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Chemical properties of soil after over 55 years of differentiated fertilization and crop rotation

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Abstract

The paper presents the results of research on chemical properties of soil, such as soil pH and the content of total nitrogen (Nt), available forms of phosphorus (P) and potassium (K) and microelements (manganese (Mn), copper (Cu), zinc (Zn) and iron (Fe)) obtained after more than 55 years of using only mineral (NPK), organic (FYM) and manure fertilization together with mineral fertilizers (½ NPK + ½ FYM) in two crop rotations: a rotation without red clover (sugar beet – spring barley – winter rapeseed – winter wheat) and a Norfolk rotation with red clover (sugar beet – spring barley with undersown red clover – red clover – winter wheat). This study was based on two long-term static field experiments established in 1955 on leached black earth (according to the World Reference Base for Soil Resources WRB – Endogleyic Phaeozems) at the Agricultural Experimental Station of the Warsaw University of Life Science – SGGW, Chylice, central Poland. The obtained results indicate that the Norfolk rotation with red clover, as well as varied fertilization and years of research, influence the chemical properties of soil. After over 55 years, the soil in crop rotation with legume (A) soil acidity and total nitrogen content was significantly higher (pH 5.7, Nt 0.76 g kg^{-1}) than in the plots without a legume plant (B) (pH 6.2, Nt 0.66 g kg^{-1}). Crop rotation with red clover also ensured a greater content of microelements (Mn, Cu, Zn, Fe) in the soil, but caused an approximately 30% decrease in the content of available phosphorus (P) and potassium (K) in the soil compared to crop rotation without the legume. It was noted that a beneficial effect of using farmyard manure on soil pH, on increasing the content of total nitrogen, content of available phosphorus (P), potassium (K), manganese (Mn), and zinc (Zn).

1. Introduction

In the face of global challenges such as climate change and degradation of soil resources, it is essential to understand the mechanisms that affect soil chemistry in the long term. Proper soil management and the use of adequate fertilization and crop rotation practices are key to maintaining and improving soil quality.

The basic element determining soil fertility is its reaction, as well as its abundance in such components as assimilable forms of phosphorus, potassium, or magnesium. Determining the soil's abundance in these components should be the initial stage of rational fertilization. Supplying these components to the soil in the event of their deficiency should be done in a way that ensures their availability to cultivated plants at the appropriate time (Fotyma, 2007; Jakubus, 2000; Kaniuczak, 1998; Kozłowska-Strawska and Kaczor, 2004).

Despite the increased use of calcium fertilizers in recent years, soil acidification remains a significant problem of contemporary agriculture in Poland (Skuta et al., 2025). Calcium fertilizer consumption in Poland is relatively low compared to needs, and over 45% of Polish soils are acidic or very acidic with pH_{KCl} below 5.6. Acidified soil responds less to applied agronomical treatments, in particular to applied mineral fertilization, causes a decrease in the absorption of most nutrients, which ultimately also contributes to a decrease in the amount and quality of the crop of cultivated plants. This is particularly important on light and very light soils, where we can observe the leaching of alkaline cations, especially calcium and magnesium. Low pH also indirectly contributes to the breakdown of the structure of secondary clay minerals and a decrease in sorption capacity. This also causes the appearance of exchangeable forms of manganese and aluminum in the soil, which are toxic to plants (Filipek et al., 2006; Filipek and Skowrońska, 2013; Tkaczyk and Bednarek, 2011). As a rule, the content of available forms of Fe, Mn, Zn and Cu in the soil increases with increasing soil acidity (Rutkowska et al. 2014).

The long-term use of manure and mineral fertilizers affects the chemical properties of the soil. Manure contributes to the increase in the content of organic carbon, alkaline cations and the capacity of the sorption complex (Mazur et al., 2015). Moreover, studies have shown that manure also affects the increase in soil content of nitrogen, phosphorus, and potassium (Sathish et al., 2016; Zemichael and Dechassa, 2018). On the other hand, mineral fertilization, despite providing the necessary macroelements needed for plant growth and development, results in a decrease in the saturation of the soil sorption complex with bases and an increase in its hydrolytic acidity. Studies show that mineral fertilizers, especially when used in combination with manure, contribute to the modification of the pH level, an increase in the content of organic carbon, total nitrogen and available forms of phosphorus and potassium, and also affect the change in the soil cation exchange capacity (Aberagi et al., 2024; Bhatt et al., 2019; Yang et al., 2024; Zhuang et al., 2024).

Legumes improve soil fertility and, consequently, crop yields through symbiotic interactions with microorganisms that fix atmospheric nitrogen and make it available to the host in a form that is available to the host and in a process known as biological nitrogen fixation (BNF) (Antonkiewicz and Łabętowicz, 2016; Kebede, 2021). Legume-based crop rotations can reduce nitrogen fertilization, limit nitrogen losses to the environment, especially in organic practices, and can be more productive than monocultures (Sainju et al., 2017). The inclusion of legumes in crop rotation not only improves soil physical properties (e.g., reduces soil bulk density), but also increases organic matter and total nitrogen (Van Der Pol et al., 2022; Wang et al., 2023). Long-term crop rotations, particularly those incorporating legumes, result in a systematic increase in organic carbon accumulation and higher levels of key soil nutrients (Domnariu et al., 2024; Liu et al., 2023; Yu et al., 2021).

In summary, it is believed that the use of manure and crop rotation with the participation of legumes brings significant benefits – both in terms of increasing the content of organic matter and improving the availability of key nutrients for plants. The changes to the soil's properties, particularly its physical and chemical characteristics, are a long-term process (Soman et al., 2017). Long-term, continuous field experiments are among the most effective means of evaluating and predicting the impacts of soil management on soil quality and plant productivity. Long-term experiments are suitable for monitoring the effects of regular treatments on soil's physical, chemical, and biological properties (Blanchet et al., 2016; Geisseler and Scow, 2014; Hungria et al., 2009).

