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Soil Chemistry

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THE INFLUENCE OF MULTI-YEAR ORGANIC AND MINERAL
FERTILISATION ON THE PHYSICOCHEMICAL PROPERTIES
OF LESSIVE SOIL

Abstract. In a multi-year field fertilisation experiment the effects of organic and mineral fertilisers on the physicochemical properties of lessive soil were compared. Manure, two doses of slurry and mineral fertilisers were applied to soil farmed in an eight-field crop rotation. Dose I of slurry, manure and mineral fertiliser were applied in doses balanced with nitrogen. Dose II of slurry was determined so that the amount of organic carbon introduced along with it was the same as in the dose of manure. To the experimental facilities with manure and slurry, additional fertilisation with phosphorus and potassium was applied. Following 36 years of annual fertilisation, samples of soil were taken from the 0-25 cm layer, determining the amount of organic carbon and the sorption properties of the soil. It was determined that as a result of applying organic fertilisers, the amount of organic carbon, sorption complex capacity and basic cation content increased whereas hydrolytic acidity decreased. Manure was found to have the most beneficial effect, which was matched by neither dose I nor II of slurry. Additional phosphorus-potassium fertilisation of soil with manure and slurry positively influenced the sum of bases and the total sorption capacity of the soil. Mineral NPK fertilisation led to the decrease in the saturation of bases of the sorption complex and the increase in hydrolytic acidity.¹

The physicochemical properties of soil are among the basic indicators of changes taking place under the influence of fertilisation. Studies on the multi-year effect of organic and mineral fertilisation on the fertility of soil have great educational and practical value [5, 7, 22]. The type of applied fertiliser influences the chemical, physical, and biological properties of soils [11, 21].

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Our research involved the application of manure, slurry and mineral fertilisers commonly used in Polish agriculture.

As a result of multi-year fertilisation, changes in the sorption capacity and saturation of the sorption complex of the soil with basic cations took place, as well as changes in pH [4, 9, 10]. In fertilisation systems, organic matter, which is the substrate for creating soil humus, is of key importance. However, fertilisation may actually sometimes lead to the dehumidification and acidification of soil.

According to Filipek and Skowrońska [8], the increased percentage share of nitrogen in NPK fertilisation has been largely responsible for the acidification of soil in Poland. Soil degradation may also take place in farms raising livestock, where large doses of organic fertilisers are applied. Large doses of these fertilisers play a role in lowering the retention of water available to plants and decreasing the content of basic cations in the sorption complex of the soil [14].

The aim of the presented studies was to assess the influence of long-term fertilisation with manure, slurry and mineral fertilisers on the sorption properties of soil.

MATERIALS AND METHODS

The field experiment was set up in 1972 in north-western Poland in Balcyny (53°35'45" N, 19°51'06" E) on lessive soil in a randomised block design of 6 repetitions. Each plot was of 45 m² in area. The 025 cm layer of soil contained 64.1% of sand fractions (2.00-0.05 mm), 29.2% of silt (0.05-0.002), and 5.5% of clay (0.002 mm). Prior to the commencement of the experiment, the pH_(KCl) soil had been determined at 5.2, and the content of available nutrients had stood at: 98.0 mg K, 53.8 mg Mg and 40.1 mg P kg⁻¹ soil. The contents of available organic carbon and total nitrogen had been at the level of 8.1 g·kg⁻¹ and 779.8 mg·kg⁻¹. The capacity of the sorption complex had been established at 74.7 mmol(+)·kg⁻¹, with a base saturation of 62.2%.

The following crop rotation was applied: potato, spring barley + undersown red clover and grasses, red clover and grasses, winter rapeseed, winter wheat + aftercrop (winter rye), corn for silage, spring barley, winter wheat. The clover and grass were planted only during the first two cycles of the crop rotation.

