

Article

The Mineral Fertilizer-Dependent Chemical Parameters of Soil Acidification under Field Conditions

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Abstract: Soil acidification in agroecosystems is a natural process that could be accelerated, mainly by the inappropriate application of mineral fertilizers, or prevented, by sustainable management practices. On the basis of a three-year field study in a grassland agroecosystem, the impact of different rates of fertilization with nitrogen (N), phosphorus (P), and potassium (K) on soil chemical parameters related to soil acidity was evaluated. It was found that high-rate fertilization with ammonium nitrate accelerated the soil acidification process, which was additionally intensified by the application of superphosphate and potassium salt. The sum of exchangeable base cations, the values of base saturation and hydrolytic acidity in the soil reflected the interactions between the applied NPK-fertilizer levels. Considering chemical parameters related to soil acidity studied in this experiment, it seems that the best strategies for mitigating soil acidification in grasslands are reducing nitrate leaching, changing fertilizer types and increasing the input of base cations.

Keywords: nitrogen fertilizers; phosphorus fertilizers; potassium fertilizers; grasslands; soil pH; acid cations; base cations

1. Introduction

Soil acidification, one of the primary constraints for the global productivity and sustainability of agriculture, affects almost 40% of the world's farmlands. It threatens agroecosystem functions and services and leads mainly to: (i) a decrease in cation exchange capacity and a reduction in the potential of soils for the retention of macro- and microelements in cation forms, which are subsequently susceptible to losses; (ii) a limitation of biological processes in soils that have remarkable cascading impacts on biodiversity and nutrient cycling, mainly nitrogen and carbon, including the formation of greenhouse gases; (iii) less availability/deficiencies of nutrients; (iv) the mobilization of potentially toxic elements and their subsequent transfer in the food chain; (v) the depression of crop growth and yields [1–7].

Although soil acidification is a naturally existing process, it has been intensified recently as a result of the overuse of nitrogen fertilizers [5,6,8–10]. Today approximately fifty percent of the world's population is provided with food obtained with the use of them. The anticipated population increase to almost ten billion by 2050 will elevate agricultural production by another 50–98%. Increased food

demand and dietary changes are likely to contribute to the further intensified use of fertilizers and thus soil acidification [11–13].

The main mechanisms of soil acidification induced by nitrogen fertilizers are connected with: (i) the displacement of acid ions and basic cations from the sorption complex, which leads to an increase in active acidity and the leaching of base cations with accompanying anions, respectively; (ii) the absorption by plants and/or microorganisms of the NH_4^+ and the secretion of H^+ (physiological acidity), $\text{NH}_4^+ + \text{ROH} \rightarrow \text{RNH}_2 + \text{H}_2\text{O} + \text{H}^+$; (iii) the nitrification of $\text{NH}_4\text{-N}$, $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$; and (iv) ammonia volatilization, $\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$. Unlike ammonium fertilizers, nitrate based fertilizers usually increase soil pH due to a combination of such processes as: nitrate uptake by plants and microorganisms, $\text{NO}_3^- + \text{ROH} + \text{H}^+ + 2\text{CH}_2\text{O} \rightarrow \text{RNH}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$ and/or denitrification, $5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O}$. However, $\text{NO}_3\text{-N}$ leaching accompanied with base cation has the potential to contribute to intensifying acidification [1,2,4,5,9,14,15]. Gundersen et al. [16] estimated that annually one kilomol of hydrogen ions per hectare can be liberated as the result of the leaching of 14 kg $\text{NO}_3\text{-N ha}^{-1}$. It is generally assumed that soil acidity rises with increasing doses of N fertilizers and their acidification potential decreases as follows: urea > ammonium nitrate = urea-ammonium nitrate > calcium-ammonium nitrate > calcium nitrate. Additionally, agroecosystems intensively fertilized with N may act as a source for acidifying gaseous pollutants (NO_x and NH_3) [12]. According to a meta-analysis made by Tian and Niu [14], soil pH dropped linearly with the rising doses of nitrogen applied, which was to a greater extent caused by ammonium nitrate and urea than by $\text{NH}_4\text{-form}$ fertilizers. The dynamics of the soil acidification in response to nitrogen application depend on abiotic as well as biotic factors (e.g., climate, land cover, and soil properties). Generally, high precipitation, especially when it outweighs evaporation, low temperatures, and plant species, found for example in the grasslands, uptaking high amounts of base cations and/or $\text{NH}_4^+\text{-N}$ or secreting organic acids, accelerate acidification, while large contents of organic and mineral colloids, particularly with a predominance of permanent, pH-independent charges on their surfaces (e.g., vermiculite and montmorillonite) and high base cation pool mitigate this process [3,10,14].

Until now, the majority of studies concerning soil acidification has focused on nonagricultural areas [10] or took into account only nitrogen fertilizers in arable lands, while very little research has attempted to assess their increasing levels and interactions with phosphorus and potassium fertilizers under grassland agroecosystems.

The aim of this study was to evaluate the impact of different rates of fertilization with nitrogen (N), phosphorus (P), and potassium (K) and their interactions on chemical parameters related to soil acidity (pH, hydrolytic acidity, exchangeable base cations, and cation exchange capacity).

