UDC 631.415:631.445.2:631.8

AN ACID-BASE BUFFERING MODEL TO DESCRIBE pH BUFFERING CAPACITY OF AN ACID ALBIC STAGNIC LUVISOL UNDER LONG-TERM AGRICULTURAL LAND USE AND MANAGEMENT

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Received September 07, 2022 / Received October 19, 2022 / Accepted November 19, 2022

Aim. To study acid-base buffering capacity depending on the intensity of different fertilization systems, including liming, with different doses of $CaCO_3$ in a long-term (55 years) stationary experiment on Albic Stagnic Luvisol (light grey forest surface-gleyed soil). This study should serve as a basis for the restoration and protection of fertility and yield and preservation of ecological restorative functions of this soil type. **Methods.** Field stationary experiment, using monitoring, laboratory-analytical and statistical-mathematical methods. **Results.** It was found that after 35 years of a seven-field crop rotation the exclusion of the intensive crops of sugar beet, potato and one winter wheat, in combination with low (2.5 time less) mineral fertilization levels, contributed to an increase in resistance to acidification over the next 20 years from 5.53 to 7.48 points (using a 100-point scale) with a simultaneous increase in soil pH_{KCl} from 3.77 to 4.12. Organo-mineral fertilization ($N_{65}P_{68}K_{68}$ + 10 t manure/ha of crop rotation area) and periodic application of $CaCO_3$ by hydrolytic acidity (6.0 t/ha) and an optimal dose of lime (2.5 t/ha $CaCO_3$) increased pH buffering over these 20 years in a four-field rotation. The general evaluation index of buffering was 21.8–21.9 points, exceeding the virgin soil by 1.9 to 2 points. In the control variants without the use of fertilizers the general evaluation index of buffering was 14.3 ± 0.3, and the coefficient of buffer asymmetry was the highest – 0.646 ± 0.013, which under these conditions indicated the danger of soil losing its ability for self-regulation and self-healing. **Conclusions.** The resistance of Albic Stagnic Luvisol to acidification increased most in the combined application of $N_{65}P_{68}K_{68}$ and 10 t/ha manure, together with an optimum calculated dose of lime in a 4-year crop rotation. An optimal dose of $CaCO_3$ (2.5 t/ha) and organo-mineral fertilizing system in a 4-year crop rotation improved the soil buffering capacity of the acid shoulder by 2.45 points compared to the mineral fertilization system. To support a determination of acid-buffering effects graphic charts representing pH buffering capacity proved to be useful and could be instrumental in diagnostics and optimization of the acid-base regime for acid forest soils in general.

Key words: liming, fertilization, short crop rotation, graphic models of pH-buffering.

DOI: https://doi.org/10.15407/agrisp9.03.018

INTRODUCTION

Global climate change, the decrease in the biodiversity potential and water and air pollution are forcing scientists to pay more attention to the ecological quality of soil (Gelybo et al, 2018; Rocci et al, 2021). For a long time, the soil has been viewed in Ukrainian society solely in terms of consumption purposes, as a means of producing food, usually neglecting its ecological functions and services. However, it is the ecological quality

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of soil that is a relevant index of stable regulation of nature management processes (Hamkalo, 2008).

The current state of Ukraine's soil resources demonstrates the environmentally risky nature of arable soil usage and the unacceptable scale of soil degradation, which threatens the livelihoods of future generations (Lykhochvor et al, 2022). The preservation of the genetic pool of the biosphere and the prevention of environmental risks is possible only through systematic systemic management of soil fertility with an obligatory application of innovative methods for proper diagnostics and optimization of all the fertility factors (Truskavetsky, 2021).

A considerable part of the soil cover structure in Ukraine, about 2.3 million ha, is represented by light grey (Albic Luvisol) and grey forest soil (Haplic Luvisol) (Polupan et al, 2005). Similar soil types are also common elsewhere in Europe (Toth et al, 2008).

The buffering capacity of soil is the ability of the soil to preserve its genetically inherent or artificially created potentials of fertility elements and to inhibit, and/or in some way, resist external factors, directed at the change in these potentials (Nadtochiy et Trembitsky, 2003; Truskavetsky, 2003).

The level of soil cultivation is primarily determined by the reliability and efficiency of the buffering mechanism functioning. The basis of soil buffering properties is the dynamic balance of chemical reactions and the processes of transformation of soil formation products which occur between the soil solution, the gas phase and microbiome, on one hand, and the organo-mineral matrix – on the other (Zheng et al, 2022).

Gradually soils lose their ecological functions if the external stress on the soil cover exceeds the relevant threshold of the buffering capacity, inherent to each specific soil type (Truskavetsky, 2003).

