

Factors Influencing the Acidification Trends in Agriculture Soils: A Case Study of Slovakia

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Abstract

This study aims to evaluate the development of soil reaction values in 15 key localities of soil Partial Monitoring System from 1994 to 2023, and to identify the most important regional drivers of pH value development. Soil samples were collected from the depth 0 - 0.10 m yearly in the spring (5 samples from each locality). In the dry soil, samples were determined actively and exchanged soil reaction. The most significant negative changes (decreases of soil reaction) were determined in Haplic Stagnosols group and Cambisols group. The pH value in topsoil is primarily controlled by soil type and soil substrate, soil management and land use, and to a lesser extent by climatic region.

Keywords

pH Value, Acidification, Climatic Region, Soil Type

1. Introduction

The optimal value of the soil reaction is one of the key aspects of the evaluation of ecosystem services resulting from natural capital stocks fulfilling human needs (Makovníková et al., 2017, 2024). This is a basic prerequisite for sustainable agriculture where soil fulfills all its functions and services to an optimal extent in a specific way of its use. Soil pH is a result of the acid-neutralizing capacity of soils that depends on the existence and reactivity of pH buffer systems and the input and production rates of acids of different strength (Bloom et al., 2005). The value of the soil reaction enters as an indicator in the evaluation of production services as well as regulating services provided by the agroecosystem (MEA, 2005). The soil reaction indicates the acid-base reactions in the soil because of the overall

balance of ions in the soil solution. Soil acidity affects the growth and activity of the root system of plants, affects the species composition of macro and microfauna in the ecosystem and conditions plant yields. Soil acidity also determines the acceptability of nutrients by plants (Leonardi, 1991), the mobility of Al, Mn and heavy metals (Yong et al., 1992; Makovníková et al., 2006, 2007), as well as several physicochemical properties of the soil (sorption capacity, cation and anion exchange capacity). The entire system of biochemical reactions in the soil/plant relationship, regulated by enzymes, is also influenced by the pH value. Acidification, the negative process of soil acidification, represents one of the serious processes of chemical degradation, which directly and indirectly affects the chemical processes in the soil. Soil acidity is characterized by the unsaturation of the sorption complex, i.e., by the majority representation of H^+ and Al^{3+} ions and the presence of free H^+ and Al^{3+} ions in the soil solution (Makovníková et al., 2006). The degree of ionization and dissociation of H^+ ions in the soil solution determines the nature of soil acidity (Čurlík et al., 2003). Current acidification is the result of cation ratios and potential anion trapping and is generally affected by disruption of element cycling in the ecosystem. The ability of the agroecosystem to cope with natural and anthropogenic acidification is determined by the capacity and potential of the buffering function of the soil, which is conditioned by functional buffering systems (Demo et al., 1998). It is the buffering function of the soil that reflects the degree of resistance of the soil to acidification. In Slovakian soils, three buffering systems are dominant (the carbonate system, the buffering system of silicates and exchangeable cations, and the aluminum buffering system) (Yang et al., 2020). Within these systems, soil organic matter acts as a separate buffering agent, while its buffering properties are primarily determined by the quality of the humus-forming material. When the soil is loaded with acid deposits, if the specific buffering capacity of a given buffering system is exceeded, the soil is acidified and degraded into another buffering system.

Acidification, the impairment of pH value, is one of the major processes of soil chemical degradation. This one indicates acid-base reactions in the soil as well as it is the result of the overall balance of ions in the soil solution. The optimal pH value is the key aspect in soil quality evaluation. Acidification reflects the interaction of soil factors and habitat factors. Acidification is a reversible process, the consequences of acidification in agro ecosystems are non-refundable:

- nutrients from the soil, and the nutrients supplied to the soil fertilizers are not at low pH value sufficiently fixed and rapidly washed out from the soil;
- bivalent cations Ca^{2+} and Mg^{2+} are extruded from the sorption complex by free Al^{3+} cations, increasing the fixation of phosphorus in forms not available to the plants (Meriño-Gergichevich, 2010);
- acidification increases the bioavailability of toxic heavy metals, aluminum ion mobility and their ability to transfers in agroecosystems.

