Mineral fertilisation as a factor determining selected sorption properties of soil against the activity of phosphatases

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ABSTRACT

The paper presents the contents of phosphorus and potassium available in soil, soil sorption properties against the activity of alkaline and acid phosphatase. The fertilisation applied involved P, K, Mg, Ca and S: (P K Mg Ca S), (K Mg Ca S), (P Mg Ca S), (P K Ca S), (P K Mg S), (P K Mg Ca) as well as nitrogen fertilisation at the following rates: 0, 50, 100, 150, 200, 250 kg N/ha. The application of high nitrogen rates with no liming applied resulted in an unfavourable increase in hydrolytic acidity and a decrease in the total bases, cation exchange capacity as well as the sorption complex saturation with bases. According to the criteria provided in PN-R-04023, the soil investigated can be classified as the 3rd class with an average available phosphorus (P_{E-R}). The analysis of Luvisol salinity demonstrated that the unbalanced mineral fertilisation applied did not trigger any chemical degradation. Significant values of the coefficients of correlation were recorded between the activity of alkaline and acid phosphatase and the parameters investigated (hydrolytic acidity, total exchangeable, base stauration, P_{E-R}). The calculated enzymatic index of soil pH (AlP/AcP) ranged from 0.11 to 0.72.

Keywords: phosphorus; potassium; alkaline and acid phosphatases; Luvisol; chemical properties

Fertilisation, especially unbalanced fertilisation, is a factor which affects the soil acidity and thus disturbs the ionic balance, deteriorates sorption properties and decreases the content of nutrients in soil (Murawska et al. 2005, Lemanowicz 2011, Radulov et al. 2011). One of the basic conditions of producing optimal yields is supplying the plants with indispensable macro- and micronutrients (Zakarauskaitė et al. 2008, Skwierawska et al. 2012). Unfortunately, recently it was observed that to increase the yields, excessive amounts of nitrogen fertilisers are applied without maintaining the right proportions with the other nutrients. Similarly, deteriorating soil sorption properties were observed; a factor regulating macro- and microelements leaching out and enhancing the effectiveness of fertilisation (Kalembasa et al. 2011). Drawing on numerous research (Sharpley et al. 2001, Lemanowicz and Siwik-Ziomek 2010,

Lemanowicz 2011, Radulov et al. 2011) it was found that the agricultural activity should be carried out according to the concept of integrated farming, combining mineral fertilisation with organic fertilisation since the fertilisers, together with growth and development of plants, provide a gradual supplementing of nutrients in soil.

The aim of the research was to determine the effect of unbalanced mineral fertilisation on changes in the basic sorption properties of Luvisols, the content of phosphorus and available potassium against the activity of alkaline and acid phosphatase.

MATERIAL AND METHODS

The research originated as a field experiment set up by the Institute of Soil Science and Plant Cultivation in Puławy in the area of the Experiment

Station in Grabów nad Wisłą, the Mazowsze province, Poland. The location of the station is determined by latitude (51°21'8''N) and longitude (21°40'8''E). The experiment was performed in a four-year crop rotation: winter wheat + intercrop, corn for grain, spring barley, winter on typical soil in Poland, classified as light loamy and sand texture according to USDA soil classification (18% silt and clay fraction and 1.39% organic matter content). According to WRB (2006) represent the type of Luvisols. The soils used for the laboratory tests were sampled in June 2008 from the 0–15 cm layer from the treatments with winter rapeseed exposed to mineral fertilisation (the first factor): P, K, Mg, Ca and S at six levels: 1 – (P K Mg Ca S); 2 – (- K Mg Ca S); 3 – (P - Mg Ca S); 4 – (P K - Ca S); 5 – (P K Mg - S); 6 – (P K Mg Ca -). The second factor was made up of nitrogen fertilisation in a form of ammonium nitrate at the following rates: 0, 50, 100, 150, 200 and 250 kg N/ha. The following fertiliser forms were applied: for the treatments with S phosphorus and potassium fertilisers containing sulphur were used: single superphosphate and potassium sulphate, for the treatment without sulphur – phosphorus and potassium fertilisers which do not include sulphur: triple superphosphate and high-percentage potassium salt, for the treatment with Ca and Mg dolomite containing 21.3% Ca and 6% Mg was applied, in the plots without Mg, lime was used at the amount of 142 kg Ca/ha, while in the case of Ca deficit, magnesium sulphate was supplied at the rate of 42 kg Mg/ha. The rates of minerals applied in the experiment were as follows: 35.2 kg P/ha, 116.2 kg K/ha, 42 kg Mg/ha, 142 kg Ca/ha. The S rate is a result of the sulphur amount introduced with adequate rates of P, K, Mg.