2. Materials and Methods

2.1. Site Description and Experimental Design

A three-year field study was conducted at the Experimental Farm in Elizówka (51°17'20.739" N 22°34'32.766" E) on Luvisol (loamy sand) with an acidic reaction ($\text{pH} = 4.9 \pm 0.05$), a low content of organic carbon according to the European Database on Soils ($10.4 \pm 0.1 \text{ g SOC kg}^{-1}$), a very high availability of phosphorus ($77.2 \pm 0.78 \text{ mg P kg}^{-1}$), a high availability of potassium ($187.0 \pm 1.23 \text{ mg K kg}^{-1}$), and a low availability of magnesium ($44.0 \pm 0.49 \text{ mg Mg kg}^{-1}$). The test plant was timothy grass (*Phleum pratense* L.), variety Skrzyszowicka. The annual precipitation was 428.4 mm, 442.4 mm and 454.0 mm in the first, second, and third year of the experiment, respectively. Average monthly temperatures in January and July were: -3.2 and 20.4 , -5.0 and 18.5 , -3.7 and 20.2 , respectively. The field experiment was set up in a split-split-plot design with four replicates. The experiment scheme included three factors: (i) three levels of nitrogen rates (120 kg N ha^{-1} (N1), 240 kg N ha^{-1} (N2), 360 kg N ha^{-1} (N3)); (ii) three levels of phosphorus rates ($39.4 \text{ kg P ha}^{-1}$ (P1), $69.8 \text{ kg P ha}^{-1}$ (P2), $104.7 \text{ kg P ha}^{-1}$ (P3)); and (iii) three levels of potassium rates (83 kg K ha^{-1} (K1), 166 kg K ha^{-1} (K2) and 249 kg K ha^{-1} (K3)). The lowest NPK rate (N1, P1, K1) was applied according to fertilizer

recommendations. The conventional rates (double and triple doses of mineral fertilizers) were in line with the farming practices. The area of each treatment was 50 m² (harvested 36 m²).

Nitrogen in the form of ammonium nitrate (AN) (34% N) was used in three split doses at the beginning of the growing season and after the first and second cut (in May and July, respectively). The whole dose of P in the form of granulated triple superphosphate (SP) (20.1% P) and a $\frac{1}{2}$ dose of K in the form of potassium salt (PS) (47.3%) were applied prior to the sowing of timothy seeds. In the second and the third year of the field study, PK fertilization was used after the 3rd cut (in September). The second rate of K was incorporated in the soil after the first cut (in May) each year.

2.2. Soil Sampling and Analysis

Soil samples were collected after each cut at the depth 0–20 cm in accordance with ISO 10381-1:2002 [17], air dried and sieved (<2 mm).

In the prepared soil samples the chemical properties were determined as follows: pH in 1 mol KCl dm⁻³ (potentiometric method) [18], hydrolytic acidity (HA) and exchangeable base cations (BC) with Kappen's method [19]. The Cation Exchange Capacity of the soil (CEC) was calculated according to the following formula: CEC = HA + BC. The data were presented in the paper in the form of the means of the three years of studies.

2.3. Statistical Analysis

The statistical analysis of the results was performed using Statistica PL software (Tulsa, OK, 78 USA). A three-way analysis of variance (ANOVA) and Tukey's mean separation were used to determine the statistical significance at $p < 0.05$. The Pearson's linear correlation coefficient was calculated with a significance level of $p < 0.05$ for all studied parameters.

3. Results and Discussion

The obtained results demonstrated that the application of NPK fertilizers accelerated the acidification process of the studied soil. The significant decrease in soil pH, by 0.5 and 0.2 units on average over three years, occurred under the influence of the triple (360 kg N ha⁻¹) and double (240 kg N ha⁻¹) doses of nitrogen, respectively (Table 1). Other authors also reported that fertilization with ammonium nitrate reduces the soil pH in timothy agroecosystems. The soil pH decreased from 5.9 to 5.3 following the applications of NH₄NO₃ in a seven-year grassland. Annual treatment with 270 kg N ha⁻¹ as AN induced the pH to drop by almost 1.3 units after 25-year-cropping of *Phleum pratense* L. [20,21]. Interestingly, a meta-analysis of 106 studies [14] showed that, due to ecosystem adaptation, a significant impact of nitrogen use on soil acidification was found in studies with a duration of less than 20 years.

Table 1. Impact of NPK fertilizers on soil pH.

Fertilization	P1			P2			P3			Mean N
	K1	K2	K3	K1	K2	K3	K1	K2	K3	
pH										
N1	5.3 ^a *	4.9 ^{b,c}	4.8 ^{c,d}	4.7 ^{d,e}	4.7 ^{d,e}	4.5 ^{f,g}	4.7 ^{d,e}	4.6 ^{e,f}	4.4 ^{g,h}	4.7 ^a
N2	4.9 ^{b,c} *	4.8 ^{c,d} *	4.6 ^{e,f} *	4.5 ^{f,g}	4.4 ^{g,h}	4.1 ⁱ	4.4 ^{g,h}	4.3 ^h	4.3 ^h	4.5 ^b
N3	4.5 ^{f,g} *	4.4 ^{g,h} *	4.4 ^{g,h}	4.3 ^h	4.1 ⁱ *	4.1 ⁱ	4.1 ⁱ	4.1 ⁱ	4.1 ⁱ	4.2 ^c
Mean P		4.7 ^a			4.4 ^b			4.3 ^c		
Mean K	4.6 ^a	4.5 ^b	4.4 ^c							

N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. * The same letter means not significantly different.

The significant differences in soil pH values observed in the experiment were undoubtedly influenced by the nitrogen rates applied (Table 1, Figure 1). Some researchers [22] stated that soil pH

declined significantly when the fertilizer level exceeded 200 kg N ha^{-1} , while below that threshold only slight changes in its value were found. Extensive inputs of ammonium based fertilizers in grasslands accelerate soil acidification predominantly by enhancing the nitrification of ammonium nitrogen to nitrate nitrogen, followed by nitrate leaching accompanied with base cations, promoting their uptake in excess of anions, and BC removal in the repeatedly harvested plant biomass [5,6,20,21,23]. Moreover, 16% of N presented in NH_4NO_3 as ammonium cation could induce physiological acidity and displace base cations binding to the soil surface, increasing their susceptibility to leaching loss and reducing acid-buffering capacity [14].

