

Influence of 96 years of mineral and organic fertilization on selected soil properties: a case study from long-term field experiments in Skierniewice, central Poland

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Abstract

Received: 2022-08-11

Accepted: 2023-03-07

Published online: 2023-03-07

Associated editor: J. Antonkiewicz

Keywords:

Agriculture

Farmyard manure

Long-term experiments

NPK fertilization

Soil properties

Long-term agricultural experiments allow for the determination of the influence of agricultural practices on soil properties. The objective of the study was to determine the effect of 96-year-old fertilization (NPK mineral fertilization and farmyard manure (FYM) use) on selected physical and chemical soil properties. The research was carried out in an experimental field in Skierniewice, central Poland, where the experiments have been conducted since 1923. Seven soil profiles (Retisols or Luvisols) were studied. Long-term fertilization caused various changes in the chemical properties of the studied soil (pH, the content of total organic carbon (TOC), total nitrogen (TN) and total sulphur (TS); exchangeable acidity (EA), total potential acidity (hydrolytic acidity) (TPA), cation exchange capacity (CEC), the total exchangeable bases (TEB), base saturation (BS)). The effect of long-term fertilization is most evident in the topsoil (the Ap horizon). The NPK fertilization led to acidification which was expressed by the decrease of soil pH (down to the value of 5.1), as well as the increase of EA, TPA, and exchangeable Al. Long-term high-dose FYM application (40 t and 60 t ha⁻¹ per year) led to the stabilization of soil pH to a level of 6.2–6.5 throughout the soil profile (down to 120 cm). The use of a combination of NPK fertilization and FYM application led to acidification of the topsoil similar to the soil in which NPK fertilizers were applied alone. Long-term FYM application led to the increase in TOC, TN, and TS concentrations in the Ap horizons of the studied soils. Long-term use of NPK fertilizers had no significant effect on soil CEC, however long-term use of FYM increased the CEC in the Ap horizon of soils. An overall positive effect has been confirmed in the use of high doses of FYM (40 t and 60 t ha⁻¹ per year), which improves the chemical properties (soil pH, TOC, TN, and TS content, as well as CEC) of the soil compared to the control plot and plots with NPK fertilization alone. These findings were confirmed by PCCA analysis.

1. Introduction

Long-term experiments in agriculture are valuable research infrastructure to reveal the long-term impact of agricultural practices on the environment. The results of the experiments are rich sources of information on how different agricultural management practices affect soil quality and their overall impact on the environment over a long time (Siebielec et al., 2020). Recently, long-term fertilizer experiments have been focused and interconnected at the national (Grosse et al., 2020; Romanenkov et al., 2020; Siebielec et al., 2020), continental (Ciaccia et al., 2020), and even at the global level (Macdonald et al., 2020).

Long-term fertilization alters soil properties. The effects of long-term fertilizer use have been demonstrated in numerous

studies. Long-term fertilization causes changes in soil reactivity, cation exchange capacity (CEC) and base saturation (BS) (Bednarek et al., 2012; Hemalatha and Chellamuthu, 2013). Fertilization improves crop supporting properties of soils. The use of fertilizers can increase plant and root biomass, eventually leading to an increase in soil organic matter (SOM) (Tian et al., 2015). Murawska et al. (2017) showed that after 36 years of applying NPK fertilizer to sandy-loamy soil with or without manure, the SOM content increased, and the humus quality in the soil also improved. The use of certain fertilizers (e.g. ammonium sulphate, urea) causes soil acidification (Barak et al., 1997). The increase in exchangeable acidity is accompanied by a decrease in the amount of exchangeable basic cations and a decrease in soil CEC. The studies of forest soils showed that the use of mineral

fertilizers, especially nitrogen fertilizers, increases the amount of SOM, carbon and nitrogen, and in some cases, the content of calcium, magnesium and phosphorus, as well as reduces the C/N ratio in the organic layer (Högberg et al., 2006; Ring et al., 2011; Saarsalmi et al., 2014).

For about 100 years, fertilization experiments have been carried out in the experimental fields in Skierniewice, central Poland, the purpose of which have been to determine, among others, the influence of different doses of mineral fertilizers and farmyard manure on the crop yield and composition of plants. Long-term experiment, have been used to investigate the effects of organic and mineral fertilizers or crop rotation on the yield and growth of vegetables (Chroboczek, 1962). However, in recent times, long-term fertilizer experiments have focused on, among others, the relationship between SOM parameters and soil structure (Šimanský et al., 2019); sorption capacity of sandy soil (Šimanský and Jonczak, 2019); effect of fertilization on physicochemical properties of the soil selected for leeks and carrots (Rumpel and Ostrzycka, 1999); the effect of long-term fertilization on physico-chemical soil properties in rye monoculture and five-year crop rotation (Stępień and Kobialka, 2019). So far, majority of papers presented results showing the effect of fertilization on topsoil (A horizon). However, less attention has been paid to the influence of long-term use of fertilizers on soil properties in the whole soil profiles in the studied experimental field. The study aims to determine the effect of 96 years of organic and mineral fertilization on select soil properties. The

author hypothesises that (1) long-term use of different fertilization treatments (NPK fertilizers alone, farmyard manure (FYM) alone, a combination of FYM and NPK) influences soil chemical properties (soil pH, contents of SOM, soil sorption complex), as well as (2) the long-term use of FYM improves these properties.

2. Materials and methods

2.1. Study area

The research was conducted in the experimental field of the Institute of Horticulture in Skierniewice, central Poland, about 66 km west of Warsaw (Fig. 1). This is an area where glacial tills of the Warthian stage (MIS 6) of the Saale glaciation covered by younger sandy loamy materials constitute the parent material of soils (Marks, 2005).

