes is a controversial matter. Adsorption may be considered as a process leading to net accumulation of nutrients in the soil solid phase, whereas precipitation should be treated as a formation of a "new solid soil phase". Both processes may result in nutrient depletion from soil solution (Sanyal and De Datta, 1991). Lin et al. (1983) reported that P adsorption dominates in soils characterized by low P content and precipitation may occur when solution concentration of P is very high. According to Nash and Halliwel (1999), adsorption is the main process which controls P transformation in soils with developed sorptive area, small changes in P solution concentration and low level of cations' concentrations in soil solution. On the basis of several processes evaluation, Ryden and Pratt (1980) have pointed out that sorption needs to keep unchanged the structure of the sorbent during sorption course and moreover surface activity towards the system decreases whereas in the case of precipitation surface activity remains steady.

P adsorption may be defined as P retention by the soil solid phase. Soluble P compounds added to soil should migrate from more concentrated medium to sites where they undergo sorption. In arable soils with pH below 7.0 sorbed P compounds dominate (Larsen, 1967 after Mengel, 1985) and sorption sites are supplied by aluminium (Al) and iron (Fe) hydroxides, clay minerals, Al and Fe organic complexes and calcium carbonate molecules (Parfitt, 1978). Phosphate anions undergo specific and nonspecific sorption in soils. Nonspecific sorption is phosphate retention by proponated hydroxyl groups (OH$^-$) at the surface of mentioned sorbents. This type of retention depends on columbic forces and is rather weak and hence nonspecific adsorption is totally reversible. Since this process is related with the protonation of OH groups, the amount of P nonspecifically retained increases with decreasing soil pH. Specific P sorption is attributed to ligand exchange between hydroxyl groups (OH$^-$) and phosphate anions. This process proceeds irrespectively of the value of surface charge and decreases quantitatively with increasing soil pH. Phosphate anions can be adsorbed by aluminium and iron hydroxyls even when the resultant charge is negative (Mengel, 1985).

The process of P adsorption in soils runs differently. Shang et al. (1992) reported that P retention during the first step (0.5 hour) was "quick" after which the reaction significantly weakened. Adsorption of phosphate anions at the sorbent surface probably proceeded at the beginning and phosphate anions earlier adsorbed diffused within the porous structures of hydroxides (Whiters and Sharpley, 1995; Hansen et al., 1999).

Practically sorption of P by soils is frequently characterized by isotherms established by the use of Langmuir and Freundlich equations (Holford and Mettingly, 1976; Holford, 1989; Pena and Torrent, 1990; Sanyal and De Datta, 1991; Breeuwsma and Silva, 1993; Tolner and Fülekey, 1995; Sharma et al., 1995; Hansen et al., 1999; Siddique and Robinson, 2003; Del Bubba et al., 2003). According to Langmuir's theory, maximal adsorption is attained at full monolayer saturation. On the other hand Freundlich assumes that the full saturation of all sorption sites in soils is never reached (Piwowarowa and Ginzburg, 1981).

Adsorption isothermes only can be determined at equilibrium state between soil solution (extractable solution, precisely) and soil solid phase. Therefore each factor impacting chemical properties of soils may lead to disturbing equilibrium state and hence changes soil capacity for supplying plants with P.

The aim of the presented work was to evaluate P sorption capacity of soils with differentiated properties as a result of 20 years of organic and mineral fertilization.

2 Materials and methods

A two-factor microplot experiment was conducted on the experimental field of the Institute of Soil Science and Plant Cultivation (IUNG) in Pulawy, Poland (51^0 25´N, 21^0 58´E). The soil was a medium sandy soil with underlying loam, pH$_{(KCl)}$ = 5.6, 6.1 g kg^{-1} organic matter and low in plant available P (2.1 mg P 100 g soil by Egner-Riehm method).