In the adequately prepared material, the following were determined: the content of available phosphorus (P_{E-R}) (PN-R-04023 1996) and the content of potassium in soil with the Egner-Riehm method – DL (PN-R-04022 1996), the activity of alkaline (AlP) [E.C. 3.1.3.1] and acid phosphatases (AcP) [E.C. 3.1.3.2] in soil with the method of Tabatabai and Bremner (1969). With the values of the activity of alkaline and acid phosphatase reported, enzymatic index of soil pH (AlP/AcP) was calculated (Dick et al. 2000), pH in 1 mol/L KCl was measured potentiometrically (ISO 10390), hydrolytic acidity (Hh) and total exchangeable bases (TEB) with the Kappen method, cation exchange capacity (CEC) and base saturation (BS) (Soil Survey Investigation 1996), salinity with the conductometric method (EC).

The results were exposed to the analysis of variance and the significance of differences between means was verified with the Tukey's test at the confidence level of P = 0.05. The calculations involved the use of ANOVA software (Krakow, Poland) based on Microsoft Excel (Krakow, Poland). Besides the results of the analyses of the features investigated, the results were exposed to the analysis of simple correlation (P < 0.05) which determined the degree of the dependence between respective features. The analysis of the correlation was made using 'Statistica for Windows Pl' software (Krakow, Poland).

RESULTS AND DISCUSSION

The values of pH determined in 1 mol/L KCl ranged from 5.2 to 5.9 (Table 1). The mineral fertilisation did not have a considerable effect on the acidity of soil which, based on the analysis made, was qualified as acid and slightly-acid soils. The lowest pH values were reported in the soil sampled from the treatments with no Ca (P K Mg - S) fertilisation, at the same time applying the highest nitrogen rates. Radulov et al. (2011) found a change in the soil reaction from slightly acid to the category of acid and very acid soils as a result of unbalanced mineral fertilisation.

One of the soil acidification indicators is the value of hydrolytic acidity. The changes in the soil pH were accompanied by an increase in the hydrolytic acidity. The Hh values ranged from 23.20 to 29.86 mmol$_+$/kg (Table 2). The mineral fertilisation applied in the experiment significantly affected the changes in the value of hydrolytic acidity. An increase in the hydrolytic acidity of the soil from the treatments with a decreased pH value was reported. The highest Hh value (29.51 mmol$_+$/kg) was recorded in the soil sampled from the treat-

Table 1. pH_{KCl} in soil

Mineral fertilisation	Nitrogen (kg/ha)					
	0	50	100	150	200	250
P K Mg Ca S	5.9	5.7	5.7	5.6	5.4	5.4
- K Mg Ca S	5.9	5.7	5.6	5.6	5.5	5.4
P - Mg Ca S	5.9	5.9	5.8	5.7	5.5	5.5
P K - Ca S	5.8	5.8	5.7	5.7	5.6	5.5
P K Mg - S	5.7	5.7	5.6	5.4	5.3	5.2
P K Mg Ca -	5.9	5.9	5.8	5.9	5.8	5.8

Table 2. Sorption properties and salinity of the soil investigated

		Hh	TEB	CEC	BS (%)	EC (mS/cm)
		(mmol$_+$/kg)				
Mineral fertilization I factor	P K Mg Ca S	28.22	37.31	63.53	44.03	0.224
	- K Mg Ca S	23.75	35.75	59.50	59.99	0.221
	P - Mg Ca S	25.72	22.68	48.40	46.50	0.253
	P K - Ca S	25.94	22.25	48.19	45.92	0.259
	P K Mg - S	29.51	24.42	50.94	41.37	0.216
	P K Mg Ca -	23.79	21.00	44.79	46.80	0.275
Nitrogen (kg/ha) II factor	0	23.20	31.77	54.97	55.58	0.257
	50	24.28	29.86	54.14	52.83	0.228
	100	25.84	27.02	52.87	46.65	0.224
	150	26.53	26.56	53.10	47.42	0.221
	200	27.21	23.07	50.28	42.75	0.225
	250	29.86	22.12	51.99	39.36	0.294
Mean		26.15	26.73	52.89	47.43	0.241
SD		3.257	8.129	7.904	8.773	0.047
LSD$_{0.05}$	I factor	0.411	0.324	0.546	0.500	0.083
	II factor	0.411	0.324	0.546	0.500	0.083