The aim of the research is to assess the impact of the fertilization system (mineral, farmyard manure and mixed mineral and farmyard manure) used in two rotations on the selected chemical properties of the soil. The paper presents research results of soil chemical properties such as soil reaction (pH) and the content of total nitrogen, available forms of phosphorus and potassium, and microelements (manganese (Mn), copper (Cu), zinc (Zn), and iron (Fe)) obtained in 2011–2014 in two long-term static experiments, in which diversified mineral and organic fertilization was used in two rotations: rotation without red clover (sugar beet – spring barley – winter rapeseed – winter wheat) and Norfolk rotation with red clover (sugar beet – spring barley with undersown red clover – red clover – winter wheat). The presented research focuses on analyzing changes in the chemical composition of the soil, which are necessary for the sustainable development of agricultural production and environmental protection. Due to the complexity of these interactions, this work aims to provide a more complete picture of the benefits of integrating different fertilization and crop rotation practices in plant cultivation

2. Materials and methods

The basis of the research was two long-term static field experiments established in 1955 at the Agricultural Experimental Station of the SGGW Chylice in Jaktorów, located in central Poland, in a plain landscape, elevated approximately 105 m above sea level (52°06' N, 20°33' E). According to Solon et al. (2018), the experimental station is located in the Central Mazovian Lowland, a mesoregion of the Łowicz-Błonie Plain (318.72). The experiments were carried out on leached black earth (Kabała et al., 2019) (according to the World Reference Base for Soil Resources WRB – Endogleyic Phaeozems), which was formed from light boulder clay. The content of sand (1–0.1 mm) in the 0–20 cm soil layer ranged from 53–66%, silt (0.1–0.02 mm) from 16% to 22%, floatable particles (<0.02 mm) from 18% to 26%, and clay particles (<0.002 mm) from 10% to 15% (Lenart, 2002). The density of the solid phase of this soil is 2.62 g cm^{-3}, and the humus horizon has a thickness of 30–35 cm. This soil is characterized by medium humus content, slightly acidic reaction, and regulated water relations. Before the experiments were carried out in 1955, the arable layer was slightly acidic (pH 6.2–6.5) and contained 1.15% organic carbon, 44 mg kg^{-1} of available phosphorus (P), and 83 mg kg^{-1} of available potassium (K) – a low content of available phosphorus and potassium (Suwara et al., 2024).

The experiments were conducted using the randomized block method with four replications. The size of the plot is 50 m^2 (12.5 m × 4 m = 50 m^2). The experiments encompass four fertilizer treatments: mineral fertilization (NPK), manure fertilization (FYM), a combination of mineral and farmyard manure fertilization (½ NPK + ½ FYM), and a control without any fertilization (0).

Composted cattle manure is plowed into the soil in autumn. The nutrient content in cattle manure was assumed based on literature data: 0.5% N, 0.11% P, and 0.5% K. Therefore, 50 kg N, 11 kg P, and 50 kg K were applied to the soil with 10 t of manure. A plow tillage system was used in the experiments (plowing depth 20 cm). All by-products, particularly straw and beet leaves, were removed from the field. Since 1955, no liming or fertilization with microelements has been used.

Fertilization is applied in two crop rotations:

A – with legume (Norfolk rotation):
- potatoes – spring barley with undersown red clover – red clover – winter wheat (from 1955 to 1989)
- sugar beet – spring barley with undersown red clover – red clover – winter wheat (since 1990, the rotation was changed and sugar beets were introduced instead of potatoes)

B – without legumes:
- potatoes – spring barley – rye (until 1989)
- Since 1990, the rotation has been changed to 4 fields: sugar beet, spring barley, winter rapeseed, and winter wheat.

Until 1962, farmyard manure in treatments with organic fertilization was used only for potatoes. In 1963, fertilization practices were modified – the doses of mineral fertilizers (pure components) were increased, and manure was applied annually to all crops grown in rotation (Table 1 and Table 2) until 1989.

Since 1990, following changes in crop rotation, the fertilization scheme presented in Tables 3 and 4 has remained in effect to date. Since 1955, liming has not been used in the experiments. Mineral fertilizers are used in the form of ammonium nitrate (mineral nitrogen 34% N), granulated superphosphate containing 18–19% P_2O_5 (8% P), and potassium salt (60% K_2O – 50% K).

Chylice Agricultural Experimental Station is located in conditions typical of Central Poland. In general, the area of central Poland is characterized by early spring, a vegetation period lasting about 200–210 days, a relatively long winter-free period of about 250 days, and a short snow cover of 35–65 days. According to data from the meteorological station at Chylice Agricultural Experimental Station, the average annual precipitation for the multi-year period 1955–2001 was 579.6 mm. The lowest precipitation was observed in January and February (25.5 and 28.9 mm), and the highest in July, at 87.4 mm. During the vegetation period, from April to September, the total average precipitation is 380 mm.

Table 1
Diagram of fertilizer experiments in crop rotation without legumes until 1989

Plant	Treatments Mineral (NPK) [kg ha^{-1}]			Organic (Farmyard manure) FYM [t ha^{-1}]	Mixed mineral with organic ½ NPK [kg ha^{-1}] + ½ FYM [t ha^{-1}]				0
	N	P	K	FYM	N	P	K	FYM	
Years 1955–1962									
Potatoes	55	18.2	104	40	27.5	9.1	52	20	–
Spring barley	35	18.2	45.5	–	17.5	9.1	22.8	–	–
Rye	35	18.2	45.5	–	17.5	9.1	22.8	–	–
1963–1989									
Potatoes	110	36.4	208	40	55	18.2	104	20	–
Spring barley	70	36.4	91	20	35	18.2	45.5	10	–
Rye	70	36.4	91	20	35	18.2	45.5	10	–

