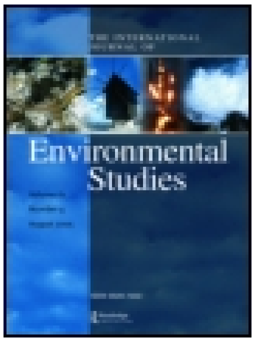

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ABSTRACT

The long-term effects of three levels of liming in combination with NPK fertiliser were studied in a field experiment on sandy Albic Retisols (sod podzolic soils) in Northwest Polissia from 2011 to 2019. Crop yields were recorded and topsoil samples collected annually and analysed for hydrolytic acidity, pH, readily hydrolysable N, labile P, and exchangeable K. The highest levels of plant nutrients were measured in plots receiving the highest doses of lime; the content of the studied elements increased during the first 4–6 years then stabilised at high levels; and this trend was shadowed by the crop yields. Grain weight varied on average from 2.07t/ha in the unfertilised control, to 3.06t/ha in plots receiving only NPK, and reached 5.30t/ha on plots receiving the maximum dose of lime.

KEYWORDS

Soil acidity; nutrient management; sod podzolic soils

Introduction

Sod-podzolic soils – *Albic Retisols* in the World Reference Base [1] – occupy 400 thousand hectares in Western Polissya – half of the arable [2,3]. They are acidic, poor in nutrients and naturally infertile [4] but until 1995 they benefitted from regular applications of lime and farmyard manure. Manure has become almost unavailable because of the rapid decline in livestock numbers, so an alternative fertilisation solution is needed.

Tomashivsky and Konik [4] assert that the most economically beneficial dose of lime on strongly acid mineral soil is about 30-50t/ha along with not less than 90 kg/ha of nitrogen (N), 90 kg/ha of phosphorus (P) and 120 kg/ha of potassium (K) applied as manure and mineral fertilisers; and Zapko et al. [5] affirm that liming also reduces the mobility of toxic heavy metals. However, liming is costly and presents practical difficulties. To avoid overliming, the rates of application should be determined by pH-buffering curves.

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Literature review

Soil acidification is characteristic of regions like Polissya where, at some seasons, excess water percolates through the soil profile, leaching bases and changing the cycling, mobility and bioavailability of plant nutrients. These changes do not benefit agricultural production [6], so soil acidity is commonly neutralised by liming, and the use of certain organic fertilisers is also effective [7]. Procedures have been tried and tested, although the zeal for liming commonly led to prodigal applications. In the more recent literature, Li et al. [8] working in the mixed farming zone of SE Australia recommend that soil should be limed regularly to maintain a pH ≥ 5.5.

Surprisingly, in view of the long history of practical and scientific experimentation, unanswered questions remain. Bolan et al. [9] and Gibbons et al. [10] highlight the need to quantify lime-enhanced mobilisation and immobilisation of nutrients. Kemmitt et al. [11] studying the dynamics of carbon (C) and nitrogen (N) in two agricultural soils under long-term field experiments (37 years) in which the pH was controlled (Rothamsted silty clay loam, pH 3.5–6.8, and Woburn sandy loam, pH 3.4–6.3) found that, although the pH had a significant effect on crop production, soil microbial biomass C and N, nitrification and soil respiration, it did not influence the total C or N contents or the level of native mineral N. Caires et al. [12], working in zero tillage systems, suggest that N fertiliser use for winter crops can be substantially reduced but highlight the importance of the form of N used in combination with lime. Kanash et al. [13] reported that the grain yield of winter wheat on sod-podzolic soil with the optimal level of N fertiliser did not change after the use of a dolomite ameliorant.

