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Formation of the acid-base buffering capacity of acid gleyed soils of the Eastern Carpathian foothills under anthropogenic influence

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ABSTRACT

The regularities of the formation of the acid-base state and acid-base buffering of brownish-podzolic gleyed soils of Eastern Carpathian Foothills, which function in their natural state under forest cover, under minimal anthropogenic influence under undrained pasture, and after drainage melioration of different durations – under haymaking since 1974 and under pasture since 1914. It was established that indicators of the potential buffer capacity in the acidic and alkaline interval, the coefficient of buffer asymmetry and the neutralization indicator objectively reflect changes in the buffering capacity of the soil under anthropogenic influence. To determine the effect of the lime, phosphorite flour, lime in combination with phosphorite flour on the transformation of acid-base buffering capacity, an indicator of the filling factor of the buffer capacity is proposed, which is calculated using the areas of the figures that are formed on the graph between the curves of the potentiometric titration of the aqueous suspension of soil and the aqueous suspension of quartz sand. The parameters of its indicators were established 1 and 2 years after the introduction of the chemical ameliorants into the soil.

Keywords: acid-base condition of the soil, lime fertilizers, phosphorite flour, neutralization index, buffering capacity.

INTRODUCTION

Soil acid-base buffering capacity refers to the soil's ability to resist pH shifts and restore its genetically inherent value (Ng et al., 2022). The parameters of indicators evaluating soil acid-base buffering reflect the balance between distinct chemical soil amendments (Ozhovan and Mikhaylyuk, 2019).

Information on quantitative and qualitative parameters and patterns of formation of acid-base buffering capacity of soils, especially with the acid reaction of the environment, has both theoretical and applied significance. Knowledge of its parameters is necessary to establish the norms of introduction of chemical ameliorants into the soil when it is necessary to optimize its acid-base state, as well as to overcome the consequences of the adverse effects of acid rain on the soil and ecosystems. Therefore, it is promising to use indicators of acid-base buffering of soils to solve general ecological problems, establish the direction and intensity of soil formation processes, assess and predict changes in agroecological condition of soil cover, etc. (Zhang et al., 2016; Nelson and Su, 2010; Truskavetskyi, 2003; Luo et al., 2015).

Acid-base buffering of the soil ensures the stability of its acid-base balance. The latter, depending on the genetic characteristics of the soil, is supported by a set of buffer systems. The change in the pH of the soil environment does not occur linearly, i.e., if one buffer system is depleted, then another begins to function. Soils with a high content of physical clay or organic matter are better able to withstand lower pH, and acidic soils that have strong buffering capacity in relation to alkalis are better able to resist its increase (Truskavetskyi, 2003).

When the soil is acidified, its mineral part is destroyed, acid-dependent differentiation of the profile is formed, and the buffer systems of the soil are degraded. When soil liming, there are changes in pH associated with buffering (Yu et al., 2022). Increasing the content of calcium ions in acidic soils leads to the reconstruction of the cation exchange hydrogen buffer system, increasing the buffer capacity in the acid range, and hence its resistance to acid loads (Hamkalo, 2004).

The acid-base status and fertility of acidic soils can be improved through lime application (Li et al., 2019). Determining lime requirements based on pH buffering capacity, as opposed to the hydrolytic acidity method, ensures the ecological stability of agroecosystems and the conservation of liming materials (Olifir Yu et al., 2022). As a result of the interaction between acidic soil and lime, the soil's ability to resist acid loading is enhanced to a greater extent (Yu et al., 2023).

After liming of soils with an acid reaction of the environment, the soil-absorbing complex is saturated with calcium ions, and the acid-base balance is shifted to the alkaline side. The consequence of these processes is the formation of hydroxides of iron and aluminium, increasing the mobility of organo-mineral complexes and reducing the content of organic matter in the soil (Marcinkonic and Tripolskaja, 2008). Over a period of time, the acid-base balance of limed soils returns to the initial level due to the presence of self-regulation mechanisms, including pH-buffer systems as a protective mechanism for acid neutralization.

Researchers have developed and tested a number of methods for determining the acid-base buffering, the use of which allows to obtain titration curves, as well as various indicators in numerical terms. The main ones are the buffer asymmetry coefficient (BAC), the buffer area (BA) and the potential buffer capacity (PBC) in the positive and negative wings of the buffer (Truskavetskyi, 2003), the neutralization indicator (NI), the degree of buffering capacity (Nadtochyi, 2013; Nadtochiy et. al**.**, 2023), buffering in relation to acid or alkali total and at intervals of pH values (Bolshanina et. al**.**, 2008), the index of acid-base balance (Nadtochyi et. al., 2010).

