

## Study of the Impact of Changes in the Acid-Base Buffering Capacity of Surface Sod-Podzolic Soils

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### ABSTRACT

The results of scientific research aimed at studying the impact of land use on the acid–base buffering capacity of gleyed sod–podzolic soils in the Carpathian region were analyzed. The transformation of these indicators was investigated using a comprehensive approach that encompasses the influence of various factors, such as agrotechnological methods and atmospheric precipitation, on the acidity and alkalinity parameters of soil solution. The research results confirm a significant influence of these factors on the acid–base characteristics, emphasizing the need for the development of a scientifically grounded approach to managing fertility and stability of the soil environment in agricultural ecosystems of the Carpathians. The study opens the perspectives for optimizing agrotechnologies and developing effective measures for the rational use of soil resources in this region.

**Keywords:** sod–podzolic soil, arable land, forest, acid–base buffering capacity, agrotechnological methods, atmospheric precipitation, fertility, soil resources.

### INTRODUCTION

The investigation of soil stability in response to environmental changes, which can be induced by both natural and anthropogenic factors, is crucial for determining the preventive measures against soil acidification and physicochemical degradation. One of the factors limiting the fertility of sod-podzolic soils in the Carpathian region is their adverse acid-base status, particularly high acidity and elevated aluminum mobility. These parameters are associated with the origin of such soils from dense acidic sedimentary, metamorphic rocks, as well as colluvial and ancient alluvial deposits under the influence of leaching water regime, predominantly under forest vegetation. In recent decades, progressive soil acidification has become one of the major problems in

agricultural land use. Therefore, it is important to determine the resistance of soils to acidification or soil solution leaching that may arise due to anthropogenic influence, including the application of acidic mineral fertilizers. To achieve this, objective indicators reflecting the acid-base buffering capacity of these soils and their parameters under different land use practices need to be established. The optimal growth of agricultural crops under production conditions crucially depends on the balance of the soil solution, which interacts with the solid part of the soil, its living components, and the air. This balance constantly changes due to root absorption, microbial emissions, precipitation, atmospheric pressure variations, soil processing, fertilizer application and irrigation [Hryhoriv et al., 2022; Hryhoriv et al., 2023; Karbivska et al., 2023]. Therefore,

the investigation of quantitative and qualitative parameters as well as patterns in the formation of the acid–base buffering capacity of soils with acidic environments holds significant theoretical and practical importance. This is associated with issues of soil acidity, chemical amelioration, as well as the adverse effects of acidic precipitation on the soil and ecosystems. The parameters characterizing acid–base buffering capacity can be utilized to address overall ecological problems, diagnose soil formation processes, contribute to agricultural soil chemistry, and assess the agroecological state of the soil [Bascompte 2010; Symochko et al., 2015].

In contemporary scientific literature exploring soil monitoring issues, particular attention is given to indicators of soil properties as a biocosmic entity. Soil monitoring in this context involves observing changes in soil properties over space and time in designated areas with the status reflecting natural diversity and all types of economic usage [Truskavetskiy and Tsapko, 2003; Tsapko, 2004; Gobat et al., 2004; Heger et al., 2012; Karbivska et al., 2020].

Developed countries have already implemented soil monitoring programs and established their networks. These programs include clearly defined monitoring objects, describing their history, purpose, quantity, and criteria for selecting sites, sample collection plans, field observations, laboratory research, soil archives, and accessible contact addresses. Ukraine is currently in the process of establishing monitoring due to various circumstances involving both subjective and objective factors. One of the main obstacles complicating its implementation is the absence of clear benchmark criteria for soil parameters. These criteria refer to fixed indicators of soil samples from genetic horizons of a certain soil variety during the initial observation period. To assess the agroecological condition of the soil, it is recommended to use parameters of virgin soil or fallow land that has not been used for agricultural purposes for 20 years or more [Medvedev, 2012; Medvedev and Laktionova, 2012; Kovalenko et al., 2024a].

Detailed experience in conducting background soil monitoring in Ukraine, including the standards for morphology and micromorphology of the profile, as well as the standards for chemical, physicochemical, and biological properties, is described in the monograph by Medvedev [2012]. However, among the standards

for physicochemical properties, only benchmark indicators of  $\text{pH}_{\text{ke1}}$  and exchangeable base content for arable soils are mentioned. This is not accidental, as not all agroecological parameters are thoroughly studied, being difficult to formalize [Frid, 2008; Radchenko et al. 2024]. Some criteria are descriptive and are based solely on practical experience without deep experimental analysis, highlighting the need for further scientific research. In this context, an extremely important indicator of the agroecological state of the soil, the acid–base buffering capacity, remains overlooked.

