Scientific Papers. Series A. Agronomy, Vol. LXVI, No. 2, 2023
ISSN 2285-5785; ISSN CD-ROM 2285-5793; ISSN Online 2285-5807; ISSN-L 2285-5785

THE INFLUENCE OF LONG-TERM ANTHROPOGENIC LOAD ON THE MIGRATION OF MOBILE ALUMINUM COMPOUNDS, PHYSICAL AND CHEMICAL PROPERTIES OF ALBIC STAGNIC LUVISOL

**Yuriy OLIFIR, Anna HABRYEL, Oleh HAVRYSHKO, Tetiana PARTYKA,
Hryhoriy KONYK, Nadiia KOZAK**

Institute of Agriculture of Carpathian Region of National Academy of Agrarian Sciences of
Ukraine, 5 Hrushevskoho Street, Obroshyne, 81115, Lviv Region, Ukraine

Corresponding author email: olifir.yura@gmail.com

Abstract

FAO singles out acidic soils, which are widespread in Ukraine, as problematic soils. At the same time, the role of aluminium in soil acidity formation and aluminium toxicity is becoming increasingly important. The study was conducted in a long-term stationary experiment and under conditions of natural analogues of Albic Stagnic Luvisol under forest and fallow land. It was found that cultivation and long-term use of different doses of fertilizers and lime change the content of mobile aluminium compounds, physical and chemical properties of not only the upper humus horizons but also affect the lower horizons and soil formation processes. The highest content of mobile aluminium compounds, 110.3-121.5 mg/kg of soil, is accumulated in the upper humus horizons in the control without fertilizers. With prolonged mineral fertilization, the highest content of mobile aluminium compounds (148.1 mg/kg) is concentrated in the illuvial-eluvial horizon. In the soil under the forest, the highest content of mobile aluminium is accumulated in the upper humus horizons AEg, Ehg and is 210.6 and 183.0 mg/kg of soil, respectively, with the lowest pH_{KCl} value of 3.72 and the highest hydrolytic acidity of 9.73 mg-eq/100 g of soil. The content of mobile aluminium ranges on the fallow land from 54.3 in AEg to 55.7 mg/kg in the Cg horizon, i.e. it is characterized by its uniform distribution.

Key words*: acidity, aluminium, Albic Stagnic Luvisol, fertilizers, liming.*

INTRODUCTION

Among the sectors of the economy, agriculture reacts most noticeably to the climatic changes of recent decades. The future of Ukraine's food security will depend on how it adapts to the transformation of weather conditions. Among the problematic soils in terms of their agricultural use, the FAO particularly highlights acidic soils, which are widespread in Ukraine (FAO & ITPS, 2015; Tkachenko & Boris, 2021). The transition to new forms of farming, climate change, increased acidity, and the use of a disproportionate ratio of fertilizers in conditions of intensive agricultural production is leading to increased soil and land cover degradation (Lykhochvor et al., 2022).

Soil acidification is becoming a growing problem for food security due to the formation of free aluminium ion (Al^{3+}), which is toxic to crops (Li et al., 2022).

However, the main goal of chemical amelioration is not to completely neutralize acidity, but primarily to reduce the level of exchangeable Al^{3+} and increase the level of exchangeable Ca^{2+} in the soil (Almaliev, 2022).

The dominant aluminium (Al^{3+}) in soil composition has a significant impact on the establishment of acid-base balance in soils, thereby playing an important role in shaping fertility. Its content varies significantly in soils of different compositions and genesis, depending on the parent material. In podzolic and sod-podzolic soils, aluminium is 1.5-2.0 times higher in the illuvial (B) than in the eluvial (E) horizons (Kyrylchuk & Bonishko, 2011).

The importance of Al in soil formation and soil fertility is very high. Firstly, aluminium plays a constitutional role, as aluminosilicates are the most abundant soil minerals - they make up nearly 85% of the Earth's crust. Secondly, Al is quite reactive and forms various compounds that migrate along the profile (Nazarenko et al., 1998). At the same time, aluminium participates in the formation of potential soil acidity (exchangeable and hydrolytic), which adversely affects the growth and development of crops. Meanwhile, the Al content affects plant nutrition by forming hardly soluble aluminium phosphates, whose phosphorus is not available to plants (Tkachenko et al., 2019). According to studies (Godsey et al., 2007; Brown et al., 2008), the physical and chemical properties of soils are significantly impaired by the presence of aluminium cations.

