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The content of mobile aluminium compounds depending on the long-term use of various fertilizing and liming systems of Albic Pantostagnic Luvisol

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Abstract. Today, climate change is exacerbating the problems of efficient and environmentally friendly use of acidic soils, which are widespread in Ukraine. At the same time, the role of mobile aluminium compounds in acidity formation is also becoming increasingly important. In this regard, chemical amelioration remains a primary and very important factor in the system of resource-saving and environmentally friendly agricultural measures for the efficient and balanced use of acidic soils. Therefore, the main objective of the research is to establish scientifically sound doses of chemical ameliorant that reduce the content of mobile aluminium compounds and ensure environmental safety and high productivity of agrocenoses on Albic Pantostagnic Luvisol. The research was carried out in a long-term stationary experiment established in 1965 with different doses of mineral fertilisers, manure and lime on an Albic Stagnic Luvisol. It was found that with a prolonged application of mineral fertilisers and the use of this soil without fertilisers, the content of mobile aluminium compounds at the end of the X rotation at pH_{KCl} 4.20 and 4.42 was 68.4 and 58.5 mg kg^{-1} respectively. Under the organo-mineral and mineral fertilisation systems with liming with 6.0 t ha^{-1} of $CaCO_3$ calculated by hydrolytic acidity, the content of mobile aluminium compounds decreased to 7.2 and 6.7 mg kg^{-1} of soil respectively. Under identical fertilisation systems with a lime application by pH-buffering capacity (2.5 t ha^{-1} $CaCO_3$), the content of mobile aluminium compounds is 10.8–10.0 mg kg^{-1} soil.

Key words: acidity, aluminium, Albic Pantostagnic Luvisol, fertilizers, liming.

INTRODUCTION

The problem of efficient and ecologically safe use of acidic soils is intensifying today due to significant climate changes. Acidic degradation, which occurs as a result of both natural (climate change) and anthropogenic (unbalanced application or complete absence of fertilizers) loads, prompts scientists to conduct theoretical and applied research aimed at understanding the processes that cause soil acidity, the nature of which is very complex and has not been finally clarified until recently. It is the acidomorphic process of soil formation, that is, the origin of soil acidity, that is important for the systematic management of the fertility of acidic soils.

Very often the acidic reaction of the soil solution is associated with the presence of potentially mobile aluminium compounds in the soil (Foy, 1996) and it is believed that the high toxicity of aluminium (Al) has the most common and very harmful effect on soil acidity and affects plants, the microbial community and the environment (Weil & Brady, 2017). Especially alumotoxicity is dangerous in soils with a low concentration of magnesium and calcium ions (Frantzios et al., 2000).

In the soil solution during acidification mobile aluminium appears below the isoelectric point, which in most soils is at a pH value below 4.5 (Truskavetskyi & Tsapko, 2016). Trivalent aluminium (Al^{3+}) is the most abundant form at low pH (approximately 4.3) and has the greatest effect on plant growth, occupying most of the negative charges in acidic soils (Martins et al., 2020). In contrast, Al precipitated or chelated with organic compounds is not toxic to plants (Nogueirol et al., 2015).

Aluminium itself by its chemical nature is an amphoteric substance that forms crystalline minerals, amorphous half-oxides and a wide range of complexes and soluble compounds. Therefore, it largely shapes the state of the surface of the soil particle and therefore various manifestations of its mobility to a certain extent also shape the conditions of the mobility of other elements (Tsapko, 2007; Cheshko, 2013).

According to (Kisnieriené & Lapeikaite, 2015) aluminium is completely released from the solution in the form of $Al(OH)_3$ at pH>5. Trivalent Al^{3+} is the most toxic form of Al to plants and animals. Al^{3+} activity at 1–10 µM in soil solution can cause damage to many crops (Hue, 2011; Blamey et al., 2015). To maintain (Al^{3+}) at submicromolar levels soil pH must be maintained above 5.0 (Hue, 2022).

However, often with the appearance of mobile aluminium further acidification of mineral soils is inhibited. Important are the studies on the role of aluminium in such complex biological objects as soils, conducted at the National Scientific Center ‘Institute of Soil Science and Agrochemistry named after O.N. Sokolovsky’. It was established as a result of the experiment that the humic acids of the soil actively neutralize the acidifying effect of aluminium. At the same time, the neutralizing capacity of fulvic acids is much higher than that of humic acids. The high buffering capacity of fulvic acids regarding aluminium is explained by their greater affinity to the ions of this element in contrast to humic acids, which more actively form organo-mineral compounds with calcium (Tsapko et al., 2018a). Therefore, humus acids despite their own relatively high acidity not only do not acidify the soil solution with aluminium compounds but play the role of a buffer mechanism concerning acid and aluminium load.