The experiment included eight experimental facilities: 1 – without fertilisation (control facility), 2 – slurry applied in the first dose (dI), 3 – slurry in the first dose with additional phosphorus and potassium fertilisation (dI+PK), 4 – slurry in the second dose (dII), 5 – slurry in the second dose with additional phosphorus and potassium fertilisation (dII+PK), 6 – manure, 7 – manure with additional phosphorus and potassium fertilisation, 8 – mineral NPK fertilisation (tab. 1). Slurry in the first dose (dI), manure and mineral fertilisation were applied in doses balanced with nitrogen. The second dose of slurry (dII) was established so that the amount of organic carbon introduced along with it would

be the same as in the case of manure. Doses of slurry and manure were calculated each year, directly prior to their application to soil on the basis of dry weight, organic carbon and nitrogen contents. All agro-technical operations were carried out at optimal times. Organic and mineral fertilisers were applied prior to the crops being sown or planted. The Table 1 presents the average yearly doses of organic and mineral fertilisers whereas the Table 2 – the average chemical composition of organic fertilisers. Soil samples of 0-25 cm layer were collected from each plot in the year 2008, after harvesting crops and after being dried at room temperature, sifted through a nylon sieve of Ø 1 mm. The input matter prepared in such a way was used to determine: organic carbon content using an elementary CNS analyser manufactured by Coestech, pH – by means of a potentiometer in 1 mol · dm⁻³ KCl solution, hydrolytic acidity (Hh) by means of Kappen's method after extraction from soil with 1 mol CH₃COONa dm⁻³, exchangeable cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) after extraction from the soil with 1 mol CH₃COONH₄ dm⁻³ solution of pH 7.0, including quantitative determination in the filtrate performed using the AAS method [16].

TABLE 1. DOSES OF FERTILIZER COMPONENTS APPLIED
IN THE EXPERIMENTS (AVERAGE FOR YEARS 1972–2008)

Fertilizers	Doses of fertilizers			
	Organic fertilizers	Mineral fertilizers		
		N	P	K
	t·ha ⁻¹ f.m.	kg·ha ⁻¹		
Manure	22.8	-	-	-
Slurry dose I (dI)	40.0	-	-	-
Slurry dose II (dII)	76.0	-	-	-
NPK	-	110	38	108

TABLE 2. CHEMICAL COMPOSITION OF ORGANIC FERTILIZERS
(AVERAGE FOR YEARS 1972–2008)

Nutrient	Cow manure	Cow slurry
	% Fresh Weight	
Dry matter	23.90	8.43
Organic carbon	8.96	3.01
Nitrogen	0.49	0.27
Phosphorus	0.15	0.11
Potassium	0.41	0.33
Magnesium	0.09	0.05

The results were verified statistically by means of the one-factorial analysis of variance. The least significant difference was assumed at $p = 0.05$ (Tukey's test). Pearson correlation coefficients were determined for selected soil properties. For these purposes, the Statistica 9 program was used.

RESULTS AND DISCUSSION

The soil organic carbon content (SOC), pH, hydrolytic acidity, and exchangeable cation content have been presented in the Table 3. Among the fertilisers, manure combined with phosphorus and potassium had the most beneficial effect on the accumulation of C-org. in the soil. A very positive combined influence of organic and mineral fertilisation on organic carbon content was confirmed by studies of Kanchikerimath and Singh [12]. According to Lorenz and Lal [13], manure leads to the growth of roots in the deeper layer of the soil as a result of improving the retention and biological properties of soil. The lowest increase in the SOC concentration in soil was recorded in the facilities fertilised with NPK. As stated by Rudrappa *et al.* [19], optimally applied mineral fertilisers increase organic carbon content in soils, which is connected with the growth of plant root systems. As a result of applying organic fertilisers and organic fertilisers with additional phosphorus and potassium fertilisation, the increase in the pH of soil was recorded, which was the highest one in soil with manure and additional PK fertilisation. Soil fertilised with NPK underwent increased acidification, which was reflected by the decrease in pH. Based on the present study, it is highly probable that the increase in the organic carbon content of soil decreases its acidification (Fig. 1).