The total concentration, composition and availability of aluminium in the soil depend on the pH and chemical environment of the solution (Bojorquez-Quintal et al., 2017; Smirnov & Taran, 2013). Al compounds are immobile in slightly alkaline and neutral environments, but gain mobility in an acidic environment, forming soluble organo-mineral complexes with fulvic acids, which causes its active migration along the profile. The resulting organic-aluminium complexes undergo various transformations depending on environmental conditions. In the soils of the podzolic zone, they are fixed in the composition of humic substances. With increasing pH, these complexes usually decompose and Al is precipitated as hydroxides (Smirnov & Taran, 2013). In studies (Schroder et al., 2011), soil acidification below pH 5.0-5.5 increases the solubility of Al^{3+} in the soil and negatively affects the growth and yield of crops. In addition, the level and toxicity of Al increase dramatically (Gillespie et al., 2021).

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

In acidic soils with a pH<5.0, phytotoxic aluminium (Al^{3+}) quickly inhibits root growth and subsequently negatively affects water and nutrient uptake by plants. This is one of the reasons why with an increased aluminium concentration in the soil profile the roots are predominantly located in the upper layer with a lower aluminium content, which is an important part of the crop's resistance to acidic soils (Smirnov et al., 2020).

According to research (Souza et al., 2023), exchangeable aluminium is significantly affected by nitrogen fertilizers, which lower the soil pH. At the same time, a higher content of organic matter on the soil surface reduces the concentration of mobile Al even at a lower pH.

The main research objective is to determine the migration of mobile aluminium compounds on Albic Stagnic Luvisol under different anthropogenic loads compared to primary soil formation under forest and fallow land (as an analogue of natural virgin soils) and to study their impact on soil formation processes.

MATERIALS AND METHODS

Long-term stationary experiments provide in-depth information on 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 classic stationary experiment of the Laboratory of Agrochemistry of the Institute of Agriculture of Carpathian region of the National Academy of Agrarian Sciences (49°47'54.3"N 23°52'26.9"E), established in 1965.

The stationary experiment consists of three fields. Each of the fields has 18 treatments in three repetitions. The arrangement of variants is single-tiered and sequential. Plot's total area is 168 m^2, and the accounting area is 100 m^2. The experiment uses a four-field crop rotation with the following crops: corn for silage - spring barley with underplanting of red clover - red clover - winter wheat. For soil cultivation, crop cultivation and crop care, we used technologies customary for the conditions of the Western Forest-Steppe zone.

The soil of the experimental site is Albic Stagnic Luvisol (WRB, 2015) (light-grey forest surface-gleyed soil by Ukrainian classification). Its arable (0-20 cm) layer had the following averaged initial fertility indicators: humus content (by Tyurin) 1.42%, pH_{KCl} 4.2, hydrolytic (by Kappen) and exchangeable acidity (by Sokolov) - 4.5 and 0.6 mg-eq/100 g of soil and 60.0 mg/kg of mobile aluminium. The content of mobile phosphorus (by Kirsanov) and exchangeable potassium (by Maslova) was 36.0 and 50.0 mg/kg of soil respectively.

As organic fertilizer semi-rotted cattle manure on straw bedding was used. Mineral fertilizers consisted of granular superphosphate (19.5%), potassium salt (40%), ammonium nitrate (34.5%) and nitroammophoska (NPK 16% each). NPK content was balanced with simple fertilizers when using nitroamophoska. Manure as organic fertilizer was applied under corn (40-60 t/ha). In the fall, phosphorus and potash fertilizers were applied during the main ploughing. Nitrogen fertilizers were used during pre-sowing cultivation in the spring. Before the start of the 9th rotation of crop rotation, liming was carried out, during which the doses of lime were adjusted. Limestone flour (93.5% $CaCO_3$) was used as limestone materials. The second mowing of red clover was ploughed as an organic fertilizer in all treatments starting from the 8th rotation.

The study of changes in the content of mobile aluminium was carried out in the soil profiles under the forest, on the fallow and the most representative treatments of the stationary experiment: absolute control (without fertilization), organo-mineral fertilization system (10 t/ha of manure per crop rotation area + $N_{65}P_{68}K_{68}$) with periodic liming with 6.0 t/ha of limestone flour (1.0 n $CaCO_3$ by hydrolytic acidity) and mineral fertilizer system ($N_{65}P_{68}K_{68}$).

Soil samples for determination of physical and chemical properties were collected on the studied variants by genetic horizons of Albic Stagnic Luvisol and prepared for analysis following DSTU ISO 11464-2001. Determination of pH_{KCl} was carried out by the potentiometric method at a ratio of soil to 1.0 n KCl solution 1:2.5 using a pH meter "pH-301" (DSTU ISO 10390:2007). Hydrolytic acidity (Ha) was determined by the titrimetric method in the extract of a 1.0 n CH_3COONa solution at a soil:solution ratio of 1:2.5, shaking for 1 hour and titration with a 0.1 n NaOH solution.

The content of mobile aluminium was determined by the 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.

The research data was processed using OriginPro 2019b software (OriginLab Corporation, USA, 2019). A comparison of the obtained data was conducted using the Tukey test ($p<0.05$). Data are presented as an arithmetic mean with standard deviation (x ± SD).