Table 2
Diagram of fertilizer experiments in Norfolk rotation until 1989

Plants	Treatments Mineral NPK [kg ha^{-1}]			Organic (Farmyard manure) FYM [t ha^{-1}]	Mixed mineral with organic ½ NPK [kg ha^{-1}]+ ½ FYM [t ha^{-1}]				0
	N	P	K	FYM	N	P	K	FYM	
Years 1955–1962									
Potatoes	55	13.6	95.8	40	27.5	6.8	47.8	20	–
Spring barley with red clover	35	13.6	33.3	–	17.5	6.8	16.7	–	–
Red clover	–	13.6	33.3	–	–	6.8	16.7	–	–
Winter wheat	35	13.6	33.3	–	17.5	6.8	16.7	–	
Years 1963–1989									
Potatoes	110	27.2	190.9	40	55	13.6	95.4	20	–
Spring barley with red clover	70	27.2	66.6	20	35	13.6	33.3	10	–
Red clover	–	27.2	66.6	–	–	13.6	33.3	–	–
Winter wheat	70	27.2	66.6	20	35	13.6	33.3	10	

Table 3
Diagram of fertilizer experiments in Norfolk rotation since 1990

Plant	Treatment Mineral (NPK) [kg ha⁻¹]			Organic (Farmyard manure) FYM [t ha⁻¹]	Mixed mineral with organic ½ NPK [kg ha⁻¹] + ½ FYM [t ha⁻¹]				0
	N	P	K	FYM	N	P	K	FYM	
Sugar beet	200	56.0	200.0	40	100	28.0	100.0	20	–
Spring barley with red clover	100	36.5	91.5	20	50	18.3	45.8	10	–
Red clover	–	36.5	91.5	–	–	18.3	45.8	–	–
Winter wheat	100	36.5	91.5	20	50	18.3	45.8	10	–

Table 4
Diagram of fertilizer experiments in crop rotation without legumes since 1990

Plant	Treatment Mineral (NPK) [kg ha⁻¹]			Organic (Farmyard manure) FYM [t ha⁻¹]	Mixed mineral with organic ½ NPK [kg ha⁻¹] + ½ FYM [t ha⁻¹]				0
	N	P	K	FYM	N	P	K	FYM	
Sugar beet	200	56.0	200.0	40	100	28.3	100.0	20	–
Spring barley	100	36.5	91.5	20	50	18.3	45.8	10	–
Winter rapeseed	100	36.5	91.5	20	50	18.3	45.8	10	–
Winter wheat	100	36.5	91.5	20	50	18.3	45.8	10	–

The average annual temperature for the multi-year period 1955–2001 was 8.44°C, with the minimum temperature in January (–1.8°C) and the maximum in July (18.7°C). In relation to the data from the multi-year period 1955–2001, recent years (2010–2014) were characterised by higher total precipitation by 50.9 mm to 261.1 mm depending on the year. The average annual temperature for recent years did not differ significantly from the average annual temperature for the multi-year period, amounting to 8.11°C (Table 5).

Soil samples were collected in the years 2011, 2012, 2013, and 2014 from the 0–20 cm topsoil (soil layer) immediately after harvesting individual crops (in the case of sugar beet, before harvesting). Soil samples for chemical analysis were collected using an Egner-Riehm stick from 20 locations in each plot, creating a mixed sample weighing 0.5 kg. These samples were air-dried and then sieved through 2 mm nylon sieves and were used to determine the following soil properties using commonly used methods:

- soil reaction (pH) in 1 M KCl dm^{-3}
- determined by the potentiometric method after extraction in 1 M KCl (ISO 10390, 2005),
- total nitrogen – determined by the Kjeldahl method (ISO 11261, 1995),
- available phosphorus – by the Egner-Riehm method (PE-R) (PN-R-04023, 1996),
- available potassium – by the Egner-Riehm method – DL (PN-R-04022, 1996),
- available forms of Zn, Fe, Cu, Mn soluble in 1M KCl in soil (according to Rinkis).

In the paper, the results of soil parameters are given as averages over the years, as no interaction with the years of research was found. For the parameters studied, means from the years 2011–2014 were calculated to compare the influence of the studied factors (fertilization and crop rotation) and their interaction. For four years, an analysis of variance and comparisons of averages were performed using the Tukey procedure,

Table 5
Average annual air temperature and annual precipitation in Chylice Experimental Station for the years 2010 – 2014

Year	Average annual air temperature [°C]	Annual precipitation [mm]
2010	6.7	840.7
2011	8.6	693.5
2012	8.3	630.5
2013	8.1	825.8
2014	8.9	638.5
Average from 2010–2014	8.1	725.8
Average from 1955–2001	8.4	579.6

and NIR values were calculated at a significance level of 0.05. Based on these analyses, homogeneous groups of averages were distinguished, i.e., groups of averages that did not differ statistically significantly were marked with the same letters. In all analyses, a significance level of 0.05 was assumed. The analyses were performed in the Statistica 13 program.

3. Results and discussion

The obtained research results indicate a significant effect of both fertilization and crop rotation on the primary parameters that determine soil fertility. One of these elements is soil pH. Our own research found a significant effect of fertilization on soil pH (Table 6). The highest soil pH (6.51) was recorded in the crop rotation without legumes in soil fertilized with manure and mineral fertilizers (½ NPK + ½ FYM). The best pH was also observed in the soil from the object fertilized with manure (FYM), both in the rotation with red clover (A) – 6.3, and in the rotation without the participation of a legume plant (B) – 6.4. In both cases, the pH of these soils is slightly acidic. In the rotation with a legume plant (A), a significantly higher soil pH was found in the objects fertilized only with manure (FYM – 6.25) compared to the other objects (NPK, ½ NPK + ½ FYM, O), where the pH ranged from 5.4 to 5.7. In the crop rotation without legumes (B), pH below 6 was found only in the soil fertilized only with mineral fertilizers (NPK), while in the remaining treatments, it was significantly higher, and the pH value ranged from 6.3 to 6.5.