Acidification is a reversible process, the consequences of acidification in the agroecosystem are irreversible. According to Act 220/2004, soil acidification

belongs to degradation processes, and every owner of agricultural land is obliged to implement agro-technical measures aimed at preserving the quality of the soil and protecting it from damage and degradation.

This study aims to evaluate the development of soil reaction values in 15 key localities of Slovak soil Partial Monitoring System from 1994 to 2023, and to evaluate the main drivers of acidification.

2. Material and Method

Currently the most consistent, and up-to-date source of data on the soil in agricultural land of Slovakia is the National Monitoring System of Agricultural Soils (CMS-P). Soil monitoring system in Slovakia consists of 2 basic subsystems: the basic network of monitoring sites in 5 years repetitions (agricultural and alpine soils together) and the key monitoring sites in repetition of every year. The key monitoring location is circular in shape with a radius of 10 m and a total area of 314 m² (Kobza et al., 2024). Each monitoring area is characterized by a pedological probe in the middle, soil type and subtype are determined according to the soil classification (WRB, 2006). The centers of the monitoring sites are geodetically focused and documented by X, Y coordinates, all monitoring sites are in WGS 84 system by GPS using. Soil sampling is carried out in a probe located in the center of the monitoring site and, in addition, from four separate places on the surface of the monitoring site in the shape of the letter Z. The value of the monitored soil parameter at the given location is represented by the average value from these five separate samples. Since 1994, we have taken soil samples at 1-year intervals in the spring from a depth of 0 - 0.10 m at 15 key locations. Sampling protocol and laboratory analysis for CMS-P have been kept standard over the whole monitoring period. In soil samples taken in the years 1994-2023 from key locations (Table 1) representing the main soil types and sub-types in Slovakia an active and exchangeable soil reaction was determined (Kolektiv, 2011). Statistical processing and evaluation of the results were carried out in the STATGRAPHICS 5.0 program. Analysis of the statistical significance of differences in soil pH value between the ČMS-P localities was carried out using Kruskal-Wallis test (non-parametric test, differences between medians) and multivariate method (cluster analysis, dendrogram).

We used a classification of agro-climatic regions provided by the Information Service of the National Agricultural and Food Centre/Soil Science and Conservation Research Institute. In this classification, 11 agro-climatic regions were identified according to long-term average temperatures in January, average growing-season temperatures, daily average temperatures sums ($T > 10^{\circ}\text{C}$), the length of period with daily temperatures $t_d > 5^{\circ}\text{C}$ and the climatic moisture indicator according to Budyko calculated by Tomlain. For our purpose, the original vector layer with 11 categories was merged into 4 categories (moderately cold regions (09, 10), moderately warm regions (06, 07, 08), warm regions (03, 04, 05), and very warm regions (00, 01, 02)) (Figure 1).

Table 1. Key localities ČMS-P.

	Key locality	Land use	Climatic region	Soil classification (WRB, 2006)
1	Topoľníky	AL	Very warm	Haplic Fluvisol (Anthric, Calcaric, Siltic)
2	Liesek	GL	Moderately cold	Haplic Stagnosol (Siltic, Eutric)
3	Voderady	AL	Very warm	Haplic Chernozem (Anthric, Siltic)
4	Dvorníky	AL	Very warm	Gleyic Fluvisol (Siltic, Eutric, Anthric)
5	Raková	GL	Moderately warm	Haplic Cambisol (Skeletal, Dystric, Siltic)
6	Malanta	AL	Very warm	Cutanic Luvisol (Anthric, Siltic, Abruptic, Hypereutric)
7	Nacina Ves	AL	Warm	Haplic Fluvisol (Anthric, Eutric, Siltic)
8	Istebné	AL	Moderately warm	Stagnic Cambisol (Siltic, Eutric)
9	Žiar n/H	GL	Warm	Luvic Stagnosol (Siltic, Albic, Anthric)
10	Krompachy	GL	Moderately warm	Stagnic Cambisol (Siltic, Eutric, Skeletic)
11	Koš	AL	Warm	Haplic Planosol (Albic, Eutric, Siltic, Anthric)
12	Moravský Ján	AL	Very warm	Regosols (Dystric)
13	Jelšava	AL	moderately warm	Luvic Stagnosol (Siltic, Eutric, Albic)
14	Sihla	GL	Moderately cold	Haplic Cambisol (Skeletal, Dystric, Siltic)
15	Spišská Belá	AL	Moderately warm	Mollic Fluvisol (Anthric, Eutric, Siltic)

Explanations: AL—arable land, GL—grassland.