At the same time, the problem of global warming also brings significant corrections to the study of the mechanisms of resistance to aluminium toxicity and the conditions that weaken or strengthen them. Therefore, the study of the mechanisms of resistance to aluminium toxicity and the factors influencing them are extremely relevant. Thus, the implementation of studies on the change in the content of mobile aluminium compounds depending on the doses of ameliorant application makes it possible to propose and put into practice technologies that are built on the principles of protecting soil resources, strengthening self-regulation processes and restoring the sustainable functioning of agroecosystems.

Therefore, the main goal of the research was to establish scientifically based doses of chemical ameliorants that reduce the content of mobile aluminium compounds and ensure the stabilization of ecological safety and high productivity of agrocenoses of Albic Pantostagnic Luvisols.

MATERIALS AND METHODS

The most representative method of researching the theoretical and practical bases of soil fertility preservation, including the origin of soil acidity and the role of aluminium in its formation, is a stationary field experiment. It is in the basic stationary experiments that you can get the most information based on deep scientific developments regarding the origin of soil acidity and the role of aluminium in its formation, as well as aluminium toxicity.

Research work was carried out in the laboratory of agrochemistry of the Institute of Agriculture of Carpathian region of the National Academy of Agrarian Sciences of Ukraine (49°47'54.3"N 23°52'26.9"E) in the classic stationary experiment established in 1965 and registered as long-term stationary field experiment in the register of the National Academy of Agrarian Sciences of Ukraine (certificate of registration NAAS No. 29).

The climate of the region is humid continental with warm summers. The average annual air temperature is +7.5 °C. The sum of active temperatures above 10 °C ranges from 2,400 to 2,800 °C, which ensures 160–175 days of active vegetation. Precipitation is 767 mm per year on average. The amount of precipitation during the warm season reaches 300–380 mm. The value of the hydrothermal coefficient ranges from 1.3 to 1.6, which indicates that the region has sufficient moisture (Shuber, 2018).

The stationary experiment was placed on three fields, each of which has 18 options in three repetitions. The arrangement of options is single-tiered and sequential. The total area of the plot - 168 m^2, and the accounting area - 100 m^2. The soil is Albic Pantostagnic Luvisol (Siltic, Aric, Katocutanic, Epidystric) (WRB, 2022), formed on a loesslike loam. Soil texture in the upper 0–32 cm layer is silt (sand fraction ($\varphi > 0.05$ mm) content is 13.0–16.0%, the silt (φ 0.05–0.001 mm) content is 78.3–81.5% and the clay ($\varphi < 0.001$ mm) content is 3.6–5.2%). In the sub-soil layers (32–150 cm) the content of clay fraction is higher (> 10%) and silt content changes from 62.9 to 73.8%, therefore soil texture is silt loam.

The agrochemical characteristics of the Albic Pantostagnic Luvisol arable layer before the start of the experiment are as follows: humus content (by Tyurin) - 1.42%, pH_{KCl} - 4.2, hydrolytic acidity (by Kappen) - 4.5, exchangeable acidity (by Sokolov) - 0.6 cmol(+) kg^{-1} of soil, the content of mobile aluminium - 60.0, mobile phosphorus (by Kirsanov) and exchangeable potassium (by Maslova) - 36.0 and 50.0 mg kg^{-1} of soil, respectively.

The experiment from the beginning was based on a seven-field crop rotation: potatoes - spring barley with clover sowing - meadow clover - winter wheat - sugar beets - corn for silage - winter wheat. Systematic liming and application of high doses of phosphorus-potassium fertilizers during five crop rotations stabilized the acidity of the soil solution and contributed to the accumulation of a significant amount of plant-available forms of phosphorus and potassium in the soil. Starting with the VI rotation a partial reconstruction of this experiment was carried out, which consisted of the study of the effectiveness and duration of the aftereffect of liming, residual phosphorus and potassium with moderate nitrogen use with a transition to a less intensive 4-field crop rotation: corn for silage - spring barley with a subsowing of meadow clover - meadow clover - winter wheat with the maintenance of fertilization and liming levels. Agricultural techniques for growing crops, soil cultivation and crop care are generally accepted for the conditions of the Western Forest-Steppe zone.

In the experiment were used cattle manure after 6 months of storage on straw bedding, ammonium nitrate (34.5%), granular superphosphate (19.5%), potassium chloride (KCl, 40%), nitroammophoska (NPK 16% each) (when using nitroamophoska, the NPK content was balanced according to the levels of fertilization with simple fertilizers). Manure (40–60 t ha^{-1}) was applied under corn. Phosphorus-potassium fertilizers were applied in the fall, nitrogen fertilizers were applied before sowing. Starting from the VIII rotation, the second mowing of meadow clover was ploughed as an organic fertilizer in all variants of the experiment.