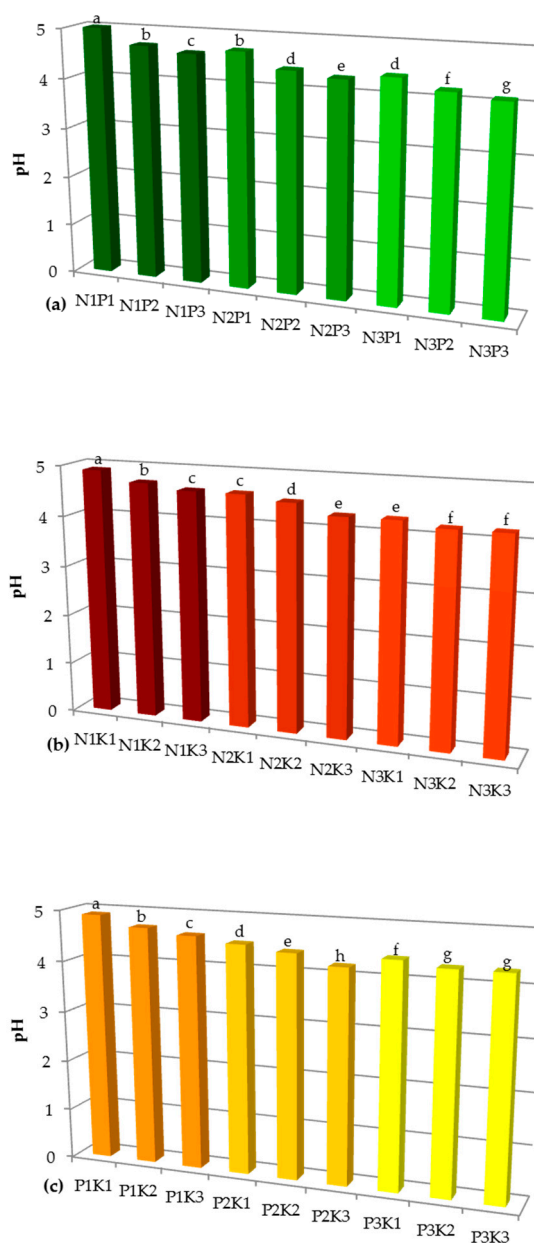


Figure 1. The interaction effect between NP (a) NK (b) and PK (c) on soil pH. N1— 120 kg N ha^{-1} , N2— 240 kg N ha^{-1} , N3— 360 kg N ha^{-1} , P1— $34.9 \text{ kg P ha}^{-1}$, P2— $69.8 \text{ kg P ha}^{-1}$, P3— $104.7 \text{ kg P ha}^{-1}$, K1— 83 kg K ha^{-1} , K2— 166 kg K ha^{-1} , K3— 249 kg K ha^{-1} . The same letter means not significantly different.

The low pH values, ranging from 5.3 to 4.1 (Table 1), found in the experiment potentially inhibited one of the main acidification drivers, i.e., nitrification. Thus, the leaching of NO_3^- originated from AN could play a dominant role in the acidification of the studied soil. It should be noted that under an acidic

environment the grass yield might be reduced, nitrogen use efficiency decreased, and the excess of reactive nitrogen that appears could be subjected to losses generating H⁺ ions [10,24]. This mechanism was not confirmed statistically in the conducted experiment, probably due to the high resistance of *Phleum pratense* L. to acidification (9 on a ten-point scale) [25].

In the present study, the acidifying effect of ammonium nitrate was intensified by phosphorus and potassium fertilization; and significant interactions between NP, NK, PK, and NPK were observed (Table 1, Figure 1). The lowest pH values (4.1) were noted in N₃P₂K₂, N₃P₂K₃, N₃P₃K₁, N₃P₃K₂ and N₃P₃K₃ treatments.

Water-soluble phosphorus fertilizers—chemically acid, but physiologically alkaline, contributed to soil acidification to a lesser extent than the nitrogen one, by approximately 0.4 unit at the highest dose (Table 1). The amount of lime required to neutralize their effect equals 15 kg CaCO₃ per 100 kg of SP, while for AN—61 kg CaCO₃ [3,6].

Additionally, the dissolution of superphosphates in soils leads to the formation of H⁺ ions. The influence of fertilization with potassium chloride on lowering the soil pH is mainly related to the activation of exchangeable and physiological acidity and the leaching of the accompanying anion (Cl). The application of potassium fertilizers also results in the displacement of Ca²⁺ ions from the sorption complex, yield increasing, and BC removal [1,3,26]. Although the low initial pH value could weaken the acidifying effect of applied NPK fertilizers in our experiment [10], their double and triple doses induced a change in acidification class of the soil from acidic to very acidic (Table 1, Figure 1).

Hydrolytic acidity as a quantitative indicator of soil acidification was closely related to the pH values ($r = -0.950$). Hence, the application of elevating doses of nitrogen, phosphorus, and potassium fertilizers contributed to a significant increase in HA, by 45.8%, 31.2%, and 12.9% respectively (Table 2), which was in line with the previous studies [27]. Blaser et al. [28] stated that the largest contents of exchangeable hydrogen ions were determined for pH < 5.2. Similarly, as in the case of the acidification qualitative indicator, i.e., pH, synergism was observed in the impact of the analyzed fertilizers on this parameter (Table 2, Figure 2). Under the combined treatments of the highest doses of NP, NK, and PK, the largest values of HA, 5.15 cm(+) kg⁻¹, 4.62 cm(+) kg⁻¹ and 4.56 cm(+) kg⁻¹, respectively, were found (Figure 2). The greatest acid saturation percentage was found in the plots with the double and triple doses of N, P, and K, which resulted in an increase in the degree of soil degradation level from very weak (25–40%) to poor (40–55%) and medium (55–70%) [3].