The acid–base status, known as acid–base buffering capacity, determines the behavior of elements in the soil and influences the regimes of organic matter and mineral nutrition, as well as the mobility of various compounds, including those toxic to plants. In acidic low buffering soils, the solubility of Mn, Fe, B, Cu, Zn increases, and their excess negatively affects the growth, development, and ultimately, the productivity of plants. Low–buffer and highly acidic soils also reduce the availability of important microelements, such as Mo [Nazarova, 1996; Kuznetsov et al., 2007; Nelson and Su, 2010; Tsyuk et al., 2022].

The buffering capacity of soil is based on the ability of elementary compounds of individual chemical elements, which are the material carriers in the soil mass of minimal volume, to retain all necessary components of the elementary system. At the same time, buffering capacity parameters determined under laboratory conditions reflect only a specific statistical description of the soil sample. Under natural conditions, acid–base buffering capacity depends not only on the solid phase of the soil but also on soil–inhabiting organisms, the intensity of moisture processes, and the  $\text{CO}_2$  content in the soil air. Thus, acid–base buffering capacity, in a broader sense, is a dynamic indicator that characterizes not only the ability of soil to react to pH changes during the addition of acid or alkali but also its ability to restore the initial pH level over time [Nadtochiy, 1998; Nadtochiy et al., 2010; Truskavetskiy and Tsapko 2016; Zhang et al., 2016; Karpenko et al., 2022].

Many processes in soil are accompanied by the release or absorption of protons, which directly or indirectly affects the formation of acid–base buffering capacity. The effective action of highly buffered soils on the productivity of phytocenosis is primarily determined by their ability to neutralize high proton activity in reactions occurring in the

soil solution, following the general scheme: acid  $\leftrightarrow$  alkali + proton [Ilyin, 1995; Balyuk et al., 2012; Radchenko et al., 2023; Kovalenko et al., 2024b]. Since acid–base buffering capacity is a key indicator of the agroecological state of the soil, the goal was set to determine its benchmark values for sod–podzolic soils, both arable and forested.

## MATERIAL AND METHODS

The objects of the study were gleyed sod–podzolic soils of the Carpathians, both natural and anthropogenically transformed lands. The subject of the research was the processes of transformation of the acid–base buffering capacity of gleyed sod–podzolic soils. To achieve the set objectives, various research methods, including field and laboratory methods, were employed.

The research was conducted on sod–podzolic soils of different land use categories in the territory of the Dolyna district, which belongs to the Ivano-Frankivsk region. The soil samples for the study were collected during soil surveys of Carpathian soils in standard landscapes of each soil type under mixed forests and arable land. The soil samples were collected with three replications. After preparation for analysis, soil samples underwent potentiometric titration with increasing concentrations of acid and alkali from 0.005 to 0.05 normality. The acid and alkali solution was prepared based on a 0.05 M solution of  $\text{CaCl}_2$ . On the basis of the constructed buffer curves, the acid–neutralizing (in the pH  $\text{CaCl}_2$  range to pH 3.0) and alkali–neutralizing (in the pH  $\text{CaCl}_2$  range to pH 8.0) capacity of soil to neutralize and absorb were determined. The pH gradients relative to pH  $\text{CaCl}_2$

(initial pH of the buffer curves) during the addition of acid and alkali at maximum concentration [Kirylichuk and Bonishko, 2011] were used as indicators of neutralization [Nadtochiy et al., 2010].

## RESULTS AND DISCUSSION

During the analytical part of the study, nine soil samples collected from different genetic horizons under the forest and arable land from two different soil profiles were analyzed. For the investigation, air–dried soil that was sieved through a 1 mm diameter sieve was used. The results of the conducted research are presented in Table 1.

The initial samples of all studied soils are characterized by an acidic pH of the environment (pH in water = 5.1–6.8), low exchangeable cation content, and high hydrolytic acidity, which significantly decreases down the soil profile, remaining higher even in the parent rocks. The exception is the arable soil horizon under cultivation. As it is known, acidity is predominantly determined by aluminum ions, indicating significant breakdown of aluminosilicates. Therefore, the inconsistency in intra–profile changes in exchange acidity and exchangeable aluminum content is a consequence of the complex multifactorial processes affecting this phenomenon and requires additional research. This trend is also attributed to the manifestation of the podzolization process in soil formation. It should be noted that the obtained research findings are supported by the works of Rusakova et al. [2012], which established that the redistribution of mobile aluminum compounds between eluvial, transitional, and transition–accumulative horizons in undisturbed natural landscapes of the southern