The low effectiveness of P fertiliser in acid soils is a long-running issue: inorganic P applied to podzolic soils binds to aluminium and iron sesquioxides, thus curtailing its availability for crop production [3,14]. Antoniadis et al. [15] found that the problem can be dealt with by applying more P fertiliser or liming, or both, but addition of P alone is more effective than liming alone unless there is a relatively high P content in the soil; and Tucher et al. [16] found that optimum efficiency required the adjustment of the soil pH to a soil-type-specific optimal level, as well as considering the susceptibility of different crop species to low soil P levels. The introduction of phosphate into soil causes a reduction in the surface charge and a decrease in the soil sorption capacity. Barrow [17] observed the strongest effect when the initial soil pH was between 3.5 and 5.0; at higher pH values, there is a smaller effect because of low charge potentials and, therefore, the additional effect of phosphate is limited; at lower pH values, previously sorbed phosphate is more easily desorbed. Therefore, liming significantly affects the mobility of phosphates and close-to-neutral soil reaction is considered optimal for phosphate uptake [18]. Simonsson et al. [19] suggested a minimum solubility level for soil P in the pH range traditionally considered the target for lime application in arable soils. Lime application did not lead to a decline in the pool of organic P; mass-balance considerations suggest that changes in organic-matter input because of liming are unlikely to result in any observable changes in the pool of organic P.

Sharifi et al. [20] tested the neutralising effects of wood ash and local sources of lime. Unsurprisingly, application of wood ash raised the K content in the soil. Moreover, it increased the soil pH to the maximum level within the first 50 days after application and, then, stabilised it for 8 months. About 38–96% of the total K in different sources of ash was found to be bioavailable to plants in 115 days and, although the soil was not P-deficient, the bioavailability of that element was enhanced by 14–48% by ash treatment.

Finally, in recent decades, the dynamics of N, P and K in the root zone increasingly depend on climate-change effects [21–23].

This article evaluates the long-term effects of the application of various doses of lime (as ground dolomite and ground limestone) in combination with NPK mineral fertilisers on the N, P and K status of arable *Albic Retisols* based on an 8-year experiment performed in north-western Polissya.

Materials and methods

The field experiment was conducted at the Experimental Station of the Institute of Agriculture of Western Polissya, National Academy of Agrarian Sciences of Ukraine, lat. 48°14’50”N, long. 31°45’15”E, at 151 m a.s.l.). The mean temperature during the historical period of observation was 7°C with mean July temperature 19.5°C and mean Jan −3.4°C, but this is changing; the regression polynomial model for temperature change was verified by an approximation coefficient of $r = 0.55$ (Figure 1). Over the study period, annual precipitation ranged from 417 to 718 mm.

Experimental plots were established in a soil complex of *Albic Retisols (Arenic, Aric)* [1] representing the typical soil of the station and, in general, for the Rivne region of Ukrainian north-western Polissya. The soil has a coarse texture, loamy sand, throughout the profile (Table 1).

The experiment conducted from 2011 to 2019 embraced various fertilisation options: control field – no fertiliser; fertiliser $N_{112}P_{87}K_{105}$ – background; $CaMg(CO_3)_2$ equivalent to half the hydrolytic acidity (0.5 Hr) + background; $CaMg(CO_3)_2$ equivalent to Hr + background; $CaMg(CO_3)_2$ equivalent to 1.5 Hr +

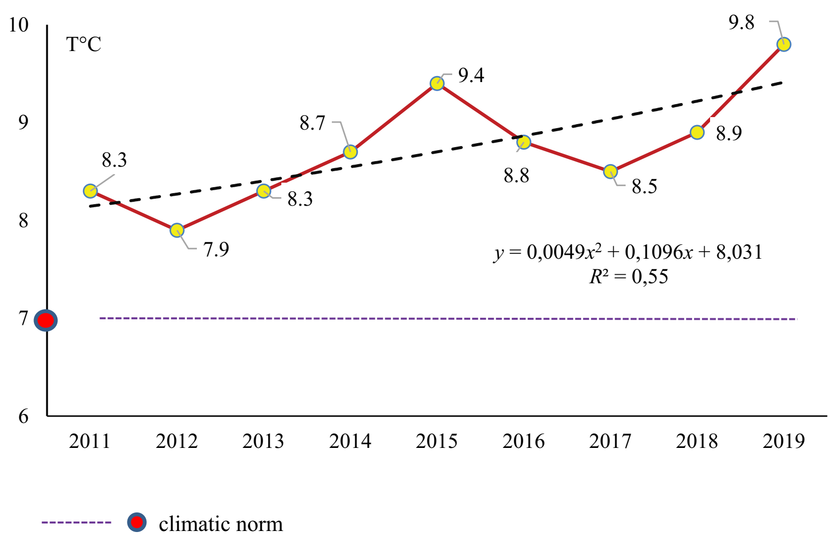

Figure 1. Regression polynomial model of the average temperature in north-western Polissya, Ukraine from 2011.