The first experimental factor was the fertilization type: cattle slurry (CS) and mineral fertilizer (NPK). Fertilizers were applied at four rates (second experimental factor): 25, 50, 100 and 200 m^3 of cattle slurry (CS) per ha and 25, 50, 100 and 200 P$_2$O$_5$ kg ha^{-1}. Nutrient content of the cattle slurry (CS) was on average: 0.4 % N, 0.2 % P$_2$O$_5$, 0.4 % K$_2$O and 10 % dry matter. In the case of NPK, the nitrogen rate (as ammonium saltpeter) was half the amount of nitrogen content of the cattle slurry (assuming nitrogen efficiency from the cattle slurry of 50 % for the first year). Potassium was supplied at rates: 50, 100, 200 and 400 kg K$_2$O ha^{-1}.

Soil samples were collected from the arable layer (0-25 cm) after 20 years of continuous cropping within a four-year rotation: potatoes – winter wheat – rye for silage + maize as second crop – oat. Organic carbon was determined according to the Tiurin method, soil pH potentiometrically in 1M KCl. Amorphous and crystalline aluminium and iron hydroxides were extracted by ammonium oxalate at pH 3.0 (FAC, 1989).

The linear form of Langmuir one-site equation was used for P sorption characterization, as follows:

$$Ce/S = (1/a_{max}*b) + (Ce/a_{max})$$

where:

C_e – P equilibrium concentration (mM dm^{-3})
S – Amount of adsorbed P (mM kg^{-1})
a_{max} – maximal amount of adsorbed P (mM kg^{-1})
b – parameter related to the energy of P adsorption "sorption strength" (dm^3 mM^{-1})

The two-site Langmuir equation implies the occurrence of two types of P sorptive surfaces (Holford and Mattingly 1976):

$$S = [(a_{max}1*b1*Ce)/(1+b1*Ce)]$$
$$+ [(a_{max2}*b2*Ce)/(1+b2*Ce)]$$

where:
1 and 2 – different P sorptive sites.

P sorption by soils was also evaluated by the Freundlich partition coefficient:

$$S = K_d * C_e{}^n$$

where:

K_d – partition coefficient (dm^3 kg^{-1})
n – dimensionless constant

Adsorption isotherms were established by equilibrating 2 g of soils with 10 cm^3 of solution containing P (as KH$_2$PO$_4$) for concentrations: 0.0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40 and 0.50 mM dm^{-3}, with CaCl$_2$ as background electrolyte. Soil samples were weighted to polyethylene centrifuge tubes and proper P solution concentrations were added and shaken for two hours after which mixtures were left to equilibrate for 24 hours. P was determined colorimetrically based on the complex obtained by adding to filtrates sulfuric acid, ascorbic acid, antimony potassium tartrate and ammonium molybdate.

Path method and variance analysis package were used for statistical analysis (Konys and Wisniewski, 1991).

3 Results and discussion

The type of fertilization - organic as well as mineral affected the chemical characteristics of the soil (Table 1). Organic carbon content resulted from interaction between both, types and rates of fertilizers. More organic matter generally was detected in treatments receiving cattle slurry (CS) except for with the lowest fertilizer rates. Application of cattle slurry at a rate of 200 m^3 increased organic carbon content by two times. The pH values found in treatments fertilized with cattle slurry were significantly higher, but did not depend on fertilizer rates. In the case of controls (NPK), soils pH decreased systematically with increasing rates. Despite the stable content of hydroxides as shown in Table 1, amounts of aluminium hydroxides fluctuated greatly, as did amorphous ones, basically. Such great variation resulted probably in complexing free

Table 1:
Chemical characteristics of the soil at Pulawy after 20 years of organic (cattle slurry) or mineral (NPK) fertilization

Rate of manure	C org.	pH	Amorphous Al hydroxides H-Al-a	Crystalline Al hydroxides H-Al-c	Amorphous Fe hydroxides H-Fe-a	Crystalline Fe hydroxides H-Fe-c
	g*kg^{-1}	1M KCl	mg*kg^{-1}			
Organic (cattle slurry) fertilization (CS) m^3 ha^{-1} [A]						
25	5.3	5.72	600	899	815	1557
50	6.3	6.02	607	769	884	1601
100	8.1	5.80	383	769	784	1759
200	11.9	6.18	402	659	857	1588
Mineral fertilization (NPK) kg ha^{-1} P$_2$O$_5$* [B]						
25	5.4	5.49	357	744	736	1664
50	5.8	5.35	367	776	751	1538
100	5.3	5.29	398	564	766	1727
200	5.8	5.07	500	543	706	1538
LSD$_{0.01}$ AxB	1.29	0.14	18	29	17	n.s.

n.s. - not significant

hydroxides by humic acids, which content was modulated by organic fertilization (Gerke, 1992).