The fertilization experiment was established in 1923 and included a field that was divided into plots where fertilization experiments were carried out in three repetitions each and among them, only one profile was selected for each fertilizer treatment. The size of a single plot was 4 m × 9 m. In the present study, 7 experimental plots were selected, where various doses of NPK fertilizers, FYM, and a combination of FYM and NPK were applied (Table 1). Fertilization was applied annually. The FYM was used in the autumn before winter plowing and NPK mineral fertilizers are applied in the spring before planting or sowing. The



Fig. 1. A view of the experimental field and the location of the study area

Table 1

Studied plots/soil profiles and detailed description of the fertilizer combinations.

Plot/Profile no.	Treatment	Doses of fertilizer per year
73	Control profile	no fertilizer
79	NPK1	60 kg N ha ⁻¹ , 30 kg P ₂ O ₅ ha ⁻¹ , 70 kg K ₂ O ha ⁻¹
80	NPK2	120 kg N ha ⁻¹ , 60 kg P ₂ O ₅ ha ⁻¹ , 140 kg K ₂ O ha ⁻¹
81	NPK3	180 kg N ha ⁻¹ , 90 kg P ₂ O ₅ ha ⁻¹ , 210 kg K ₂ O ha ⁻¹
83	FYM2	Manure 40 t ha ⁻¹ per year
84	FYM3	Manure 60 t ha ⁻¹ per year
65	FYM3 + NPK1 (in year 2018)	Manure 60 t ha ⁻¹ per year + NPK1 (in year 2018)

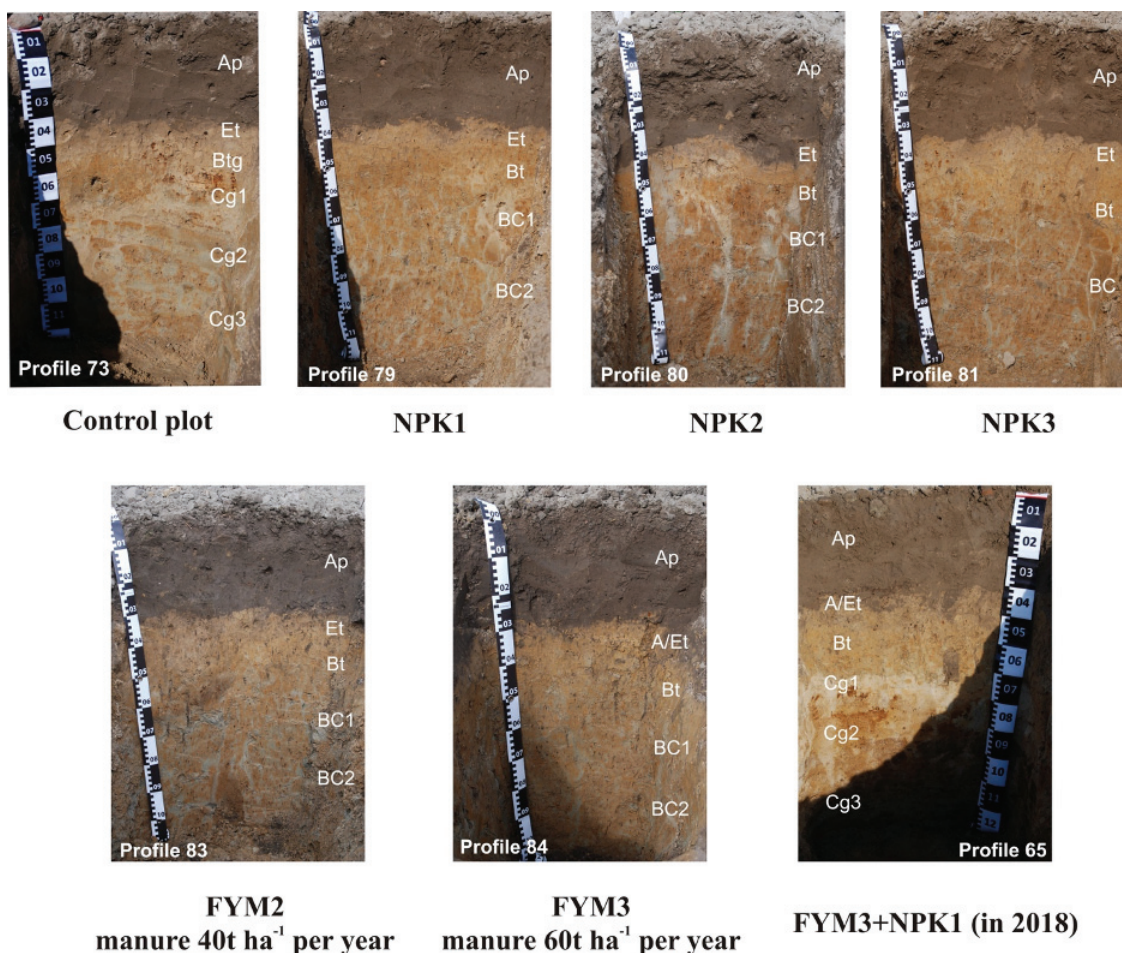


Fig. 2. Studied soil profiles

mineral fertilizers used were ammonium nitrate (34% N), triple superphosphate (46% P_2O_5), and potassium sulphate (50% K_2O) (Rumpel and Ostrzycka, 1999). One of the plots (no. 73) was the control plot (a plot without any fertilization and manuring). Plot no. 65 was a plot where both NPK fertilizers, and FYM were applied. This plot was characterized by high-dose manuring (FYM3 – 60 t ha^{-1} per year) and a change of NPK fertilizer formula alternating between NPK1, NPK2, and NPK3 with a frequency of every 3 years.