Table 1. Particle-size distribution of experimental site.

Sampling depth, cm	Particle-size, mm/%						Particle-size <0.01 mm, %
	Sand		Silt			Clay	
	1–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	
0–20	62.8	20.2	8.9	5.1	1.2	1.8	8.1
30–40	69.8	19.6	3.1	3.5	1.2	2.8	7.5
50–60	65.3	14.3	11.5	2.7	2.0	4.2	8.9
130–140	70.5	18.5	4.3	2.0	1.4	3.3	6.7

Table 2. Fertilisation options and average crop productivity for the years 2012–2019.

Fertilisation option	Crop yield, grain units t/ha	Dose of ground dolomite	
		t/ha	%
No fertilisers	2.07	–	–
$N_{112}P_{87}K_{105}$ – background	3.06	0.99	48
Background + $CaMg(CO_3)_2$ (0.5 Hr)	4.02	1.95	94
Background + $CaMg(CO_3)_2$ (1.0 Hr)	4.55	2.48	120
Background + $CaMg(CO_3)_2$ (1.5 Hr)	5.33	3.26	157

background. Each experimental option included three replicates. The crop rotation during the experiment period was winter wheat – maize for grain – spring barley – winter rape. Table 2 shows the average yields of the crops in grain units.

Mineral fertilisers were applied to winter wheat at 120 kg/ha N, 60 kg/ha P and 90 kg/ha K; to maize at 120, 90 and 120 kg/ha; to spring barley at 90, 90 and 90 kg/ha; and to rape at 120, 90 and 120 kg/ha. The average annual dose of fertiliser under the full crop rotation (4 years) was 112 kg/ha N, 82 kg/ha P, and 105 kg/ha K. PK fertilisers were applied during pre-sowing cultivation, and N fertilisers were applied during the pre-cropping treatment.

Ground dolomite ($CaMg(CO_2)_{2,}$ 21% calcium and 12% magnesium) or ground limestone ($CaCO_{3,}$ 60.1% calcium) was applied at the outset to reduce soil acidity. The dose of each ameliorant (D_a) was calculated according to the formula D_a (t/ha) = 1.5 × H_h, where H_h is hydrolytic acidity. The initial soil pH_{KCl} was 4.3 and the H_h varied from 2.80 to 2.97 $cmol^{(+)}$/kg soil. Three doses of ground dolomite were tested: $D_{d0.5}$ = 2.23 t ha^{-1} (Ca_{478} + Mg_{269} kg ha^{-1}), $D_{d1.0}$ = 4.74 t ha^{-1} (Ca_{1015} + Mg_{572} kg ha^{-1}) and $D_{d1.5}$ = 6.70 t ha^{-1} (Ca_{1435} + Mg_{809} kg ha^{-1}). Ground limestone was applied at a dose of $D_{l1.0}$ = 4.940 t ha^{-1} (Ca_{2998} kg ha^{-1}).

Soil samples were collected from 0 to 20 cm from each option in three replicates at the start of the experiment and after harvesting each crop each year. Laboratory analyses were performed in duplicate according to standard methods: pH_{KCl} by the potentiometric method [24]; H_h by Kappen's method; exchangeable Ca^{2+} and Mg^{2+} by atomic-absorption spectrometry (NPP AKADEMPRYBOR, OOO 40031, Vul. Kurska, Sumy) after sample extraction in molar ammonium acetate adjusted to pH 7.0; easily hydrolysable forms of N (EHN) after sample extraction in 0.1 molar sodium hydroxide solution. Statistical analysis of the obtained data was carried out using STATISTICA 12 [25].

Results and discussion

The EHN content in the variants of the experiment over the years of observation ranged from 34.6 to 58.8 mg/kg soil (Figure 2). Averaged over the 8 years, the lowest supply of