The use of mineral fertilization only (NPK), regardless of crop rotation, resulted in significantly higher soil acidification compared to both the control object (0) and the other fertilization systems. The highest pH, regardless of the crop rotation, was recorded in objects fertilized only with manure (FYM).

The inclusion of a legume plant in the crop rotation had an adverse effect on the formation of soil pH. In the case of a crop rotation without a legume plant (B), soil acidity was significantly lower (pH 6.2) than in the plots with a legume plant (A) (pH 5.7). The soil in all the studied plots had not been limed since 1955,

Table 6
Soil pH (pH in 1M KCl), depending on the fertilization system and crop rotation (means of 2011–2014)

Fertilization	Crop rotation A with legume	 B without legume	Mean
O	5.7 b*	6.3 a	6.0 b
NPK	5.4 b	5.7 b	5.6 c
FYM	6.3 a	6.4 a	6.3 a
½ NPK + ½ FYM	5.6 b	6.5 a	6.1 b
Mean	5.7 B	6.2 A	–

*– individual letters indicate homogeneous groups of means; mean values marked with the same letters do not differ significantly at α = 0.05
– Lower-case letters refer to the comparison of fertilization in columns
– Upper-case letters refer to the comparison of crop rotations in rows

while clovers with a strongly developed root system take up large amounts of calcium from the upper layers of the soil.

The obtained results concerning soil pH are confirmed in the literature. According to Mazur and Sądej (Mazur and Sądej, 1989), the use of organic fertilization causes beneficial changes in soil pH, which is particularly important on light soils (Gawrońska-Kulesza et al., 1989). According to Sienkiewicz (2003) and Blecharczyk et al. (2005), manure has a stabilizing effect on soil pH, a finding confirmed by our own studies. Earlier studies by Gawrońska-Kulesza and Lenart on the same experiment also confirm these results (Gawrońska-Kulesza and Lenart, 1987; Lenart, 2002). In the above studies, the authors noted a beneficial effect of using manure in a legume crop rotation on soil pH (pH 6.4) and a negative effect of mineral fertilization (pH 6.1). In objects fertilized with manure in combination with mineral fertilizers, the soil pH was 6.3. According to researchers such as Luo et al. (2024) and Fan et al. (2012), omitting the introduction of manure to the soil during intensive use of nitrogen fertilizers contributes to increased soil acidification. This is confirmed by the results of the studies by Wojnowska et al. (1993). According to Kuszelewski and Łabętowicz (1991), manure weakens the acidifying effect of mineral fertilization. Additionally, according to Jaskulska and Jaskulski (2003), the most beneficial fertilization system is mineral-organic fertilization, as it prevents sudden changes in the chemical properties of the soil. On the other hand, Koper and Lemanowicz (2006) in their studies on lessive soil also did not find any effect of using higher doses of manure on changes in soil pH. However, they observed that increasing the dose of mineral nitrogen caused a slight decrease in pH. The acidifying effect of using only mineral fertilization in long-term studies established on lessive soil developed from light clayey sand was noted by Stanisławska-Glubiak and Wróbel (1999). After 20 years of no liming and using only mineral fertilization, the researchers found a decrease in pH by 1.9 units. In contrast, objects fertilized with manure and manure combined with mineral fertilizers showed decreases of 1.6 and 1.7 units, respectively. Filipek (2001) also observed in their studies that mineral fertilization with NPK causes a decrease in soil pH. The adverse effect of clover cultivation on soil pH was noted by Nowosielski (1974). According to the researcher, clover is a plant that strongly acidifies the soil. Wang et al. (2023) and Pikuła and Rutkowska (2020) also confirm that crop rotation with legumes significantly reduces pH. In summary, it is reported that treatments with a significant impact on maintaining soil pH include liming and fertilization with manure (Blecharczyk et al., 2005; Mazur et al., 2015; Menšík et al., 2018; Nazarkiewicz and Kaniuczak, 2012).

A very important indicator that allows determining the fertility of a given soil is its abundance of three primary macronutrients, such as total nitrogen, available phosphorus, and potassium. They are required in large amounts by plants and are growth-limiting factors.

Crop rotation, alongside the use of organic fertilization, is one of the most essential components for developing a sustainable agricultural production system (Giacometti et al., 2021; Wortman et al., 2011). In general, the selection of plants in crop rotation and the application of farmyard manure help to preserve soil quality, and according to many researchers, they play a main role in the accumulation of nutrients necessary for plants (Blecharczyk et al., 2005; Giacometti et al., 2021; Mercik et al., 2005; Pikuła and Rutkowska, 2020).

In our own studies, it was found that the soil from the object fertilized only with manure (FYM) had the highest total nitrogen content (0.81 g kg^{-1}), regardless of the crop rotation (Table 7). The total N content in the soil increased as a result of FYM applications and NPK fertilization. In the rotation with red clover, the highest total N content was found in soil fertilized with FYM (0.89 g kg^{-1}), followed by soil fertilized with a combination of manure and mineral fertilizers – ½ NPK + ½ FYM (0.79 g kg^{-1}). In the rotation without legumes, the highest total N content was also found in the object fertilized with manure – FYM (0.72 g kg^{-1}).

In the crop rotation with legumes (A), the nitrogen content when fertilized with manure (FYM) was 39% higher, while in the crop rotation without red clover (B), it was 18% higher compared to the control (0).

The use of manure fertilization, combined with mineral fertilizers (½ NPK + ½ FYM), also increased the total nitrogen content in the soil compared to the control object and exclusive NPK fertilization. The obtained results confirm the beneficial effect of manure (FYM) and organic-mineral fertilization (½ NPK + ½ FYM) on the fertility of the tested soil. The introduction of only mineral fertilizers (NPK) in the experiment with legumes (A) resulted in a slight increase in nitrogen content; however, these changes were not statistically significant compared to the unfertilized control (0).