One of the parameters describing soil capacity for P adsorption is the Langmuir constant a_{max}. The impact of fertilization on a_{max} value was found to result from the application of fertilizers, whereas differences among treatments increased with increasing fertilizers inputs (Table 2). At the cattle slurry (CS) rate of 200 m^3 ha^{-1}, the difference was estimated for 11% in comparison with the NPK object. The analysis of these results aimed at looking for any causes, which could modify soil sorption capacities as a result of a 20 year continuous organic and mineral fertilization. Coefficients of correlation listed in Table 3, reveal that a_{max} was controlled by different soil parameters. In treatments receiving cattle slurry (CS) a_{max} values were first influenced by organic matter and aluminium hydroxides and further by soil pH. P adsorption did not show a direct relationship with organic matter after application of mineral fertilization (NPK).

Holford et al. (1997) reported on changes of soil sorptive properties as a result of organic fertilization. According to Siddique and Robinson (2003) cattle slurry and KH_2PO_4 had a marked negative effect on P sorption and a positive effect on P availability (the decrease in P sorption

Table 2:

Parameters of the Langmuir and Freundlich equations for phosphate adsorption in a soil after 20 years of organic (cattle slurry) or mineral (NPK) fertilization

Rate of manure	a_{max}	a_{max1}	a_{max2}	b	b_1	b_2	Kd
	mM$_*$kg^{-1}			dm$^3_*$mM^{-1}			dm3*kg-1
	Organic (cattle slurry) fertilization (CS) [A]						
1	2.74	1.53	1.43	32.2	92.3	11.3	5.53
2	3.04	1.51	1.48	32.3	126	13.6	5.53
3	3.66	1.94	1.53	31.3	140	14.2	5.68
4	5.26	3.19	1.54	22.5	79.9	11.1	7.78
	Mineral fertilization (NPK) [B]						
1	2.74	1.32	1.47	29.9	93.6	13.5	5.00
2	3.15	1.29	1.55	36.2	158	15.8	5.21
3	3.83	2.33	1.37	37.5	129	14.9	5.51
4	4.72	2.90	1.49	31.3	121	13.0	6.41
LSD$_{0.01}$AxB	0.24	0.21	n.s.	7.6	45.1	2.5	0.71

Table 3:

Correlations between soil characteristics and parameters for P adsorption in a soil after 20 years of organic (cattle slurry) or mineral (NPK) fertilization

Soil Properties	a_{max}	a_{max1}	a_{max2}	b	b_1	b_2	Kd
	Organic (cattle slurry) fertilization (CS)						
C org.	0.94**	0.80**	0.21	-0.44	0.00	-0.10	0.83**
pH	0.69*	0.70*	-0.21	-0.24	-0.14	-0.18	0.63*
H-Al-a	-0.72**	-0.61*	-0.13	0.33	-0.07	-0.08	-0.51
H-Al-c	-0.86**	-0.75**	-0.04	0.36	-0.04	-0.08	-0.72**
H-Fe-a	0.17	0.16	-0.06	0.00	0.00	-0.11	0.21
H-Fe-c	0.10	0.09	-0.09	0.30	0.41	0.37	-0.19
	Mineral fertilization (NPK)						
C org.	0.33	0.29	0.07	-0.02	0.21	-0.02	0.15
pH	-0.74**	-0.70*	-0.13	0.09	-0.25	0.22	-0.53
H-Al-a	0.96**	0.91**	0.05	-0.02	-0.14	-0.40	0.78**
H-Al-c	-0.83**	-0.86**	0.27	-0.30	-0.02	0.17	-0.53
H-Fe-a	-0.27	-0.24	0.04	0.14	-0.19	0.11	-0.33
H-Fe-c	-0.18	-0.11	-0.18	0.14	-0.18	-0.19	-0.23
** $P \leq 0.01$ * $P \leq 0.05$							