The background for the territory of Eastern Carpathian Foothillsis brownish-podzolic gleyed soils, which have a number of unfavourable properties for plants, such as excess water content and the development of podzolization and gleying processes, high acidity and a high content of exchangeable aluminium, undersaturation of bases, low supply of elements of mineral nutrition for plants. Despite certain negative consequences, hydrotechnical melioration helps remove excess moisture from the soil and reduce the intensity of gley-forming processes but does not eliminate soil acidity and does not inactivate mobile aluminium. In turn, liming reduces hydrolytic acidity, eliminates exchange acidity, and reduces the amount of mobile aluminium. To reduce the toxicity of mobile aluminium in acidic soils, it is recommended to carry out phosphating. Its combination with liming is an effective measure (Begei and Karasevych, 2023). Therefore, our research is aimed at establishing the acid-base buffering capacity of the brownish-podzolic gleyed soils of the Eastern Carpathian Foothills in their natural state (under forest cover), under the influence of drainage amelioration and chemical ameliorants. This will make it possible to establish the regularities of its formation under different land use methods and when applying chemical ameliorants.

The purpose of the article is to establish the specifics of formation and parameters of acid-base buffering indicators of brownish-podzolic gleyed soils of Eastern Carpathian Foothills under various types of anthropogenic influence and patterns of its transformation during chemical reclamation.

The subject of research is indicators of acid-base buffering properties of soils.

MATERIALS AND METHODS

Field studies of the soil cover were carried out within the Vyzhnytskyi-Storozhynetsky physical-geographical district of the Eastern Carpathian Foothills' highland region (Marynych et al., 2003). In order to identify the distribution areas of brownish-podzolic glaciated soils, a series of excavations was carried out, and representative key areas were selected at the facility near the village Ispas on soils occupied by natural forest and herbaceous phytocenoses. When choosing them, the principle of homogeneity of relief conditions, parent rock, and depth of groundwater was observed as much as possible. Soil cross sections were established within each group of representative key plots (forest, undrained pasture, hayfield drained by closed tile drainage in 1974, and pasture drained by closed tile drainage in 1914). Soil sections on drained lands were done in the middle of the inter-drainage distance – 6 meters.

Morphological properties of soils were studied in the field, and soil samples for laboratory and analytical studies were selected in 3 replicates according to genetic horizons.

The influence of chemical ameliorants (lime and phosphorite flour) on the processes of formation of acid-base buffering of the soil was studied in micro-plot experiments on undrained pasture and drained hay. The area of the experimental site is 50 m^2. Scheme of the experiment: option 1) control – without chemical ameliorants; option 2) lime – 3 rates calculated according to hydrolytic acidity; option 3) phosphorite flour – 3 standards, designed to neutralize movable aluminum; option 4) lime – 1.5 standards + phosphorite flour – 1.5 standards. Chemical ameliorants were introduced in the autumn under the main tillage. Their physical mass per area of the experimental plot was determined based on the content of the active substance and the calculated application rate. Soil samples for laboratory and analytical studies were taken from the upper humus-eluvial horizon 1 and 2 years after the experiment was started in 3 repetitions.

In the soil samples prepared for analysis, the acid-base buffering capacity of the soil was determined according to DSTU (National Standard of Ukraine) 4456:2005 (Quality of the Soil, 2006). The method is based on measuring the change in the pH of the soil suspension due to the addition of acid (HCl) and alkali (NaOH) of different concentrations. The introduction of the maximum concentration of acid and alkali into the soil suspension was 12.5 mg-eq./100 g of soil, which provides the study of the buffering capacity of soils in the pH range from 1.3 to 12.7. The results are presented graphically as a dependence of pH on the dose of the additive. The characteristics of the obtained curve are the characteristics of pH-buffering of the soil. Indicators of acid-base buffer properties were calculated according to the instructions (Nadtochyi, 2013; Truskavetskyi, 2003) in 3 analytical repetitions.

To determine the parameters of the buffer properties, based on the results of the titration of the water suspension of the soil, the buffer curve of the soil and the titration curve of the water suspension of the unbuffered substrate – washed quartzsand (Figure 1) were constructed.