SD – standard deviation; Hh – hydrolytic activity; TEB – total exchangeable bases; CEC – cation exchange capacity; BS – base saturation; EC – salinity

ments non-fertilised with Ca (P K Mg - S). In the other cases liming decreased the Hh value significantly. The effect of mineral fertilisation on Hh changes was also noted by Szymańska et al. (2008). In the present research it was found that increasing the nitrogen rate resulted in an increase in hydrolytic acidity in soil. Having applied nitrogen at the rate of 250 kg N/ha, Hh was highest (29.86 mmol$_+$/kg on average for mineral fertilisation). Generally, once higher nitrogen rates are applied, a loss of calcium cations from the sorption complex is reported, which, as a result, leads to soil acidification and an increase in hydrolytic acidity.

Total exchangeable bases in the soil were significantly modified by the experiment factors (Table 2). The TEB value in the soil was 26.73 mmol$_+$/kg (average for fertilisation). The highest TEB value was noted in the soil with full mineral fertilisation (P K Mg Ca S) and without P (- K Mg Ca S) where rapeseed was fertilised without magnesium (P K - Ca S). The lowest TEB values (22.12 mmol$_+$/kg) were reported following the application of the highest nitrogen rate (250 kg/ha). Similar results were recorded by Murawska et al. (2005). The authors claim that it must have been due to the higher uptake of base cations with crop yields fertilised with high nitrogen rates as well as the possible base cation leaching.

The cation exchange capacity depended significantly both on the varied mineral fertilisation and the nitrogen rates and their interaction. The highest values of sorption capacity (63.53 mmol$_+$/kg on average for mineral fertilisation) were recorded in the soil from the treatments with full mineral fertilisation (P K Mg Ca S) (Table 2). Lower values were noted from the treatments where rapeseed was not fertilised with potassium (48.40 mmol$_+$/kg) and magnesium (48.19 mmol$_+$/kg). The fertilisation with increasing nitrogen rates regularly decreased the CEC value, which was due to high Hh and, at the same time, a low TEB content. The average value of base saturation was 47.43%. The lack of liming (P K Mg - S) resulted in a decrease in the degree of sorption complex saturation of the soil (41.37%). The highest degree of sorption

complex saturation was observed in the soil from the plots where winter rapeseed was not fertilised with nitrogen (55.58%). The application of higher nitrogen rates resulted in a successive decrease in the value of complex saturation.

Mineral fertilisation is one of the causes of soil salinity since considerable amounts of salts containing phosphorus, nitrogen and potassium are introduced into soil together with fertilisers. Soil salinity, measured as electric conductivity (EC), was changing significantly as affected by the experimental factors (Table 2). The EC values ranged from 0.216 to 0.294 mS/cm (0.241 mS/cm on average for the experiment). According to the salt concentration harmfulness range (Kotuby-Amacher et al. 1997, Corwim and Lesch 2005), the effect of the salinity was non-significant since the electrolytic conductivity of soil water extracts was definitely lower than the average threshold value of saline soils (4 mS/cm). Increasing nitrogen rates showed a significant effect on the changes in the salinity of the soil, however, the effect was unclear. The rates of 50, 100, 150 and 200 kg N/ha

resulted in a respective 11, 13, 14 and 12% decrease in the salinity, as compared with the soils non-fertilised with that nutrient. However, an increase in the nitrogen rate up to 250 kg N/ha increased the salinity of the soil sampled from those treatments by 15%.

The content of available potassium in soil ranged from 65.43 to 110.6 mg K/kg. The soil samples analysed showed a very low, average and high richness in available potassium. The lowest K content was found in the soil sampled from the treatments where rapeseed was not fertilised with potassium (P - Mg Ca S) (65.43 mg K/kg on average for nitrogen fertilisation). The soil represented the 4th low richness in that nutrient (Table 3). The fertilisation without sulphur (P K Mg Ca -) increased the potassium content in soil (104.91 mg K/kg on average for nitrogen rates). Kaczor and Łaszcz-Zakorczmenna (2009) also observed a clear increase in the content of available potassium in the soil from the treatments fertilised with potassium without sulphur fertilisation, which was connected with the fact that the nutrient

Table 3. Content of available phosphorus (P_{E-R}); potassium (K); the activity of alkaline (AlP); acid (AcP) phosphatases and the enzymatic index of soil pH (AlP/AcP)