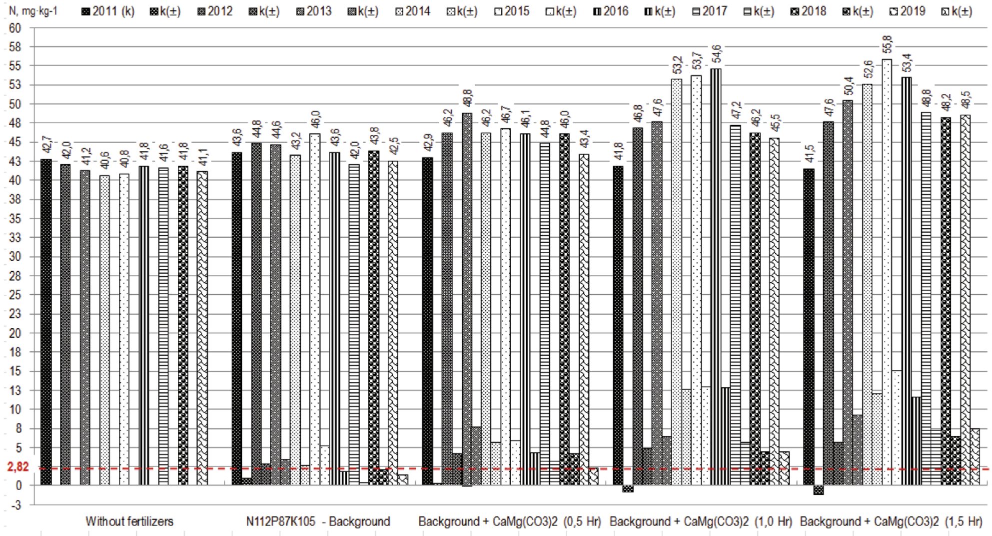

Figure 2. Temporal dynamics of EHN in soils under various fertilisation practices (all analytical parameters on ANOVA were within the 0.05 level of statistical accuracy: experiment error: 0.99; error of the difference of means: 1.4; ALSD: 2.82 - the red pecked line; RLSD: 6.22%).

EHN was 40.4 mg/kg of soil in the control without mineral fertilisation; EHN increased to 43.8 mg/kg with the introduction of $N_{112}P_{87}K_{105}$ per 1 ha of crop rotation; liming the soil with the 0.5 dose of $CaMg(CO_3)_2$, in combination with a certain dose of fertiliser, contributed to a significant increase in N content. Absolute least significant difference (ALSD) was calculated in ANOVA as 2.82 mg/kg soil. Subsequently, we noted that this occurred almost proportionally with the increase in dose of ameliorant from 0.5, 1.0 and 1.5 doses of $CaMg(CO_3)_2$.

Analysis of the EHN dynamic during the experimental period for each fertilisation option and after reclamation revealed a tendency to increase in 2014–2016, which coincided with the period of the most effective action of the ground dolomite. Thus, the background application of $N_{112}P_{87}K_{105}$ in combination with the 0.5, 1.0 and 1.5 doses of $CaMg(CO_3)_2$ increased the content of EHN in the soil by 8.4%, 13.9%, 20.8% and 24.8%, respectively. Relative least significant difference (RLSD) was calculated in ANOVA as 6.22%. EHN remained stubbornly low.

The supply of labile P to the soils of north-western Polissya in Ukraine was much better compared to N and K. This can be attributed to the recommendation of adding high doses of P fertilisers to cropland over the last few decades; the norms exceeded the removal by crops 1.5 or 2-fold and because of the low mobility of P, even in coarse-textured soils, this element was hardly leached from the topsoil (Figure 3). The soils of the experimental plots were characterised by medium security, based on the scale adopted in Ukraine [14].

Prior to the experiment, the content of labile P ranged from 67.7 to 103.6 mg/kg of soil. Low crop yields in unfertilised areas removed little P from the soil and its content remained relatively stable over time, reaching values of 72.0–76.6 mg/kg over the 8 years of the study. The average application of $N_{112}P_{87}K_{105}$ per hectare during crop rotation