maximum and binding energy). In his work, Niskanen (1990) analyzed the influence of several factors on soils sorptive capacity, differentiated by soil texture, organic matter content and pH. He concluded that the content of aluminium and iron hydroxides as well as clay and pH were soils' factors which at about 80 % were responsible

path coefficients allowed to point out direct and indirect influences of the independent variable on a given soil property. Values of indirect path coefficients for H-Al-a (Fig. 1A) demonstrate the interaction between aluminium hydroxides and humic acids. Negative values indicate interactions limiting the maximum P adsorption. Data
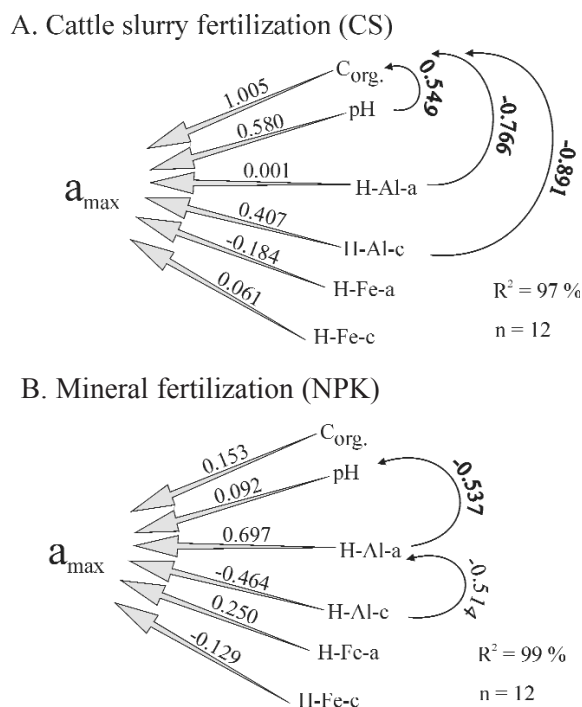
Table 4:

Multiple regression analysis with stepwise exclusion for Corg., pH, amorphous aluminium and iron hydroxides (H-Al-a, H-Fe-a) and chrystalline aluminium and iron hydroxides (H-Al-c, H-Fe-c) in a soil after 20 years of organic (cattle slurry) or mineral (NPK) fertilization

Number of independent variable	Stepwise variable selection for amax						R^2 (%)
Organic (cattle slurry) fertilization (CS)							
1	$C_{org.}$	pH	H-Al-a	H-Al-c	H-Fe-a	H-Fe-c	97.5
2	$C_{org.}$	pH		H-Al-c	H-Fe-a	H-Fe-c	97.5
3	$C_{org.}$	pH	H-Al-a	H-Al-c			97.3
4	$C_{org.}$	pH			H-Fe-a		95.8
5	$C_{org.}$	pH					93.6
6	$C_{org.}$						89.2
Mineral fertilizatoion (NPK)							
1	$C_{org.}$	pH	H-Al-a	H-Al-c	H-Fe-a	H-Fe-c	98.7
2	$C_{org.}$		H-Al-a	H-Al-c	H-Fe-a	H-Fe-c	98.4
3	$C_{org.}$		H-Al-a	H-Al-c	H-Fe-a		97.9
4			H-Al-a	H-Al-c	H-Fe-a		96.7
5			H-Al-a	H-Al-c			94.8
6			H-Al-a				91.3

for P adsorption in sandy soils and in organic matter rich soils, the role of organic carbon in modulating soil capacity for P adsorption was preponderant. In contrast Laverdiere and Karam (1984); Sanyal (1990) after Sanyal and De Datta (1991) reported that maximal P adsorption referred to a_{max} and K_d increased with increasing organic matter content and active aluminium and iron oxides levels. Moughli et al., (1993) showed that maximal P adsorption depended on clay and organic matter content, but did not exhibit a relationship with amounts of amorphous and crystalline iron oxides. P maximal adsorption in Alfisols was correlated with oxalate-extractable aluminium oxide, clay and organic matter (Indiati et al., 2002). The role of soil physical and chemical properties in the process of P adsorption was widely pointed out by Del Bubba et al. (2003). The results presented in this paper a complex relationship between investigated soil properties and maximum P adsorption (a_{max}). The stepwise variable selection analysis (Table 4) reveals that in treatments with cattle slurry organic matter was the most important factor which influenced the a_{max} values. As Fig. 2A shows this was a linear relationship. The maximal P adsorption for the NPK treatments was found to be primarily influenced by the content of aluminium hydroxides (H-Al-a), as described by the 2º degree polynomial function (Fig. 2B). At this level a question arises about the lower sorption capacity of hydroxides in soils fertilized with cattle slurry. Analysis of