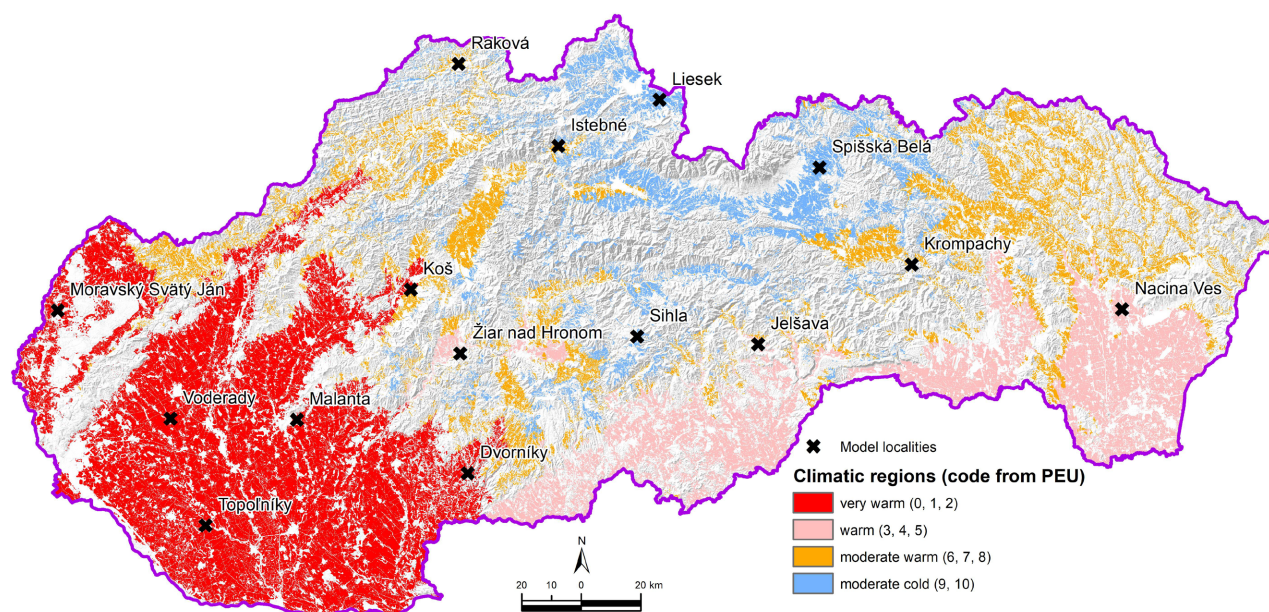


Figure 1. Categories of climatic regions in the Slovak Republic with model localities.

Data Sources

Soil monitoring network in Slovakia is constructed using ecological principle, considering all main soil groups and subgroups, climatic regions as well as various agricultural land use. All used methods (chemical and physical indicators) are described in more details in publication (Kobza et al., 2024).

Measured data were statistically processed by the program Statgraphics Centurion XVI. To compare files in the process of stratification, we used non-parametric tests of agreement because the assumption of the normality of files was not met (differences between medians; Kruskal-Wallis Test). To compare model regions, we used multivariate methods (cluster analysis, dendrogram).

3. Results and Discussion

The pH of agricultural soil in Europe depends mainly on the bioclimatic conditions that determine the agroecological zones. According to the standard agroecological zoning, Slovakia belongs to the Temperate sub-continental region (Fischer et al., 2002). The degradation process of acidification and its direct or indirect impact on the fulfillment of ecosystem services are presented in **Table 2** (Dominati et al., 2010, 2014; Orwin & Wardle, 2004).

Table 2. Direct and indirect impact of acidification on agroecosystem services.