ABC and ADE are the area characterizing alkaline and acidic maximum buffer capacities, respectively (ABC + ADE = Smax); A´BG and A´DH – the area characterizing the buffering area of the conditional soil in the alkaline (Sal) and acidic intervals (Sa); F is the initial value of the degree of actual acidity; I – the transition point of the buffer curve through the standard line with

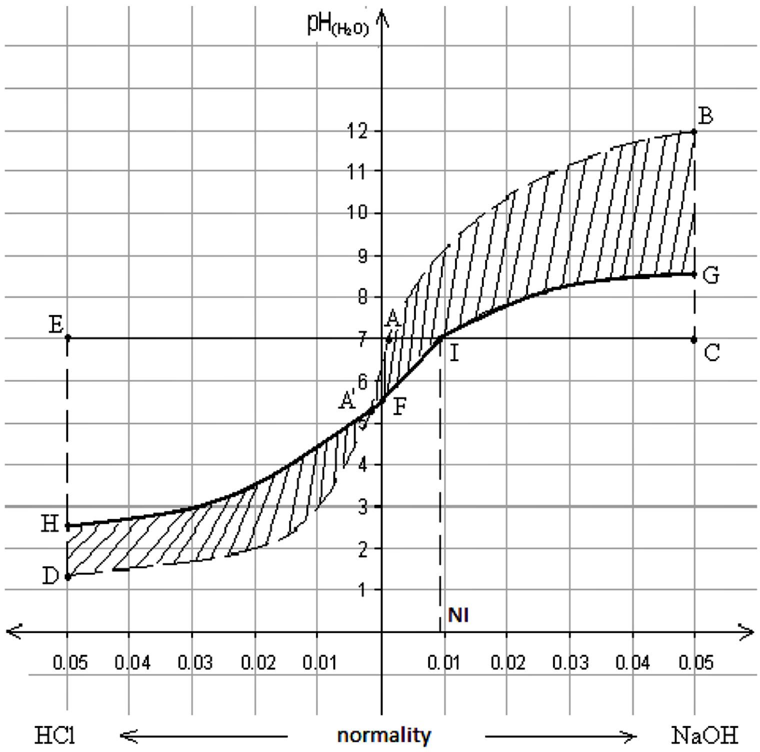

Figure 1. Graphical model for determining buffer areas and neutralization rate

pH 7.0 (neutralization indicator); A′ is the point of intersection of the buffer curve of the soil with the buffer curve of the unbuffered substrate.

The indicator of acid-base buffering is the area of the figure formed between the titration curves of the specified objects: A′DH in the acid interval and ABGI in the alkaline interval. Based on the buffering curves and the areas of the indicated figures, the potential buffer capacity in the acidic (PBCa) and alkaline (PBCal) intervals, the coefficient of buffer asymmetry (CBA) were calculated (Truskavetskyi, 2003).

The potential PBCa and PBCal intervals is calculated as a percentage of the buffer area in the corresponding interval to the total buffer area: PBCa = Sk·100/Smax and PBCal = Sl·100/Smax. At the same time, Sa = A′DH, Sal = ABGI, and Smax = Sa + Sal.

The segment FI on the buffer curve is used to calculate the neutralizing ability of the soil, which was called the neutralization index (Nadtochyi et al., 2010). The indicated parameter numerically corresponds to the amount of acid (acidic pH) or alkali (alkaline pH) per 100 g of soil, which ensures a neutral reaction of the soil suspension.

RESULTS AND DISCUSSIONS

To obtain comparative data on physico-chemical properties and acid-base buffering in the natural state and under minimal anthropogenic load, soils under forest cover and under undrained pasture were studied. To determine the effect of drainage reclamation, soils under hayfields and pastures drained by closed tile drainage were studied. The acid-base state of the soil is determined by the direction of the soil-forming process, the properties of the parent rocks, vegetation cover, and other factors. It is likely that the intensive leaching of exchangeable cations of calcium and magnesium with drainage waters from the upper layer of drained soil can reduce its ability to resist both acidification and alkalinization of the environment, and therefore to form its acid-base buffering parameters.

The mobility and availability of almost all elements of mineral nutrition to plants, the rate of mineralization of organic substances and the dissolution of poorly soluble compounds, the state of soil colloids, and the intensity of the development of processes of soil oxidization depend on the reaction of the soil environment (Marcinkonic and Tripolskaja, 2008). It is known that in soils with an acidic reaction of the environment there are unfavorable conditions for the growth of most agricultural crops and the functioning of microbial coenoses, physical properties deteriorate, and organic substances are poorly fixed. Therefore, indicators of the acid-base state of the soil provide an objective characteristic of changes in the soil-forming process due to anthropogenic influence (Paas, 1986).