Chemical amelioration, especially given the global climatic changes, remains an important factor in the systematic control of acidic soil fertility. However, traditional chemical amelioration of acidic soils, in particular liming with lime doses calculated according to hydrolytic acidity, in practice leads to both excessive consumption of limestone materials and over-liming, which is extremely negatively reflected in the environmental situation (Patra et al., 2021). A decisive factor for preserving and improving fertility, and ensuring soil stability is the stability of the optimal calcium content in it (Loide, 2010). In the seven-field crop rotation, liming was carried out according to the experiment scheme with 0.5; 1.0 and 1.5 norms of $CaCO_3$ calculated by hydrolytic acidity (Ha). The norm of lime by hydrolytic acidity was calculated according to the formula $D_{CaCO3} = 1.5 \times Ha$ (t ha^{-1}). But it was found in previous research that there is a significant excess of lime ameliorants in Albic Pantostagnic Luvisol when norms of lime are calculated according to hydrolytic acidity compared to the norms determined by pH-buffering capacity graphs (Tsapko & Desyatnik, 2013). Therefore, before the start of the IX crop rotation, another liming was carried out according to both hydrolytic acidity (the common method) and pH-buffering capacity (the more environmentally friendly method) on identical fertilizer systems. The method of calculating the dose of lime according to the pH-buffering capacity graphs was developed at the the National Scientific Center ‘Institute of Soil Science and Agrochemistry named after O.N. Sokolovsky’ (Truskavetskyi, 2003). The measurement of pH buffering capacity was determined by adding increasing amounts of 0.1 mol dm^{-3} HCl (0; 1.0; 2.0; 3.0; 4.0; 5.0 mL) and 0.03 mol dm^{-3} $Ca(OH)_2$ (0; 4.0; 8.0; 12.0; 16.0; 20.0 mL) to a dried, crushed and sifted through a 1 mm sieve soil samples. Distilled water was used to bring the volume to 50.0 mL. The solution was shaken on a rotary shaker for one hour at 60 rpm at room temperature, and the pH of the filtrate was measured potentiometrically. For a comparative assessment of the buffering capacity of the soil, pure quartz sand was used as a non-buffering substrate for a zero standard curve. Buffering capacity was then calculated by plotting the pH values on a graph and determining the area between the buffering curve and a standard curve to calculate buffering indices. Using the pH buffering curves we determine the amount of $CaCO_3$ required by measuring the required amount of $Ca(OH)_2$ to bring a pH to the desired optimal pH in a particular soil type. For Albic Pantostagnic Luvisol this amount was 2.5 t of $CaCO_3$ per ha of crop rotation area.

Ground limestone (93.5% $CaCO_3$) was used as limestone material for the entire period of research.

Research on changes in the content of mobile aluminium depending on long-term fertilization and periodic liming was carried out in all variants. In the article, we present the most representative options: control (without fertilizing) (C); organic fertilization system (10 t ha^{-1} of crop rotation area of manure) (O); organo-mineral fertilizing system (10 t of manure per ha of crop rotation area + $N_{65}P_{68}K_{68}$) with periodic liming by 1.0 norm of $CaCO_3$ (6.0 t of ground limestone per ha) according to hydrolytic acidity (OM1); the same fertilizing system with an optimal dose of lime (2.5 t ha^{-1}), calculated according to acid-base buffering capacity (OM2); mineral fertilizing system ($N_{105}P_{101}K_{101}$) with liming by 1.5 norms of $CaCO_3$ (9.0 t ha^{-1}) according to hydrolytic acidity (M1); the same fertilizing system with applying $CaCO_3$ (2.5 t ha^{-1}) according to acid-base buffering capacity (M2); mineral ($N_{65}P_{68}K_{68}$) fertilizing system (M) (Table 1).

Table 1. Scheme of the studied variants of the stationary field experiment (IX, X rotations)

Fertilization system		Per 1 ha of crop rotation area			Corn for silage	Spring barley + meadow clover	Meadow clover	Winter wheat
		rate of lime	Manure, t	NPK, kg of active substance				
Without fertilizers (control)	C	0	0	0	0	0	0	0
Organic	O	0	10	0	Manure, 40 t ha^{-1}	0	0	0
Organo-mineral with liming	OM1	1.0 norm by hydrolytic acidity (6.0 t ha^{-1})	10	$N_{65}P_{68}K_{68}$	Manure, 40 t ha^{-1}+ $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
	OM2	Optimal by the acid-base buffering capacity (2.5 t ha^{-1})	10	$N_{65}P_{68}K_{68}$	Manure, 40 t ha^{-1}+ $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
Mineral	M	0	0	$N_{65}P_{68}K_{68}$	$N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
Mineral with liming	M1	1.5 norms by hydrolytic acidity (9.0 t ha^{-1})	0	$N_{105}P_{101}K_{101}$	$N_{180}P_{135}K_{135}$	$N_{120}P_{135}K_{135}$	0	$N_{120}P_{135}K_{135}$
	M2	Optimal by acid-base buffering capacity (2.5 t ha^{-1})	0	$N_{105}P_{101}K_{101}$	$N_{180}P_{135}K_{135}$	$N_{120}P_{135}K_{135}$	0	$N_{120}P_{135}K_{135}$

Soil samples for determination of physicochemical properties were taken after the end of each of the following rotations on the studied treatments from the arable layer of Albic Pantostagnic Luvisol (0–25 cm) and prepared for analysis per DSTU ISO 11464-