Degradation process	Influence	Ecosystem services		
		provisioning	Regulating	Cultural
Acidification	direct	x	x	
	indirect			x

Changes in soil reaction values led to an unfavorable trend resulting in a decrease in soil reaction values at up to 10 locations (comparison of year 1994 and year 2023 in **Figure 2**). The most significant negative changes (decrease in soil reaction values reactions by 1.49 units) were determined in the Moravsky Jan site (Regosol) and in the group of Cambisols (the Rakova by 0.85 units and the Krompachy by 0.53 units). Regozems are, in terms of buffering capacity, a variable soil type, depending on the parent substrate. Regosols on non-carbonate eolic sediments have a lower resistance to acidification and lower soil reaction value. In Cambisols developed on flysch (Rakova), the dominant activity is the buffering system of silicates and exchangeable cations, in Cambisols developed on acidic substrates (Krompachy), the dominant activity is the buffering system of silicates, exchangeable cations and aluminum. These soils belong to more labile ecosystems, with a tendency to acidification. Changes in the value of soil reaction on arable soils were in the interval from -0.74 (Jelsava) to 0.51 (Nacina Ves), and on grassland in wider interval from -1.49 (Moravsky Jan) to 0.30 (Sihla). Changes in soil reaction values during monitoring are conditioned by the capacity and potential of the buffering system of the monitored soils, represented by the system of carbonates, silicates, exchangeable cations and aluminum. When the value of the active soil reaction is lower than 6.5, the bioavailability of risk elements increases, resulting in exceeding the limit values for individual inorganic pollutants in the soil system (Makovnicková et al., 2007).

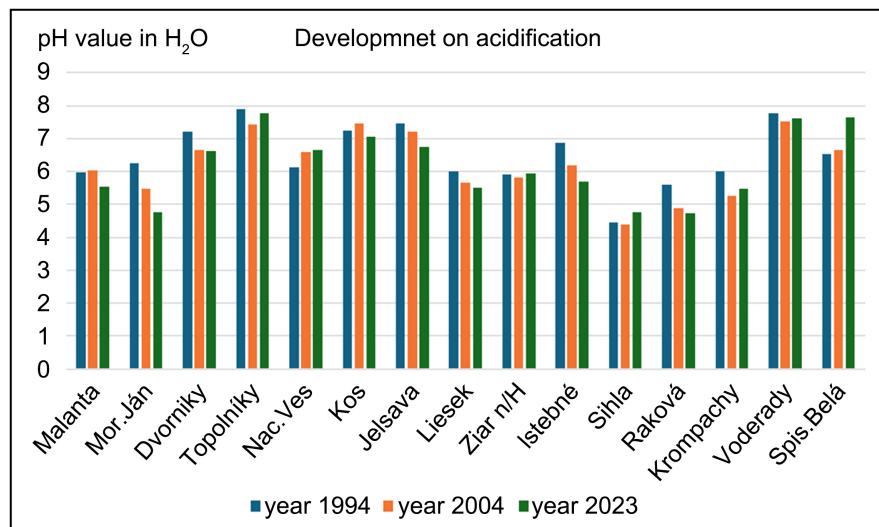


Figure 2. Development of pH value within key localities.

Chernozem (Voderady), Mollic Fluvisol (Spis. Bela) can be classified as soil types resistant to acidification. The carbonate buffer system should stabilize soil pH (H_2O) between 6.2 and 8.6. The buffering system of carbonates manifests itself by dampening acidification tendencies, the value of the soil reaction during the monitored period in the case of these soils oscillates in the interval determined by the measurement error (**Figure 3**).