The beneficial effect of manure fertilization on increasing the total nitrogen content was also demonstrated in the studies of Körschens and Buś (1982), Bokhtiar and Sakurai (2005), Ahmed et al. (2023), Aksahin et al. (2023), and Wu et al. (2024). Some researchers claim that the application of mineral and organic fertilizers significantly increased the contents of phosphorus (P) and total N (Zemichael and Dechassa, 2018).

Table 7
Total nitrogen content in soil (Nt) depending on fertilization and crop rotation (means of 2011–2014)

Fertilization	Crop rotation A with legume N_t [g kg^{-1}]	B without legume	Mean
0	0.64 c*	0.61 b	0.63 c
NPK	0.70 cb	0.63 b	0.66 c
FYM	0.89 a	0.72 a	0.81 a
½ NPK + ½ FYM	0.79 b	0.64 b	0.72 b
Mean	0.76 A	0.66 B	–

*– individual letters indicate homogeneous groups of means; mean values marked with the same letters do not differ significantly at α = 0.05
– Lower-case letters refer to the comparison of fertilization in columns
– Upper-case letters refer to the comparison of crop rotations in rows

Regardless of the fertilization used, the soil from the object with the rotation with red clover (A) was characterized by a significantly higher total nitrogen content compared to the soil from the rotation without the legume plant (B). Higher nitrogen content in crop rotation A was a consequence of including legumes in crop rotation. These results are confirmed by other studies (Lenart, 2002; Mercik et al., 2005; Pikuła and Rutkowska, 2020; Suwara and Gawrońska-Kulesza, 1994).

Siwik-Ziomek and Koper (2013) in an experiment on lessive soil using different fertilization and crop rotation systems also noted a higher total nitrogen content in the soil from the object with rotation with undersown red clover fertilized with manure compared to the soil from the object without the use of manure and legumes in the rotation, and the difference in the value of these parameters between the rotations was 12%. Sosulski et al. (2005) showed a significant effect of manure application and legume cultivation on increasing the nitrogen content in the soil by 51–56% compared to the object fertilized only with minerals. According to Wang et al. (2023), Pikuła and Rutkowska (2020), Lenart (2002), and Bałuch and Benedycki (2004), the crop rotation with legumes significantly increased the soil total N.

Both crop rotation and fertilization significantly differentiated the content of available phosphorus and potassium in the soil (Table 8). The highest content of available phosphorus in the soil among the tested fertilization systems, both in the rotation with legumes (A) and in the rotation without legumes (B), was recorded in the soil fertilized with manure – FYM (83.5 mg kg^{-1} and 111.9 mg kg^{-1}, respectively) and mineral-organic – ½ NPK + ½ FYM (78.8 mg kg^{-1} and 109.6 mg kg^{-1}). Only mineral fertilization (NPK) also had a beneficial effect on the content of available phosphorus in the soil (74.6 mg kg^{-1} and 92.4 mg kg^{-1}), and the soil from the control object (0) was characterized by significantly the lowest content of this element (29.6 mg kg^{-1} and 63.1 mg kg^{-1}).

To sum up, on average for the crop rotations, the highest phosphorus content was recorded in the soil fertilized with manure – FYM (97.7 mg kg^{-1}), followed by the soil fertilized with manure combined with mineral fertilizers – ½ NPK + ½ FYM (94.2 mg kg^{-1}). The use of only mineral fertilization (NPK) also had a positive effect on the content of this macroelement in the soil (83.5 mg kg^{-1}). The significantly lowest content of this element was recorded in the unfertilized soil – 0 (46.4 mg kg^{-1}). Furthermore, regardless of the fertilization system, a significantly higher phosphorus content was recorded in the soil from the crop rotation object without a legume plant (B), where the phosphorus content was 94.3 mg kg^{-1}, while in the crop rotation objects with the participation of a legume plant (A), it was 66.6 mg kg^{-1}.

Fertilization with manure, both exclusively and in combination with mineral fertilizers (FYM and ½ NPK + ½ FYM) in both crop rotations, also provided the highest content of available potassium in the soil. A significantly lower potassium content was observed in the soil from the object fertilized exclusively with mineral fertilizers (NPK), and the lowest potassium content was noted in the control (0) in relation to all other objects.

Table 8
Content of available phosphorus (P) and potassium (K) depending on the fertilization and crop rotation (means of 2011–2014)

Fertilization	P [mg kg⁻¹]			K		
	Crop rotation		Means	Crop rotation		Mean
	A with legume	B without legume		A with legume	B without legume	
O	29.6 b*	63.1 b	46.4 b	49.1 c	91.1 c	70.1 c
NPK	74.6 a	92.4 a	83.5 a	80.3 b	143.7 b	112.0 b
FYM	83.5 a	111.9 a	97.7 a	142.7 a	217.9 a	180.3 a
½ NPK + ½ FYM	78.8 a	109.6 a	94.2 a	163.2 a	186.5 a	174.9 a
Mean	66.6 B	94.3 A	–	108.8 B	159.8 A	–

*– individual letters indicate homogeneous groups of means; mean values marked with the same letters do not differ significantly at α = 0.05
– Lower-case letters refer to the comparison of fertilization in columns
– Upper-case letters refer to the comparison of crop rotations in rows

On average, regardless of the crop rotation, the highest potassium content was recorded in soil fertilized with manure – FYM (180.3 mg kg^{-1}) and manure combined with mineral fertilizers – ½ NPK + ½ FYM (174.9 mg kg^{-1}). The use of only mineral fertilization – NPK (112.0 mg kg^{-1}) also resulted in an increase in the content of available potassium in the soil compared to the control (0), where the content of this element was (70.1 mg kg^{-1}).