The studied soils, regardless of the degree of anthropogenic load, are characterized by an acidic reaction of the environment. The lowest values of the indicator of the degree of actual acidity ($pH_{(H2O)}$) are characteristic of the soil under the forest cover (Table 1). A natural increase of this indicator with depth is noted. This is due to the acidic nature of plant waste and its decomposition by fungal microflora in the upper layer of the soil. A certain increase in $pH_{(H2O)}$ values in the soil of an undrained pasture can be explained by the fact that herbaceous plants, unlike trees, have a cationic-anionic type of nutrition, i.e., they actively release into the environment, in addition to H^+, also OH^- and $HCO3^-$ and cause a smaller effect of "trophic acidification" (Shum and Bedernichek, 2013). Similar regularities regarding the value and profile distribution of this indicator were established for the soil of the drained hayfield. In the soil of the drained pasture, where tile drainage has been in operation for more than 100 years and, accordingly, significant leaching of exchangeable cations has occurred, the value of $pH_{(H2O)}$ is the lowest within the entire profile among all soils.

Differences in the parameters of the acid-base buffering capacity of the studied soil depending on the conditions of its functioning, in particular the potential buffer capacity in the acid and alkaline interval, the coefficient of buffer asymmetry, as well as the neutralization index, were established.

The lowest values of the potential buffer capacity in the acid interval are characteristic of the soil functioning in conditions of long-term (since 1914) drainage – 6.5–10.3 points. Such soil will be less resistant to acidification. During less long-term drainage (since 1974), a decrease to 29.4–40.9 points in the potential buffer capacity in the alkaline interval was noted in the upper layer of the soil compared to the soil of undrained pasture, where its value within the profile is 31.3–41.5 points. The values of this estimated indicator of acid-base buffering were the highest in the

Table 1. The degree of actual acidity and estimated indicators of acid-base buffering of the soil under various anthropogenic loads

Horizon	$pH_{(H2O)}$	Neutralization index, mg-eq 100 g^{-1}	Potential buffer capacity, points		Coefficient of buffer asymmetry
			Acidic	Alkaline	
Forest					
HE	4.1	5.0	12.1	40.2	0.78
Egl	4.8	4.8	12.4	40.1	0.70
Eigl	5.5	5.4	14.0	37.4	0.73
Igl	5.3	4.5	13.6	35.9	0.68
Pgl	5.7	1.7	15.8	28.6	0.64
Undrained pasture					
HE	4.3	3.5	11.4	43.5	0.57
Egl	5.4	2.8	10.3	39.1	0.58
Eigl	5.5	2.9	12.8	41.5	0.53
Igl	5.9	2.1	15.6	31.3	0.37
Pgl	6.3	1.3	14.2	31.6	0.39
Hayfield drained by closed tile drainage in 1974					
HE	4.6	2.9	13.1	32.2	0.42
Egl	5.4	3.3	12.2	29.4	0.42
Eigl	5.4	3.7	10.8	40.9	0.61
Igl	5.7	3.7	9.7	39.0	0.60
Pgl	6.1	1.8	12.0	33.4	0.48
Pasture drained by closed tile drainage in 1914					
HE	4.7	6.3	10.3	40.2	0.61
Egl	4.8	5.6	7.6	43.5	0.71
Eigl	4.7	6.4	8.5	42.6	0.66
Igl	4.8	6.2	8.2	45.2	0.71
Pigl	5.0	5.9	6.5	40.4	0.72

case of long-term soil drying and changed little within the profile (40.2–45.2 points). Thus, long-term drying of the soil leads to an increase in its buffering capacity against bases.

Close parameters of acid-base buffering indicators are formed in the soil under the forest cover and undrained pasture. There is a clear consistency between the values of the potential buffer capacity in the alkaline interval and the neutralization index. Their values decrease from the upper genetic horizons to the lower ones. Therefore, the soil under grassy vegetation acquires the ability to better neutralize alkaline loads compared to acid loads.

In the soil of the drained lands, a more uniform distribution of the values of the potential buffer capacity in the acidic and alkaline interval was noted. In particular, for more than a century of operation of tile drainage within the entire soil profile, the potential buffer capacity in the acidic interval has significantly decreased and increased in the alkaline interval. The values of the neutralization index are 5.6–6.4 mg-eq/100 g of soil, that is, they are the highest of all soils. This indicates an increase in the neutralizing ability of the soil to alkali.