RESULTS AND DISCUSSIONS

Studies conducted in a stationary experiment have shown that long-term ploughing and the use of different doses of fertilizers and lime on an Albic Stagnic Luvisol (compared with the primary soil formation under the forest and fallow - analogues of natural virgin soils) changes the content of mobile aluminium compounds, physical and chemical properties of the upper humus horizons. At the same time, it has an intense impact on the horizons below, thereby affecting soil formation processes that occur under different anthropogenic loads.

The obtained indicators of the physicochemical characteristics of the control and fallow land variants indicate the low agroecological quality of Albic Stagnic Luvisol due to high acidity.

Characterizing the distribution of mobile aluminium in the soil profile, it should be noted that with the introduction of different doses of fertilizers and lime, the largest amount of it is concentrated in the illuvial weakly eluviated gleyed horizon (Beg). At the same time, the highest value of 148.1 mg/kg of soil mobile aluminium in the profile was determined by the long-term application of only mineral fertilizers (Table 1).

With long-term use of the organo-mineral fertilizer system and liming, the content of mobile aluminium in the humus-eluvial arable horizon is the lowest - 26.1 mg/kg. This is because, with a slightly acidic reaction of the soil solution (pH_{KCl} - 5.18), the content of organic matter in the upper horizon increased to 1.90%, which contributed to a decrease in the concentration of mobile aluminium and a reduction in its toxicity due to the formation of aluminium-humus complexes. Similar results were obtained in studies (Li et al., 2022), where the presence of more organic matter in the soil not only improved their acid buffering capacity but also suppressed the accumulation of exchangeable and soluble Al.

With the depth of the soil profile under this fertilization system, the content of mobile aluminium in the humus-eluvial subsoil, eluvial, and weakly eluvial horizons increases to 64.8-79.7 mg/kg. In the lower horizons, the content of mobile aluminium compounds decreases more than twice to 24.3-43.2 mg/kg in parallel to the increase in the number of absorbed bases to 18.9-16.3 mg-eq/100 g of soil.

This is primarily due to a small amount of organic matter, represented mainly by mobile fulvic acids, with which aluminium forms complex organo-mineral compounds.

Table 1. Changes in the physical and chemical properties of the genetic horizons of the Albic Stagnic Luvisol under the long-term anthropogenic influence, the end of the 9th rotation (x ± SD, n = 6)

Genetic horizons	Sampling depth, Cm	pH_{KCl}	Hydrolytic acidity	A sum of absorbed bases	Mobile aluminium, mg/kg of soil	Humus, %
			mg-eq/100 g of soil			
1	2	3	4	5	6	7
No fertilizers (control)						
AEg (arable)	0-18	4.22±0.14a	5.11±0.59a	3.0±0.1a	110.3±15.3a	1.48±0.04a
AEg (sub-arable)	18-31	4.18±0.37a	4.94±0.10a	2.4±0.6a	121.5±9.8a	1.40±0.07a
Ehg	31-64	4.31±0.09a	3.58±0.42a	5.2±0.5a	65.3±1.9a	0.48±0.03a
Beg	64-110	4.13±0.18a	4.20±0.17a	10.4±1.2a	91.8±0.2a	0.28±0.02a
Bg	110-131	4.22±0.08a	3.23±0.10a	6.9±0.1a	68.4±1.7a	0.28±0.01a
BCg	131-180	4.47±0.03a	1.40±0.04b	6.0±0.7a	27.5±2.0a	0.47±0.02a
CBg	180-200	4.35±0.07a	2.62±0.44a	8.0±0.1a	36.5±2.6a	0.26±0.02a
	LSD_{05}	*0.15*	*1.72*	*3.66*	*46.50*	*0.70*
Organo-mineral fertilizer system ($N_{65}P_{68}K_{68}$ + 10 t/ha of manure + $CaCO_3$ 1.0 n by Ha)						
AEg (arable)	0-20	5.18±0.10b	2.77±0.22b	10.6±0.5b	26.1±1.4b	1.90±0.05b
AEg (sub-arable)	20-35	5.05±0.07b	2.86±0.15b	7.5±0.5b	64.8±0.1b	1.61±0.16b
Ehg	35-55	4.90±0.12b	3.11±0.05a	8.5±0.2b	71.1±9.3a	0.83±0.15b
Beg	55-81	4.78±0.21b	3.46±0.21a	9.0±1.9a	79.7±1.6a	0.64±0.10b
Bg	81-150	4.90±0.13b	3.15±0.04a	11.9±0.8b	43.2±5.8b	0.55±0.06b
BCg	150-193	4.85±0.06a	2.98±0.01a	16.3±1.2b	32.4±4.2a	0.51±0.00a
CBG	193-215	4.87±0.12b	2.95±0.04a	18.9±0.1b	24.3±2.1a	0.40±0.01a
	LSD_{05}	*0.18*	*0.30*	*5.59*	*29.88*	*0.77*
Mineral fertilizer system ($N_{65}P_{68}K_{68}$)						
AEg (arable)	0-22	4.03±0.07a	5.11±0.92a	3.0±0.5a	75.2±5.1c	1.57±0.03a
AEg (sub-arable)	22-35	3.98±0.09a	5.20±0.07a	2.8±0.2a	99.5±0.9c	1.45±0.03ab
Ehg	35-61	4.17±0.04a	4.54±0.06b	1.5±0.1c	126.5±3.8b	0.63±0.06a
Beg	61-87	4.00±0.02a	5.25±0.06b	5.7±0.2b	148.1±3.0b	0.37±0.03a
Bg	87-150	4.07±0.10a	2.97±0.02a	8.0±1.3a	66.2±2.8a	0.26±0.02a
BCg	150-180	4.04±0.05b	2.97±0.10a	13.8±0.3c	54.5±6.1b	0.21±0.01b
CBG	180-200	4.11±0.04a	2.80±0.05a	15.2±0.5c	36.0±0.9a	0.31±0.02a
	LSD_{05}	*0.09*	*1.51*	*7.17*	*52.59*	*0.76*