Table 2. Impact of NPK fertilizers on the soil hydrolytic acidity.

Fertilization	P1			P2			P3			Mean N
	K1	K2	K3	K1	K2	K3	K1	K2	K3	
cmol(+) kg⁻¹										
N1	2.23 ^{n*}	2.70 ^m	2.69 ^m	3.28 ^{jk}	3.11 ^{kl}	3.72 ^{gh}	3.27 ^{jk}	3.41 ^{lj}	3.63 ⁿⁱ	3.12 ^b
N2	2.891 ^m	3.08 ^{kl}	3.51 ^{n,lj}	3.93 ^{fg}	4.25 ^{de}	5.07 ^b	3.91 ^{fg}	4.12 ^{ef}	4.45 ^{cd}	3.91 ^a
N3	3.60 ⁿⁱ	4.24 ^{de}	4.23 ^{de}	4.49 ^{cd}	4.27 ^{de}	4.65 ^c	5.11 ^{ab}	5.37 ^a	4.99 ^b	4.55 ^a
Mean P		3.24 ^b			4.08 ^a				4.25 ^a	
Mean K	3.63 ^c	3.84 ^b	4.10 ^a							
Saturation of Acid Cations [%]										
N1	26.1	28.4	31.2	40.4	36.5	47.8	34.1	37.4	40.8	35.7
N2	32.1	37.5	41.1	45.8	52.1	59.9	41.6	43.1	47.5	44.3
N3	39.1	49.5	46.9	52.1	59.5	59.2	55.1	56.5	54.5	52.2
Mean P		36.9			50.4				45.6	
Mean K	40.7	40.2	47.7							

N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. * The same letter means not significantly different.

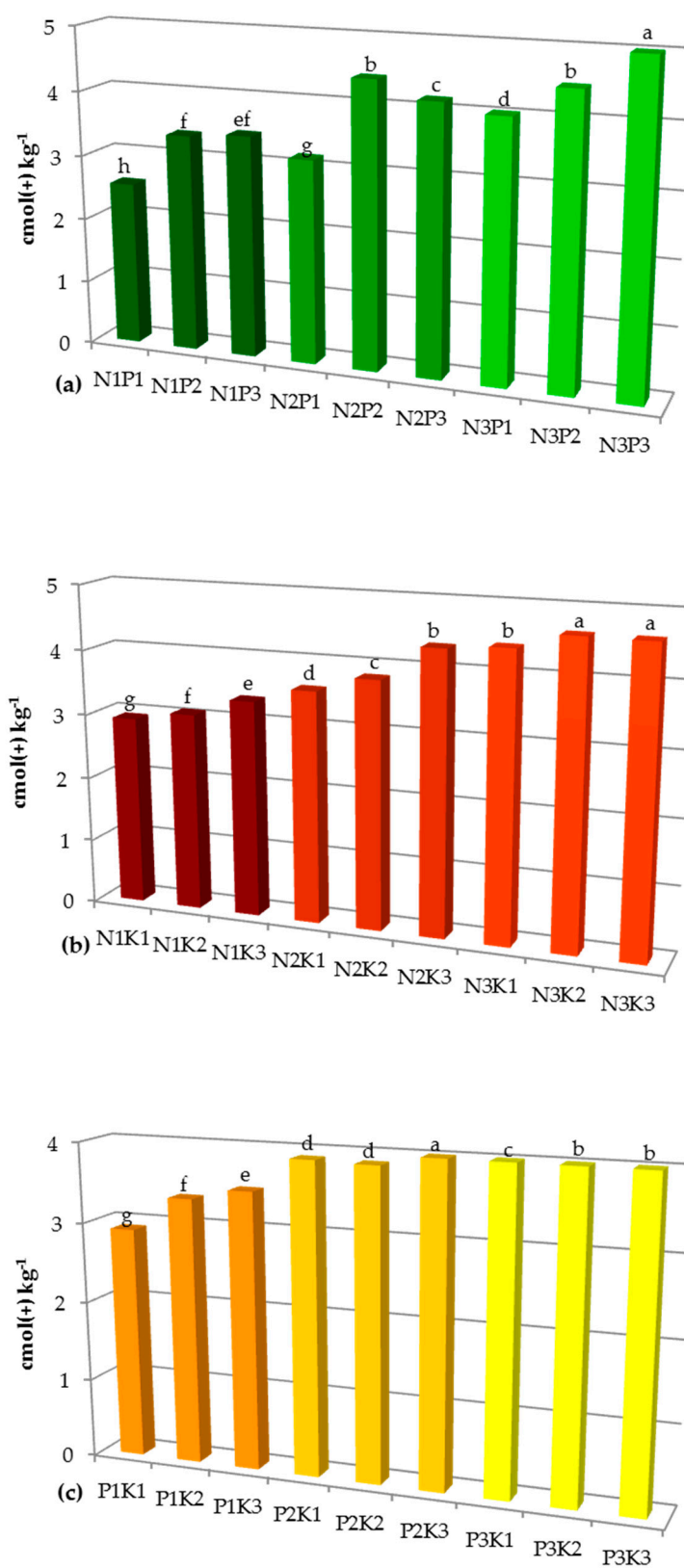


Figure 2. The interaction effect between NP (a) NK (b) and PK (c) on the soil hydrolytic acidity. N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. The same letter means not significantly different.