When soil is degrading, usually the buffering capacity of the soil also degrades, weakening the ecological functions and services of soil, and its resistance to unfavourable factors reflected in the performance of the crops in the end (Lal, 1997).

Recent changes in climate towards warming and longer dry seasons have shifted the acid-base balance of soils to some degree (Polovyy et al, 2022). Moreover, the acid-base balance, genetically inherent to soils, is disrupted by agricultural activities such as the introduction of fertilizers and ameliorants and the type of crop rotation (Smaga et al, 2017). Recent uncontrolled intensification of agriculture accelerated the acidification of soils, mainly related to acid precipitation, the excessive introduction of nitrogen, physiological acid mineral fertilizers, and a considerable removal of calcium by crops (Liu et al, 2005; Zhu et al, 2018).

Buffering parameters are integral indices of the balance between chemical components of the soil themselves as well as between them and fertilizers and ameliorants (Ozhovan et Mikhaylyuk, 2019). Essentially acid-base buffering capacity is a dynamic index, characterizing the ability of soil to resist the changes in pH and to restore previous genetically inherent pH values (Nadtochiy et Trembitsky, 2003; Ng et al, 2022). Graphic models could help establish which agro-technical actions are necessary to maintain or enhance soil buffering capacity (Barouchas et al, 2013).

Liming is the most common measure to improve the acid-base properties and fertility of acidic soils (Nduwumuremyi, 2013; Zaryshniak et al, 2018; Li et al, 2019). The problem of determining the lime rate for each soil type has been widely studied, resulting in numerous methods for determining it (Barouchas et al, 2013; Godsey et al, 2007; Kissel et al, 2012). In Ukraine in the practice of chemical reclamation of acidic soils, the main criterion for determining the rate of lime application is still the hydrolytic acidity (Ha), though it usually leads to the application of excessive doses of lime (Baliuk et Truskavetskyi, 2018). This conventional system of cultivating acid soils and increasing their pH based on liming with $CaCO_3$ is unfortunately accompanied by a considerable washing-out of calcium, excessive mineralization, and emission of CO_2. This creates serious environmental problems, polluting the underground waters and increases the emission of carbon dioxide, thus increasing the concentration of greenhouse gases and air temperature (West et McBride, 2005; Goulding, 2016; Olego et al, 2021).

Thus, it is necessary to change the methodological approach to the evaluation of soil acidification, in particular, its ecologic role and increase the focus on the buffering properties of soil. Under these conditions, the study of the impact of agrotechnical factors on the buffering ability of soil becomes especially urgent and promising.

Currently, in cooperation with National Scientific Centre (NSC)'s Institute for Soil Science and Agrochemistry, named after O.N. Sokolovsky at Kharkiv, we have been researching in more depth and detail the possibilities and effects of liming on the fertility and acid-base buffering capacity of acid Albic Stagnic Luvisol in the Carpathian region (Olifir et al, 2020 and 2021).

Timely correction of the norms of differentiating agrotechnological measures requires permanent agroecological monitoring, which can be achieved by long-term stationary field studies (Grahmann et al, 2022). Although the effect of liming on acid Stagnic Luvisol has been studied before (Mazur, 2008; Tkachenko et al, 2020), this was not done for the Carpathian region and under such long-term agricultural land use and management. Therefore, the objectives of the present study were to: (i) study the acid-base buffering capacity depending on the intensity of different fertilization systems, including liming with different doses of $CaCO_3$, and (ii) facilitate the detection methods in use for determining the buffering status of our soil. This in the context of a long-term experiment (55 years), which could serve as a basis to improve the agroecological state, restoration and protection of fertility, preservation of ecological restorative functions and obtaining high performance of Albic Stagnic Luvisol.

MATERIALS AND METHODS

A long-term stationary experiment on the effects of agricultural activities on the acid-base buffering capacity of Luvisols is performed by the Institute of Agri-culture of the Carpathian Region, of the National Academy of Agrarian Sciences (NAAS). It was launched in 1965 on 3 ha in the municipality of Obroshyne in Lviv region, where in a 7-field rotation with potatoes – spring barley with additional sowing of meadow clover – meadow clover – winter wheat – sugar beets – corn for silage – winter wheat different doses and ratios of mineral fertilizers, manure, and lime are applied in combination with different methods of ploughing and other field operations (Zaryshniak et al, 2016). After 35 years and a number of 7-field rotations (up to rotation VI, 2000), the scheme was reduced to 4 crops, excluding potato, sugar beet and one winter wheat crop, to relax the stress on the soil (**Table 1**). The presented results of the research are based on data on the dynamics in the change of pH-buffering and the index of pH_{KCl} in the variants of different fertilization and liming systems after 35 years (1999, end of rotation V) and 55 years (2019, end of rotation X) of their usage.