		K	P_{E-R}	AlP	AcP	AlP/AcP
		(mg/kg)		(mmol pNP/kg/h)		
Mineral fertilization I factor	P K Mg Ca S	89.36	55.30	0.610	1.258	0.48
	- K Mg Ca S	90.06	39.28	0.778	2.427	0.32
	P - Mg Ca S	65.43	52.98	0.537	1.081	0.50
	P K - Ca S	89.30	56.38	0.475	1.976	0.24
	P K Mg - S	92.91	50.00	0.424	2.341	0.18
	P K Mg Ca -	104.9	46.68	0.523	1.869	0.28
Nitrogen (kg/ha) II factor	0	110.6	70.01	0.707	1.611	0.44
	50	93.87	56.83	0.643	1.688	0.38
	100	89.61	50.61	0.585	1.774	0.33
	150	78.28	46.54	0.522	1.876	0.28
	200	79.05	40.56	0.468	1.960	0.24
	250	80.53	36.06	0.421	2.045	0.21
Mean		88.66	50.10	0.558	1.825	0.31
SD		20.43	13.53	0.156	0.535	
$LSD_{0.05}$	I factor	0.160	2.059	0.011	0.018	
	II factor	0.160	2.059	0.011	0.018	

SD – standard deviation

concentration in soil is mostly determined by its amount in fertilisers. The nitrogen rates increasing to 200 kg N/ha resulted in a regular decrease in the K content in soil. However Radulov et al. (2011) find think following the application of high amounts of nitrogen, potassium may be released causing increase of the potassium content in soil.

According to the criteria provided for in PN-R-04023 (1996), the soil can be classified as the third class with an average content of P_{E-R} (50.10 mg P_{E-R}/kg) (Table 3). The lack of phosphorus fertilisation (K Mg Ca S) changed the class of the soil richness in phosphorus from average to low. According to Yang et al. (2007), as for the application of high rates of nitrogen fertilisers, it is recommended to apply phosphorus fertilisers at the rates increased by balance surplus. Similarly, nitrogen fertilisation at the rates of 200 and 250 kg N/ha changed the class from average to low even when exposed to phosphorus fertilisation which, in that case, should be increased. Earlier reports by Lemanowicz (2011) also pointed to the unbalanced winter wheat fertilisation due to the lack of phosphorus fertilisation and due to the application of high nitrogen rates which can deplete the soil of that nutrient. A significant decrease was founded in the phosphorus content in soil from the treatment without liming (P K Mg - S).

Drawing on the analysis of variance, a significant effect of the fertilisation applied on the changes in the activity of alkaline and acid phosphatase was found (Table 3). Both the alkaline and (0.778 mmol pNP/kg/h on average for nitrogen fertilisation) acid activity (2.427 mmol pNP/kg/h on average for nitrogen fertilisation) of phosphatase was highest in the soil where no phosphorus fertilisation was applied (- K Mg Ca S). In general, the activity of soil phosphatases is inversely proportional to the content of available phosphorus (Lemanowicz 2011) since the deficit of this nutrient in soil increases the production and secretion of extracellular phosphatases to the substrate through the crop roots. The fertilisation with increasing nitrogen rates inhibited the activity of alkaline phosphatase. However, an increased activity of acid phosphatase was noted as affected by N fertilisation (Table 3). A higher activity of acid phosphatase comes from the fact that phosphomonoesterases are the enzymes most susceptible to the changes in the soil reaction; the optimum pH of soil for the activity of alkaline phosphatase is 9.0–11.0, and for acid phosphatase is 4.0–6.5 (Dodor and Tabatabai 2003,

Koper and Lemanowicz 2008, Lemanowicz and Siwik-Ziomek 2010).

Based on the values of the activity of both phosphatases reported, the enzymatic index of soil pH (AlP/AcP) was calculated. When the value of the AlP/AcP ratio is lower than 0.50, it points to the acid reaction of soil and soil liming is recommended (Dick et al. 2000). In the present research the AlP/AcP value ranged from 0.18 to 0.50. The nitrogen application already at the rate of 100 kg N/ha and higher resulted in a lower value of the enzymatic index of soil pH below 0.5. The lowest values were recorded for the fertilisation of winter rapeseed with nitrogen at the rate of 250 kg N/ha (0.21). Similarly, in the soil from the treatments where rapeseed was treated with mineral fertilisation without Ca (P K Mg - S), the AlP/AcP value –0.18. The enzymatic index of soil pH can be used as an alternative method to determine soil pH as well as the changes in soil (Dick et al. 2000, Lemanowicz 2011, Krzyżaniak and Lemanowicz 2013).