TABLE 3. ORGANIC CARBON CONTENT, pH, HYDROLYTIC ACIDITY AND EXCHANGEABLE CATION CONTENT

Objects	SOC g·kg ⁻¹	pH _(KCl)	Hh	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺
			mmol(+)-kg ⁻¹				
1 Without fertilization	8.59	4.82	30.58	42.09	2.84	2.80	1.09
2 Slurry dI	9.91	5.09	25.37	42.36	4.22	4.36	1.15
3 Slurry dI + PK	10.09	4.90	26.30	44.58	4.48	5.20	1.54
4 Slurry dII	10.64	4.99	27.75	44.98	4.38	5.31	1.66
5 Slurry dII + PK	10.65	5.23	28.53	46.26	4.51	5.62	1.98
6 Manure	12.12	5.31	24.22	50.73	6.45	8.69	1.72
7 Manure + PK	12.42	5.65	26.62	51.66	6.29	9.36	1.69
8 NPK	9.37	4.38	37.15	41.14	4.17	6.92	1.50
LSD _{0.05}	1.32	0.51	1.82	2.47	0.69	1.65	0.36

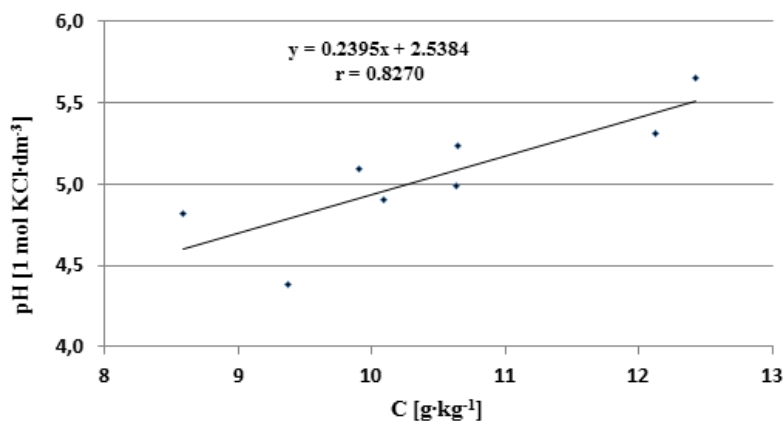


Fig. 1. Influence of organic carbon content of soil on pH.

Hydrolytic acidity (Hh) of the soil was highest in the soil of the facilities fertilised with NPK, in which the increase in Hh of $6.57 \text{ mmol}(+) \text{ kg}^{-1}$ in relation to unfertilised soil was noted. Among the organic fertilisers, manure had the most beneficial effect (decrease in Hh of $6.36 \text{ mmol}(+) \cdot \text{kg}^{-1}$ soil). An adverse impact of mineral fertilisers on the hydrolytic acidity of soil dependent on the N:P:K ratio and on the pH of the soil were confirmed during a 4-year experiment by Nazarkiewicz and Kaniuczak [15]. Potarzycki [17] also showed that 20-year long application of cow slurry resulted in decreasing hydrolytic acidity of soil by $10 \text{ mmol}(+) \cdot \text{kg}^{-1}$ in relation to soil fertilised with NPK. Bednarek *et al.* [4], on the other hand, stated that multi-year fertilisation with slurry and NPK did not result in significant changes in hydrolytic acidity regardless of the doses whereas mineral fertilisers caused it to increase.