2001. Laboratory and analytical studies were performed in the certified laboratory of the Institute of Agriculture of Carpathian Region of the National Academy of Sciences of Ukraine. Determination of pH_{KCl} was carried out by the potentiometric method at a 1:2.5 ratio of soil to a solution of 1.0 n KCl using a pH-meter ‘pH-301’ and glass electrodes (DSTU ISO 10390:2007). Hydrolytic acidity was determined by the titrimetric method with the extraction of 1.0 n CH_3COONa at a 1:2.5 soil:solution ratio, shaking for 1 hour and titration with a 0.1 n NaOH. The content of mobile aluminium was determined by Sokolov method (extraction with 1.0 n KCl (1:2.5), shaking for 1 h, followed by titration after boiling for 5 min in a hot state with a 0.02 n NaOH solution).

For the comparative assessment of crops of different biological groups in a crop rotation and the calculation of the overall productivity of crop rotation, the yield of each crop was converted into grain units using the established conversion coefficients (corn for silage - 0.17, spring barley - 0.8, meadow clover - 0.5, winter wheat - 1). A grain unit is a unit of measurement of crop rotation productivity that corresponds to 1 kg of winter wheat grain (Ivanyuk, 2009). The obtained values were added, divided by the number of crops in the rotation, and the total yield of grain units per 1 ha of crop rotation area was determined.

Statistical processing of the obtained research results was carried out using the software OriginPro 2019b (OriginLab Corporation, USA, 2019). Data were compared using the Tukey test. Differences between samples were considered statistically significant at $p < 0.05$. Data in the tables are presented as an arithmetic mean with standard deviation (x ± SD).

RESULTS AND DISCUSSION

For the theoretical substantiation of many processes that occur in the soil at various stages of evolution, including the results of intense anthropogenic influence, acid-base properties are also important. They are the most dynamic indicators of the physical and chemical properties of soils, they change intensively in space and time depending on the transformation of elementary soil processes and under the influence of the agrogenic evolution of soils (Pidvalna & Pozniak, 2004).

Studies have shown that in the conditions of Albic Pantostagnic Luvisol, the content of mobile aluminium compounds is closely related to the acidity (by pH_{KCl} and hydrolytic), fertilization systems, their aftereffects, and the crop rotation factor.

The inclusion of Albic Pantostagnic Luvisol in the system of intensive farming without the application of fertilizers and lime, and the one-sided application of mineral fertilizers leads to further deterioration of its properties and an increase in the content of mobile aluminium compounds.

The highest content of mobile aluminium compounds was 92.0 and 132.0 mg kg^{-1} of soil in the control treatment and the mineral fertilization system after five seven-field rotations at pH_{KCl} of 4.1 and 3.8, respectively, hydrolytic acidity (Ha) of 5.20 and 6.43 cmol(+) kg^{-1} of soil (Fig. 1, Table 2). According to studies (Chen et al., 2018), a decrease in pH also led to the release of exchangeable Al into the soil solution, as a result of which its concentration in the soil increased.

In our previous studies of the humic state of the specified treatments at the end of the V rotation, the content of fulvic acids in the composition of organic carbon was 0.54–0.63%, the content of humic acids - 0.26% and the ratio of $C_{\text{humic acids}}$: $C_{\text{fulvic acids}}$ was

0.48–0.41, which according to the classification of V.K. Pestryakov characterizes the fulvate type of humus. At the same time, in the fraction of fulvic acids, the content of the most mobile and ‘aggressive’ FAs was the highest and amounted to 0.11–0.13% in the control and 0.23% under the mineral fertilizer system (Habriel et al., 2006). It contributed to additional humus mineralization (Olifir et al., 2021). After all, it is known that soluble organic matter is easily washed away and transported by wind and water (erosion), due to which soil fertility decreases (Loide, 2010).