The field works were carried out in April 2019. Seven soil profiles (about 110–120 cm deep) were prepared (one profile for each experimental plot) (Fig. 2). Soil horizons were distinguished in the soil profiles. The profiles were described according to the Guidelines for soil description (2006). Soil samples were taken from each soil horizon distinguished in the field.

2.2. Field studies and analytical methods

Soil samples taken from each soil horizon were subject to laboratory analyses. In total, 36 soil samples were investigated. In the laboratory, living roots were removed from soil samples and then the samples were dried at room temperature and sieved through a 2 mm sieve to obtain fine earth (<2 mm) from soil samples. Contents of rock fragments (>2 mm) were deter-

mined by dry sieving. The properties of fine earth were determined utilizing common pedological methods (Pansu and Gautheyrou, 2006). Soil samples were analyzed with 2 replications for each selected soil property.

Soil colour was determined in the field based on slightly moist samples with the application of the Munsell Soil Colour Charts (2009) (Table 2). Particle size distribution was determined by Bouyoucos–Casagrande hydrometer method as modified by Prószyński (Brogowski and Czerwiński, 2016). Soil textural classes were defined according to the U.S.D.A. classification (Soil Survey Division Staff, 1993). Soil pH was measured using the potentiometric (electrometric) method in H_2O and 1 mol $KCl \cdot dm^{-3}$. Carbonate content (in %) was determined as a calcium carbonate equivalent using the Scheibler volumetric method (Brogowski and Czerwiński, 2016). Total carbon (TC), total nitrogen (TN), and total sulphur (TS) contents were determined using CHNS elemental analyzer (the vario MACRO cube, Elementar). In samples containing no carbonates, TC values from CHNS elemental analyzer were assumed as total organic carbon (TOC) contents. The TOC concentration in carbonate-bearing samples was measured using dichromate oxidation techniques (Tyurin method; digestion reagent: $K_2Cr_2O_7$ and H_2SO_4 ; titrant: $FeSO_4 \cdot 7H_2O$) (Brogowski and Czerwiński, 2016). The C/N ratio was calculated based on TOC and TN contents.

Table 2

Select physical properties of the studied soils

Profile	Treatment*	Depth (cm)	Horizon	Rock fragments (>2 mm) (%)	Particle size distribution (%)			Soil textural class (USDA)
					Sand (2–0.05 mm)	Silt (0.05–0.002 mm)	Clay (<0.002 mm)	
73	Control profile	0–30	Ap	4.8	78	13	9	Sandy Loam
		30–45	Et	4.8	83	10	7	Loamy Sand
		45–60	Btg	4.4	73	12	15	Sandy Loam
		60–70	Cg1	7.3	91	4	5	Sand
		70–100	Cg2	2.8	71	12	17	Sandy Loam
		100–120	Cg3	2.5	70	14	16	Sandy Loam
79	NPK1	0–35	Ap	4.5	75	16	9	Sandy Loam
		35–50	Et	2.4	68	16	16	Sandy Loam
		50–60	Bt	2.3	65	12	23	Sandy Clay Loam
		60–80	BC1	2.4	58	19	23	Sandy Clay Loam
		80–120	BC2	2.2	58	20	22	Sandy Clay Loam
80	NPK2	0–35	Ap	5.3	75	17	8	Sandy Loam
		35–50	Et	5.4	73	16	11	Sandy Loam
		50–60	Bt	3.4	76	8	16	Sandy Loam
		60–80	BC1	2.8	60	20	20	Sandy Clay Loam
		80–110	BC2	3.1	64	18	18	Sandy Loam
81	NPK3	0–30	Ap	3.0	76	15	9	Sandy Loam
		30–50	Et	3.1	79	15	6	Loamy Sand
		50–70	Bt	2.7	69	14	17	Sandy Loam
		70–110	BC	2.4	63	18	19	Sandy Loam
83	FYM2	0–30	Ap	5.2	73	20	7	Sandy Loam
		30–40	Et	12.0	67	19	14	Sandy Loam
		40–60	Bt	3.3	65	18	17	Sandy Loam
		60–80	BC1	3.1	60	17	23	Sandy Clay Loam
		80–100	BC2	3.4	61	19	20	Sandy Clay Loam
84	FYM3	0–30	Ap	5.4	73	18	9	Sandy Loam
		30–40	A/Et	3.4	66	17	17	Sandy Loam
		40–60	Bt	2.9	61	18	21	Sandy Clay Loam
		60–80	BC1	2.4	62	18	20	Sandy Clay Loam
		80–110	BC2	3.4	62	19	19	Sandy Loam
65	FYM3 + NPK1	0–30	Ap	5.2	79	14	7	Loamy Sand
		30–40	A/Et	6.2	75	15	10	Sandy Loam
		40–60	Bt	3.7	66	15	19	Sandy Loam
		60–70	Cg1	0.9	95	2	3	Sand
		70–105	Cg2	1.6	97	1	2	Sand
		105–120	Cg3	38.8	85	3	12	Loamy Sand

* Explanations of treatment as in Table 1.