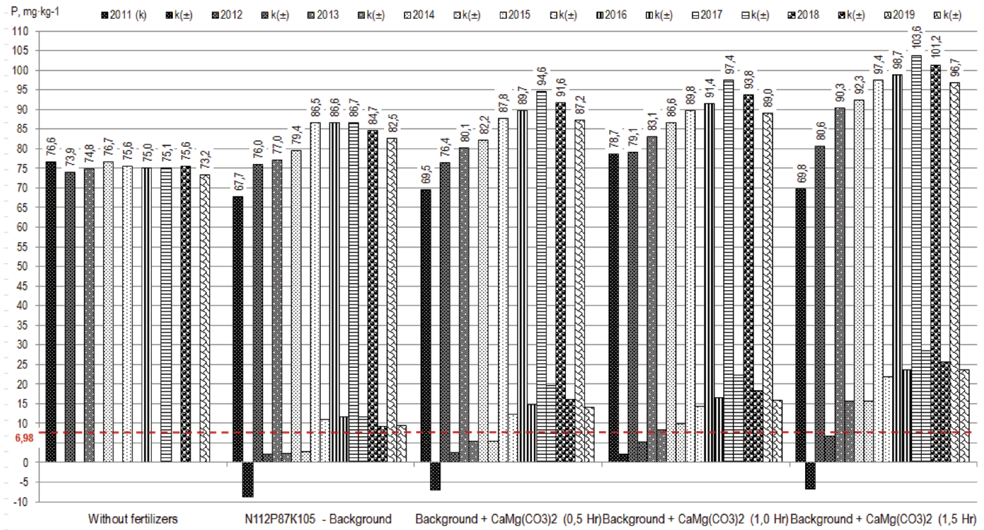

Figure 3. Temporal dynamics of labile P in soils under various fertilisation practices (all analytical parameters on ANOVA were within the 0.05 level of statistical accuracy: experiment error: 2.44; error of the difference of means: 3.45; ALSD: 6.98 - the red pecked line; RLSD: 8.31%).

without liming resulted in an increased P content of up to 86.7 mg/kg, a gain of 19 mg/kg after the 8 years of the experiment. ALSD was calculated in ANOVA as 6.98 mg/kg.

The introduction of 0.5, 1.0 and 1.5 doses of ground dolomite contributed to an increase in the content of labile P to 94.6, 97.4 and 103.6 mg/kg, respectively. The most significant changes in the P content were noted in the soil with background values of $N_{112}P_{87}K_{105}$, both with liming and without liming, in the first 4 years of the study period, with the content becoming relatively stable over the next 4 years. This is a high value of P availability compared to the recommended limiting value of labile P in Albic Retisols in Ukraine of 43.6–65.4 mg/kg of soil [14].

The coarse-textured Albic Retisols of north-western Polissya are poor in exchangeable K. Combined with N and P deficiencies, this results in low crop yields. Soil monitoring showed that the average K content in this region was 52.7–56.9 mg/kg of soil compared with the optimal content estimated as 100–130 mg/kg [14]. The studied topsoils contained 43.7–46.9mgK/kg at the beginning of the experiment (Figure 4). The fertiliser system adopted in the experiments contained, on average, $N_{112}P_{87}K_{105}$ per 1 ha of crop rotation, which significantly increased the content of the exchangeable K pool in the soil. During the 8 years of the study, the K content decreased in the unfertilised soils from an initial 45.6 mg/kg to 43.7 mg/kg. However, it increased with a background of $N_{112}P_{87}K_{105}$ application from 46.9 to 72.9 mg/kg. Reducing the soil acidity through the use of ground dolomite with the background fertilisers further increased the stocks of exchangeable K in spite of intensive removal of the element through high crop yields: liming at doses of 0.5 1.0 and 1.5 $CaMg(CO_3)_2$ increased K content from 43.7 to 80.3, from 45.1 to 84.5, and from 46.9 to 89.4 mg/kg, respectively. ALSD was calculated in ANOVA as 9.54 mg/kg.

Acid, nutrient-poor soils respond very positively to the application of N, P and K fertilisers and liming. In our study, these additives significantly increased crop yields