The CBA shows how much the soil's ability to deposit a fertility element outweighs its ability to supply this element back into the soil solution or convert it into a form available to plants: CBA = (Sal – Sa)/(Sal + Sa). The zero level of this indicator indicates that the soil has achieved full symmetry and the best ability to self-regulate the corresponding mode. If the coefficient of buffer asymmetry (BA) approaches unity, then in such a soil the conditions are mainly for deposition (accumulation) of an element with a limited ability to release it into the soil solution. At negative maximum asymmetry (CBA = -1), the soil has the highest ability to convert the element into an available form. In this case, external loads on such soil become more dangerous, because at the slightest acid impact, its acid-base balance is already shifted, which causes a decrease in fertility (Truskavetskyi et al., 2007). The best condition of the acid-base buffer systems of the soil was noted under undrained pasture and hayfield drained, where the values of CBA within the soil profile are 0.37–0.58 and 0.42–0.61, respectively. In the soil of the drained pastures, the value of CBA increases compared to these areas, but remains lower than in the soil under the forest.

So, with a relatively short duration of tile drainage (40–45 years), there is a slight deterioration of the acid-base buffer capacity of the soil compared to non-drained lands. Long-term drainage (more than 100 years) of the soil by closed earthen drainage leads to significant disturbances in the functioning of its buffer mechanisms, in particular, its ability to resist acidification decreases and its ability to resist alkalization increases. Therefore, it is necessary to carry out additional measures to stabilize, first of all, the acid-base state of the soil. In addition, since indicators of the potential buffer capacity in the acidic and alkaline intervals clearly respond to the change in vegetation and the duration of the drainage systems, it is advisable to use their parameters to establish the orientation of the soil-forming process under the corresponding types of anthropogenic influence compared to the soil in natural state (under forest cover).

It has been established that lime effectively reduces soil acidity (Marcinkonic and Tripolskaja, 2008). However, in the acidic gleyed soils of Eastern Carpathian Foothills, the processes of gley formation and acid hydrolysis cause the destruction of clay minerals and the accumulation of mobile forms of aluminum, which, increases the acidification of the soil solution as a result of hydrolysis. Aluminum has both direct and indirect effects on plants. To reduce the toxicity of aluminum, to reduce the acidity of the soil, it is necessary to apply phosrorite flour, under the influence of which aluminum phosphate intracomplex compounds are formed. In them, aluminum is a component of the anionic part, loses its ability to undergo hydrolysis and does not acidify the soil solution. The simultaneous application of lime and phosphorite flour proved to be effective, which ensures a decrease in both soil acidity and the content of mobile aluminum (Begei and Karasevych, 2023).

The study of the influence of chemical meliorants according to the scheme of the experiment on the formation of the acid-base buffering capacity of the soil under undrained pasture and hay drained was carried out. For this purpose, we propose to determine the filling factor of the buffer capacity (FFBC), which can be acidic (FFBCa) and alkaline (FFBCal). For this, it is necessary to determine the buffer area in the acidic (Sa) and alkaline (Sal) intervals: Sa= A´DH, and Sal = A´BG. When determining the area of buffering in the alkaline interval, we suggest taking into account the area of the figure A´AIF, which is located below the EC line on the graph, i.e., the standard with pH 7. FFBCa is calculated as the ratio of the actual area of buffering in the acid interval (Sa) to the maximum possible buffer capacity: $FFBCa = Sa \cdot 100/Sa_{max}$, and FFBCal – as the ratio of the actual area of buffering in the alkaline interval (Sal) to the maximum possible buffer capacity: $FFBCal = Sal \cdot 100/ Sl_{max}$.

In the investigated soil under the grassland, the FFBCa is 0.21–0.23 and 0.24–0.26 for the non-drained pasture and the drained hayfield, respectively (Table 2), i.e., the filling of the buffer capacity in the acidic range is very low. The filling factor of the buffer capacity in the alkaline range has several times higher values. For undrained pasture, they are 0.79–0.89, and for drained hay – 0.59–0.65.

After a year of interaction of the soil with chemical ameliorants in different variants of the experiment, the values of FFBCa increased by 1.5–2 (pasture not drained) and by 2–3 (hayfield drained). In addition, there was a decrease in the values of FFBCal by almost 2 and 1.5–2 times for these lands. In most cases, its highest values were during liming. The most significant decrease in the values of FFBCal in the soil of the undrained pasture occurred when lime was applied to the soil, as well as lime with phosphorite flour. This indicator clearly reflects the degree of transformation of the acid-base buffering capacity of the soil when calcium-containing compounds are introduced.