With increasing hydrolytic acidity, decreasing amounts of base cations remained in the exchangeable form ($r = -0.788$). Liberated hydrogen ions undoubtedly replaced the exchange sites of base cations in the colloids, and displaced the BC into the soil solution, liable to leaching losses, which implied a reduction in the acid buffering capacity of the soil [10,26]. According to Bolan [2], for each kmol of hydrogen ion remaining in the soil following nitrate leaching 50 kg of CaCO_3 is required to neutralize the acidifying effect that arises. The obtained linear relationship between BC and soil pH ($r = 0.799$) in the experiment demonstrated that soil pH was predominantly influenced by the exchange of base cations with H^+ ions in the range of pH from 4 to 7 [14,29]. The magnitude of leaching loss of BC cations is usually as follows: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$, i.e., in the order they are present in soils. In the conducted experiment, the exchangeable base cations capacity was also determined mainly by the contents of calcium ($r = 0.989$) and magnesium ($r = 0.804$) ions.

Increasing mineral nitrogen additions resulted in a significant decrease, by 25.9%, in the contents of BC (Table 3). The application of phosphorus and potassium fertilizers intensified this process and statistically significant interactions between NP, NK, PK, and NPK were found (Table 3, Figure 3). The lowest value of BC ($2.91 \text{ cm} (+) \text{ kg}^{-1}$) and base saturation were observed in the $\text{N}_3\text{P}_2\text{K}_2$ treatment. Long-term applications of ammonium nitrate greatly reduced the levels of exchangeable calcium and magnesium in other experiments [30]. Under NP and NPK treatment, BC contents decreased sometimes by over 80% [9,10,31]. The meta-analysis made by Lucas et al. [16] suggested that nitrogen fertilization in grasslands caused a decrease in exchangeable forms of calcium, magnesium, and potassium by about 24% only in experiments which lasted less than 5 years.

Table 3. Impact of NPK fertilizers on the content of exchangeable base cations in the soil.

Fertilization	P1			P2			P3			Mean N
	K1	K2	K3	K1	K2	K3	K1	K2	K3	
	cmol(+) kg⁻¹									
N1	6.31 ^{a,b,*}	6.82 ^a	5.94 ^{b,c,d}	4.83 ^{l,j,k}	5.42 ^{c,f,g}	4.06 ^{m,n}	6.33 ^a	5.71 ^{c,d,e}	5.26 ^{f,g,h,i}	5.63 ^a
N2	6.12 ^{a,b,c}	5.13 ^{g,h,l,j}	5.02 ^{h,l,j}	4.66 ^{k,l}	3.91 ⁿ	3.39 ^{o,p}	5.49 ^{e,f,g}	5.44 ^{e,f,g}	4.92 ^{ij,k}	4.92 ^b
N3	5.60 ^{d,e,f}	4.33 ^{l,m}	4.79 ^{j,k}	4.12 ^{m,n}	2.91 ^r	3.20 ^{p,r}	4.17 ^{m,n}	4.14 ^{m,n}	4.17 ^{m,n}	4.17 ^c
Mean P		5.56 ^a			4.05 ^c			5.09 ^b		
Mean K	5.29 ^a	4.87 ^b	4.55 ^c							
	Base Saturation [%]									
N1	73.9	71.6	68.8	59.6	63.5	52.2	65.9	62.6	59.2	64.3
N2	67.9	62.5	58.9	54.2	47.9	40.1	58.4	56.9	52.5	55.7
N3	60.9	50.5	53.1	47.9	40.5	40.8	44.9	43.5	45.5	47.8
Mean P		63.1			49.6				54.4	
Mean K	59.3	59.8	52.3							

N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. * The same letter means not significantly different.

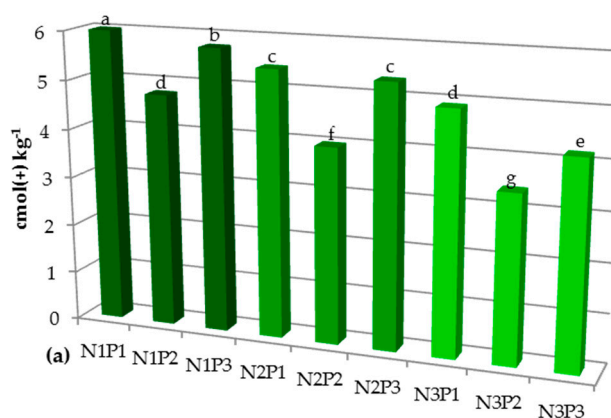


Figure 3. Cont.