Multi-year fertilisation had a positive effect on the content of all four exchangeable cations, except for calcium in soil fertilised with NPK. The content of exchangeable calcium in soil was most positively increased with manure along with additional PK fertilisation, resulting in the increase by $9.57 \text{ mmol}(+) \cdot \text{kg}^{-1}$. In soils with slurry applied at the dose balanced with manure in terms of nitrogen content (dI) as well as in soil fertilised with NPK, significant differences in Ca^{2+} content were not observed. The increase in the content of exchangeable calcium was confirmed by Hemalatha and Chellamuthu [9] in a 36-year study using mineral fertilisers and manure. The highest increase in Ca^{2+} (by 32.3%) was obtained in soil fertilised with manure + NPK. Potarzycki [17] obtained a significant increase in exchangeable calcium content in the soil sorption complex fertilised with cow slurry ($36.6 \text{ mmol}(+) \cdot \text{kg}^{-1}$) as compared to soil fertilised with NPK ($11.6 \text{ mmol}(+) \cdot \text{kg}^{-1}$).

Fertilisation had a positive effect on the content of exchangeable magnesium in the soil sorption complex. Among the applied organic fertilisers, the

content of exchangeable magnesium was most positively affected by manure. In soil fertilised with slurry, this increase ranged from $1.38 \text{ mmol}(+)\cdot\text{kg}^{-1}$ for soil fertilised with the first dose of slurry balanced with the nitrogen content of manure (dI), to $1.67 \text{ mmol}(+)\cdot\text{kg}^{-1}$ for soil fertilised with a dose of slurry balanced with manure in terms of organic carbon with additional PK fertilisation (dII+PK). The lowest increase in Mg^{2+} content ($1.33 \text{ mmol}(+)\cdot\text{kg}^{-1}$) was confirmed in soil fertilised with NPK. Similarly, Hemalatha and Chellamuthu [9] obtained the lowest increase in exchangeable magnesium (13%) in soil fertilised with a low dose of NPK, and the highest one (35%) – in that fertilised with manure along with additional NPK fertilisation. Bednarek *et al.* [4] reported a positive correlation of the Mg^{2+} content of soil and the dose of slurry. Similar effects were obtained by Potarzycki [17]. It turned out that 20-year long application of cow manure was more beneficial than NPK when it came to the content of exchangeable magnesium in the sorption complex of soil.

The highest increase (of $6.56 \text{ mmol}(+)\cdot\text{kg}^{-1}$) in the content of exchangeable potassium in relation to the control was confirmed in soil fertilised with manure along with phosphorus and potassium. The only mineral fertilisation resulted in the increase in K^+ concentration by 4.12 whereas the effect of slurry was the increase by $1.56\text{--}2.82 \text{ mmol}(+)\cdot\text{kg}^{-1}$. Mineral PK fertilisation applied with slurry and manure did not have a significant impact on exchangeable potassium content. Similar effects may be found in studies of other authors researching the content of exchangeable potassium following fertilisation with manure [6, 18, 23] or slurry [4, 17].

As a result of fertilisation, the concentration of exchangeable sodium increased from 0.06 to $0.89 \text{ mmol}(+)\cdot\text{kg}^{-1}$ and was found to be the highest in soil fertilised with the dose of slurry balanced with manure in terms of organic carbon, with additional PK fertilisation (dII+PK). In studies conducted by Enujeke *et al.* [6], the increased content of Na^+ was observed in soil fertilised with manure and mineral fertilisers. A dose of pig manure at $30 \text{ t}\cdot\text{ha}^{-1}$ led to the increase by $0.12 \text{ mmol}(+)\cdot\text{kg}^{-1}$ whereas the dose of 450 kg NPK – the increase by $0.18 \text{ mmol}(+)\cdot\text{kg}^{-1}$. Potarzycki [17] reported a similar increase ($0.5 \text{ mmol}(+)\cdot\text{kg}^{-1}$) in the content of exchangeable sodium in soil fertilised with slurry and NPK for 20 years.