The stationary experiment is located on three fields, each including 18 variants in three repeats. The total area of a plot is 168 m^2, and the registration area is 100 m^2 The four-field crop rotation has the following sequence of crops: corn for silage – spring barley with the additional sowing of meadow clover – meadow clover – winter wheat. The agrotechnology of crop and soil cultivation, and field treatment is common for the Western Forest-Steppe (Zubets, 2010).

The agrotechnical characteristics of the arable layer of Albic Stagnic Luvisol (World Reference Base for Soil Resources, 2015), before launching the experiment in 1965, were as follows: humus content (according to Tyurin, 1937) – 1.42 %, pH_{KCl} ((potentiometric method) – 4.2, hydrolytic acidity (according to Kappen, 1929) – 4.5 $cmol.kg^{-1}$, exchangeable acidity (by Sokolov, 1939) – 0.6 $cmol.kg^{-1}$, the content of exchangeable aluminium (according to Sokolov, 1939) – 60.0 $mg.kg^{-1}$, available phosphorus (according to Kirsanov, 1931) and exchangeable potassium (according to Maslova, 1935) – 36.0 and 50.0 $mg.kg^{-1}$ of soil respectively.

Table 1. The scheme of variants in a 4-year crop rotation of a field stationary experiment, 2016-2019 (rotation X), located at Obroshyne municipality

Variant	Type of fertilization	Per ha of crop rotation area			Corn for silage	Spring barley + meadow clover	Meadow clover	Winter wheat
		Lime dosage	Manure, t	NPK, kg of active substance				
1	No fertilizers, no liming (control)	0	0	0	0	0	0	0
7	Organic-mineral with liming	By hydrolytic acidity (6.0 t/ha)	10	$N_{65}P_{68}K_{68}$	Manure, 40 t/ha + + $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
8	Organic-mineral with liming	Optimal by acid-base buffering (2.5 t/ha)	10	$N_{65}P_{68}K_{68}$	Manure, 40 t/ha + + $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
15	Mineral only, no liming	0	0	$N_{65}P_{68}K_{68}$	$N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$

Half-decayed cattle manure (over 6 months old) in straw, ammonium-nitrophosphate (ANP) fertilizer (NPK, 16 %), were used in the experiment. When ANP fertilizer was used, NPK content was balanced with simple fertilizers: ammonia nitrate, granulated superphosphate, and potassium chloride, according to the fertilizer rates. The 40 t/ha of manure was added at once before corn, which is 10 t per ha of crop rotation area. Phosphate-potassium fertilizer was introduced in autumn and nitrogen fertilizer – prior to pre-sowing harrowing. The liming of the upper 0–20 cm layer was done in 2012 (before the beginning of crop rotation IX). At the same time, the doses of the introduced fertilizers were adjusted to the relevant crops. Limestone powder obtained from Additional Liability Company Pustomyty plant management of lime plants was used as calciferous material (93.5 % $CaCO_3$). The dose of lime by hydrolytic acidity (Ha) was calculated according to the formula $D_{CaCO_3} = 1.5 \times Ha$ ($t \cdot ha^{-1}$). Starting from 2008 (crop rotation VIII), the second mowing of meadow clover was ploughed in as an organic fertilizer in all the experiment variants.

The acid-base buffering was determined in the following variants (Table 1):

a) Negative control (no fertilizers, no liming, variant 1)

b) Organic-mineral fertilization (10 t/ha of cattle manure per crop rotation area + $N_{65}P_{68}K_{68}$) with periodic liming with $CaCO_3$ by Ha (6.0 t/ha of limestone powder, var. 7)

c) Organic-mineral fertilization with an optimal dose of lime, calculated as per acid-base buffering (2.5 t/ha, var. 8)

d) Mineral fertilization only, without liming ($N_{65}P_{68}K_{68}$, var. 15).

Soil samples for the determination of exchangeable acidity were selected, after collecting the harvest of winter wheat, from the arable layer of Albic Stagnic Luvisol (0–20 cm). Per treatment 9 composite soil samples were collected according to a zig-zag sampling pattern with an auger, each sample weighed approximately 1 kg). The pH_{KCl} was determined using the potentiometric method according to at the ratio between soil and the solution of 1 : 2.5 in the salt extract of 1 mol/l KCl solution at 20 °C.