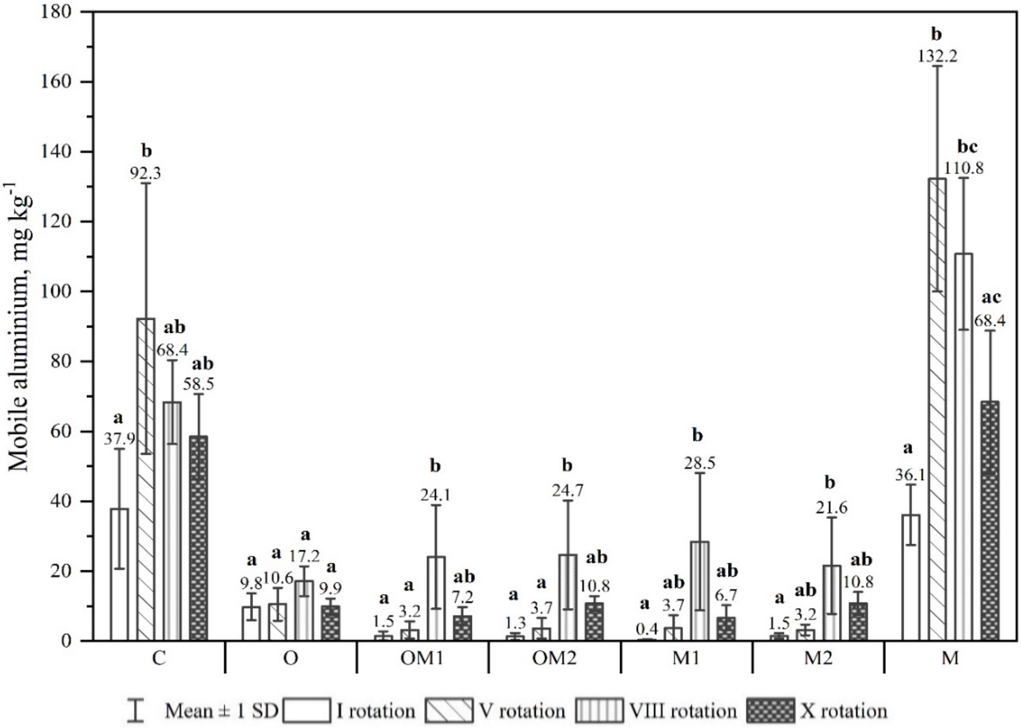

Figure 1. Dynamics of mobile aluminium in rotations depending on long-term anthropogenic influence, mg kg^{-1} (x ± SD, $n = 6$). Fertilization systems: C – without fertilizers (control); O – organic; OM1 – organo-mineral with liming by 6.0 t ha^{-1} $CaCO_3$; OM2 – organo-mineral with liming by 2.5 t ha^{-1} $CaCO_3$; M – mineral; M1 – mineral with liming by 9.0 t ha^{-1} $CaCO_3$; M2 – mineral with liming by 2.5 t ha^{-1} $CaCO_3$. Mean values labelled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test ($P < 0.05$) within each fertilization system.

In the variants of the organo-mineral and mineral fertilization systems with liming with 6 and 9 t ha^{-1} of $CaCO_3$ at the end of the V seven-field rotation the content of mobile aluminium compounds decreased to 3.2 and 3.7 mg kg^{-1} of soil respectively. Soil pH was 5.4, and hydrolytic acidity in these variants reached 2.4 and 2.27 cmol(+) kg^{-1} of soil respectively. Under such conditions, the content of aggressive fulvic acids decreased to 0.03–0.09% with a sufficiently high 0.2–0.15% content of the mobile fraction of fulvic acids (Habriel et al., 2006). Obviously in this case the high buffering effect of fulvic acids is manifested concerning the aluminium load with the formation of complex organo-mineral compounds, which is also mentioned in the studies (Tsapko et al., 2018b).

According to the research of the NSC 'Institute of Soil Science and Agrochemistry named after O.N. Sokolovsky' aluminium in these complex heterogeneous salts is very tightly bound. Within the pH range of 4.5–7.5, it is located in the inner part of the molecule, so it cannot acidify the soil environment. The destruction of these complexes is possible at a pH of the soil solution < 4.5 (a very acidic reaction), which is observed in our case in the variants of control and mineral fertilization.

Table 2. Dynamics of acidity by rotation depending on long-term anthropogenic influence (x ± *SD*, *n* = 6)