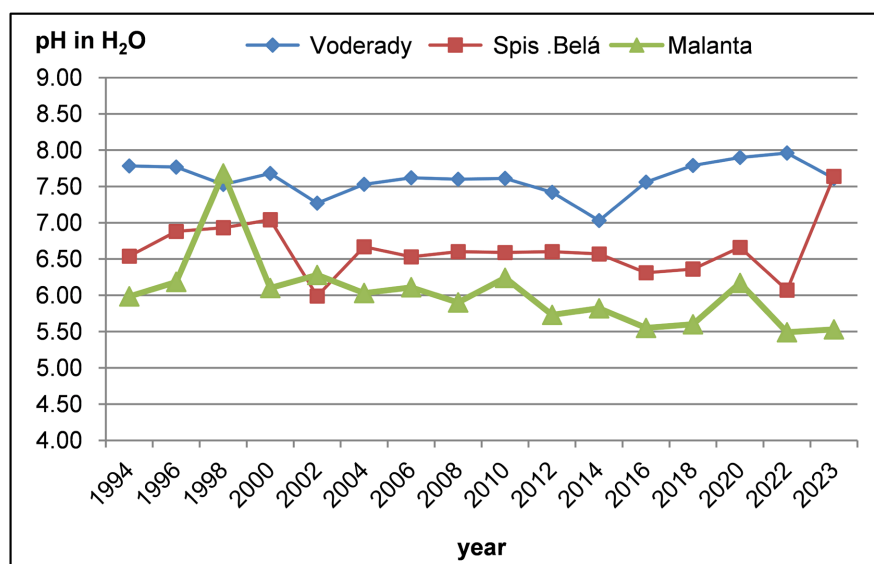


Figure 3. Development of pH value at key localities Voderady, Spisska Bela, Malanta.

Soil type, land use and climatic region belong to the important drivers leading to differences in acidification trends. Soil type and soil substrate affect the value of the soil reaction, as well as the buffering mechanisms in the soil.

The Chernozem (Voderady), Mollic Fluvisol (Spisska Bela) and Cutanic Luvisol (Malanta) localities with a pH value in the slightly alkaline area (**Figure 4**), located in different climate regions, showed statistically significant differences in pH values during the monitored period (**Table 3**). The soil reaction values at these sites with similar pedogenesis are in the neutral to weakly alkaline range. The locations are used as arable land, but they are located in different climatic regions. According to several authors (Jaradat & Boody, 2011; Montoya & Raffaelli, 2010; Birkhofer & Wolters, 2011; Diehl et al., 2013), climate has a significant impact, affects the management possibilities and land use and thus the acidification process (Makovníková et al., 2024).

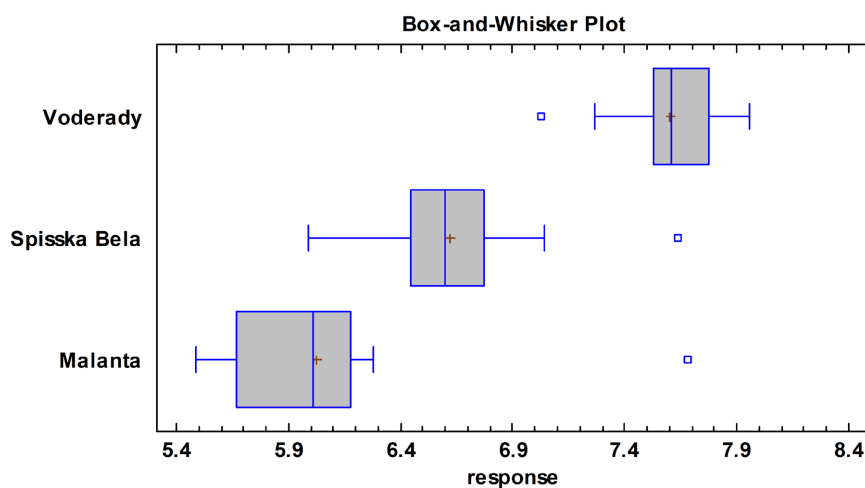


Figure 4. Box and Whisket plot (years 1994-2023) of pH value at key localities Voderady, Spisska Bela and Malanta.

Table 3. Statistical significance of differences between means of the pH value at key localities (Multiple range Test) between individual soil types.

Measure	Stratification level	Kruskal-Wallis Test	Test statistic	P-value
Comparison of pH value development	Chernozems and	1	32.5903	8.37739E-8
	Fluvisols	1	30.6255	2.23744E-7
	Pseudogleje	1	48.6446	1.55266E-10
	Cambisols	1	50.9611	4.98633E-11

1: statistically significant difference amongst the medians at the 95.0% confidence level.

We noticed a slight trend towards acidification at the Dvorníky site (Fluvisol on non-carbonate fluvial sediments), however, this trend has significant negative consequences, as the site belongs to contaminated sites with combined geo-chemical and anthropogenic contamination (Figure 5). The decrease in the soil pH can significantly increase the mobility and bioavailability of heavy metals (Bolan et al., 2003).