Total potential acidity (TPA) (so-called hydrolytic acidity) was measured by the Kappen method (extraction using $1 \text{ mol} \cdot \text{dm}^{-3}$ calcium acetate and titration using $0.1 \text{ mol NaOH} \cdot \text{dm}^{-3}$) (Brogowski and Czerwiński, 2016). Exchangeable acidity (EA), including exchangeable H^+ and Al^{3+} , was determined by the Sokolov method (extraction using $1 \text{ mol} \cdot \text{dm}^{-3}$ potassium chloride and titration using $0.05 \text{ mol NaOH} \cdot \text{dm}^{-3}$) (Brogowski and Czerwiński, 2016). Total exchangeable bases (TEB), i.e. Ca^{2+} , Mg^{2+} , K^+ , and Na^+ , were extracted using ammonium acetate ($\text{pH}=7.0$) and ammonium chloride ($\text{pH}=8.2$) in non-carbonate and carbonate-bearing soil samples, respectively (Brogowski and Czerwiński, 2016). Contents of Ca^{2+} and Mg^{2+} in extracts were determined using atomic absorption spectrometry (AAS) (PERKIN ELMER 2100 apparatus) and contents of K^+ and Na^+ were measured using the emission (flame) spectrophotometry (BWB XP apparatus). The total of exchangeable bases (TEB) was then calculated. Cation exchange capacity (CEC) was obtained as a sum of EA and TEB. Base saturation (BS) was calculated as a percentage of TEB in CEC.

The soil profiles were classified according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2022) and Polish Soil Classification (Systematyka Gleb Polski), (2019).

Selected properties of soils (pH, TPA, TOC, TN, TS, CEC) were used for statistical analysis. For this study, Principal Component Analysis and Classification (PCCA) was applied in order to find the most important factors controlling the properties of studied soils. Before the analysis, the data was standardized. The number of factors was selected based on the eigenvalues. The analysis was done in STATISTICA 13 (StatSoft).

3. Results

3.1. Morphology and classification of the studied soil profiles

The morphology of the individual profiles is very similar (Fig. 2). Their thickness is all up to 120 cm. Clearly visible soil horizons were distinguished in soil profiles by their colour. Typically, from 4 to 6 genetic horizons were distinguished, most often with distinct or sharp transitions. Soil profiles had a general sequence of soil horizons as follows: Ap-Et-Bt-C. The Ap surface horizons were characterized by the accumulation of humified SOM and dark colour. The Et horizons were recognized by the occurrence of a soil material with pale brown colour immediately below the Ap horizon. The Bt horizons were layers of illuvial concentration of clay minerals and more orange colour than the overlying and underlying horizons. The interfingering of coarser-textured grey material into a finer-textured Bt horizons occurred in some soil profiles (Fig. 2). The C horizons were distinguished in the subsoil of each soil profile.

Small rock fragments (mostly igneous rocks coming from the glacial till) were found in all soil profiles. Roots were present in the entire soil profiles; however, the majority of roots were found at a depth of 30 cm (Ap horizon).

The soil profiles were classified as different variants of Retisols or Luvisols (IUSS Working Group WRB, 2022). According to

the Polish Soil Classification (2019), the soils can be classified as different variants of “gleby płowe” (typical clay illuvial soils and tonguing clay-illuvial soils).

3.2. Particle size distribution

Rock fragment content did not exceed 7% in the majority of soil horizons with some exception in a few horizons (Table 2). Studied soils were characterized by the texture of sandy loam, loamy sand, sand, and sandy clay loam (Table 2). Although the studied soils occurred in a small area, they showed a relatively big diversity of textures of materials constituting the soil substrate. The most common situation occurring in the majority of the studied soils was that the topsoil (Ap, sometimes also Et horizons) had the texture of sandy loam (or loamy sand) with a clay content of 6–9%, whereas the subsoil had the heavier texture (sandy clay loam or sandy loam) with clay content 15–23%. In some soil profiles (e.g. profile 65 and 73) there were sandy layers (C horizons) in the subsoil.

3.3. Soil chemical properties

The value of $\text{pH}_{\text{H}_2\text{O}}$ of the studied soils was in the range of 5.1–6.5 (Table 3). The $\text{pH}_{\text{H}_2\text{O}}$ in profile 73 (control plot) was between 5.5 and 6.2. The soil profiles on plots where NPK fertilizers were used alone, showed the most acidic reaction ($\text{pH}_{\text{H}_2\text{O}}$ 5.1–6.0) among all studied soils. There was a trend of the pH decrease in A horizons of soil profiles 79, 80, and 81 with the increasing dose of NPK mineral fertilizers. The highest $\text{pH}_{\text{H}_2\text{O}}$ values (from 6.2 to 6.5) was detected in profiles 83 and 84 on plots where FYM was added alone (Table 3). Relatively high pH in these two soils occurred throughout both soil profiles. Profile 65 on a plot with a combination of NPK fertilizers and FYM was characterized by low pH (5.5) in the topsoil similar to that in profiles where NPK mineral fertilizers were applied. Very small contents of carbonates occurred in the topsoil (A horizon) of several soil profiles with the highest contents of 0.18% (Table 3).

The TOC, TN, and TS contents in the studied soils were in the ranges of 0.05–1.15%, 0.02–0.12% and 0.003–0.02%, respectively. The highest TOC, TN, and TS contents were noted in the A horizons of the studied soils (Table 3). All studied soil profiles were characterized by a decrease in TOC, TN, and TS contents with the depth of the soil profile. In soil on plots where FYM was applied, contents of TOC, TN, and TS were the highest (1.15%, 0.12%, and 0.02%, respectively).

3.4. Sorption properties of the studied soils

The EA in the studied soil was in the range from 0.04 to 0.32 cmol kg^{-1} (Table 4). Exchangeable H^+ predominated in EA of all studied soils except for profiles 80 and 81 on plots where the highest doses of NPK fertilizers were applied. In these two profiles, exchangeable Al^{3+} predominated over H^+ . The highest contents of exchangeable Al^{3+} were determined in Bt horizons of soils on control plot and plots with NPK fertilization. Exchangeable H^+ predominated over exchangeable Al^{3+} in profiles 83 and 84 on plots where FYM was applied (Table 4).