Variants	I rotation		V rotation		VIII rotation		X rotation	
	pH_{KCl}	Ha, cmol(+) kg^{-1} of soil	pH_{KCl}	Ha, cmol(+) kg^{-1} of soil	pH_{KCl}	Ha, cmol(+) kg^{-1} of soil	pH_{KCl}	Ha, cmol(+) kg^{-1} of soil
Control (without fertilizers)	4.2 ± 0.1^{a}	$4.50 \pm 0.42^{\underline{a}}$	4.1 ± 0.1^{a}	$5.20 \pm 1.31^{\underline{a}}$	4.4 ± 0.1^{a}	$4.69 \pm 0.23^{\underline{a}}$	4.4 ± 0.1^{a}	$4.29 \pm 0.16^{\underline{a}}$
Manure 10 t ha^{-1}	4.4 ± 0.2^{a}	$4.70 \pm 0.23^{\underline{a}}$	4.8 ± 0.1^{b}	$3.47 \pm 0.67^{\underline{b}}$	4.7 ± 0.1^{ab}	$3.85 \pm 0.17^{\underline{ab}}$	4.9 ± 0.2^{b}	$2.57 \pm 0.34^{\underline{b}}$
$N_{65}P_{68}K_{68}$ + manure 10 t ha^{-1} + $CaCO_3$ 1.0 norm by Ha (6.0 t ha^{-1})	5.1 ± 0.2^{abc}	$3.40 \pm 0.76^{\underline{a}}$	5.4 ± 0.3^{ab}	$2.40 \pm 0.70^{\underline{a}}$	4.8 ± 0.1^{ac}	$4.04 \pm 0.74^{\underline{a}}$	5.0 ± 0.1^{abc}	$3.59 \pm 0.67^{\underline{a}}$
$N_{65}P_{68}K_{68}$ + manure 10 t ha^{-1} + $CaCO_3$ optim. by pH buff. (2.5 t ha^{-1})	4.8 ± 0.2^{a}	$4.80 \pm 0.41^{\underline{a}}$	5.3 ± 0.4^{a}	$2.67 \pm 0.85^{\underline{b}}$	4.8 ± 0.3^{a}	$3.94 \pm 0.76^{\underline{ab}}$	5.0 ± 0.2^{a}	$3.85 \pm 0.86^{\underline{ab}}$
$N_{105}P_{101}K_{101}$ + $CaCO_3$ 1.5 norms by Ha (9.0 t ha^{-1})	5.4 ± 0.1^{a}	$5.40 \pm 0.57^{\underline{a}}$	5.4 ± 0.1^{a}	$2.27 \pm 0.49^{\underline{b}}$	4.7 ± 0.2^{b}	$3.90 \pm 0.51^{\underline{c}}$	5.4 ± 0.2^{a}	$3.41 \pm 0.61^{\underline{bc}}$
$N_{105}P_{101}K_{101}$ + $CaCO_3$ optim. by pH buff. (2.5 t ha^{-1})	5.0 ± 0.4^{a}	$5.00 \pm 0.23^{\underline{a}}$	5.8 ± 0.3^{a}	$2.97 \pm 0.61^{\underline{b}}$	4.9 ± 0.2^{a}	$3.40 \pm 0.43^{\underline{bc}}$	5.2 ± 0.4^{a}	$4.55 \pm 0.74^{\underline{ac}}$
$N_{65}P_{68}K_{68}$	4.1 ± 0.3^{a}	$4.10 \pm 0.47^{\underline{a}}$	3.8 ± 0.1^{a}	$6.43 \pm 1.42^{\underline{b}}$	4.2 ± 0.1^{a}	$5.78 \pm 0.37^{\underline{ab}}$	4.2 ± 0.1^{a}	$4.63 \pm 0.4^{\underline{ab}}$

Note: values that have at least one identical letter within a table line do not differ in the *Tukey test* ($P < 0.05$).

All this confirms the unconvincingness of the theory of the origin of soil acidity due to aluminium and coincides with the views of Z. M. Tomashivskyi that the acidity of the soil is the result of a long-term process of leaching calcium and magnesium from the soil by precipitation and enriching it with hydrogen ions - the primary source of the acidic reaction of the soil (Tomashivskyi et al., 2021).

Studies have shown that the organic fertilization system (introduction of 40 t ha^{-1} of manure in a crop rotation) on Albic Pantostagnic Luvisol increases pH_{KCl} at the end of I and V rotations to 4.4 and 4.8 units and reduces hydrolytic acidity to 4.70 and 3.47 cmol(+) kg^{-1} of soil respectively. As a result, the content of mobile aluminium compounds decreased to 9.8 and 10.6 mg kg^{-1}. It is known that cattle manure increases soil pH (Dai et al., 2021; Naramabuye et al., 2008; Whalen et al., 2002; Whalen et al., 2000). Obviously, in this case, the acid-neutralizing ability is associated with organic matter. Al is known to tend to bind to organic matter, forming strong insoluble complexes (Patra et al., 2020; Yang et al., 2022). Other major mechanisms responsible for the elevated pH were the proton consumption capacity of humic material present in the manure and the decarboxylation of organic acid anions during its decomposition (Mokolobate & Haynes, 2002).

An invaluable advantage of stationary experiments is that with the duration of use, you can always make the necessary adjustments to the requirements of time and thereby increase the effectiveness of research.

At the end of the VIII rotation in the control, in the arable layer, a decrease in hydrolytic acidity to 4.69 cmol(+) kg^{-1} of soil is observed compared to the end of the V seven-field rotation. At the same time, there is an increase in the pH index to 4.4 against 4.1 and a decrease in the content of mobile aluminium compounds to 68.4 mg kg^{-1} of soil. In the case of mineral fertilizer, the pH_{KCl} increased to 4.20 against 3.8 (end of V rotation), hydrolytic acidity decreased to 5.78 cmol(+) kg^{-1} of soil against 6.43 cmol(+) kg^{-1} respectfully. Meanwhile, the content of mobile aluminium decreased to 110.8 compared to 132.0 mg kg^{-1} at the end of V rotation.

This was largely facilitated by the replacement of a seven-field crop rotation with a four-field one before the start of the VI rotation with the exclusion of energy-intensive crops, in particular, sugar beets and potatoes and winter wheat after corn. This was accompanied by a decrease in the intensity of cultivation and a significant amount of organic root residues accumulated during the four-field crop rotation (corn for silage - spring barley - meadow clover - winter wheat) significantly affected the cycle of nutrients, physicochemical and agrochemical indicators, primarily of control and under low levels of fertilization.