Note. Values labelled with the same letter within one soil horizon are not significantly different from each other according to the Tukey test ($p<0.05$).

It is known from studies (Berggren & Mulder, 1995) that the solubility of Al in acidic mineral soil horizons is controlled by the reaction of complexation with soil organic matter. After all, the pool of organically bound soil Al strongly controls the solubility of Al in acid soil suspensions.

In the soil under the forest and the control without fertilizers, the highest content of mobile aluminium is accumulated in the upper humus horizon - 210.6 mg/kg of soil under the forest and 110.3-121.5 mg/kg in the control without fertilizers. On the fallow land, the content of mobile aluminium ranged from 54.3 mg/kg of soil in AEg to 55.7 mg/kg in the Cg horizon, i.e., its uniform distribution along the profile is characteristic (Table 2).

Studies in a stationary experiment have shown that at the end of the IX rotation of four-field crop rotation, the acidity (pH_{KCl}) of the soil profile does not change significantly. In the humus-eluvial arable horizon (AEg arable.), the pH_{KCl} is 4.22. With depth, the pH value of the salt extract changes unevenly from 4.31 in the eluvial weakly humic gleyed (Ehg) horizon to 4.13 in the illuvial slightly eluviated gleyed (Beg) and to 4.35 in the CBg horizon at a depth of 181 cm. Hydrolytic acidity decreases from 5.11 in the humus-eluvial horizon to 1.40-2.62 mg-eq/100 g of soil in the BCg and CBg horizons (Table 1).

It was established that the soil under the forest is characterized by a very strongly acidic reaction of the soil environment of all genetic horizons (3.72-3.94 units of pH_{KCl}). At the same time, the upper AEg horizon is characterized by the lowest pH_{KCl} value of 3.72 and the highest hydrolytic acidity - 9.73 mg-eq/100 g of soil (Table 2).

Table 2. Changes in the physical and chemical properties of the genetic horizons of the Albic Stagnic Luvisol under the forest and fallow (x ± SD, n = 6)

Genetic horizons	Sampling depth, cm	pH_{KCl}	Hydrolytic acidity (Ha)	The sum of absorbed bases	Mobile aluminium, mg/kg of soil	Humus, %
			mg-eq/100 g of soil			
1	2	3	4	5	6	7
			Forest			
AEg	5-26	3.72±0.12	9.73±0.08	1.1±0.2	210.6±1.7	2.07±0.08
Ehg	26-47	3.86±0.04	6.49±0.01	0.9±0.2	183.0±0.9	1.23±0.06
Beg	47-64	3.78±0.02	4.51±0.04	1.0±0.1	90.1±1.3	0.53±0.07
Bg	64-96	3.83±0.01	4.60±1.14	6.8±0.2	77.7±3.4	0.33±0.05
Bcg	96-122	3.83±0.05	3.79±0.04	11.2±0.4	53.7±0.1	0.29±0.07
Cbg	122-150	3.89±0.01	3.42±0.02	11.9±0.6	48.7±1.3	0.26±0.05
Bg	150-173	3.94±0.01	3.15±0.02	13.7±0.1	37.6±1.2	0.22±0.04
	LSD_{05}	*0.09*	*3.04*	*7.44*	*90.08*	*0.91*
			Fallow			
AEg	5-30	4.25±0.05*	5.59±0.02*	5.6±0.1*	54.3±2.6*	1.74±0.11*
Ehg	30-40	4.35±0.03*	3.41±0.00*	5.2±0.4*	45.3±0.1*	0.46±0.05*
Beg	40-61	4.23±0.07*	3.85±0.03*	11.2±0.8*	51.6±1.5*	0.41±0.13
Bg	61-102	4.21±0.23*	3.50±0.17*	11.4±1.1*	50.9±0.7*	0.28±0.08
Bcg	102-129	4.48±0.05*	1.31±0.02*	5.6±0.3*	20.0±2.4*	0.21±0.04
Cbg	129-150	4.32±0.14*	2.80±0.20*	7.4±0.6*	36.7±1.0*	0.26±0.03
Cg	150-180	4.23±0.27	3.58±0.30*	11.4±2.5	55.7±1.4*	0.19±0.01
	LSD_{05}	*0.13*	*1.67*	*3.88*	*16.68*	*0.72*