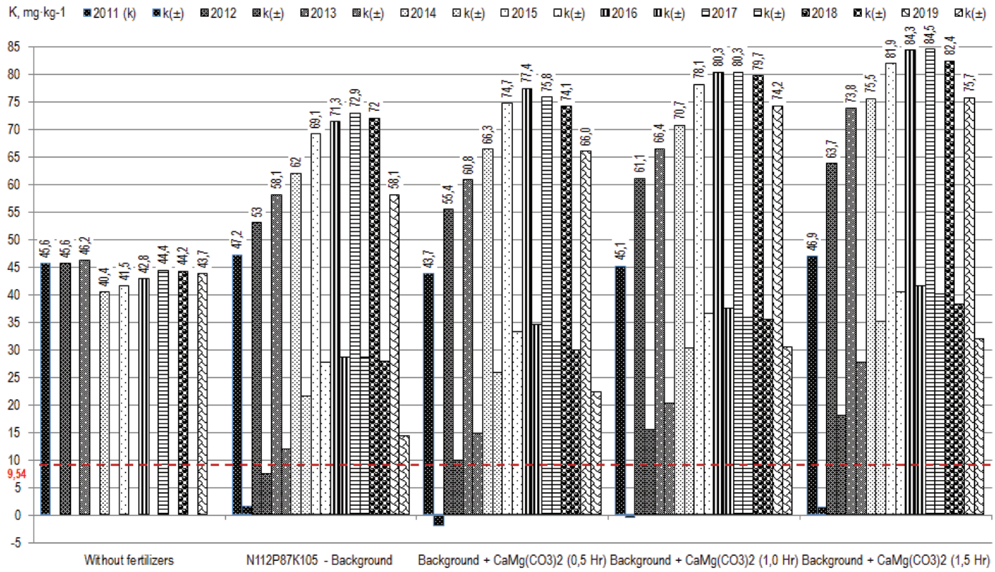

Figure 4. Temporal dynamics of exchangeable K in soils under various fertilisation practices (all analytical parameters on ANOVA were within the 0.05 level of statistical accuracy: experiment error: 3.34; error of the difference of means: 4.72; ALSD: 9.54 - the red pecked line; RLSD: 15.03%).

(Table 2). Over the 8 years of the experiment, the productivity of soils with background $N_{112}P_{87}K_{105}$ fertiliser application increased from 2.07 to 3.06t/ha (48% compared with the unfertilised control). Liming with 0.5, 1.0 and 1.5 $CaMg(CO_3)_2$ rates in combination with $N_{112}P_{87}K_{105}$ mineral fertiliser brought about a gradual increase in crop-rotation productivity at 4.02, 4.55 and 5.14t/ha amounting to 2.20–2.57 times the yield of the control: clear evidence of the effectiveness of improving the nutrient regime and optimising the soil acidity.

However, in our study, the EHN content in the studied Albic Retisol hardly changed (from 41.5 to 43.6 mg/kg). Our experimental data on the content of hydrolysable N in an alkaline solution, and its dynamics, confirmed the low supply of that element in the Albic Retisol over 8 years, covering two full crop rotations (Figure 2), compared with the average EHN supply of 150–200 mg/kg according to the assessment scale used in Ukraine [2,5].

The dynamics of exchangeable K under the influence of fertilisers and liming were much more positive. Slowly decreasing stocks of K in 2012–2015 were recorded in the unfertilised soils. Average annual applications of $N_{112}P_{87}K_{105}$ per 1 ha during the crop rotation period, both alone and in combination with lime, resulted in the content of exchangeable K increasing to maximum values in the first 4 years. The obtained results show that the average application of K_{105} during crop rotation was enough to achieve the highest content of labile K in the soil. The use of such K doses over the longer term can, however, contaminate groundwater.

In this study, we analysed the temporal changes in N, P and K in an initially strongly acidic Albic Retisol in response to the application of various doses of ground dolomite, ground limestone, and NPK fertilisers. Table 3 lays out the very strong relationships

Table 3. Relationships between changes in pH_{KI} and changes in nutrient content with the introduction of dolomite to Albic Retisol soils, Pearson's correlation coefficient ±*r*.

Nutrient	Dolomite application	Correlation coefficient, ± *r* (Chaddock, 1925)
EHN	Without fertilisers	0.22 (weak connection)
	Background + $CaMg(CO_3)_2$ (1.5 Hr)	0.72 (strong connection)
Labile P	Without fertilisers	0.61 (significant connection)
	Background + $CaMg(CO_3)_2$ (1.5 Hr)	0.76 (strong connection)
Exchangeable K	Without fertilisers	0.91 (very strong connection)
	Background + $CaMg(CO_3)_2$ (1.5 Hr)	0.93 (very strong connection)

revealed between the dynamics of N, P and K and soil pH_{KCl} on the background dose + $CaMg(CO_3)_2$ (1.5 Hr).