Including a legume plant (A) in the crop rotation resulted in a decrease in the potassium content in the soil by about 30% (108.8 mg kg^{-1}) compared to the crop rotation without a legume plant (B) (159.8 mg kg^{-1}).

Comparing the results obtained on the content of available phosphorus and potassium obtained in these experiments in the past, it is stated that after many years of using manure fertilization (FYM and ½ NPK + ½ FYM), the content of these components in the soil increases, while in objects fertilized only with mineral fertilizers (NPK), it decreases. In 1981, the highest phosphorus content in the soil from the rotation with legumes (A) was noted in objects fertilized with manure combined with mineral fertilizers – ½ NPK + ½ FYM (96.4 mg kg^{-1}) and fertilized only with mineral fertilizers – NPK (94.2 mg kg^{-1}), then with manure – FYM (77.4 mg kg^{-1}), and the lowest in the control objects – 0 (51.5 mg kg^{-1}) (Gawrońska-Kulesza and Lenart, 1987). After 13 years of using the same fertilization system, the content of available phosphorus in the same experiments was, respectively, in the objects fertilized with mineral-organic fertilizers (½ NPK + ½ FYM) (80.7 mg kg^{-1}), mineral fertilizers (NPK) (79.4 mg kg^{-1}), manure (FYM) (74.6 mg kg^{-1}) and the control (0) (49.3 mg kg^{-1}), while in the B crop rotation it was the highest in the object fertilized with mineral-organic fertilizers (½ NPK + ½ FYM) (86 mg kg^{-1}) (Lenart, 2002). In 1981, the content of available potassium in the soil from the Norfolk crop rotation treatments was the highest in the treatments fertilized with manure (FYM) (83 mg kg^{-1}), then in the treatments fertilized with mineral-organic fertilizers (½ NPK + ½ FYM) (68 mg kg^{-1}), and the lowest content of this element was recorded in the control treatment (0) (55 mg kg^{-1}) (Gawrońska-Kulesza and Lenart, 1987). Similar trends in the accumulation of this element in the soil were noted by Lenart (2002) and Pikuła and Rutkowska (2020).

Many authors confirm the beneficial effect of manure application on increasing the content of available phosphorus and potassium in the soil (Aksahin et al., 2023; Alzamel et al., 2022; Han et al., 2021; He et al., 2022; Kotwica et al., 2021; Rutkowska et al., 2002; Wortman et al., 2011; Zhao et al., 2024). Harasimowicz-Herman (1989) observed that the application of organic fertilization and the cultivation of legumes resulted in an increase in the content of available forms of phosphorus and potassium in the soil. In turn, Pikuła and Rutkowska (2020) found a decrease in the available forms of P and K in soil in crop rotation with legumes, contrary to crop rotation without legumes. Only mineral fertilization resulted in an increase in the soil's potassium content compared to the control object; however, this increase was smaller than that observed with the other fertilization systems.

In the studies by Jaskulska et al. (2020), the use of manure fertilization in combination with mineral fertilizers significantly increased the content of available phosphorus and available magnesium in the soil compared to mineral fertilization alone. Fertilization studies conducted by Mercik et al. (2009) in Chylice on black earth developed from light silty boulder clay and Mochełek on typical lessive soil developed from strong and light clayey sand showed that the accumulation of both phosphorus and potassium in both types of soil was most beneficially influenced by manure fertilization in combination with mineral fertilizers. In reference to our own results (Table 8) to the results of studies conducted by other researchers on the same long-term experience, it can be observed that the use of long-term manure fertilization has a beneficial effect on the formation of soil phosphorus and potassium content, and over the years, the soil content in these components shows an increasing trend.

In the conducted experiments, the content of available forms of micronutrients, such as manganese, copper, zinc, and iron, was also determined. It was found that all analyzed objects

Table 9
Content of available manganese (Mn). copper (Cu). zinc (Zn) and iron (Fe), depending on the fertilization and crop rotation (means of 2011–2014)

Fertilization	Mn [mg kg^{-1}]			Cu			Zn			Fe		
	Crop rotation		Mean	Crop rotation		Mean	Crop rotation		Mean	Crop rotation		Mean
	A with legume	B without legume		A with legume	B without legume		A with legume	B without legume		A with legume	B without legume	
0	116.81c*	109.58b	113.20c	6.08ab	4.84a	5.46ab	10.93a	7.89b	9.41b	806.25a	634.38a	720.32a
NPK	126.44ab	112.06b	119.25b	6.23a	4.83a	5.53a	9.31a	7.83b	8.57c	707.66b	586.88ab	647.27b
FYM	131.81a	121.16a	126.49a	5.34b	4.69a	5.02b	10.58a	9.36a	9.97a	612.81c	550.63b	581.72c
½ NPK + ½ FYM	123.65b	122.69a	123.17ab	5.38ab	4.58a	4.98b	9.93a	8.99ab	9.46b	660.94bc	538.44b	599.69bc
Mean	124.67A	116.37B	–	5.76A	4.74B	–	10.19A	8.52B	–	696.92A	577.58B	–

*– individual letters indicate homogeneous groups of means. Mean values marked with the same letters do not differ significantly at α = 0.05
– Lower-case letters refer to the comparison of fertilization in columns
– Upper-case letters refer to the comparison of crop rotations in rows

were characterized by an average content of manganese, zinc, and copper (Korzeniowska et al., 2021). However, long-term fertilization, regardless of crop rotation, had an influence on changes in micronutrient contents (Table 9).