A. Cattle slurry fertilization (CS)

B. Mineral fertilization (NPK)

Fig. 1:

Path coefficients between Langmuir one-site (a_{max}) parameter and chemical characteristics in a soil after 20 years of organic (cattle slurry) or mineral (NPK) fertilization
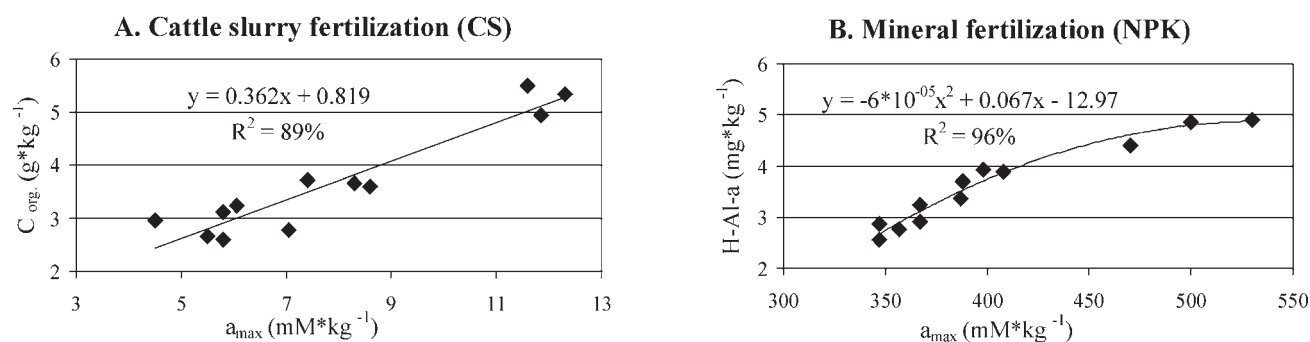
A. Cattle slurry fertilization (CS)

$y = 0.362x + 0.819$

$R^2 = 89\%$

$C_{org.}$ $(g*kg^{-1})$

a_{max} $(mM*kg^{-1})$

B. Mineral fertilization (NPK)

$y = -6*10^{-05}x^2 + 0.067x - 12.97$

$R^2 = 96\%$

H-Al-a $(mg*kg^{-1})$

a_{max} $(mM*kg^{-1})$

Fig. 2:
Relationship between amax and chemical characteristics in a soil after 20 years of organic (cattle slurry) or mineral (NPK) fertilization
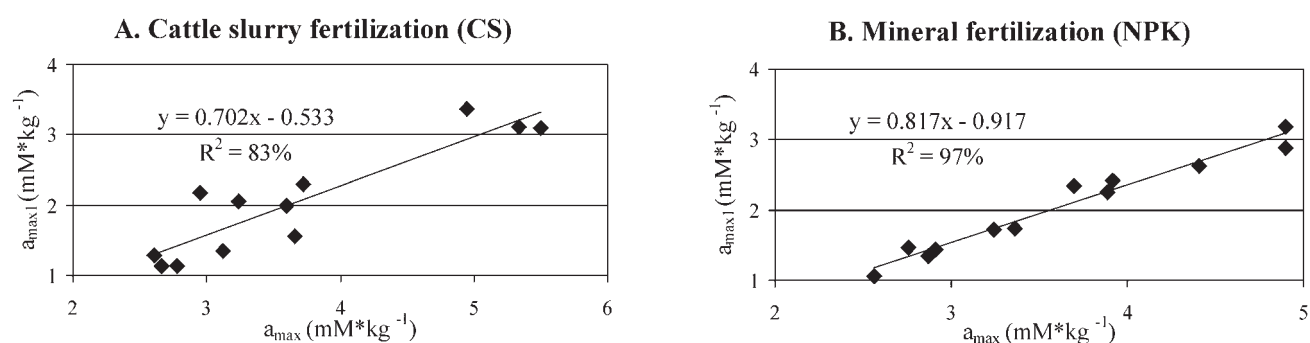
A. Cattle slurry fertilization (CS)