The highest increase in the total amount of bases (BEC), amounting to $20.19 \text{ mmol}(+)\cdot\text{kg}^{-1}$ was noted in soil fertilised with manure and additional PK fertilisation (Fig. 2). The application of slurry resulted in the increase in BEC from $3.27 \text{ mmol}(+)\cdot\text{kg}^{-1}$ in soil with slurry applied at the dose balanced with manure in terms of nitrogen (dI) to $18.77 \text{ mmol}(+)\cdot\text{kg}^{-1}$ in soil with slurry applied at the dose balanced with manure in terms of organic carbon along with additional PK fertilisation (dII+PK). Additional phosphorus and potassium fertilisation applied with manure or slurry did not significantly influence basic cation content.

NPK fertilisation for a period of 36 years resulted in the increase by $4.92 \text{ mmol}(+)\cdot\text{kg}^{-1}$ in the sum of $\text{Ca}^{2+}+\text{Mg}^{2+}+\text{K}^++\text{Na}^+$ as compared to unfertilised soil.

Bakayoko *et al.* [2], applying cow manure for 10 years at the dose of $10 \text{ t} \cdot \text{h} \cdot \text{a}^{-1}$ achieved the increase in the sum of bases of $9.4 \text{ mmol}(+) \cdot \text{kg}^{-1}$ as compared to the control facility. Enujeke *et al.* [6] confirmed that manure fertilisation lead to a higher increase in the sum of cations than mineral fertilisers.

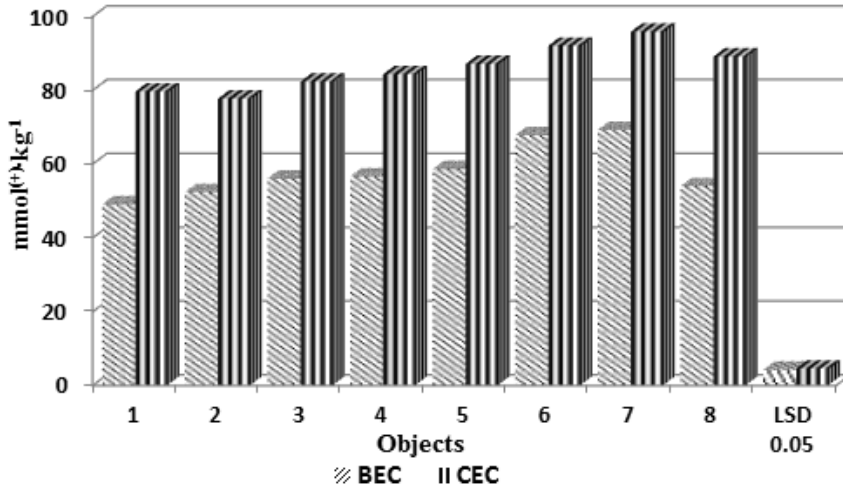


Fig. 2. Sum of bases (BEC) and sorption complex capacity (CEC).

The total capacity of the sorption complex (CEC) was highest in soil fertilised with manure and PK ($95.61 \text{ mmol}(+) \cdot \text{kg}^{-1}$), and lowest in soil fertilised with the dose of slurry matching manure in terms of the amount of nitrogen that had been applied (dI) ($77.45 \text{ mmol}(+) \cdot \text{kg}^{-1}$) – Fig. 2. Bednarek *et al.* [4], when applying slurry in various doses over a few dozen years, did not confirm significant differences in the capacity of the sorption complex of the surface layer of soil. In studies by Potarzycki [17], the total sorption capacity of soil fertilised with cow slurry over 20 years was found to stand at $101.3 \text{ mmol}(+) \cdot \text{kg}^{-1}$ whereas that of soil fertilised with only NPK – $85.3 \text{ mmol}(+) \cdot \text{kg}^{-1}$. A positive influence of cow manure on the increase in sorption complex capacity was also confirmed in the research of Sienkiewicz [20] and Bakayoko *et al.* [2].