Table 3
Chemical properties of the studied soils

Profile	Treatment*	Depth (cm)	Horizon	pH _{H₂O}	pH _{KCl}	eq. CaCO ₃	TOC	TN	TS	C:N
						(%)				
73	Control profile	0–30	Ap	6.2	5.8	0.18	0.47	0.05	0.009	9.5
		30–45	Et	5.9	5.0	–	0.14	0.03	0.005	5.1
		45–60	Btg	5.5	4.2	–	0.15	0.03	0.004	4.5
		60–70	Cg1	6.1	4.8	–	0.05	0.02	0.003	2.6
		70–100	Cg2	6.1	4.7	–	0.07	0.03	0.003	2.5
		100–120	Cg3	6.1	4.7	–	0.07	0.03	0.003	2.6
79	NPK1	0–35	Ap	6.0	5.5	–	0.66	0.07	0.012	9.9
		35–50	Et	5.7	4.5	–	0.18	0.04	0.006	4.7
		50–60	Bt	5.4	4.2	–	0.18	0.04	0.006	4.6
		60–80	BC1	5.7	4.4	–	0.12	0.03	0.005	3.5
		80–120	BC2	5.9	4.5	–	0.08	0.03	0.004	2.4
80	NPK2	0–35	Ap	5.4	4.6	0.08	0.50	0.06	0.009	8.9
		35–50	Et	5.2	4.2	–	0.15	0.04	0.005	4.2
		50–60	Bt	5.2	4.1	–	0.12	0.03	0.005	3.6
		60–80	BC1	5.3	4.2	–	0.11	0.04	0.006	3.1
		80–110	BC2	5.4	4.3	–	0.07	0.03	0.005	2.1
81	NPK3	0–30	Ap	5.3	4.3	–	0.45	0.05	0.008	8.9
		30–50	Et	5.1	4.3	–	0.12	0.02	0.005	4.9
		50–70	Bt	5.3	4.2	–	0.11	0.03	0.005	3.6
		70–110	BC	5.7	4.5	–	0.08	0.03	0.005	2.7
83	FYM2	0–30	Ap	6.5	6.4	–	1.14	0.11	0.020	10.2
		30–40	Et	6.3	5.7	–	0.20	0.04	0.005	4.8
		40–60	Bt	6.4	5.5	–	0.16	0.04	0.005	4.6
		60–80	BC1	6.5	5.2	–	0.12	0.04	0.004	3.1
		80–100	BC2	6.2	5.1	–	0.09	0.03	0.003	3.2
84	FYM3	0–30	Ap	6.5	6.3	–	1.15	0.12	0.020	10.0
		30–40	A/Et	6.4	5.7	–	0.20	0.04	0.005	5.0
		40–60	Bt	6.5	5.7	–	0.17	0.04	0.004	4.6
		60–80	BC1	6.5	5.5	–	0.10	0.03	0.003	3.3
		80–110	BC2	6.5	5.4	–	0.08	0.03	0.003	2.6
65	FYM3 + NPK1	0–30	Ap	5.5	4.9	0.12	0.65	0.07	0.012	9.4
		30–40	A/Et	5.8	4.9	–	0.23	0.04	0.006	6.2
		40–60	Bt	5.9	4.7	–	0.20	0.04	0.006	4.8
		60–70	Cg1	5.9	5.0	–	0.06	0.02	0.004	2.6
		70–105	Cg2	6.0	5.1	–	0.06	0.02	0.004	2.5
		105–120	Cg3	6.1	5.1	–	0.09	0.03	0.004	3.5

Explanations of symbols: eq. CaCO₃ – calcium carbonate equivalent; TOC – total organic carbon; TN – total nitrogen; TS – total sulphur; C:N – the TOC to TN ratio.

* Explanations of treatment as in Table 1.