The acid-base buffering of soil was determined by the potentiometric (titration) method according to the method described in (Truskavetsky, 2003). For this purpose, a series of 5 soil samples per experimental plot, 5 g each, was taken and dried, crushed and sieved through a 1 mm sieve to which the following solutions were added: 0.1 mol/l HCl (5.0; 4.0; 3.0; 2.0; 1.0; 0 ml, respectively) and 0.03 mol/l $Ca(OH)_2$ (0; 4.0; 8.0; 12.0; 16.0; 20.0 ml). 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 pH was measured potentiometrically in the filtrate. For comparative evaluation of the buffering capacity of the soil, pure silica sand with an average particle size of 250 μm was used as a non-buffered substrate, while building the "zero" standard curve. Buffering curves were built based on the obtained data, using the specialized program "Buff-pH" (developed at NSC's Institute for Soil Science and Agrochemistry, named after O.N. Sokolovsky) by calculating the following buffering indices:

a) Buffering area (in the acid and base intervals) – areas between the zero standard curve and soil buffering curve (A′BG (S_b) and A′DH (S_a) in **Figure**)

b) Buffering capacity (in points, out of 100):

$$\text{base} - \beta_b = \frac{S_b \cdot 100}{S_{tot}}; \ \text{acid} - \beta_a = \frac{S_a \cdot 100}{S_{tot}};$$

where $S_{tot} = S_a + S_b$

c) Coefficient of buffering asymmetry (CBA):

$$CBA = \frac{\beta_b - \beta_a}{\beta_b + \beta_a};$$

d) General evaluation index of buffering (GEIB):

$$GEIB = (\beta_b + \beta_a) * (1 - CBA).$$

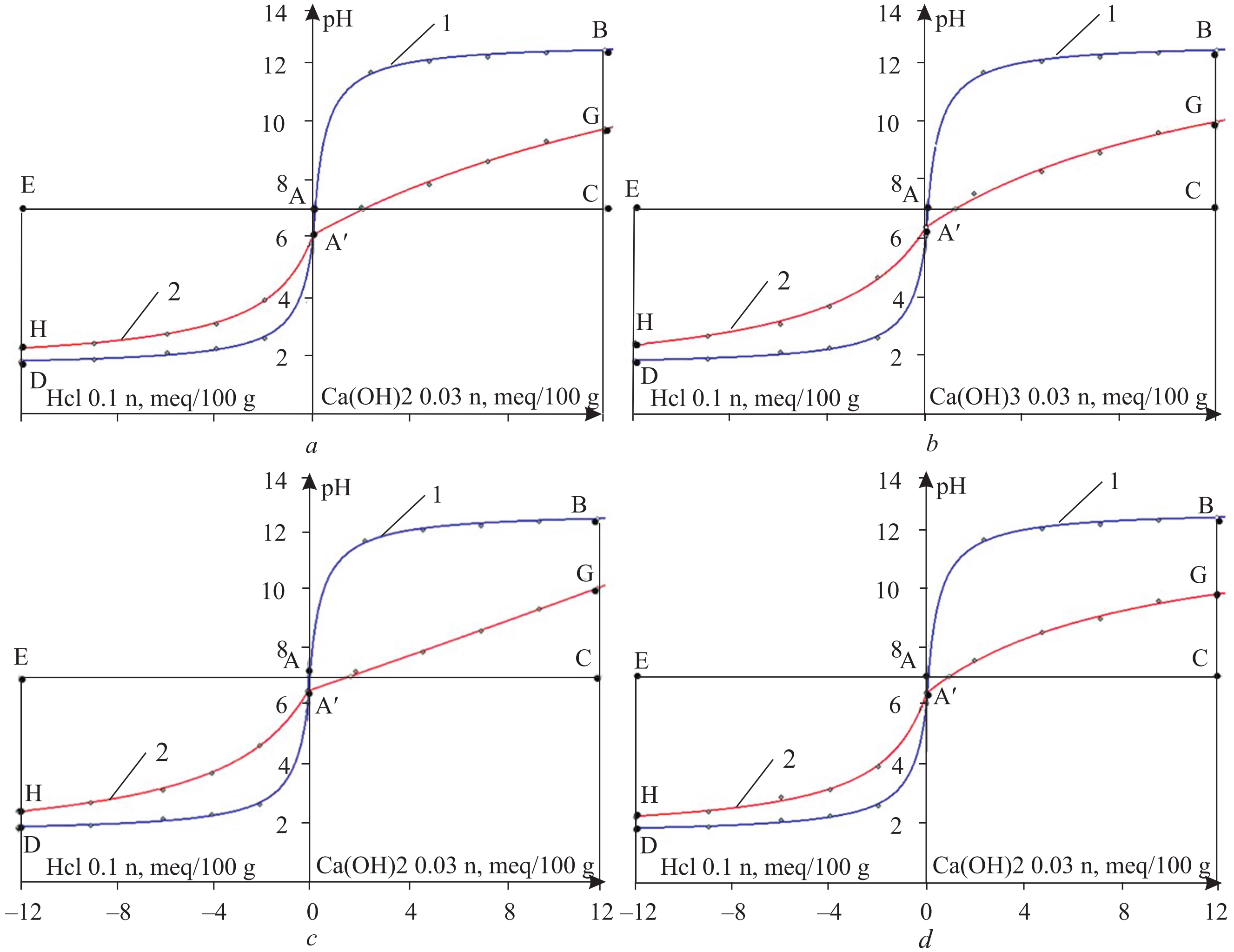
A similar series of control soil samples were taken from virgin soil, and their pH-buffering capacity was studied as well.