In three-dimensional regression planes for pH_{KCl} with each soil fertility index, N and P showed their interdependence on the degree of neutralisation of the soil acidity with $CaMg(CO_2)_2$ (1.5 Hr) + $N_{112}P_{87}K_{105}$ (Figure 5) [25]. There was a similar relationship between the dynamics of the available forms of P and K with pH_{KCl}, which is associated with the dynamics of the nutrients in 2011–2019 with the introduction of $CaMg(CO_2)_2$ (1.5 Hr) + $N_{112}P_{87}K_{105}$.

We watched the weather for 8 years (Figure 1). The mean annual temperature increased steadily and each year was higher than the climatic norm of 7°C from 2011. The regression polynomial model of temperature change $Y = -0.0186x^2 + 0.4139x + 6.9983$ is verified by the approximation coefficient of $R^2 = 0.55$. The amount of annual precipitation tended to decrease. We calculated the tightness of the links of climate change with fluctuations in the indicators of resources N, P, K in the soil (Table 4).

Pearson's correlation between the parameters of climate and fluctuations in the stocks of the studied forms of N, P and K in the soil (Table 4) highlights the

a) b)

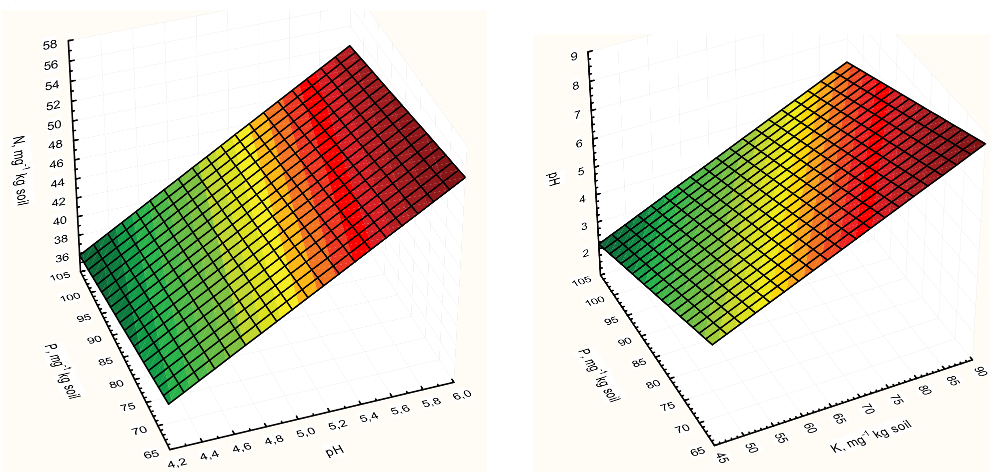

Figure 5. 3D model of the relationship between changes in pH_{KCl} and changes in nutrient content through the introduction of ground dolomite to an Albic Retisol: a) plane of regression for N and P from pH_{KCl}; and b) plane of regression for pH_{KCl} and P from K ($N_A = 5.9747 + 8.9896*ph - 0.0754*P$ and $pH_{KCl\ B} = 4.696 + 0.0889*K - 0.0621*P$ – distance weighted least squares).

Table 4. Significant and more significant correlation coefficients between soil nutrient contents and weather conditions.

Weather indicators	Nutrients[1]								
	No fertilisers			$N_{112}P_{87}K_{105}$ – control			Control + $CaMg(CO_3)_2$ (1.5 Hr)		
	N	P	K	N	P	K	N	P	K
Average T, °C	**0.32**[5]	–0.17[6]	**0.296**	–0.10[6]	**0.684**	**0.42**[5]	**0.46**[5]	**0.723**	**0.51**[4]
Maximum T, °C	**0.723**	–0.21[6]	–0.02[7]	0.15[6]	**0.34**[5]	0.14[6]	0.27[6]	0.18[6]	0.06
Precipitation, mm	**–0.67**[4]	–0.22[6]	–0.04[7]	**-0.28**[5]	0.02[7]	0.02[7]	–0.09[7]	–0.02[7]	0.13[6]

[1]Moderate and higher correlations in bold.
[2]Tightness of communication according to Chaddock R. E. *Principles and Methods of Statistics*, 1925:
[3]–Strong; [4]–Considerable; [5]–Moderate; [6]–Weak; [7]–no connection.

significance of temperature and precipitation as factors influencing the elemental contents, and in particular N and P, although these effects are masked by any substantial input of fertilisers. It was found that the dynamics at average temperatures are most closely correlated with the dynamics of P on the background + CaMg $(CO_2)_2$ (1.5 Hr) ($r = 0.72$). The dynamics of the EHN were closely related to the maximum temperature ($r = 0.72$) and precipitation ($r = 0.67$) only in the non-fertilised soil.