Mult-year fertilisation varied the share of base saturation (BS) in the total sorption complex capacity of the soil (Fig. 3). In soil fertilised with slurry and manure, the saturation of the sorption complex with bases was higher than in the case of the control facility, and fell within the range of 64.88% (slurry applied at the dose balanced with manure in terms of nitrogen) to 73.04% (manure). This was connected mainly with the increase in Ca^{2+} content in the sorption complex and decrease in hydrolytic activity [1]. In soil fertilised with NPK the decrease in BS by 3.5% occurred. According to Barak *et al.* [3], fertilisation with nitrogen in the form of ammonia over many years decreases the content of Ca^{2+} in the

sorption complex and increases hydrolytic acidity. Such a dependency has been confirmed in these studies – the increase in hydrolytic acidity notably decreased the amount of Ca^{2+} cations in the sorption complex (Fig. 4). On the other hand, it's worth highlighting that calcium content plays a large role in determining the sorption capacity of soil (Fig. 5).

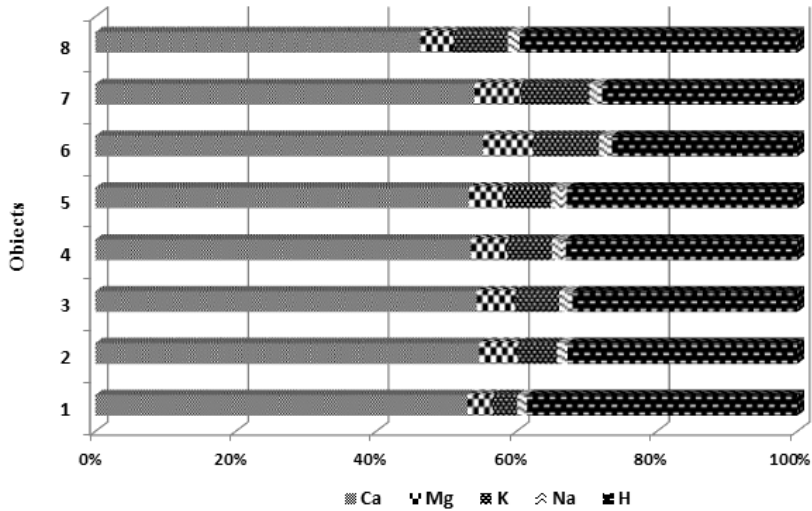


Fig. 3. Percentage share of cations in sorption complex.

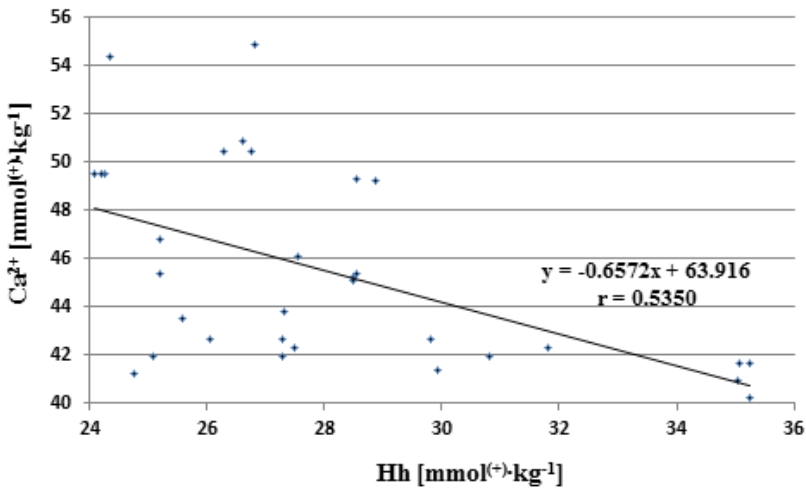


Fig. 4. Influence of hydrolytic acidity on Ca^{2+} content in the sorption complex.