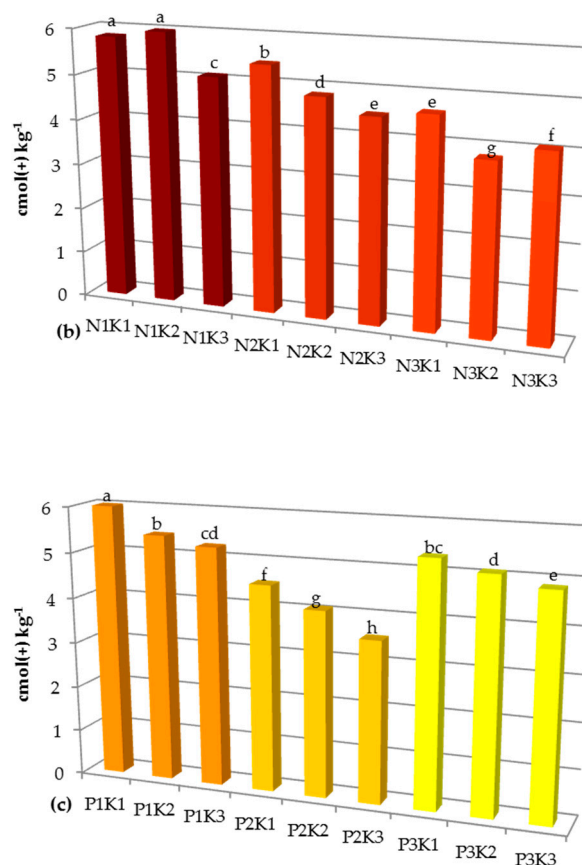


Figure 3. The interaction effect between NP (a) NK (b) and PK (c) on the content of exchangeable base cations in the soil. N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. The same letter means not significantly different.

In the present study, changes in the contents of BC were closely related to cation exchange capacity ($r = 0.570$). The influence of mineral fertilizers on this parameter, with the average value of 8.76 cm (+) kg⁻¹, showed less differentiation than in the case of the other properties discussed (Table 4, Figure 4). In a previous study, cation exchange capacity was not influenced by nitrogen doses [32] or NPK fertilization [33]. According to Šimanský et al. [34], statistically significant changes in CEC values occur only at certain doses of nitrogen fertilization.

Table 4. Impact of NPK fertilizers on Cation Exchange Capacity in the soil.

Fertilization	P1			P2			P3			Mean N
	K1	K2	K3	K1	K2	K3	K1	K2	K3	
	cmol(+) kg ⁻¹									
N1	8.54 ^{f,g,h,i} *	9.52 ^{a,b}	8.63 ^{e,f,g}	8.11 ^{ij,k}	8.53 ^{f,g,h,i}	7.78 ^k	9.60 ^a	9.12 ^{b,c,d}	8.89 ^{d,e,f,g}	8.75 ^{a,b}
N2	9.01 ^{c,d,e}	8.21 ^{h,l,j,k}	8.53 ^{f,g,h,i}	8.59 ^{e,f,g,h}	8.16 ^{h,l,j,k}	8.46 ^{g,i}	9.40 ^{a,b,c,d}	9.56 ^{a,b}	9.37 ^{a,b,c,d}	8.83 ^a
N3	9.20 ^{a,b,c,d}	8.57 ^{e,f,g,h}	9.02 ^{c,d,e}	8.61 ^{e,f,g,h}	7.18 ^l	7.85 ^{j,k}	9.28 ^{a,b,c,d}	9.51 ^{a,b}	9.16 ^{a,b,c,d}	8.72 ^b
Mean P		8.80 ^b			8.14 ^c			9.32 ^a		
Mean K	8.92 ^a	8.71 ^b	8.63 ^b							

N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. * The same letter means not significantly different.