$y = 0.702x - 0.533$

$R^2 = 83\%$

a_{max1} $(mM*kg^{-1})$

a_{max} $(mM*kg^{-1})$

B. Mineral fertilization (NPK)

$y = 0.817x - 0.917$

$R^2 = 97\%$

a_{max1} $(mM*kg^{-1})$

a_{max} $(mM*kg^{-1})$

Fig. 3:
Relationship between amax and amax1 and chemical characteristics in a soil after 20 years of organic (cattle slurry) or mineral (NPK) fertilization

from literature underline that the role of organic matter during P adsorption is frequently referred to its stabilizing effect on aluminium and iron oxides (Al_2O_3 and Fe_2O_3). According to Bennoah and Acquaye (1989) oxides of these metals when directly bound to organic matter may adsorb more phosphates than in their free state. The increase in their activity should be explained by a delay in the crystallization process (Williams et al., 1958; Schwertmann et al., 1968, after Niskanen, 1990) rather by the increase in the sites for P sorption. Recently Holford et al., (1997) reported that application of organic fertilizers may result in a limitation of P sorption throughout complexation of iron compounds by organic matter. Cations occurring in plant rhizosphere and constituting specific bridges between sorbents and phosphates can be bound during chelating processes resulting in a direct increase of phosphate activity (Breeuwsma et al., 1993). According to this hypothesis, organic acids modulate the amounts of plant available P by reducing P adsorption and simultaneously increasing phosphate dissolution in the soil. As reported by Harter (1969) after Sanyal et al., (1991), the effect of organic matter on P sorption consists of substituting hydroxyl ions (OH⁻) bound on humic acids by phosphate anions throughout anionic exchange. It follows that organic matter may modulate P adsorption by direct binding

phosphates to humic compounds. Another effect of organic matter in this context could be the creating additional suitable conditions for P binding by other sorbents such as aluminium hydroxides.

In the treatments receiving NPK, maximum P adsorption (a_{max}) was not related to humus content but with aluminium hydroxides (Table 4) of which amorphous forms increased P sorption (Fig. 1B). The negative indirect influence of pH could be explained by the reduction in the activity of aluminium compounds as a result of pH rise. According to Shang et al. (1992) for P adsorption aquo groups on the surfaces are more reactive than hydroxo groups and dominated the initial fast reaction. Increasing the pH decreased the quality of aqua groups and therefore pH had more influence on reaction rates.

Several authors emphasize the effect of aluminium and iron oxides on P bindings by soils: Bolan (1985), Goldberg et Sposito (1985), Borggaard (1983 and 1986), Van der Zee and Van Riemsdijk (1988), Niskanen (1990), Pena and Torrent (1990), Sanyal and De Datta (1991), Espejo and Cox (1992), Jorgensen and Borggaard (1992) and Breeuwsma and Silva (1993). In the study presented here, the effect of aluminium oxides in the minerally (NPK) fertilized plot was specific and depended probably only on the degree of their crystallization. The necessity to con-

sider the degree of crystallization of hydroxides during experiments on P sorption was pointed out by Borggaard (1986). According to Ryden and Pratt (1980), the P sorbing capacity of amorphous hydroxides is 10 to 100 greater than the one of crystalline species. However, the question which of the metal hydroxides, i.e. aluminium or iron influences P adsorption more still remains unanswered. The works of Ryden and Pratt (1980), Espejo and Cox (1992), Niskanen (1990) and Fernandes and Warren (1994) are pointing towards a greater role of aluminium hydroxides in P binding, whereas Pena and Torrent (1990) and Borggaard (1986) attributed it to iron hydroxides. A greater P adsorption in the presence of aluminium hydroxides was explained by Niskanen (1990) as a tendency to form films over clay particles resulting in an increase of adsorbent surface.