* - differences significant between forest and fallow soil according to Tukey test ($p < 0.05$)

It should be noted that the upper horizons (AEg, Ehg and Beg) of the soil under the forest are characterized by a very low sum of absorbed bases, which ranges from 0.9 to 1.1 mg-eq/100 g of soil. Starting from the illuvial gleyed horizon (Bg), the amount of absorbed bases increases from 6.8 mg-eq/100 g of soil in this horizon to 13.7 mg-eq/100 g of soil in the parent material (Cg) due to their enrichment with silt factions.

The Albic Stagnic Luvisol of the fallow is characterized by an acid reaction of the soil environment in all horizons where the pH_{KCl} value is below 4.5 (Table 1). With depth, the reaction of the soil solution decreases. In the illuvial glaciated horizon (Bg) it is 4.21, closer to the parent material it increases to 4.32-4.48 units.

Also, in the Albic Stagnic Luvisol under the fallow, compared to the forest, an increase in the sum of absorbed bases in the upper horizons was noted. Thus, in the humus-eluvial and eluvial horizons, it amounts to 5.6 and 5.2 mg-eq/100 g of soil, respectively, which characterizes such soils with a low degree of supply of bases. Due to the increase of silty fractions with depth in the fallow, as well as under the forest, an increase in the sum of absorbed bases to 11.4 mg-eq/100 g of soil was noted (Table 2). According to (Guo et al., 2010), soil acidification in natural conditions is slow and can be caused by decomposition of organic matter and the leaching of cations by excessive precipitation.

The Albic Stagnic Luvisol with a genetically inherent acid reaction of the soil solution in the control without fertilizers is characterized by a very low degree of the sum of absorbed bases in the upper humus horizons. Thus, in the arable and subarable layers, it is 3.0 and 2.4 mg-eq/100 g of soil, respectively. It is lower than on the fallow in the AEg horizon, which is associated with the removal of Ca and Mg by crops. This once again indicates the importance and expediency of mandatory periodic liming of acidic Albic Stagnic Luvisols. With the depth of the control soil in the lower genetic horizons, the amount of absorbed bases increases but does not differ significantly from virgin soil under forest and fallow land.

The long-term use of organic and mineral fertilizers in the crop rotation at a dose of $N_{65}P_{68}K_{68}$ + manure 10 t/ha of the crop rotation area on the background of applying 1.0 norm of lime by Ha had a positive effect on the reaction of the soil solution in all genetic horizons. This creates favourable conditions for the development and growth of crops. The pH_{KCl} value of the arable and subarable layers is 5.18 and 5.05 units, respectively. The seasonally gleyed Ehg and Beg horizons under this fertilizer are characterized by lower pH_{KCl} values of 4.90 and 4.78 units. At the same time, the hydrolytic acidity within the soil profile did not exceed 3.46 mg-eq/100 g of soil (Table 1).

Systematic application of mineral and organic fertilizers in crop rotation on the background of periodic liming with $CaCO_3$ (1.0 n by Ha) increases the sum of absorbed bases within the entire soil profile. Thus, the humus-eluvial arable horizon (AEg_{arable}) is characterized by an average degree of availability of the sum of absorbed bases, which is 10.6 mg-eq/100 g of soil. It decreases to 7.5 mg-eq/100 g of soil in the sub-arable humus-eluvial horizon ($AEg_{sub-arable}$) and increases with depth, including to 18.9 mg-eq/100 g of soil in the heavily gleyed parent material. This creates certain agroecological problems due to their leaching into groundwater. It was found that under the mineral fertilization system, the sum of absorbed bases changed minimally in the 0-35 cm soil layer. Most of them are concentrated in the lower horizons, which is associated with the removal of a significant amount of bases by flows of matter and energy in conditions of periodic overwetting and acidification by mineral fertilizers. This distribution in the profile is also typical for the soil under forests.

Long-term application of only mineral fertilizers in crop rotation causes significant acidification of the soil solution. Therefore, the value of pH_{KCl} throughout the soil profile is in the range of 3.98-4.17 units (Table 1).