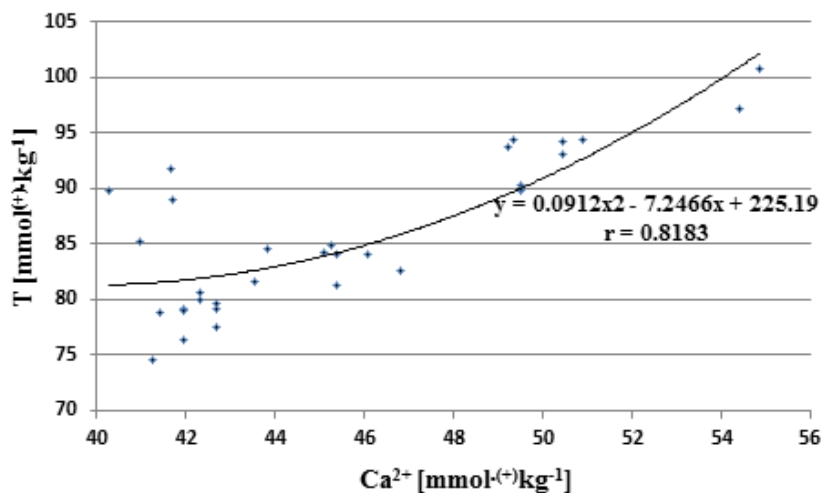


Fig. 5. Dependency of sorption capacity of soil on Ca^{2+} .

CONCLUSIONS

1. The application of organic fertilisers and organic fertilisers with additional phosphorus and potassium fertilisation for a period of many years led to the increase in the content of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^{+} + \text{Na}^{+}$ in the sorption complex and the decrease in hydrolytic acidity (Hh).

2. Slurry applied at the dose balanced with manure in terms of nitrogen content as well as organic carbon did not have as beneficial effect as manure had on the sum of bases (BEC) or total sorption complex capacity (CEC) and its saturation with bases (BS).

3. Additional phosphorus-potassium fertilisation with manure and slurry had a positive effect on the total amount of bases (BEC) and total sorption capacity (CEC) of the soil.

4. Mineral fertilisation (NPK) resulted in the increase of hydrolytic acidity, as well as the decrease in the content of Ca^{2+} and base saturation of the sorption complex.

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WPLYW WIELOLETNIEGO NAWOŻENIA ORGANICZNEGO I MINERALNEGO NA WŁAŚCIWOŚCI FIZYKOCHEMICZNE GLEBY PŁOWEJ

W wieloletnim polowym doświadczeniu nawozowym porównano działanie nawozów naturalnych i mineralnych na właściwości fizykochemiczne gleby płowej. Pod rośliny uprawiane w 8-polowym zmianowaniu stosowano obornik, gnojowicę w dwóch dawkach i nawozy mineralne. Gnojowicę w dawce I, obornik i nawożenie mineralne stosowano w dawkach zrównoważonych azotem. Wielkość dawki II gnojowicy określono tak, by ilość wprowadzanego z nią węgla organicznego była taka sama jak w dawce obornika. W obiektach z obornikiem i gnojowicą stosowano dodatkowe nawożenie fosforem i potasem. Po 36 latach corocznego nawożenia pobrano próbki gleby z warstwy 0-25 cm i oznaczono zawartość węgla organicznego oraz właściwości sorpcyjne gleby. Stwierdzono, że w wyniku stosowania nawozów organicznych wzrosła zawartość węgla organicznego, pojemność kompleksu sorpcyjnego i zawartość kationów zasadowych,

a zmalała kwasowość hydrolityczna. Najkorzystniej na badane właściwości gleby działał obornik, któremu ustępowała gnojowica w dawce II i gnojowica w dawce I. Dodatkowe nawożenie fosforowo-potasowe w obiektach z obornikiem i gnojowicą działało korzystnie na sumę zasad i całkowitą pojemność sorpcyjną gleby. Nawożenie mineralne NPK spowodowało zmniejszenie wysycenia kompleksu sorpcyjnego zasadami i wzrost kwasowości hydrolitycznej.