The statistical processing of results was done using one-way ANOVA on OriginPro 2019b (OriginLab Corporation, USA, https://www.originlab.com/2019b). Post-hoc analysis was performed using the Tukey HSD test. The differences between the samples were deemed statistically significant at $p < 0.05$. The data in the tables are presented as the arithmetic mean with standard deviation (x ± SD).

RESULTS

Data presented in **Table 2** and graphs in Figure, *a–d* on pH-buffering of acid Albic Stagnic Luvisol of different cultivated variants demonstrate that soil has a high buffering capacity under alkaline conditions and low buffering capacity under acid conditions.

The study of the acid-base buffering capacity of the control variants without fertilizers and under different



1 – the curve of “zero” pH buffering (sand) 2 – the curve of pH buffering of soil

Graph representing pH buffering of Albic Stagnic Luvisol under *a* – control without fertilizers (var. 1, Table 1, end of rotation X, red line); *b* – organo-mineral fertilization system with the introduction of $CaCO_3$ by Ha (var. 7, Table 1, end of rotation X, red line); *c* – organo-mineral fertilization system against the introduction of the optimal dose of $CaCO_3$ by pH buffering (var. 8, Table 1, end of rotation X, red line); *d* – long-term use of the mineral fertilization system (var. 15, Table 1, end of rotation X, red line) compared to pH buffering in the sand (“zero” standard curve, blue line). ABC and ADE – the area which characterizes the alkali and acid standard buffering capacities, respectively; A′BG – the area which characterizes the alkali buffering capacity of Albic Stagnic Luvisol; A′DH – the area which characterizes the acid buffering capacity of Albic Stagnic Luvisol

fertilizer systems after 55 years of soil cultivation (2019, end of rotation X) showed that the buffering capacity of the acid shoulder in control was 7.15 points and that of the alkali shoulder, – 33.22 points. The general evaluation index of buffering (GEIB) was 14.3 points (Table 2, Figure, *a*). Mineral fertilization only minimally and insignificantly changed the GEIB (Table 2, Figure, *d*).

Positive changes in pH buffering capacity were primarily due to the change in crop rotation (exclusion of potato, sugar beet and one winter wheat) and optimal fertilization levels. It led to an increase of pH from 3.8–4.0 to 4.2–4.3 in control without fertilization and with fertilization, respectively, at a high level and an increase of GEIB of var. 7 (Table 2).

In the control variant (var. 1) and the variant with the mineral fertilization only (var. 15) the coefficients of buffering capacity are the highest, amounting to 0.646–0.596 respectively (Table 2). It is a sign that the soil under these conditions is at risk of losing the mechanisms of self-regulation and self-restoration.

There were considerable changes in physical-chemical properties which had a significant impact

Table 2. The indices of acid-base buffering of acid Albic Stagnic Luvisol as determined under different agricultural management and fertilization/liming conditions over a period of 55 years (2019, end of rotation X), n = 5

No of var.	Fertilization per 1 ha of crop rotation area	Buffering capacity, points (out of 100)		Coefficient of buffering asymmetry (CBA)	General evaluation index of buffering (GEIB), points
		alkali	acid		
1	Control (no fertilizers)	33.22 ± 1.97^{a}	7.15 ± 0.14^{a}	0.646 ± 0.013^{a}	14.3 ± 0.3^{a}
7	$N_{65}P_{68}K_{68}$ + manure 10 t/ha + $CaCO_3$ 1.0 n by Ha	29.96 ± 0.88^{a}	10.92 ± 0.51^{b}	0.466 ± 0.01^{b}	21.8 ± 1.0^{b}
8	$N_{65}P_{68}K_{68}$ + manure 10 t/ha + $CaCO_3$ optim. by acid-base buffering	32.66 ± 1.37^{a}	10.93 ± 0.79^{b}	0.498 ± 0.042^{bc}	21.9 ± 1.6^{b}
15	$N_{65}P_{68}K_{68}$	29.54 ± 1.51^{a}	7.48 ± 0.36^{ac}	0.596 ± 0.008^{ac}	15.0 ± 0.7^{ac}
	Virgin Albic Stagnic Luvisol	28.7 ± 1.7 ^{b}	8.4 ± 0.21^{c}	0.55 ± 0.03^{c}	16.9 ± 0.4^{c}