**Table 1.** Physicochemical properties of sod–podzolic gleyed soils under different land uses

Section, land	Genetic horizon	Depth, cm	pH		Acidity		Exchangeable			
			H <sub>2</sub> O	KCl	HA	OA	Al <sup>3+</sup>	H <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
meq/100 g soil										
Arable land	He <sub>arable</sub>	0–30	6.80	5.78	2.17	0.88	0.51	0.33	8.10	0.7
	Ehgl	30–59	6.75	4.65	4.81	2.46	2.11	0.35	7.10	7.91
	Igl	59–109	5.85	4.74	5.25	5.53	5.25	0.28	10.66	5.86
	Pgl	> 109	6.55	4.21	3.89	2.03	1.74	0.28	10.10	9.21
Forest	He	4–25	5.13	4.36	7.56	1.15	0.72	0.41	4.49	2.70
	Eh	25–50	6.35	4.24	7.02	1.87	1.43	0.42	8.26	0.92
	Ei	50–74	6.36	4.31	5.23	2.31	2.01	0.28	11.26	4.68
	Igl	74–115	6.36	4.35	6.11	3.34	3.04	0.8	10.12	4.58
	Pgl	> 115	6.58	4.25	4.81	2.31	1.43	0.86	11.68	0.87

taiga leads to significant spatial differentiation of the acid-base buffering capacity of mineral soil layers with a substantial increase in soil buffering within the boundaries of transition-accumulative relief positions. Changes in the pH level and its distribution along the soil profile indicate a tendency towards pH neutralization with the intensive use of sod-podzolic soils (Table 1). This is mainly explained by the activation of the podzolization process, chemical amelioration of arable soils, and the partial application of organic fertilizers. The reaction of the soil solution directly affects the amount of exchanged cations and their chemical composition. During the research, both the total amount of absorbed bases and the degree of their saturation depended on the soil acidity and the intensity of its use. The exchangeable hydrogen content in the studied samples of sod-podzolic soils ranges from 0.28 to 0.86 meq/100 g soil, which is significantly lower than the level of available exchangeable aluminum, the main factor in acidity formation.

It is worth noting that soil clearing from the forest, its amelioration, and active use contribute to the reduction of hydrolytic and exchange acidity, which is mainly confirmed by the data of the conducted research. The drawn conclusions are also supported by the research of Kuznetsov et al. [2007], which revealed a direct correlation between soil acidity buffering capacity and the total content of exchangeable bases and the content of oxalate-soluble aluminum compounds in the soil. When analyzing the buffer capacity of soils under the influence of proton loading, the main focus was on assessing the intensity of shifts in the pH level of soil suspension depending on the proton concentration in it. The results of the conducted

studies regarding the determination of key parameters of the buffer properties of sod-podzolic gleyed soils in different land uses are presented in Table 2.

Through the identification of segments on the buffer curves within the respective pH values, it was possible to calculate the acid-neutralizing (from  $\text{pH}_{\text{CaCl}_2}$  to  $\text{pH}_{5.0}$ ) and alkali-neutralizing (from  $\text{pH}_{\text{CaCl}_2}$  to  $\text{pH}_{8.0}$ ), as well as the neutralizing and absorbing capacity of the soil towards acid and alkali in the specified pH ranges. The gradients of pH concerning  $\text{pH}_{\text{CaCl}_2}$  at maximum acid or alkali input were also determined. These gradients indicate the buffering capacity of soil under extreme acid and alkaline loads, as a higher pH gradient corresponds to lower buffering capacity.

Comparing the data on the buffer properties of soils in different land uses, it was found that  $\text{pH}_{\text{CaCl}_2}$  changed from acidic (3.81–5.40) closer to weakly acidic (3.82–6.28) in the fields. This confirms that soil cultivation not only improves its properties but also contributes to increased soil stability, leading to an increase in its buffering capacity. The obtained findings are consistent with the research of Nadochiy et al. [2010], who established that, according to the scale for assessing acid-base buffering capacity, the degree of buffer capacity in the acid interval throughout the soil profile is very low, while it is moderate in the alkaline interval. Additionally, the neutralization index does not exceed 1.9 meq/100 g soil. Its maximum value was found in the upper soil layer.