A similar pattern can be observed regarding the change in hydrolytic acidity (Ha). Long-term application of only mineral fertilizers in the recommended dose of $N_{65}P_{68}K_{68}$ without liming increased with a depth the Ha value from 5.11 to 5.25 mg-eq/100 g of soil in the Beg horizon. Changes in the pH values of saline and hydrolytic acidity can be caused not only by the long-term anthropogenic impact but also by a change in the climatic and agroecological state of the Western Forest-Steppe zone, due to increased heat and moisture supply of the territory (Poliovyi et al., 2019).

In studies (Souza et al., 2023), long-term application of mineral nitrogen fertilizers significantly reduced soil pH in the top layer (0-15 cm) and deeper soil layers, especially at higher application rates. Regardless of the depth of soil sampling, the decrease in pH was significantly related to the amount of N applied. In addition, nitrogen fertilization significantly increased exchangeable Al but decreased the sum of $Ca^{2+} + Mg^{2+} + K^{+} + Na^{+}$ throughout the topsoil and deeper layers.

In studies (Ghimire et al., 2017), soil acidification also occurred primarily on the soil îsurface up to 20 cm deep, potentially affecting nutrient dynamics, growth, development and yield of wheat.

The correlation coefficients between humus content and soil physicochemical parameters varied significantly across treatments, indicating the close nature of the relationship between them. Under the organic-mineral fertilizer system, a close correlation between humus content and pH_{KCl} (r = 0.927-0.970) was found, and the dose of lime does not affect the closeness of this relationship (Table 3). This indicates a significant role of liming in general not only for regulating the acid-base regime but also for improving the conditions of humus formation in the soil profile.

Table 3. Correlation of humus with physical and chemical parameters in the profile of Albic Stagnic Luvisol

Treatment	pH_{KCl}	Hydrolytic acidity	The sum of absorbed bases	Mobile aluminium
		mg-eq/100 g of soil		mg/kg of soil
Forest	-0.684	0.987	-0.728	0.963
Fallow	-0.229	0.791	-0.420	0.368
No fertilizers (control)	-0.301	0.697	-0.865	0.747
Organo-mineral fertilization system	0.927	-0.597	-0.570	-0.004
Mineral fertilization system	-0.386	0.711	-0.670	0.151

In the soil under the forest, close correlations were found between humus content and mobile aluminium (r = 0.963), and hydrolytic acidity (r = 0.987), as well as a close negative relationship with the sum of absorbed bases (r = -0.728).

This indicates the formation of organo-mineral compounds in the soil under the forest, which are associated with aluminium.

On the control without fertilizers, there is also a close correlation between humus content and mobile aluminium, hydrolytic acidity and the sum of absorbed bases, but they are weaker than under the forest (correlation coefficient is 0.747, 0.697 and -0.865, respectively). On fallow and with the introduction of only $N_{65}P_{68}K_{68}$ a close relationship was found only with hydrolytic acidity (0.791 and 0.711). Based on the results of the research, a mathematical model was created based on correlation and regression analysis that reproduces the link between the physical and chemical properties of Albic Stagnic Luvisol's genetic horizons under the forest, on the fallow and under different fertilization systems in the experiment (Table 4). The resulting equation is reliable at 95% of the probability level according to Fisher's test (Ffact.>F05), and the coefficient of the equations is reliable according to Student's test. The multiple correlation coefficient given in Table 4 (R = 0.730-0.996) validate close relationship between the indicators included in the equations. The coefficient of determination (D = 53.3-99.2%) indicates a significant influence of pH_{KCl} (argument - X_1) and Ha (argument - X_2) on humus content (function - Y).

Table 4. Models of the relationship between physical and chemical properties of Albic Stagnic Luvisol

Treatment	Regression equation	R	D, %
Forest	$Y = 124.4395–66.5722X_1+8.8218X_1^2+0.3827X_2–0.0054X_2^2$	0.992	98.4
Fallow	$Y = –180.5181+82.6632X_1–9.4211\ X_1^2–0.5715X_2+0.1375\ X_2^2$	0.995	99.0
Organo-mineral fertilization system	$Y = –271.3405+126.9458X_1–12.3350\ X_1^2–35.0755X_2+5.7108\ X_2^2$	0.978	95.6
Mineral fertilization system	$Y = –529.0588+259.2015X_1–31.9601\ X_1^2+1.8293X_2–0.1775\ X^2_2$	0.730	53.3

Note: Y - humus content, %; X_1 - pH_{KCl}; X_2 - hydrolytic acidity (Ha), mg-eq/100 g of soil.

Therefore, the physicochemical parameters of the genetic horizons of the control without fertilizers and the mineral fertilization system indicate low agroecological quality, low fertility potential and the further development of the podzolic process in the Albic Stagnic Luvisol in the process of its agricultural use. Measures to increase fertility and counteract intra-soil degradation processes in Albic Stagnic Luvisol under the long-term anthropogenic influence are an organo-mineral fertilization system with the application of optimal doses of mineral and organic fertilizers, in particular, $N_{65}P_{68}K_{68}$ + manure 10 t/ha of crop rotation area on the background of periodic liming. This fertilization system helps to reduce the content of mobile aluminium compounds, optimize physicochemical parameters and create conditions for activating humus formation.