Note. Variables which have at least one similar letter within a column do not differ significantly.

on the formation of the nutrition regime of Albic Stagnic Luvisol: the content of exchangeable aluminium compounds decreased down to 59.9–75.0 mg/kg of soil in the variants of control and the mineral fertilization system after 55 years of cultivation (2019) compared to 92.3–132.2 mg/kg of soil after the completion of the seven-field crop rotation (rotation V,1999, after 35 years of ploughing and cultivation). The sum of the absorbed bases increased in 2019 up to 3.27–2.01 compared to 2.7–2.2 cmol.kg^{-1} of soil in 1999, and the hydrolytic acidity decreased down to 4.48–4.69 compared to a corresponding 5.20–6.43 cmol.kg^{-1} soil at the end of rotation V (1999).

In the variants with identical organic-mineral fertilization systems of $N_{65}P_{68}K_{68}$ + 10 t of manure on ha of crop rotation area with the periodic introduction of $CaCO_3$ by Ha for 20 years (6.0 t/ha, var. 7) and the optimal dose of $CaCO_3$ by pH buffering capacity (2.5 t/ha, var. 8) the general evaluation index of buffering was insignificantly different. By 2019 (end X rotation X), indices are 21.8–21.9 points and exceed the virgin analogue by 1.9 to 2 points (Figure, *b*, *c*).

Table 3. The change in the physical-chemical properties of Albic Stagnic Luvisol from 1999 to 2019, n =9

No of var.	Fertilization of 1 ha of the crop rotation area	pH_{KCl}		Hydrolytic acidity (Ha)		The sum of absorbed bases		Exchangeable aluminium mg/kg of soil	
		1999 (end of rotation V)	2019 (end of rotation X)	1999 (end of rotation V)	2019 (end of rotation X)	1999 (end of rotation V)	2019 (end of rotation X)	1999 (end of rotation V)	2019 (end of rotation X)
1	Control (no fertilizers)	4.14 ± ± 0.14^{a}	4.30 ± ± 0.18^{a}	5.20 ± ± 1.31^{a}	4.48 ± ± 0.55^{a}	2.70 ± ± 0.61^{a}	3.27 ± ± 0.47^{a}	92.3 ± ± 38.7^{a}	59.9 ± ± 1.4^{a}
7 8	$N_{65}P_{68}K_{68}$ + manure 10 t/ha + + $CaCO_3$ by Ha	5.42 ± ± 0.26 ^{b}	5.38 ± ± 0.22 ^{b}	2.40 ± ± 0.72 ^{b}	2.28 ± ± 0.44^{a}	7.07 ± ± 0.31 ^{b}	8.20 ± ± 1.06 ^{b}	3.2 ± ± 2.4 ^{b}	4.6 ± ± 2.3 ^{b}
15	$N_{65}P_{68}K_{68}$ + manure 10 t/ha + + $CaCO_3$ optim. by acid-base buffering	5.30 ± ± 0.43 ^{b}	5.03 ± ± 0.15 ^{b}	2.67 ± ± 0.85 ^{b}	3.13 ± ± 0.69^{a}	6.80 ± ± 0.69 ^{b}	5.57 ± ± 0.57 ^{c}	3.7 ± ± 2.9 ^{b}	6.8 ± ± 2.6 ^{b}
	$N_{65}P_{68}K_{68}$	3.77 ± ± 0.06^{a}	4.12 ± ± 0.11^{a}	6.43 ± ± 1.42^{a}	4.69 ± ± 0.58^{a}	2.20 ± ± 0.20^{a}	2.01 ± ± 0.20^{a}	132.2 ± ± 32.2^{a}	72.6 ± ± 5.2^{a}

Note. The variables which have at least one similar letter within a column of the Table do not differ significantly.

There is only an insignificant difference between the physical-chemical properties of the mentioned variants (**Table 3**).

The results obtained in the long-term stationary experiment on Albic Stagnic Luvisol, with the initial pH 4.3, demonstrate that the use of the organo-mineral fertilization system with the introduction of $N_{65}P_{68}K_{68}$ and 10 t/ha manure in a four-field crop rotation with liming (with the lime dose, calculated by pH buffering) decreased the content of exchangeable aluminium compounds and the hydrolytic acidity by the end of rotation X (2019), and promoted the increase in the sum of absorbed bases and acid-base buffering at pH 5.0 in general (Table 3).