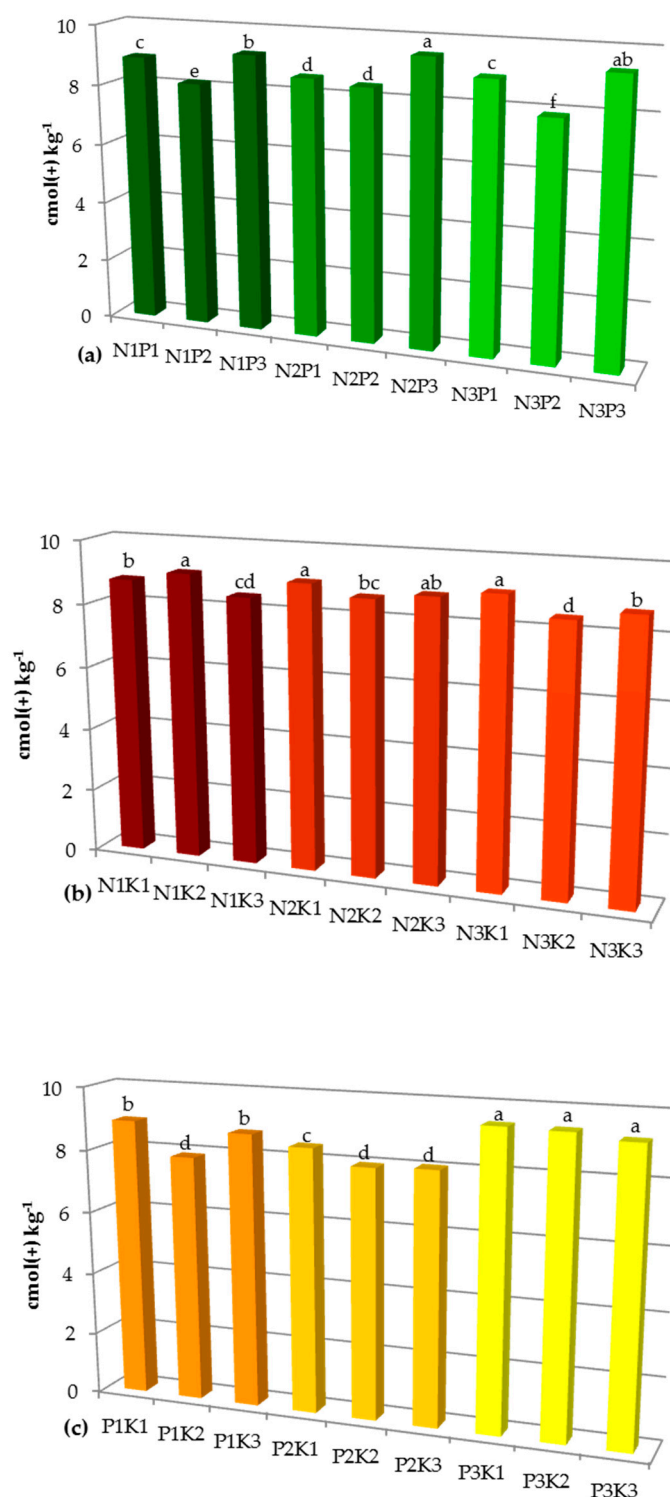


Figure 4. The interaction effect between NP (a) NK (b) and PK (c) on Cation Exchange Capacity (CEC) in the soil. N1—120 kg N ha⁻¹, N2—240 kg N ha⁻¹, N3—360 kg N ha⁻¹, P1—34.9 kg P ha⁻¹, P2—69.8 kg P ha⁻¹, P3—104.7 kg P ha⁻¹, K1—83 kg K ha⁻¹, K2—166 kg K ha⁻¹, K3—249 kg K ha⁻¹. The same letter means not significantly different.

4. Conclusions

The study revealed that high-rate fertilization with ammonium nitrate accelerated the soil acidification process, which was additionally intensified by the application of superphosphate and

potassium salt. The lowest pH values noted in $N_3P_2K_2$, $N_3P_2K_3$, $N_3P_3K_1$, $N_3P_3K_2$, and $N_3P_3K_3$ treatments were predominantly influenced by the exchange of base cations with hydrogen ions. The values of exchangeable base cations, their saturation levels and hydrolytic acidity in the soil reflected the interactions between the applied NPK-fertilizer rates.

Taking into account chemical parameters related to soil acidity as studied in this experiment, it seems that the best strategies for mitigating soil acidification in grasslands, recommended for further research, are: reducing nitrate leaching mainly by balancing fertilization and improving nitrogen use efficiency; changing fertilizer types to those that induce lesser acidification, e.g., phosphate rock; and increasing the input of base cations via liming or organic fertilization.

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References

1. Bolan, N.S.; Adriano, D.C.; Curtin, D. Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. *Adv. Agron.* **2003**, *78*, 215–272.
2. Bolan, N.S.; Adriano, D.C.; Curtin, D. Acidity. In *Encyclopedia of Soils in the Environment*; Hillel, D., Ed.; Academic Press: Cambridge, MA, USA, 2004; pp. 11–17.
3. Filipiek, T.; Badora, A.; Lipiński, W.; Brodowska, M.S.; Domańska, J.; Harasim, P.; Kozłowska-Strawska, J.; Skowron, P.; Skowrońska, M.; Tkaczyk, P. *Acidification and Liming of Soils*; FAPA: Warsaw, Poland, 2015; p. 236. (In Polish)
4. Goulding, K.W.T. Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom. *Soil Use Manag.* **2016**, *32*, 390–399. [[CrossRef](#)] [[PubMed](#)]
5. Hao, T.; Zhu, Q.; Zeng, M.; Shen, J.; Shi, X.; Liu, X.; Zhang, F.; de Vries, W. Impacts of nitrogen fertilizer type and application rate on soil acidification rate under a wheat-maize double cropping system. *J. Environ. Manag.* **2020**, *270*, 110888. [[CrossRef](#)] [[PubMed](#)]
6. Kunhikrishnan, A.; Thangarajan, R.; Bolan, N.; Xu, Y.; Mandal, S.; Gleeson, D.; Seshadri, B.; Zaman, M.; Barton, L.; Tang, C.; et al. Functional relationships of soil acidification, liming, and greenhouse gas flux. In *Advances in Agronomy*; Sparks, D.L., Ed.; Elsevier Inc.: Amsterdam, The Netherlands, 2016; pp. 1–71.
7. Verma, P.; Sagar, R. Effect of nitrogen (N) deposition on soil-N processes: A holistic approach. *Sci. Rep.* **2020**, *10*, 10470. [[CrossRef](#)] [[PubMed](#)]
8. Abdulaha-Al Baquy, M.; Li, J.; Shi, R.; Kamran, M.A.; Xu, R. Higher cation exchange capacity determined lower critical soil pH and higher Al concentration for soybean. *Environ. Sci. Pollut. Res.* **2018**, *25*, 6980–6989. [[CrossRef](#)]
9. Cai, Z.; Wang, B.; Xu, M.; Zhang, H.; He, X.; Zhang, L.; Gao, S. Intensified soil acidification from chemical N fertilization and prevention by manure in an 18-year field experiment in the red soil of southern China. *J. Soils Sediments* **2015**, *15*, 260–270. [[CrossRef](#)]
10. Zhang, Y.; de Vries, W.; Thomas, B.W.; Hao, X.; Shi, X. Impacts of long-term nitrogen fertilization on acid buffering rates and mechanisms of a slightly calcareous clay soil. *Geoderma* **2017**, *305*, 92–99. [[CrossRef](#)]
11. Piesse, M. *Global Food and Water Security in 2050: Demographic Change and Increased Demand. Strategic Analysis Paper. 4 February 2020*; Future Directions International Pty Ltd.: Nedlands, Australia, 2020; p. 6.
12. Skowrońska, M.; Filipiek, T. Life cycle assessment of fertilizers: A review. *Int. Agrophys.* **2014**, *28*, 101–110. [[CrossRef](#)]
13. Thangavel, P.; Sridevi, G. Soil Security: A Key Role for Sustainable Food Productivity. In *Sustainable Agriculture towards Food Security*; Dhanarajan, A., Ed.; Springer: Singapore, 2017.