Acidity and the content of mobile aluminium at the end of the VIII four-field rotation (in which we studied the effect of applying lime and mineral fertilizers) indicate that periodic liming was and remains the most reliable and effective measure for fundamentally improving the agro-ecological condition and increasing the fertility of soils with an acidic reaction.

With the duration of the after-effect of lime, the content of mobile aluminium compounds at the end of the VIII rotation increases to 24.1 and 24.7 mg kg^{-1} of soil against 3.2–3.7 mg kg^{-1} at the end of the V rotation in variants of the organo-mineral system of fertilization and liming according to Ha.

At the end of the X crop rotation in the variant of the combined application of the organo-mineral fertilization system with the introduction of the full rate of NPK, 10 t ha^{-1} of manure and 6.0 t ha^{-1} of $CaCO_3$ by Ha, the content of mobile aluminium compounds is 7.2 mg kg^{-1} of soil, Ha decreased to 3.59 and pH is 5.0. With an identical fertilization system with liming by the pH buffering capacity the content of mobile aluminium compounds is 10.8 mg kg^{-1} of soil, Ha is 3.85 cmol(+) kg^{-1} and pH_{KCl} 5.0.

Mineral fertilizer system plus liming with 9.0 t ha^{-1} of $CaCO_3$, the pH value is 5.4, and with the addition of lime by the pH-buffering capacity - 5.2. At the same time, hydrolytic acidity is 3.41 and 4.55 cmol(+) kg^{-1} of soil respectively. The content of mobile aluminium decreased to 6.7 and 10.8 mg kg^{-1} of soil respectively.

Similar results were obtained in studies (Polovyy et al., 2022), in which the concentration of Al^{3+} was the highest in unlimed and fertilized areas. And the use of limestone fertilizers (ground limestone and dolomite) with the application of mineral fertilizers led to an increase in the value of pH_{KCl}, saturation with bases and at the same time a decrease in the content of exchangeable Al^{3+} in the soil.

In studies (Szara et al., 2019) liming in combination with mineral fertilizers also reduced the sorption capacity of the soil, especially as a result of fixing amorphous (hydro)oxides of Al and Fe into more crystalline forms.

Further ploughing of the second mowing of the meadow clover green mass as fertilizer also contributed to the stabilization of the pH_{KCl} to 4.40 in the control and 4.20 in the mineral fertilizer treatment at the end of X rotation, and a decrease in hydrolytic acidity to 4.29 in the control and 4.63 cmol(+) kg^{-1} of soil in mineral fertilization systems. Meanwhile, the content of mobile aluminium compounds at the end of the X rotation is 58.5 and 68.4 mg kg^{-1} of soil under control and mineral fertilizer treatment respectively

Under the mineral fertilisation system, the introduction of the optimal dose of lime (2.5 t ha^{-1}) calculated by pH buffering capacity increased the pH_{KCl} from 4.9 at the end of the VIII rotation to 5.2 at the end of the X rotation. With an identical fertilisation system but the application of 9.0 t ha^{-1} of lime increased the pH_{KCl} value to 5.4 against 4.7 at the end of the VIII rotation. It is obvious that under conditions of a periodically leaching water regime, the mineral fertilisation system with high doses of lime will contribute to the additional leaching of calcium to a greater extent.

The use of an organo-mineral fertilisation system with the application of the full norm of NPK, 10 t ha^{-1} of manure with liming with a dose of $CaCO_3$ calculated by pH-buffering capacity (2.5 t ha^{-1}) is more efficient and environmentally friendly on Albic Pantostagnic Luvisol compared to the mineral fertilisation system with liming with high doses of lime (9.0 t ha^{-1}). This is due to the systematic application of organic fertilisers, which play a more important role in these low-fertile soils due to the formation of complex organic-mineral compounds compared to the application of high doses of lime, which is subject to significant leaching under the conditions of periodically leaching water regime.

Phytotoxicity of aluminium is one of the main problems related to the formation of productivity of crops on acidic soils (Martins et al., 2020).

Research conducted in the conditions of a long-term stationary experiment shows that systematic fertilization and periodic liming, improving the physicochemical properties of Albic Pantostagnic Luvisol primarily due to a decrease in the acidity of the soil solution and mobile aluminium compounds, ensures a sufficiently high level of productivity: 5.66–7.09 t ha^{-1} of grain units (g.u.). Long-term mineral fertilization on this type of soil creates a level of productivity of 1.45 t ha^{-1} g.u. higher than in the control without fertilizers and is 3.99 t ha^{-1} of organic matter at the end of X rotation. Under the organic-mineral and mineral fertilization systems with liming with a dose of $CaCO_3$ by Ha, the level of productivity is only 0.57–0.50 t ha^{-1} g.u. higher than the identical fertilizer system with liming by the pH buffering capacity (Fig. 2).

The systematic long-term application of 40 t ha^{-1} of manure in the crop rotation since 1965 has reduced acidity (hydrolytic acidity, pH_{KCl}) and the content of mobile aluminium, but the productivity of crop rotation under this fertilisation system is significantly lower compared to the organic-mineral fertilisation system with liming.