Table 4
Sorptions properties of the studied soils

Profile	Treatment*	Depth (cm)	Horizon	EA		TPA	TEB				CEC	BS (%)
				H ⁺	Al ³⁺		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺		
(cmol kg ⁻¹)												
73	Control profile	0–30	Ap	0.03	0.01	1.35	3.19	0.59	0.07	0.01	3.91	98.98
		30–45	Et	0.03	0.02	1.12	2.14	0.34	0.04	0.01	2.58	98.45
		45–60	Btg	0.04	0.16	1.62	7.27	0.66	0.15	0.03	8.31	97.59
		60–70	Cg1	0.03	0.02	0.67	1.82	0.16	0.03	0.02	2.07	98.06
		70–100	Cg2	0.05	0.00	1.15	9.57	0.80	0.20	0.03	10.65	99.53
		100–120	Cg3	0.05	0.00	1.02	8.67	0.72	0.19	0.03	9.67	99.38
79	NPK1	0–35	Ap	0.04	0.03	1.71	4.18	0.73	0.15	0.02	5.16	98.64
		35–50	Et	0.04	0.05	1.71	5.80	0.78	0.14	0.02	6.84	98.68
		50–60	Bt	0.05	0.11	1.90	9.27	1.06	0.21	0.03	10.73	98.51
		60–80	BC1	0.06	0.03	1.68	10.62	1.18	0.24	0.04	12.16	99.26
		80–120	BC2	0.04	0.05	1.43	9.97	1.17	0.22	0.04	11.50	99.22
80	NPK2	0–35	Ap	0.06	0.07	2.40	2.52	0.51	0.27	0.01	3.44	96.22
		35–50	Et	0.05	0.15	1.61	3.41	0.67	0.13	0.02	4.43	95.48
		50–60	Bt	0.04	0.25	1.70	5.87	0.56	0.17	0.02	6.92	95.81
		60–80	BC1	0.06	0.10	1.68	9.78	0.76	0.22	0.03	10.96	98.54
		80–110	BC2	0.05	0.13	1.61	9.07	0.83	0.20	0.04	10.31	98.25
81	NPK3	0–30	Ap	0.04	0.25	2.58	2.15	0.44	0.40	0.01	3.30	91.20
		30–50	Et	0.06	0.26	1.61	1.28	0.29	0.11	0.01	2.02	84.12
		50–70	Bt	0.04	0.16	1.55	6.72	0.79	0.30	0.02	8.03	97.51
		70–110	BC	0.04	0.03	1.37	10.01	0.91	0.29	0.03	11.31	99.38
83	FYM2	0–30	Ap	0.06	0.03	1.38	6.66	1.38	0.41	0.03	8.58	98.95
		30–40	Et	0.06	0.01	1.10	5.28	1.47	0.40	0.04	7.26	99.04
		40–60	Bt	0.04	0.01	1.17	6.82	1.73	0.48	0.04	9.13	99.34
		60–80	BC1	0.05	0.00	1.11	10.85	2.02	0.38	0.09	13.39	99.63
		80–100	BC2	0.04	0.01	0.99	10.37	1.61	0.23	0.10	12.36	99.60
84	FYM3	0–30	Ap	0.07	0.00	1.49	7.06	1.39	0.46	0.03	9.01	99.22
		30–40	A/Et	0.06	0.00	1.31	6.30	2.02	0.58	0.04	9.01	99.33
		40–60	Bt	0.06	0.01	1.25	8.18	2.30	0.84	0.07	11.45	99.39
		60–80	BC1	0.04	0.03	1.01	9.04	1.94	0.64	0.09	11.79	99.41
		80–110	BC2	0.06	0.00	0.86	9.43	1.51	0.38	0.10	11.48	99.48
65	FYM3 + NPK1	0–30	Ap	0.06	0.02	2.33	2.51	0.48	0.30	0.01	3.38	97.63
		30–40	A/Et	0.05	0.02	1.91	3.18	0.86	0.30	0.02	4.43	98.42
		40–60	Bt	0.04	0.04	2.00	6.35	1.73	0.65	0.02	8.83	99.21
		60–70	Cg1	0.01	0.03	0.77	1.03	0.27	0.12	0.02	1.48	97.29
		70–105	Cg2	0.00	0.04	0.76	1.00	0.24	0.11	0.02	1.41	97.16
		105–120	Cg3	0.03	0.01	1.24	4.88	1.07	0.46	0.04	6.48	99.38

Explanations of symbols: EA – exchangeable acidity; TPA – total potential acidity (hydrolytic acidity); TEB – total exchangeable bases; CEC – cation exchange capacity; BS – base saturation.

* Explanations of treatment as in Table 1.

The TPA (hydrolytic acidity) was in the range of 0.67–2.58 cmol kg⁻¹ (Table 4). The highest TPA values were determined in the topsoil of profiles 79, 80, and 81 on plots with NPK fertilization, as well as in the topsoil of profile 65 on a plot with a combination of NPK fertilization and FYM.

The TEB was in the range of 1.37 to 13.34 cmol kg⁻¹ (Table 4). The highest TEB values were determined in the subsoil horizons, except for profile 65, where the subsoil was built of sandy material. The predominating base cation was Ca²⁺, followed by Mg²⁺, K⁺, and Na⁺.

The CEC in the studied soils was in the range of 1.41 to 13.39 cmol kg⁻¹ (Table 4). Similar to the TEB, high CEC values were determined in the subsoil horizons, except for profile 65. Considering A horizons alone, the highest CEC was detected in A horizons in profiles 83 and 84 where FYM was applied. However, it does not apply for A horizon of profile 65 where a combination of NPK fertilizers and FYM was added.

The BS values were in the range of 84.1–99.6% (Table 4). The lowest BS values were determined in the topsoil of profile 81 on a plot where the highest doses of NPK fertilizers were applied.

4. Discussion

The effects of 96 years of mineral and organic fertilizers application were recognized in the studied soils. The long-term NPK fertilization and FYM application had an impact on soil chemical and sorption properties. Statistical analysis revealed

that there are two factors controlling the effect of fertilization on the properties of soils (Fig. 3). First factor explained 53% of data variability and there was related to the TOC, TN, and TS content in soils. The second factor, related to pH and TPA, explained 29% of data variability.

The study showed that there was a strong influence of mineral and organic fertilization on soil pH. In all soil samples studied, there was a clear difference in soil pH between the soil profiles using NPK fertilizers and the soil profiles with FYM compared with the control profile (Table 3). The former soils had the lowest pH among all soils studied. Furthermore, the PCCA analysis showed that the NPK fertilizers mostly affected the Ap horizons, where the TPA is the highest amongst studied horizons. On the other hand, soils on plots where FYM was applied alone had a slightly acidic to near-neutral reaction. That feature is well expressed in Ap horizons of the studied soils. The pH_{H2O} of Ap horizon was as follows: 6.2 (control plot), 6.0 (low NPK1 dose), 5.4 (medium NPK2 dose), 5.3 (high NPK3 dose), 6.5 (both soils with FYM), and 5.5 (FYM + NPK). The results presented herein are in the line with the results by Blecharczyk (1999) who showed that FYM application makes a higher pH value than the use of mineral fertilizers (alone or in combination with FYM). In a field experiment of long-term slurry fertilization, FYM and NPK conducted over 21 years the authors showed the effect of fertilizer application on hydrogen ions and the soil TPA had an increase in all soil horizons of the profile using NPK compared to the profile using FYM (Mazur and Sądej, 1996). Besides, the study results also show that the effect of long-term fertilization with reasonable NPK dosage