In the rotation with legumes (A), the highest contents of available manganese (Mn) were recorded in the soil of objects fertilized with manure – FYM (131.81 mg kg^{-1}) and exclusively with minerals (126.44 mg kg^{-1}), and significantly the lowest content of this element was recorded in the control object (0). In the rotation without legumes (B), the highest content of this microelement was recorded in the soil fertilized with mineral-organic fertilizers – ½ NPK + ½ FYM (122.69 mg kg^{-1}) and exclusively with manure – FYM (121.16 mg kg^{-1}). The use of mineral fertilization (NPK) did not significantly increase the content of available manganese in the soil (112.06 mg kg^{-1}) in relation to the control object. On average, for the crop rotations, the significantly highest content of available manganese was noted in the soil fertilized with manure – FYM (126.49 mg kg^{-1}) and manure combined with mineral fertilizers – ½ NPK + ½ FYM (123.17 mg kg^{-1}), and then mineral fertilized – NPK (119.25 mg kg^{-1}). Among all treatments, the soil that had not been fertilized since 1955 (0) showed the significantly lowest content of available manganese.

The content of copper (Cu) was significantly differentiated by fertilization only in the rotation with the participation of a legume plant (A). The significantly highest copper content was recorded in the soil from the object fertilized with mineral – NPK (6.23 mg kg^{-1}) and from the control object – 0 (6.08 mg kg^{-1}), followed by the mineral-organic fertilization – ½ NPK + ½ FYM (5.38 mg kg^{-1}). Fertilization only with manure (FYM) resulted in a significant decrease in the content of this microelement in the soil compared to mineral fertilization (NPK). In the rotation without the participation of a legume plant (B), the fertilization used did not significantly differentiate the copper content in the soil. Regardless of crop rotation, significant differences in the content of available copper in the soil occurred only between the object fertilized with mineral fertilization (NPK), where the content of this element in the soil was the highest, and the mineral-organic fertilization (½ NPK + ½ FYM) and manure (FYM), where the soil was the poorest in copper.

The zinc content in the soil from the objects with the legume crop rotation (A) was not significantly differentiated by the applied fertilization and ranged from 9.31 mg kg^{-1} to 10.93 mg kg^{-1}. It should be noted, however, that the introduction of mineral fertilizers resulted in a decrease in the content of available zinc in the soil. In the rotation without the legume crop (B), the applied fertilization significantly differentiated the zinc content in the soil. The significantly highest content of this element was recorded in the objects fertilized with manure – FYM (9.36 mg kg^{-1}) and mineral-organic – ½ NPK + ½ FYM (8.99 mg kg^{-1}), and significantly lower was recorded in the soil from the control objects – 0 (7.89 mg kg^{-1}) and mineral-fertilized – NPK (7.83 mg kg^{-1}). Regardless of the crop rotation used, under the influence of exclusive mineral fertilization (NPK), the significantly lowest content of available zinc (Zn) in the soil was found, while fertilization exclusively with manure provided the significantly highest content of this element.

In both crop rotations, the iron (Fe) content in the soil was significantly differentiated by the applied fertilization, and the soil from the control object (0) was characterized by the highest content (in the rotation with legumes – 806.25 mg kg^{-1}; in the rotation without legumes – 634.38 mg kg^{-1}). The introduction of manure resulted in a decrease in the content of this microelement in the soil, and in the rotation without legumes it was 550.63 mg kg^{-1} in the crops fertilized with manure (FYM) and 538.44 mg kg^{-1} in the crops fertilized with mineral-organic fertilizers (½ NPK + ½ FYM), and in crop rotation with legumes the lowest content of this element was recorded in the soil fertilized only with manure – FYM (612.81 mg kg^{-1}).

Regardless of the crop rotation, the soil from the unfertilized object (0) had the highest iron content – 720.32 mg kg^{-1}. A significantly lower iron content was recorded in the soil fertilized with mineral fertilizers – NPK (647.27 mg kg^{-1}) and mineral-organic fertilizers – ½ NPK + ½ FYM (599.69 mg kg^{-1}), and the lowest content of this element was recorded in the object fertilized with manure – FYM (581.72 mg kg^{-1}). Including legumes (A) in the crop rotation ensured a significantly higher content of available forms of all tested microelements —manganese, copper, zinc, and iron — in the soil compared to objects with a crop rotation without the participation of a legume plant (B).

The impacts of fertilization on available micronutrients varied with cropping systems (Wei et al., 2006). The beneficial effect of legume crops in crop rotation on the content of available micronutrients is confirmed by Benchaar et al. (2001) and Szulc et al. (2007). The higher content of available forms of micronutrients in the soil from objects with legumes compared to objects without legumes may be caused by the large amount of post-harvest residues rich in nutrients left by red clover. As a result, this may contribute to an increase in the soil's sorption capacity (Czekała, 2003).

According to Thapa et al. (2021), soil organic matter can meet the micronutrient requirements of many crops. It has been observed that the use of organic amendments, such as compost, manure, green manure, and the incorporation of plant residues into the soil, is beneficial as they provide essential micronutrients for plants (Dhaliwal et al., 2019).

The application of manure increases the content of organic matter in the soil and, according to Parat et al. (2005) and Zhang et al. (2001), has a significant direct effect on the availability of Mn and Zn. In turn, Fan et al. (2012) claim that the long-term application of horse manure can increase the availability of Zn in the soil. Additionally, the application of mineral fertilizers increases the extractable Fe, Mn, and Cu in the soil by lowering the soil pH. According to Wei et al. (2006), the content of available forms of Zn and Fe was higher in the fertilized compared to the unfertilized treatments, but the content of available Cu was not significantly affected by fertilization. The effect of fertilization on the content of available manganese (Mn) depended on the crop rotation. The application of fertilization tended to increase the available Mn in continuous wheat and maize cultivation, but decreased the content of available Mn in continuous clover and legume rotation. Wei et al. (2006) demonstrated that soil organic matter has a significant and direct impact on the availability of Zn, Mn, and Fe, but has a minimal effect on the available Cu content.