After 2 years of interaction of the soil with chemical meliorants, tendencies to decrease the values of FFBCa and increase thos of FFBCal became noticeable in most variants of the experiment. In our opinion, the indicator obtained as the ratio of FFBCa to FFBCal is important for establishing the effect of «overliming» of reclaimed soil. Such a phenomenon is noted when its values are higher than 1. In this case, the area of buffering

Table 2. Indicators of acid-base buffer transformation soil capacity after interaction with chemical ameliorants

Variant of Experiment	The filling factor of the buffer capacity				FFBCa /FFBCal	
	Acidic		Alkaline			
	1 year	2 years	1 year	2 years	1 year	2 year
Undrained pasture						
Control	0.23	0.23	0.89	0.89	0.26	0.26
Lime, standard rate	0.34	0.31	0.33	0.56	1.03	0.56
Phosphate, standard rate	0.34	0.28	0.49	0.64	0.70	0.44
Lime + phosphate, each at half standard	0.41	0.35	0.46	0.58	0.93	0.60
Hayfield drained						
Control	0.26	0.26	0.65	0.65	0.41	0.41
Lime, standard rate	0.67	0.54	0.49	0.80	1.41	0.68
Phosphate, standard rate	0.57	0.54	0.41	0.66	0.96	0.83
Lime + phosphate, each at half standard	0.41	0.29	0.34	0.49	1.24	0.59

in the acid range exceeds the area of buffering in the alkaline range, which is not characteristic of the soil in its natural state.

In the first year after applying high rates of lime to the soil, its acid-base buffer mechanisms begin to function in conditions atypical for the natural state. In the version of the experiment with the introduction of lime, the value of the FFBCa/FFBCal ratio exceeded one both in the soil of the undrained pasture and the drained hayloft. In the version of the experiment with the simultaneous introduction of both lime and phosphorite flour, the effect of «recalcification» was noted only in the soil of the drained hayloft. After the second year of interaction of the soil with calcium-containing compounds, a decrease by 1.5–2 times in the value of this indicator compared to the first year was recorded in almost all variants of the experiment. The soil functions in the direction of returning to the natural state of its buffer mechanisms.

CONCLUSIONS

The peculiarities of the manifestation of acid-base buffering capacity and the specificity of its indicators in the studied soils are the asymmetry of the buffer areas with high values in the alkaline and low values in the acidic interval, which causes values of the coefficient of buffer asymmetry close to one.

When forest vegetation is changed to herbaceous with minimal anthropogenic influence, a tendency to improve the values of indicators of acid-base buffering of the soil is outlined. Drainage of the soil with closed earthen drainage for 45 years did not lead to a significant deterioration of its buffering functions in relation to acid-alkaline loads, and after 100 years, the weakening of their manifestation is diagnosed by a decrease in the potential buffering capacity in acid and an increase in alkaline interval, as well as the values of the neutralization index and buffer asymmetry coefficient.

The studied soils, in the case of agricultural use, drainage by closed tile drainage, interaction with lime, phosphorite flour, both lime and phosphorite flour (1:1), are able to retain the genetically determined ability to show more intense anti-base than anti-acid buffering capacity. The most favorable effect on the manifestation of soil buffering in relation to acid-alkaline loads is exerted by liming in combination with phosphating.

After 1 year of the experiment, in the variants with liming and liming in combination with phosphating, 1.5-2 times increase in the values of the buffer areas in the acidic range was recorded, with their less significant decrease in the alkaline range, weakening of the buffer asymmetry and strengthening the ability of the soil to resist a change in the acid-base balance under minimal acid or alkaline influence. After a one-year interaction of the soil with phosphorite flour, there were slight similar changes in the indicators of its acid-base buffer capacity, and after a two-year interaction, their parameters acquired values close to the control.

After 2 years of interaction of the soil with lime, its anti-acid neutralizing and absorbing capacity and buffering capacity increased. During the same period, from the introduction of lime in combination with phosphorite flour, the parameters of the indicators of the acid-base buffering capacity of the soil became close to the genetically determined level.

The dynamics of the acid-base buffering capacity of the soil under the influence of calcium-containing chemical ameliorants is proposed to be carried out by the filling coefficient of the buffer capacity (acidic and alkaline), and the dynamic of the effect of "overliming" of the soil is to be carried out by the ratio of the values of this indicator in the acidic to the values in the alkaline interval.

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