It should be noted that following the dynamics of changes in the productivity of crop rotation by rotations, its gradual growth was noted in almost all variants, including the control without fertilizers. This happened primarily due to the influence of the crop rotation factor, which contributes to the accumulation of a significant amount of organic residues, including meadow clover, and the correct selection of cultivated crops. All this, together with the use of science-based fertilization systems, ensured a decrease in the content of mobile aluminium compounds, and an improvement in physicochemical and agrochemical properties, which made it possible to obtain sufficiently high yields of cultivated crop rotations on infertile soils.

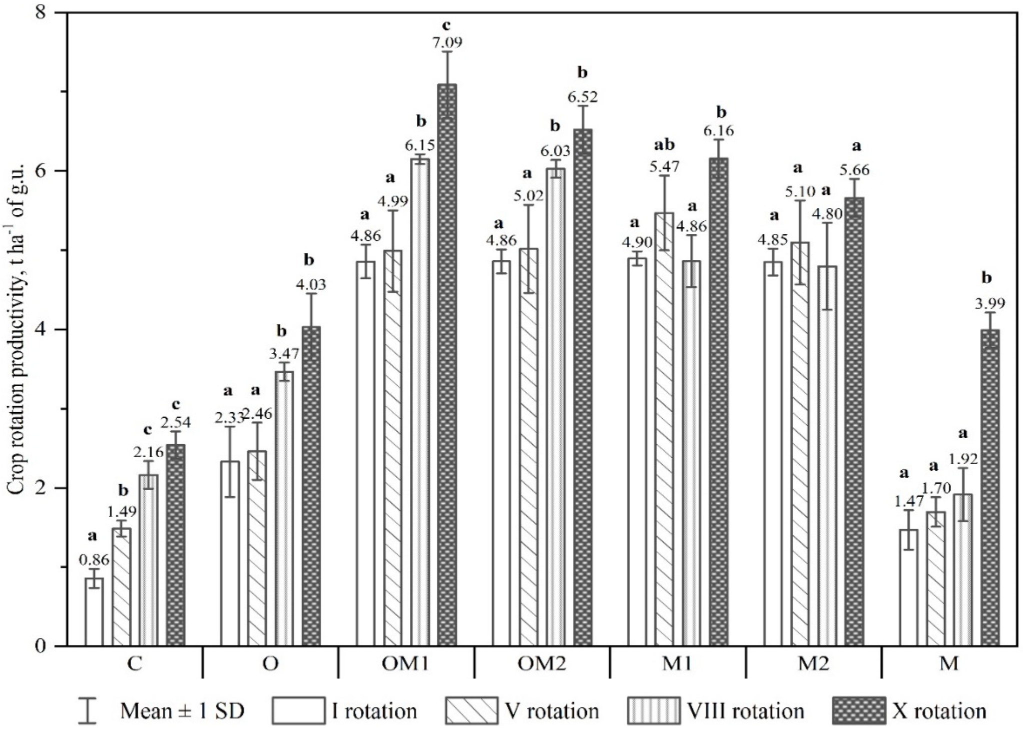

Figure 2. Change in crop rotation productivity by rotations, t ha^{-1} of grain units (x ± SD, *n* = 6). Fertilization systems: C – without fertilizers (control); O – organic; OM1 – organo-mineral with liming by 6.0 t ha^{-1} $CaCO_3$; OM2 – organo-mineral with liming by 2.5 t ha^{-1} $CaCO_3$; M – mineral, M1 – mineral with liming by 6.0 t ha^{-1} $CaCO_3$; M2 – mineral with liming by 2.5 t ha^{-1} $CaCO_3$. Mean values labelled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test ($P < 0.05$) within each fertilization system.

In short crop rotations on Albic Pantostagnic Luvisol the periodic application of a chemical ameliorant with a dose calculated by the pH-buffering capacity ensures the reduction of the content of mobile aluminium to harmless values, the improvement of physicochemical properties, ensuring a high level of crop rotation productivity of 5.66–6.52 t ha^{-1} grain units.

CONCLUSIONS

Based on the studies conducted in a long-term stationary experiment on Albic Pantostagnic Luvisol, it was found that the dose of chemical ameliorant calculated based on pH-buffering capacity graph (2.5 t ha^{-1}) in a 4-year crop rotation ensures a reduction in the content of mobile aluminium compounds to harmless levels (10.8 mg kg^{-1} soil), a high level of agrocenosis productivity (6.52 t ha^{-1} of grain units), economical use of fertilisers and ameliorants, and stabilisation of environmental safety. With the unilateral long-term application of high doses of mineral fertilisers and intensive use of Albic Pantostagnic Luvisol without fertilisers, the content of mobile aluminium increased to 58.5–132.0 t ha^{-1}, which contributed to the further humus fulvatization with the formation of mobile aluminium fulvates and increased acidity.

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