DISCUSSION

Due to current notable climate changes, the problem of efficient and environmentally friendly use of acid soils has become much more acute. The solution to this issue lies in the development and application of innovative agricultural measures which would promote the balanced use of acid soils (Wang et al, 2021). In general, soils with low anti-acid buffering capacity may be quickly acidified, which decreases the number of gleyed minerals and cation exchange capacity and, as a result, impacts soil fertility (Wei et al, 2022; Curtin and Trolove, 2013).

Our study, demonstrated that a dose of lime, calculated by acid-base buffering capacity (2.5 t/ha $CaCO_3$), introduced before the beginning of each four-field rotation, is the most optimal under organic-mineral fertilization, It excludes negative consequences of modern agrotechnical management and is a prerequisite of environmental stability of the agroecosystem. In our present and previous studies, it was in the control variants and those of mineral fertilization systems only, that we observed the highest losses of carbon dioxide, especially after the soil tillage in spring and autumn (Olifir et al, 2020).

This is why accurate determination of the pH buffering capacity of soil in agriculture systems is important for the evaluation of the need for lime and forecasting the rate of soil acidification (Wang et al, 2015; Wong et al, 2013). The effect of soil liming can be long-lasting or unstable. In the absence of periodic liming, the acidity returns to its original state, i.e., the effect of re-acidification (Hamkalo, 2008).

Wei et al, 2022 determined that several processes promote the increase in the acid buffering ability of soil in different pH ranges, and the global analysis of data demonstrated that a pH value of 5.5 may be a key threshold value; different buffering systems are active under pH > 5.5 and pH < 5.5. Also according to Goulding and Blake (1998), different buffering processes in soils occur in this order: 1) dissolution of carbonates and other base minerals; 2) replacement of exchange base cations by H^+ and Al^{3+} in the exchange complex; 3) dissolution of Al, which is followed by the dissolution of iron-containing minerals. In the same order as given above, these processes tend to buffer soil pH at about 7.0, 6.0–5.0 and 4.0–3.0. Therefore, in the soils of the control variant and mineral fertiliser at pH < 4.5, the content of exchangeable aluminium increases sharply, unlike in other variants.

After 35 years in a seven-field crop rotation system, Albic Stagnic Luvisol without fertilizers had pH 4.1, the content of mobile aluminium compounds increased to 92.0 mg/kg of soil, and the sum of absorbed bases was 2.70 $cmol.kg^{-1}$ of soil. It had a lower buffering capacity than the virgin analogue. In the variant of applying a double dose of mineral fertilisers for 35 years in an intensive seven-field crop rotation, the buffer capacity of the acid shoulder significantly decreased not only compared to the virgin soil but also compared to the control. This indicates a significant loss of soil resistance to acid exposure and the emergence of environmental risks, accompanied by a loss of self-regulation mechanisms. Under such conditions, sugar beet died at the first stages of growth and development, while crops of meadow clover and spring barley produced yields below those of the control (Truskavetsky et al, 2005).

In soils with a pH between 4.5 and 6.0 soil organic matter (SOM) also plays an important role in soil pH buffering (Aitken et al, 1990; Yang, 2022). Change in crop rotation (exclusion of potato, sugar beet and winter wheat) and optimal fertilization levels influenced soil organic matter. resulted in a considerable improvement in the humus state of the Albic Stagnic Luvisol, due primarily to a decrease in the number of “aggressive” fulvic acids.

In the previous studies of the humus state after five seven-field crop rotations (in 1999) in the variants of control and mineral fertilization, the ratio of C_{HA}:C_{FA} was 0.48 and 0.41, respectively. The content of “aggressive” fulvic acids increased up to 15 % in the humus of the control without fertilizers and 13.4 % in the variant of intense mineral fertilization (Habriel et al, 2006). After the completion of rotation X (2019), the ratio of C_{HA} : C_{FA} in control increased up to 0.59, and in the variant with mineral fertilization up to 0.62. The content of aggressive fulvic acids decreased down to 8.0–7.5 % (Snitynsky et al, 2014). Bergelin et al, 2000 have also shown that low molecular weight organic acids play a more important role in pH buffering than the mass of dissolved organic carbon.

Yang et al (2020) developed a model of surface complex formation, which was used for further evaluation (illustration) of acid-base buffering properties of soils, assuming that the buffering system is a process of protonation-deprotonation. The constants of complex formation on the surface may be used for the quantitative evaluation of the acid-base process of buffering and accurate forecasting of the potential needs in lime for acid soils.

One of the important targets to counteract effects of global climate change is to try to create a higher buffering capacity for poor (acid) soils (Truskavetsky, 2021). Further research on the nature of buffering mechanisms, and the functional stability of soil fertility is important. Therefore, further studies of our Institute will be aimed at more fully understanding the processes that determine soil acidity and the role of Al, Fe, and Mn in the formation of acidity and acid-base buffering capacity.Moreover, the mechanisms of stability of aluminium toxicity, content, forms, quantitative ratio of iron and manganese compounds, their interdependence and connection with redox potential will be investigated.