CONCLUSIONS

The involvement of Albic Stagnic Luvisol in agricultural use, depending on the intensity of the impact, is accompanied by changes in the content of mobile aluminium compounds and the physical and chemical properties of both humus and lower horizons. The organic-mineral fertilizer system with periodic liming, positively affecting the reaction of the soil solution (pH_{KCl} = 5.18, Ha = 2.37 mg-eq/100 g of soil), reduces the content of mobile aluminium compounds within the genetic profile from 26.1 in upper to 79.7 mg/kg in the Beg horizon. At the same time, the amount of absorbed bases increases to 10.6-18.9 mg-eq/100 g of soil.

Long-term use of the mineral fertilizer system, accompanied by acidification of the soil profile to pH_{KCl} 3.98-4.17, an increase in Ha to 5.11-5.25 mg-eq/100 g of soil, a decrease in the sum of absorbed bases of the upper horizons to 1.5-3.0 mg-eq/100 g of soil, increases the content of mobile aluminium to 126.5-148.1 mg/kg in the Ehg and Beg horizons to the greatest extent. On the control without fertilizers, the content of mobile aluminium is the highest in the arable and sub-arable horizons and amounts to 110.3-121.5 mg/kg of soil at pH_{KCl} 4.22-4.18, Ha 5.11-

4.94 mg-eq/100 g of soil, the sum of absorbed bases 3.0-2.4 mg-eq/100 g of soil.

In the Albic Stagnic Luvisol under the forest, the highest aluminium content is accumulated in the upper humus horizon and amounts to 210.6 mg/kg of soil. On fallow land, a uniform distribution of mobile aluminium compounds is characteristic of the Albic Stagnic Luvisol: 54.3 mg/kg of soil in AEgl to 55.7 mg/kg in the parent material (Pgl).

REFERENCES

Almaliev, M. (2022). Research the variation of exchange calcium along the depth of the soil profile after the application of ameliorants. *Scientific Papers. Series A. Agronomy, LXV*(1), 25–29.

Baquy, M. A. A., Li, J. Y., Jiang, J., Mehmood, K., Shi, R.Y., Xu, R.K. (2018). Critical pH and exchangeable Al of four acidic soils derived from different parent materials for maize crops. *Journal of Soils and Sediments,* 18. 1490–1499. DOI: https://doi.org/10.1007/s11368-017-1887-x.

Berggren, D. & Mulder, J. (1995). The role of organic matter in controlling aluminium solubility in acidic mineral soils horizons. *Geochimica et Cosmochimica Acta, 59*. 4167–4180.

Bojorquez-Quintal, E., Escalante-Magaña, C., Echevarría-Machado, I., Martínez-Estévez, M. (2017). Aluminum, a friend or foe of higher plants in acid soils. *Frontiers in Plant Science, 8*. 1767.

Brown, T. T., Koenig, R. T., Huggins, D. R., Harsh, J. B., Rossi, R. E. (2008). Lime effects on soil acidity, crop yield, and aluminum chemistry in direct seeded cropping systems. *Soil Science Society of America Journal, 72*. 634–640. DOI: https://doi.org/10.2136/sssaj2007.0061.

Ghimire, R., Machado, S., Bista, P. (2017). Soil pH, soil organic matter and crop yields in winter wheat–summer fallow systems. *Agronomy Journal, 109*(2), 706–717. DOI: https://doi.org/10.2134/agronj2016.08.0462.

Gillespie, C. J., Antonangelo, J. A., Zhang H. (2021). The response of soil pH and exchangeable Al to alum and lime amendments. *Agriculture, 11*(6), 547. DOI: https://doi.org/10.3390/agriculture11060547.

Godsey, C. B., Pierzynski, G. M., Mengel, D. B., Lamond, R. E. (2007). Changes in soil pH, organic carbon, and extractable aluminium from crop rotation and tillage. *Soil Science Society of America Journal, 71*. 1038–1044. DOI: https://doi.org/10.2136/sssaj2006.0170.

Guo, J. H., Liu, X. J., Zhang, Y., Shen, J. L., Han, W. X., Zhang, W. F., Christie, P., Goulding, K. W. T., Vitousek, P. M., Zhang F. S. (2010). Significant acidification in major Chinese croplands. *Science, 327*(5968), 1008–1010. DOI: https://doi.org/10.1126/science.1182570.

Kyrylchuk, A. A. & Bonishko, O. S. (2011). Khimiia gruntiv: osnovy teorii i praktykum [Soil chemistry: the basics of theory and practice]. Lviv: LNU imeni Ivana Franka. pp. 354. ISBN 978-966-613-893-7 [in Ukrainian].