Another key indicator indicating the soil's acid-base buffering capacity is the pH gradient of the suspension after the introduction of the maximum amount of acid or alkali (12.5 meq HCl and NaOH). It was found that the smaller this gradient, the higher the buffering capacity of soil, and

**Table 2.** Indicators of buffer properties of sod-podzolic gleyed soils under different land uses

Section, land	Genetic Horizon	Depth, cm	$\text{pH}_{\text{CaCl}_2}$	Neutralizing capacity, meq/100 g soil		Buffering capacity, meq/100 g soil $\Delta\text{pH}$		pH Gradient of suspension from input	
				In the range from $\text{pH}_{\text{CaCl}_2}$ to				12.5 meq/100 g HCl	12.5 meq/100 g NaOH
				$\text{pH}_{5.0}$	$\text{pH}_{8.0}$	$\text{pH}_{5.0}$	$\text{pH}_{8.0}$		
Arable Land	He <sub>arable</sub>	0–30	6.28	1	1.30	0.76	0.75	4.17	3.84
	Ehgl	30–59	5.08	0.5	1.50	4.50	0.51	2.54	5.21
	Igl	59–109	3.82	-	2.24	-	0.53	1.40	7.93
	Pgl	> 109	4.56	-	1.50	-	0.43	2.21	6.11
Forest	He <sub>arable</sub>	4–25	3.81	-	2.24	-	0.53	2.05	8.15
	Eh	25–50	4.74	-	1.50	-	0.45	2.71	6.27
	Igl	74–115	4.96	-	1.24	-	0.40	2.76	6.66
	Pgl	> 115	5.40	0.53	0.64	1.20	0.24	3.35	6.10

**Table 3.** Estimated indicators of acid-base buffering capacity of podzolized gley soils under different land use types

Section, land	Genetic horizon	Depth, cm	Buffer area, cm <sup>2</sup>		ABB*
			Against acidification	Against alkalization	
Arable land	He <sub>arable</sub>	0–30	4.50	9.94	0.37
	Ehgl	30–59	5.94	10.24	0.26
	Igl	59–109	4.64	9.91	0.35
	Pgl	> 109	4.71	8.14	0.26
Forest	He <sub>arable</sub>	4–25	1.51	6.81	0.63
	Eh	25–50	3.11	7.41	0.40
	Igl	74–115	3.64	7.41	0.35
	Pgl	> 115	2.14	3.91	0.28

**Note:** \*ABB – acid-base buffering.

vice versa. The data obtained confirm that the buffering capacity in the acidic range is higher both in the forest and in the fields. However, it is worth noting that under cultivation in the humus–eluvial horizon, the buffering capacity is higher than under leaching, indicating a gradient of 3.85 meq NaOH versus 4.18 meq HCl.

Using pH–buffer curves of soils in 0.01 M CaCl<sub>2</sub> solution, the buffering area against acid and alkali loads was calculated. The buffering asymmetry coefficient was calculated based on these indicators. The results of these studies are presented in Table 3.

The conclusions that can be drawn based on the results of the study are as follows: both in fields and in the forest, the buffer area is larger under cultivation, which is explained by the genetic nature of these soils. Even though the values are slightly higher under cultivation, they remain within the range of 8.14 to 10.24 cm<sup>2</sup>, compared to the forest, where these indicators range from 3.91 to 7.41 cm<sup>2</sup>.

It is worth noting that buffer asymmetry is clearly expressed both in forest soil, where ABB = 0.28–0.63, and in fields, where ABB is 0.26–0.37. However, unlike forest soil, this asymmetry is less pronounced in cultivated soil.

According to the research results of Smaha and Kazymyr [2022] Podkarpattia podzolized chernozems, occurring in different land use types, are characterized by the same type of buffer curves in all genetic horizons and a similar distribution of neutralization indicators and pH in a CaCl<sub>2</sub> solution. The magnitude of the soil neutralization capacity to acids depends on the land use type and decreases in the following order: forest – arable land – pasture. As for the soil neutralization capacity to alkalis, it decreases in the

order: pasture – arable land – forest. Determining the buffer capacity of soil by isolating its neutralization capacity in mg–eq./100 g based on the “delta” pH is impractical. The values of the pH suspension gradient when introducing the minimum concentration of acid or alkali relative to the initial titration point objectively reflect the buffering capacity of soil in acidic and alkaline ranges [Smaha and Kazymyr, 2022].

## CONCLUSIONS

According to the results of the horizontal analysis of the acid–base buffering capacity, it can be noted that the podzolized chernozems under the forest and cultivation have the same genetic nature and orientation in the formation of soil processes. The calculated parameters indicate that the buffering capacity of the studied soils is higher with respect to alkalization than with respect to acidification. For example, the buffer areas range from 1.50 to 5.94 cm<sup>2</sup> and from 3.91 to 10.24 cm<sup>2</sup>, respectively. It was also found that in terms of the structure of the anti–acid and anti–alkaline buffering capacity, the studied podzolized chernozems did not differ significantly.

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