Drawing on the significant values of the coefficients of correlation reported, the relationship between the features of the sorption properties of the soil, the content of P_{E-R}, K and the activity of phosphatases was evaluated (Table 4). A significant negative value of the coefficient of correlation was reported between Hh and the enzymatic index of soil pH (AlP/AcP) ($r = -0.43$; $P < 0.05$). The decrease in the value of soil pH was accompanied by an increase in hydrolytic acidity and, at the same time, a decrease in the value of the AlP/AcP ratio was found. A negative relationship was also observed between the activity of alkaline phosphatase in soil and hydrolytic acidity ($r = -0.63$; $P < 0.05$) since in acid soils the inhibition of the activity of alkaline phosphomonoesterase usually occurs. Similar results were recorded by Wyszkowski and Kucharski (2004).

A significant negative value of the coefficient of correlation between the content of available phosphorus and the activity of acid phosphatase ($r = -0.48$; $P < 0.05$) points to the participation of that enzyme in the soil phosphorus transformations. Usually in the soils with acid reaction the activity of acid phosphatase is high since the enzyme, similarly as alkaline phosphatase, is sensitive to pH changes (Dodor and Tabatabai 2003, Lemanowicz 2011, Krzyżaniak and Lemanowicz 2013), whereas the content of available phosphorus can decrease since in acid soils phosphates form very complex and insoluble compounds with iron, aluminium and

Table 4. Person's correlation coefficients (*n* = 36)

	Hh	TEB	CEC	BS	K	P$_{E-R}$	AlP	AcP	AlP/AcP
AlP/AcP	–0.43	0.57	ns	0.50	ns	0.44	ns	ns	1.00
AcP	ns	ns	ns	ns	ns	–0.48	ns	1.00	–
AlP	–0.63	0.79	0.54	0.82	ns	ns	1.00	–	–
P$_{E-R}$	–0.38	ns	ns	ns	0.41	1.00	–	–	–
K	–0.37	ns	ns	ns	1.00	–	–	–	–
BS	–0.77	0.63	0.33	1.00	–	–	–	–	–
CEC	ns	0.91	1.00	–	–	–	–	–	–
TEB	ns	1.00	–	–	–	–	–	–	–
Hh	1.00	–	–	–	–	–	–	–	–

Significant at $P < 0.05$; ns – not-significant; Hh – hydrolytic acidity; TEB – total exchangeable bases; CEC – cation exchange capacity; BS – base saturation; EC – salinity; AlP/AcP – enzymatic index of soil pH

manganese. A significant relationship between the value of AlP/AcP and the total exchangeable bases ($r = 0.57$; $P < 0.05$) and base saturation ($r = 0.50$; $P < 0.05$) was found, which points to the fact that investigating the activity of phosphatases, and the enzymatic index of soil pH calculated based on it, can be used as an indicator of the effect of unbalanced fertilisation on soil fertility.

The research results coincide with the results reported by many authors (Sharpley et al. 2001, Yang et al. 2007, Sienkiewicz et al. 2009, Radulov et al. 2011) demonstrating that agricultural activity should comply with the principle of integrated farming which considers mineral and organic fertilisation.

The application of high nitrogen rates accompanied by the lack of liming triggered an unfavourable increase in hydrolytic acidity and a decrease in total bases, cation exchange capacity and the sorption complex saturation with bases. The lack of phosphorus and potassium fertilisation accompanied by the application of high nitrogen rates changed the class of the soil richness in selected nutrients from average to low. Investigating the activity of alkaline and acid phosphatase can be used to evaluate the changes in soils due to unbalanced fertilisation, which is seen from significant values of the coefficients of correlation. The mineral fertilisers applied changed the salinity of Luvisol significantly; however, they did not lead to its chemical degradation and thus that effect showed to be non-significant for winter rapeseed growth and development. The calculated enzymatic index of the soil pH demonstrated to be a significant

measure of the state of soil salinity and, as such, it can be used as an alternative method to measure the soil pH. Long-term mineral fertilisation significantly influenced soil properties, which may lead to the change of phosphatases activity of soil as well as the contents of the nutrients in soil. The results of the study show that it is necessary to continue research on soil chemical and enzymological properties during application of fertilisers for the selection of the proper management system.

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