Szulc et al. (2004) noted a negative balance of copper and zinc in their studies under the influence of mineral fertilization. The use of mineral fertilization in conjunction with manure to some extent reduced this balance difference. When using only manure fertilization, the researchers observed a positive balance of manganese and zinc, indicating the buffering effect of manure. Rutkowska et al. (2002) found that fertilization only slightly modified the content of available microelements; however, they observed a tendency for the content of available forms of manganese, zinc, and copper in the soil to increase in objects fertilized with manure compared to those where manure was not used. The negative effect of mineral fertilization on the content of these microelements in the soil was also demonstrated in Kaniuczak's studies (1996). According to Czuba (1996), with the increase in the nitrogen dose, the uptake of microelements by the plant increases, up to the point of their deficiency in the soil.

According to many researchers, soil pH plays a crucial role in regulating the availability of microelements for plants, and consequently, their amount remaining in the soil (Jakubus et al., 1996; Rutkowska et al., 2014). Rutkowska et al. (2014) noted the highest contents of available forms of Cu, Fe, Mn and Zn in soil with the lowest pH. Most studies show that the solubility of microelements decreases with increasing soil pH (Herms, 1982). Our own studies showed a higher iron content in objects with lower pH values. The lowest content of this microelement was noted in soil fertilized with manure and manure combined with mineral fertilizers, while the highest was noted in the control object. The highest iron content in the control object was likely due to the lowest plant yields obtained on unfertilized control objects and the low uptake of this element in the yields.

Different results were obtained in studies by Jakubus et al. (1996) and Czekała et al. (1996), who found the highest iron content in soil from objects fertilized with manure. In their studies, the application of manure resulted in an increase in the content of all microelements in the soil compared to NPK fertilization. In contrast, our own studies showed an increase in the content of manganese and zinc in the soil under the influence of manure fertilization.

4. Conclusions

Based on two long-term static field experiments established in 1955 on leached black earths (Endogleyic Phaeozems), our results, obtained in 2011–2014, showed that the Norfolk rotation with red clover, as well as mineral and organic fertilization, affect the chemical properties of the soil. All kinds of fertilization used (NPK, FYM, ½ NPK + ½ FYM) lead to a significant increase in the content of available phosphorus and potassium in the soil compared to the object that has not been fertilized since 1955. Fertilization with manure (FYM) and mineral-manure (½ NPK + ½ FYM) of black earth has a stabilizing effect on the soil reaction, causing a significant increase in total nitrogen and available manganese in the soil compared to the object that is not fertilized and is fertilized only with mineral fertilizers. To sum up, the combined application of manure and mineral fertilizer increased the content of available nutrients and, as a consequence, improved soil properties. Exclusive mineral fertilization (NPK) of black earth has an acidifying effect on the soil; however, it does not significantly affect the total nitrogen content compared to the control object. The use of red clover in crop rotation results in a decrease in soil pH, a reduction in the content of available phosphorus and potassium, but an increase in the total nitrogen content in the soil. Crop rotation with red clover also ensured a higher content of available microelements (Mn, Cu, Zn, Fe) in the soil.

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Conflict of interest

The authors declare no conflict of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. This research did not involve human or animal subjects.

Author Contributions

Irena Suwara – Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review and editing. **Katarzyna Pawlak-Zaręba** – Conceptualization, Investigation, Methodology, Supervision, Visualization, Writing – review and editing. **Dariusz Gozdowski** – Data curation, Methodology, Visualization, Writing – original draft. **Szymon Młynek** – Writing – original draft.

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Właściwości chemiczne gleby po ponad 55 latach zróżnicowanego nawożenia i zmianowania roślin

Słowa kluczowe:

Nawożenie mineralne
Nawożenie obornikiem
Rośliny strączkowe
Wieloletnie doświadczenie polowe
Zmianowanie

Streszczenie

W pracy przedstawiono wyniki badań właściwości chemicznych gleb, takich jak pH gleby oraz zawartość azotu ogólnego (Nt), przyswajalnych form fosforu (P) i potasu (K) oraz mikroelementów (manganu (Mn), miedzi (Cu), cynku (Zn) i żelaza (Fe)) uzyskanych po ponad 55 latach stosowania nawożenia wyłącznie mineralnego (NPK), organicznego (OB) i obornikiem łącznie z nawozami mineralnymi (½ NPK + ½ OB) w dwóch zmianowaniach: zmianowaniu bez koniczyny czerwonej (burak cukrowy – jęczmień jary – rzepak ozimy – pszenica ozima) oraz zmianowaniu norfolskim z koniczyną czerwoną (burak cukrowy – jęczmień jary z wsiewką koniczyny czerwonej – koniczyna czerwona – pszenica ozima). Badania te oparto na dwóch wieloletnich statycznych doświadczeniach polowych założonych w 1955 roku na czarnej ziemi wyługowanej wytworzonej z gliny zwałowej lekkiej, pylastej i odgórnie spiaszczonej (według World References Base for Soil Resources WRB – Endogleyic Phaeozems) w Stacji Doświadczalnej SGGW (52°06'N, 20°33'E). Uzyskane wyniki wskazują, że zmianowanie z koniczyną czerwoną oraz wieloletnie zróżnicowane nawożenie wpływają na właściwości chemiczne gleby. Po ponad 55 latach gleba w zmianowaniu z rośliną bobowatą charakteryzowała się istotnie wyższą kwasowością i zawartością azotu ogólnego (pH 5,7, Nt 0,76 g kg^{-1}) niż na poletkach bez rośliny bobowatej (pH 6,2, Nt 0,66 g kg^{-1}). Zmianowanie z koniczyną czerwoną zapewniło również większą zawartość przyswajalnych mikroelementów (Mn, Cu, Zn, Fe) w glebie, ale spowodowało około 30% obniżenie zawartości przyswajalnego fosforu (P) i potasu (K) w glebie w porównaniu do zmianowania bez rośliny bobowatej. Odnotowano korzystny wpływ stosowania obornika na pH gleby, na zwiększenie zawartości azotu ogólnego, zawartości przyswajalnego fosforu (P), potasu (K), manganu (Mn) i cynku (Zn).