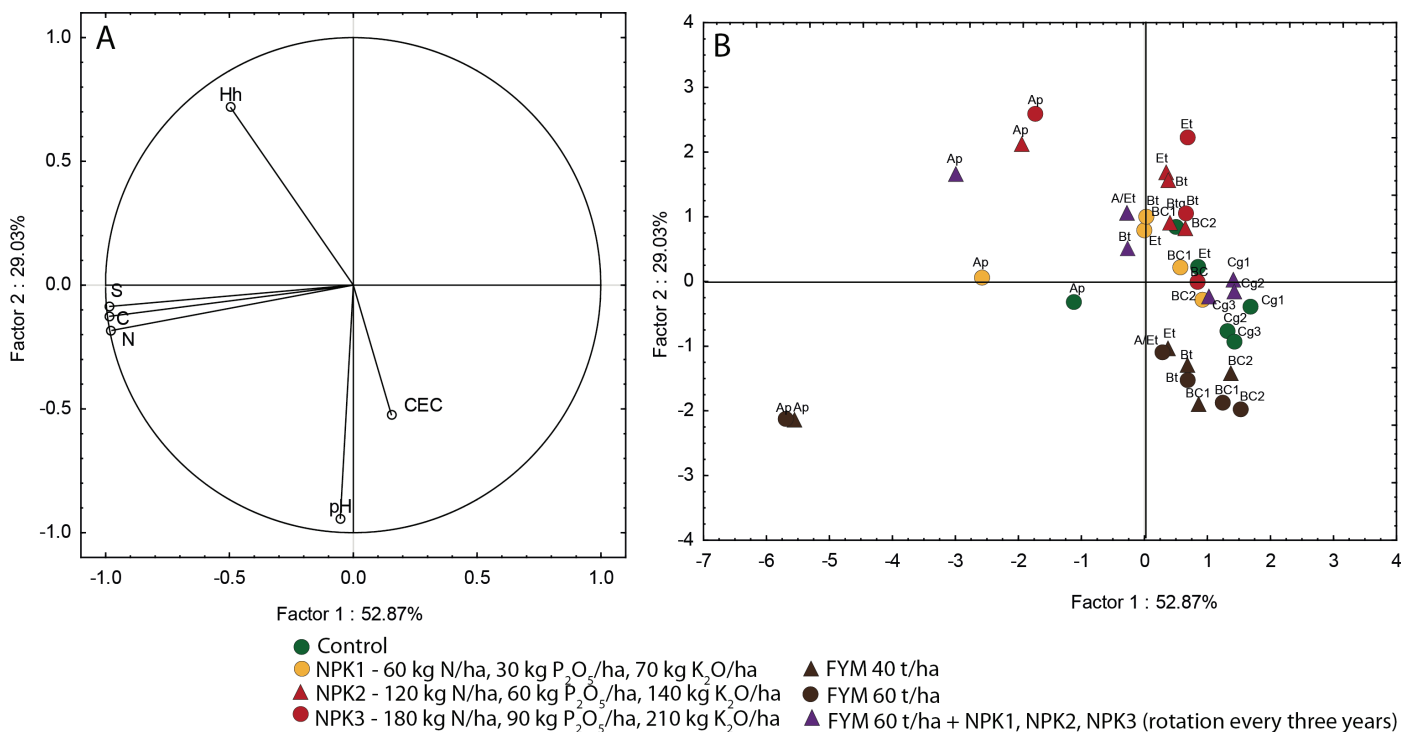


Fig. 3. Principal Component Analysis and Classification (PCCA) of the studied soils (A – projection of variables onto the plane of factors; B – projection of cases onto the plane of factors)

(NPK1) seems to have lower effect on soil acidity compared to NPK2 and NPK3 (Fig. 3). This is also consistent with a 28-year fertilization experiment, which showed that the long-term mineral fertilizer use decreases the pH value of the soil (Ge et al., 2018). The study results showed that high-dose FYM application (without NPK fertilization) mitigates soil acidification. Moreover, the effect of the application of high doses (40 and 60 t ha⁻¹ per year) of FYM seems to be a slight increase of soil pH not only in the topsoil but also throughout the soil profile (down to 120 cm) what was confirmed during PCCA analysis (Fig. 3). It is commonly known that the use of certain fertilizers (e.g. ammonium sulphate, urea) causes soil acidification (Barak et al., 1997). Acidification of soils may accelerate the weathering of minerals, as well as may cause the transformation of the clay minerals and the formation of non-exchangeable hydroxy-Al complexes in the interlayers of swelling clay minerals (smectite and vermiculite). Clay minerals are a very sensitive indicators of changes in soil properties under the influence of long-term K fertilization (Holthusen et al., 2012).

The study showed that there was an influence of organic fertilization on an accumulation of SOM expressed by the increase of TOC, TN, and TS content due to long-term high-dose FYM application. This was true for an 8-year experiment in which manure increased soil TOC (average 4 to 14%) while slurring at a dose equivalent to NPK in manure did not change the amount of this ingredient (Jarecki and Krzywy, 1991). This relationship was clearly visible in this study in Ap horizons, where 40 t FYM ha⁻¹ and 60 t FYM ha⁻¹ was added to soils (Fig. 3). It is commonly known that long-term use of manure increases the content of various components in the soil (e.g. soil organic carbon (SOC), TN, as well as macronutrients and micronutrients) (Wang et al., 2009; Li et al., 2010; Kołodziejczyk et al., 2017; Murawska et al., 2017). Besides, the application of completely NPK mineral fertilizers for a long time also increases the SOM (Mercik et al., 2005). Other similar results were obtained in other long-term experiments (Jenkinson et al., 1994; Weigel et al., 1998; Blecharczyk, 1999). SOC is an important constituent of soil because it regulates soil moisture and structure, and influences the availability of nutrients and microbial activity (Krull et al., 2003). The studies by Šimanský and Jonczak (2019) indicate the importance of the quantity and quality of SOM related to CEC, especially in sandy soils that have been fertilized with mineral fertilizers for a long time. Long-term fertilization influences not only agricultural soils but also forest soils. After a 19-year experiment at Lipki Experimental Station, Krzywy et al. (1989) showed that the use of NPK had no discernible effect on soil TN content, however, the use of FYM demonstrated that had a positive effect on the TN content.