In any case, understanding the above-mentioned processes, including the functioning of the various redox-systems, requires their analysis in space and time.This can only be realised in long-term experiments, one of which is thestationary experiment at our Institute with different doses and ratios of mineral fertilisers, manure and lime.

CONCLUSIONS

It was established that the addition of calcium-containing substances to Albic Stagnic Luvisol together with a balanced organic-mineral fertilization system is an important condition to improve the soil resistance to external influences and to provide an optimal soil pH buffering system. The resistance of Albic Stagnic Luvisol to acidification increased most in combination with the application of $N_{65}P_{68}K_{68}$, 10 t/ha manure and an optimum calculated dose of lime in a 4-year crop rotation. Moreover, the buffer capacity of an acid shoulder increased up to 10.93 points against the corresponding indices of 7.15 in the control and 7.48 points under the mineral fertilization system.

Thus, modelling pH buffering capacity in graphs proved to be useful in the determination of acid-buffering effects and could be instrumental in diagnostics and optimization of the acid-base regime for acid forest soils in general. Our graphic model could assist in achieving economic rationalization of fertilization resources and ameliorants, and in improving the agroecological state, and ecologic services of acid soils.

ACKNOWLEDGEMENT

The authors express their sincere gratitude to Prof. R.S. Truskavetsky, Doctor of Agricultural Science, the corresponding member of the National Academy of Agrarian Sciences of Ukraine, for his invaluable support and experience throughout the entire research.

Conflict of interests. The authors deny any conflict of interest.

Compliance with standards of working with animals. This article does not relate to any studies involving the use of animals as objects of study.

Financing. This study was not financed by any specific grant from financing institutions in the state, commercial or non-commercial sectors.

Модель кислотно-основної буферності для опису рН-буферної здатності кислого ясно-сірого лісового ґрунту в умовах довготривалого сільськогосподарського використання та управління

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Мета. Дослідити в умовах тривалого стаціонарного досліду (55 років) агрогенну зміну кислотно-основної буферності ясно-сірого лісового грунту залежно від інтенсивності впливу систем удобрення на фоні вапнування різними дозами $CaCO_3$. Це послужить основою покращення агроекологічного стану, відтворення та охорони родючості, збереження екологовідтворних функцій і отримання високої продуктивності ясно-сірих лісових ґрунтів. **Методи.** Польовий стаціонарний дослід, інструментальний моніторинг, лабораторно-аналітичний, статистично-математичний. **Результати.** Встановлено, що після 35 років п'ятирічної семипільної сівозміни виключення інтенсивних культур цукрових буряків, картоплі та однієї озимої пшениці у поєднанні з внесенням у 2,5 рази меншої дози мінерального удобрення сприяло підвищенню стійкості до підкислення впродовж наступних 20 років з 5,53 до 7,48 бала (за 100-бальною шкалою) з одночасним зростанням pH_{KCl} ґрунту з 3,77 до 4,12. Органо-мінеральне удобрення ($N_{65}P_{68}K_{68}$ + 10 т гною на 1 га сівозмінної площі) та періодичне внесення $CaCO_3$ за гідролітичною кислотністю (6,0 т/га) і оптимальної дози вапна (2,5 т/га $CaCO_3$) сприяли підвищенню буферності pH за ці 20 років у чотирипільній сівозміні. Загальний оціночний показник буферності становив 21,8–21,9 бала, що перевищувало показник цілини на 1,9–2 бали. У контрольних варіантах без застосування добрив загальний показник буферності становив 14,3 ± 0,3, а коефіцієнт асиметрії буферності був найвищим – 0,646 ± 0,013, що за цих умов свідчить про небезпеку втрати ґрунтом здатності до саморегуляції та самовідновлення. **Висновки.** Стійкість ясно-сірого лісового ґрунту до підкислення найбільше зростала у поєднанні внесення $N_{65}P_{68}K_{68}$, 10 т/га гною та оптимальної розрахункової дози вапна у 4-річній сівозміні. Оптимальна доза $CaCO_3$ (2,5 т/га) та органо-мінеральна система удобрення в 4-пільній сівозміні покращила буферність ґрунту кислотного плеча на 2,45 бала порівняно з мінеральною системою удобрення. Для визначення кислотно-буферних ефектів корисними виявилися графічні діаграми, які відображають буферність pH і можуть бути корисними для діагностики та оптимізації кислотно-основного режиму кислих лісових ґрунтів загалом.

Ключові слова: вапнування, короткоротаційна сівозміна, кислотно-основна буферність, буферна ємність, графічні моделі pH-буферності.

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