Li, K.-wei, Lu, H.-long, Nkoh, J. N., Hong, Z.-neng, Xu, R.-kou (2022). Aluminum mobilization as influenced by soil organic matter during soil and mineral acidification: A constant pH study. *Geoderma, 418*. 115853. DOI: https://doi.org/10.1016/j.geoderma.2022.115853.

Lykhochvor, V., Hnativ, P., Petrichenko, V., Ivaniuk, V., Szulc, W., Rutkowska, B., Veha, N., Olifir, Y. (2022). Threat of degradation of agricultural land in Ukraine through a negative balance of nutritional elements in growing of field cultures. *Journal of Elementology, 27*(3), 695–707. DOI: 10.5601/jelem.2022.27.2.2290 http://jsite.uwm.edu.pl/articles/view/2290/.

Nazarenko, I. I., Bespalko, R. I., Stankevich, I. I. (1998). Formy ta spoluky aliuminiiu v buruvato-pidzolystykh ohleienykh hruntakh Peredkarpattia riznoho vykorystannia [Forms and compounds of aluminum in brownish-podzolic glaciated soils of Precarpathia of various uses]. *Naukovyi visnyk Chernivetskoho universytetu: Biolohiia,* 38. 83–94 [in Ukrainian].

Poliovyi, V. M., Lukashchuk, L. Ya., Lukianyk, M. M. (2019). Vplyv zmin klimatu na rozvytok roslynnytstva v umovakh zakhidnoho rehionu [The influence of climate change on the development of crop production in the conditions of the western region]. *Visnyk Ahrarnoi Nauky, 9*. 29–34. DOI: https://doi.org/10.31073/agrovisnyk201909-04 [in Ukrainian].

Schroder, J. L., Zhang, H., Girma, K., Raun, W. R., Penn, C. J., Payton, M. E. (2011). Soil acidification from long-term use of nitrogen fertilizers on winter wheat. *Soil Science Society of America Journal, 75*. 957–964. DOI: https://doi.org/10.2136/sssaj2010.0187.

Smirnov, O. E., Kosyan, A. M., Kosyk, O. I., Batsmanova, L. M., Mykhalska, L. M., Schwartau, V. V., Taran, N. Y. (2020). Effect of aluminium on redox-homeostasis of common buckwheat (*Fagopyrum esculentum). Biosystems Diversity, 28*(4), 426–432. DOI: https://doi.org/10.15421/012055.

Smirnov, O. E. & Taran N. Y. (2013). Fitotoksychni efekty aliuminiiu ta mekhanizmy aliumorezystentnosti vyshchykh roslyn [Phytotoxic effects of aluminum and mechanisms of aluminum resistance of higher plants]. *Fiziolohiia roslyn i henetyka, 45*(4), 281–289 [in Ukrainian].

Souza, J. L. B., Antonangelo, J. A., Zhang, H., Reed, V., Finch, B., Arnall, B. (2023). Impact of long-term fertilization in no-till on the stratification of soil acidity and related parameters. *Soil and Tillage Research,* 228, 105624. DOI: https://doi.org/10.1016/j.still.2022.105624.

Szara, E., Sosulski, T., Szymańska, M. (2019). Impact of long-term liming on sandy soil phosphorus sorption properties. *Soil Science Annual, 70*(1), 13–20. DOI: https://doi.org/10.2478/ssa-2019-0002.

Tkachenko, M. A. & Boris N. E. (2021). Optymizatsiia zhyvlennia silskohospodarskykh kultur za fizykokhimichnoi dehradatsii kyslykh gruntiv [Optimizing the nutrition of agricultural crops during physical and chemical degradation of acidic soils]. *Visnyk Ahrarnoi Nauky,* 1. 15–22. DOI: https://doi.org/10.31073/agrovisnyk202101-02 [in Ukrainian].

Tkachenko, M. A., Kondratyuk, I. M., Borys, N. E. (2019). Khimichna melioratsiia kyslykh gruntiv [Chemical reclamation of acidic soils]. Vinnytsia: TOV «TVORY». pp. 318. ISBN 978-966-949-306-4 [in Ukrainian].

Truskavetsky, R. S., Tsapko, Yu. L. (2016). Osnovy upravlinnia rodiuchistiu gruntiv [Fundamentals of soil fertility management]. Kharkiv: Brovin O. V. pp. 386. ISBN: 978-617-7256-41-9 [in Ukrainian].

***FAO and ITPS (2015). Status of the world's soil resources (SWSR) – Main report. Food and Agriculture Organization of the United Nations and Intergovernmental Technical Panel on Soils. Rome, Italy. Available: https://www.fao.org/3/i5199e/i5199e.pdf.

***IUSS Working Group WRB (2015). World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports. 106. FAO, Rome. http://www.fao.org/3/i3794en/I3794en.pdf.