The study showed that there is an influence of mineral and organic fertilization on sorption properties. The results show that in soil profiles on the experimental plots using only mineral NPK fertilization, the EA and TPA values are higher than in the control plot (Table 4). In a study of the most important effects of long-term fertilizer application on soil properties, Mercik (1994) showed that compared to mineral fertilizers, manure resulted in increased humus content, CEC, and total

exchange base cation. The increase in EA is accompanied by a decrease in the amount of exchangeable basic cations and a decrease in the CEC of the soil. This is particularly well expressed in Ap horizons of soils treated with increasing doses of NPK in comparison with a soil on control plot (Table 4). Moreover, the study showed that the acidification related to the application of the highest doses of NPK fertilizers causes the release of exchangeable Al to the soil. The profile 81 with the highest dose of NPK fertilizers and the lowest pH_{H2O} in the topsoil (Ap and Et horizons) (Table 3), had also the highest contents of exchangeable Al and the lowest BS of sorption complex (Table 4). The use of mineral fertilizers (NK, NP, and NPK) led to changes in the chemical properties of the soil studied compared to FYM alone such as a decrease in soil pH, an increase in exchangeable Al, a decrease in available Mg, an increase in TOC and of P and K available (Wenglikowska, 1986). When the dose of K applied to the soil was increased, the exchange rate of K in the soil increased significantly. This is clearly shown in the NPK2, and NPK3 treatments and most clearly in the treatment with the highest fertilizer dose (NPK3). In the entire study profile, the K content tends to increase gradually with the depth of the earth horizons. Meanwhile, Ca and Mg contents tend to decrease gradually, which is completely consistent with the research of Stępień (1989). This is an adverse phenomenon in soil, as exchangeable Al damages soil roots. Also, a study by Caires et al. (2008) showed that the exchangeable Al level in the soil of 3 mmol_(,) dm⁻³ is considered to be very important for wheat root development. Wheat grain yield correlates well with root length per soil surface area. The results show that aluminium toxicity is low in no-till systems during seasons with suitable and well-distributed rainfall, but under unfavourable rain conditions, aluminium toxicity severely affects root growth and yield. Contrary to NPK fertilization and soil acidification, the application of high doses of FYM has a positive effect on sorption properties as it increases the CEC of soils (Fig. 3). The results by Reeves (1997) showed that the CEC increased after fertilization with organic fertilizers and NPK fertilizer. Using FYM significantly increased the adsorption capacity of experimental soil compared to using NPK. The degree of soil saturation with alkalinity was also highest in the case of FYM. The ratio of exchangeable cations in the soil absorption complex is as follows: Ca²⁺>Mg²⁺>K⁺>Na⁺. However, there was no obvious difference in effect between the treatments using FYM (Mazur and Sądej, 1989). The CEC depends on soil pH, quantity and quality of clay minerals and Fe, Al, and Si compounds, as well as the type of humic substances in the soil. It was shown (Tombácz et al., 2004) that the of humic acids in the interaction with clay minerals and iron oxide have an important influence on the adsorption capacity of the soil.

In this paper, the influence of the long-term application of different mineral and organic fertilizers on soil properties was investigated. However, further studies should be conducted focusing on the influence of long-term use of mineral and organic fertilizers on the mineral composition of clay fraction, as well as micromorphological features of soils.

5. Conclusions

The obtained results permit drawing the following conclusions:

1. The present study showed that 96-year use of mineral (NPK) and organic (FYM) fertilizers had a distinct influence on soil chemical and sorption properties. The effect of fertilization was best expressed in the topsoil (in particular in A horizon).
2. Long-term use of mineral (NPK) fertilization led to the decrease of soil pH down to the value of 5.1, whereas long term high-dose FYM application led to the stabilization of soil pH throughout the soil on a level of 6.2–6.5.
3. Long-term high-dose FYM application (40 t and 60 t ha⁻¹ per year) led to the significant accumulation of SOM expressed by the increase of TOC, TN, and TS concentrations in the Ap horizons of the studied soils.
4. The NPK fertilization led to the acidification of the whole soil profiles which was expressed by the increase of exchangeable acidity and total potential acidity (hydrolytic acidity). Acidification led to the release of exchangeable Al. Long-term high-dose use of FYM increased the CEC in Ap horizons of soils.

Acknowledgments

The study was financed by the subvention of the Polish Ministry of Education and Science for the Institute of Agriculture and Doctoral School of the Warsaw University of Life Sciences – SGGW, Poland. The author thanks Prof. Wojciech Stępień (Warsaw University of Life Sciences – SGGW) and Dr. Kazimierz Felczyński (Institute of Horticulture in Skierniewice) for their helpful comments and a help during the field works. The author also thanks Dr. Artur Pędziwiatr (Warsaw University of Life Sciences – SGGW) for a help in statistical analyses. Three anonymous reviewers are acknowledged for their valuable comments.

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