14. Tian, D.; Niu, S. A global analysis of soil acidification caused by nitrogen addition. *Environ. Res. Lett.* **2015**, *10*, 024019. [[CrossRef](#)]
15. Zhou, J.; Xia, F.; Liu, X.; He, Y.; Xu, J.; Brookes, P.C. Effects of nitrogen fertilizer on the acidification of two typical acid soils in South China. *J. Soils Sediments* **2014**, *14*, 415–422. [[CrossRef](#)]
16. Lucas, R.W.; Klaminder, J.; Fitter, M.N.; Bishop, K.H.; Egnell, G.; Laudon, H.; Högberg, P. A meta-analysis of the effects of nitrogen additions on base cations: Implications for plants, soils, and streams. *For. Ecol. Manag.* **2011**, *262*, 95–104. [[CrossRef](#)]
17. ISO 10381-1:2002. *Soil Quality—Sampling—Part 1: Guidance on the Design of Sampling Programs*; International Organization for Standardization: Geneva, Switzerland, 2002.
18. ISO 10390:2005. *Soil Quality—Determination of pH*; International Organization for Standardization: Geneva, Switzerland, 2005.
19. Soil Survey Laboratory Methods Manual. *Soil Survey Investigation Report*; United States Department of Agriculture, Natural Resources Conservation Service, National Soil Survey Center: Washington, DC, USA, 1996; p. 42.
20. Messiga, A.J.; Ziadi, N.; Belanger, G.; Morel, C. Soil Nutrients and Other Major Properties in Grassland Fertilized with Nitrogen and Phosphorus. *Soil Sci. Soc. Am. J.* **2013**, *77*, 643–652. [[CrossRef](#)]
21. Stroia, C.; Morel, C.; Jouany, C. Nitrogen fertilization effects on grassland soil acidification: Consequences on diffusive phosphorus ions. *Soil Sci. Soc. Am. J.* **2011**, *75*, 112–120. [[CrossRef](#)]
22. Liu, X.; Shi, H.; Bai, Z.; Liu, X.; Yang, B.; Yan, D. Assessing Soil Acidification of Croplands in the Poyang Lake Basin of China from 2012 to 2018. *Sustainability* **2020**, *12*, 3072. [[CrossRef](#)]
23. Zeng, M.; De Vries, W.; Bonten, L.T.C.; Zhu, Q.; Hao, T.; Liu, H.; Xu, M.; Shi, X.; Zhang, F.; Shen, J. Model-based analysis of the long-term effects of fertilization management on cropland soil acidification. *Environ. Sci. Technol.* **2017**, *51*, 3843–3851. [[CrossRef](#)] [[PubMed](#)]
24. Cai, Z.; Wang, B.; Xum, M.; Zhang, H.; Zhang, L.; Gao, S. Nitrification and acidification from urea application in red soil (Ferralic Cambisol) after different long-term fertilization treatments. *J. Soils Sediments* **2014**, *14*, 1526–1536. [[CrossRef](#)]
25. Hojito, M. Productivity of acidified grassland caused by acidic nitrogen fertilizer and aluminum tolerance of grasses and legumes. *JARQ* **1998**, *32*, 87–96.
26. Yang, X.-D.; Ni, K.; Shi, Y.-Z.; Yi, X.-Y.; Zhang, Q.-F.; Fang, L.; Ma, L.-F.; Ruan, J. Effects of long-term nitrogen application on soil acidification and solution chemistry of a tea plantation in China. *Agric. Ecosyst. Environ.* **2018**, *252*, 74–82. [[CrossRef](#)]
27. Šimanský, V.; Jonczak, J. Sorption capacity of sandy soil under long-term fertilisation. *Agriculture* **2019**, *65*, 164–171. [[CrossRef](#)]
28. Blaser, P.; Walthert, L.; Zimmermann, S.; Graf Pannatier, E.; Luster, J. Classification schemes for the acidity, base saturation, and acidification status of forest soils in Switzerland. *J. Plant Nutr. Soil Sci.* **2008**, *171*, 163–170. [[CrossRef](#)]
29. Xu, D.; Carswell, A.; Zhu, Q.; Zhang, F.; de Vries, W. Modelling long-term impacts of fertilization and liming on soil acidification at Rothamsted experimental station. *Sci. Total Environ.* **2020**, *713*, 136249. [[CrossRef](#)] [[PubMed](#)]
30. Schroder, J.L.; Zhang, H.; Girma, K.; Raun, W.R.; Penn, C.J.; Payton, M.E. Soil acidification from long-term use of nitrogen fertilizers on winter wheat. *Soil Sci. Soc. Am. J.* **2011**, *75*, 957–964. [[CrossRef](#)]
31. Cai, J.; Luo, W.; Liu, H.; Feng, X.; Zhang, Y.; Wang, R.; Xu, Z.; Zhang, Y.; Jiang, Y. Precipitation-mediated responses of soil acid buffering capacity to long-term nitrogen addition in a semi-arid grassland. *Atmos. Environ.* **2017**, *17*, 312–318. [[CrossRef](#)]
32. Reeves, J.L.; Liebig, M.A. Soil pH and exchangeable cation responses to tillage and fertilizer in dryland cropping systems. *Commun. Soil Sci. Plant Anal.* **2016**, *47*, 2396–2404. [[CrossRef](#)]
33. Šimanský, V.; Lukáč, C. Soil structure after 18 years of long-term different tillage systems and fertilisation in Haplic Luvisol. *Soil Water Res.* **2018**, *13*, 140–149.
34. Šimanský, V.; Kováčik, P.; Jonczak, J. The effect of different doses of N fertilization on the parameters of soil organic matter and soil sorption complex. *J. Ecol. Eng.* **2017**, *18*, 104–111. [[CrossRef](#)]