The decisive role of pH is not to be omitted since iron compounds exhibit their greater activity in strongly acidic soils (pH < 4.0), whereas the pH of the soils in the investigation presented here ranged within 5.1 – 6.2 (Table 1).

Maximum P adsorption (a_{max}) increased on all treatments with increasing amounts of applied phosphorus. In the works of Mullins (1991) and Sharma et al., (1995) it was shown that added mineral P decreased its maximal adsorption. Such apparent discrepancy should be explained by the fact that in both experiments mentioned, other soil properties than the amount of plant available P did not change. In the current study, a 20 year fertilization has significantly changed basic soil properties, which means that chemical soil properties more than the amounts of incorporated P where responsible for the maximum P adsorbtion.

In both experimental objects positive relationships were found between a_{max} and K_d as shown below:

$$a_{max\ CS} = 0.87\ K_d - 1.65\ R^2 = 83\ \%$$
$$a_{max\ NPK} = 0.86\ K_d - 1.22\ R^2 = 54\ \%$$

where: a_{max} (mM kg^{-1}), K_d (dm^3 kg^{-1}).

The close relationship between these parameters allows also to use the partition coefficient K_d for soil characterization referring to the maximum amount of P the soil may adsorb.

The Langmuir two-site equation implies the occurrence of surfaces differing in their energy for P binding. Holford and Mattingly (1976) reported that adsorption parameters of this equation (a_{max1}, b_1 and a_{max2}, b_2) characterize high and low energetic adsorption levels, respectively, what could be referred to as specific and nonspecific sorption. This is ascertained by the fact that values of the specific energy bonding term (b_1) were on average 10 times higher comparing to b_2 (Table 2).

Analysis of a_{max1} and a_{max2} parameters indicated that both mechanisms were occurring in investigated soils. Values of a_{max1} referring to as specific adsorption increased in all soils with increasing fertilizer rates, whereas a_{max2} did not show marked changes related to cattle slurry and mineral fertilizer rates. This means that for the investigated soils, all sites at which P was nonspecifically i.e. reversibly adsorbed, were inaccessible just at low soil fertility towards phosphorus. Therefore long-term fertilization has basically modulated soil capacity for specific P retention. This hypothesis is supported by the linear relationship between Langmuir one-site adsorption parameter (a_{max}) and a_{max1} (Fig. 3 A-B). In all objects, a_{max1} values were modulated by the same soil properties responsible for the maximal adsorption expressed by the parameter a_{max}. In soils of South America, Houghes and Le Mare (1982) found a greater dependence of nonexchangeable P on the aluminium hydroxide contents than on iron, which fully confirms the results of this work for the NPK treatments.

According to Breeuwsma and Silva (1993) about 1/3 of the maximum P adsoprtion capacity may be irreversible adsorption. Piwowarowa and Ginzburg (1981) reported from a literature review that the amount of chemically (specific) adsorbed P represents 40-52 % of the total adsorption capacity for P leaving the rest for physical (nonspecifical) tetention. In this study, the share of maximum adsorption parameter a_{max1} – characteristic for specific sorption, fluctuated between 50 and 66 % accordingly for the lowest and highest fertilizer rates, irrespective of the type of fertilizers.

4 Conclusions

A 20 year organic and mineral fertilization by inducing changes in chemical soil properties simultaneously influenced soils sorptive capacity towards P. Cattle slurry throughout controlling the content of organic matter in the soil potentially increased possibility of P retention. The significance of organic matter in the process of P adsorption is thought to create sorption sites and to modify sorptive capacity of other sorbents such as aluminium hydroxides. In soils treated with mineral fertilizers (NPK) the organic matter content remained stable over time and the maximum P adsorption was influenced by amorphous aluminium hydroxides. In questions related to P adsorption the degree of hydroxides crystallization should be considered.

The share of specifically retained P did not depend on the kind of fertilization, but increased with fertilizer rates, indicating that the applied rates did not saturate all sites available for P retention.

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