It is hard to find studies of the impact of climate change on the dynamics of nitrogen, phosphorus and potassium as nutrients for field crops, but we see a lot of ecological research data in the wild. In particular, Koller & Phoenix [26] showed that delayed snowmelt caused net N mineralisation to be highest at the warmest site and the site with the most productive vegetation. At the same time, P was strongly immobilised at all sites, both in winter and summer, and N:P ratios indicated that plants were generally P limited at all sites, likely through strong P immobilisation.

Weedon et al. [27] showed that summer warming accelerates nitrogen cycling in subarctic peatlands without changing enzyme pools or microbial community structure. Simultaneous measurements allowed the authors to determine the level of the organic components at which the impact of climate change is evident. Organic nitrogen pools and fluxes were an order of magnitude larger at 1°C warming than inorganic nitrogen stocks and fluxes. Summer warming approximately doubled the fluxes of organic nitrogen and ammonia in the soil during the growing season.

Matías et al. [28] investigated the availability of different soil C, N and P fractions under a global change scenario in a Mediterranean mountain ecosystem. Nutrient content in soil and microorganisms varied with seasons, habitats, and climate scenarios. Soil nutrient fractions increased with lower soil moisture conditions (dry scenario and summer), while microbial nutrients increased under wet summer and spring scenarios. These results suggest that higher rainfall improves nutrient uptake by microbes and plants, and thus nutrient cycling; conversely, reduced rainfall results in soil nutrient accumulation, increasing the risk of nutrient loss through leaching or erosion. These results show that projected climate change will have significant effects on nutrient cycles and ecosystem functioning.

From our research on the liming standards of arable soils, we should expect a significant impact of climate change on the efficiency of liming and the reserves of nitrogen, phosphorus and potassium in limed soils under field crops.

Conclusions

- Appropriate liming, whether using ground dolomite or ground limestone, greatly improves the nutrient status of arable Albic Retisols/Sod-podzolic soils. Overall, with the addition of background mineral fertiliser, crop yields increased with an increasing application of ground dolomite. On average, over the 8 years, the largest harvest of grain units (5.33 tonne/ha) was obtained by applying 1.5 aliquots of CaMg $(CO_2)_2$ to the soil with a background fertilisation of $N_{112}P_{87}K_{105}$, compared to 2.07 t/ha in the unfertilised control and 3.06 with NPK alone.
- At the beginning of the experiment, the soils were strongly acidic and poor in N, P and K. Liming contributed to higher contents and stocks of EHN, labile P and exchangeable K. The nutrient elements in the limed soils were raised higher than in the control (non-fertilised) soil, as well as in plots fertilised with NPK, but not limed. The highest elemental contents were recorded in plots where the highest doses were applied.
- Nutrient status increased considerably in the first 2 years of the experiment. Depending on the element, after 4–6 years, levels stabilised at relatively high levels, indicating that the soil system had reached a new equilibrium. The relatively rapid stabilisation can be explained by the sandy soil texture, with weakly developed sorption capacity and buffering.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Appendix.

Advisory materials

(ANOVA)

N	P	K
F actual significance: 12.91	Criterion of materiality: 6.99	Criterion of materiality: 12.62
F at the 5% significance level: 2.12	Criterion F at the 5% significance level: 2.12	Criterion F at the 5% significance level: 2.12
Experiment error: 0.99	Experiment error: 2.44	Experiment error: 3.34
Error of the difference of means: 1.4	Error of the difference of means: 3.45	Error of the difference of means: 4.72
Relative error of the difference of means: 3.08%	Relative error of the difference of means: 4.11%	Relative error of the difference of means: 7.43%
Absolute least significant difference: 2.82	Absolute least significant difference: 6.98	Absolute least significant difference: 9.54
Relative least significant difference: 6.22%	Relative least significant difference : 8.31%	Relative least significant difference : 15.03%
Coefficient of variation: 6.53%	Coefficient of variation: 8.72%	Coefficient of variation: 15.77%