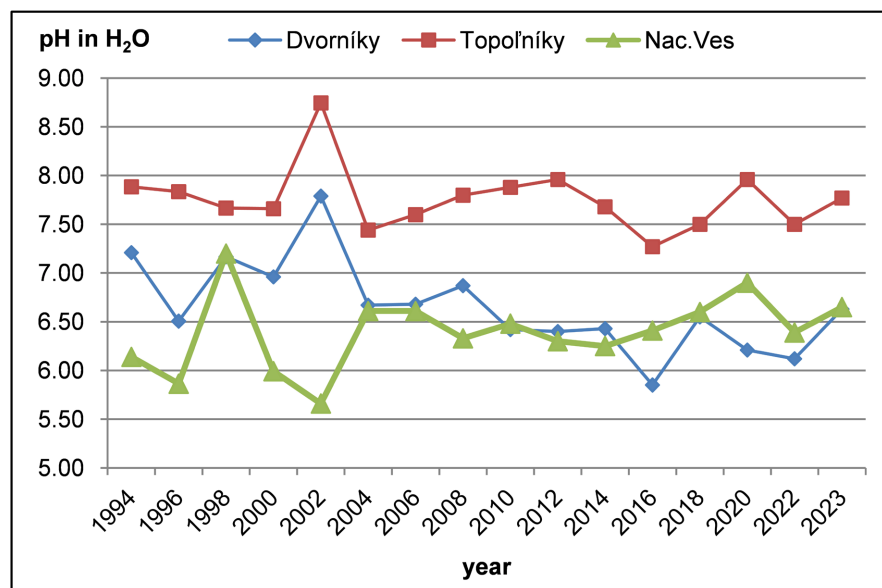


Figure 5. Development of pH value at key localities—Fluvisols.

The monitored Fluvisols are used as arable soils, the value of the soil reaction ranges from neutral to weakly acidic; the main difference is their location in different climatic regions. Fluvisols located in different climate regions, show statistically significant differences in pH values during the monitored period (Figure 6, Table 3).

The buffering systems of Stagnosols (silicates and exchangeable cations) indicate that these soils belong to more labile ecosystems, with a stronger tendency to

acidification (Bedrna, 2003). This trend is also confirmed at key localities representing pseudogleys, where we noted deviations towards acidification at all monitored localities when comparing the years 1994 and 2022 (Figure 7). In 2023, we noted a slight increase in the soil reaction value.

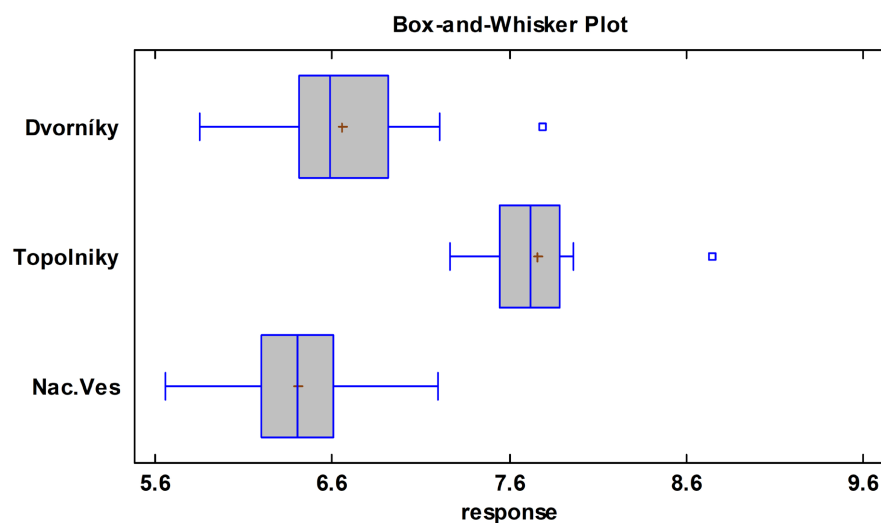


Figure 6. Box and Whisker plot (years 1994–2023) of pH value—Fluvisols.

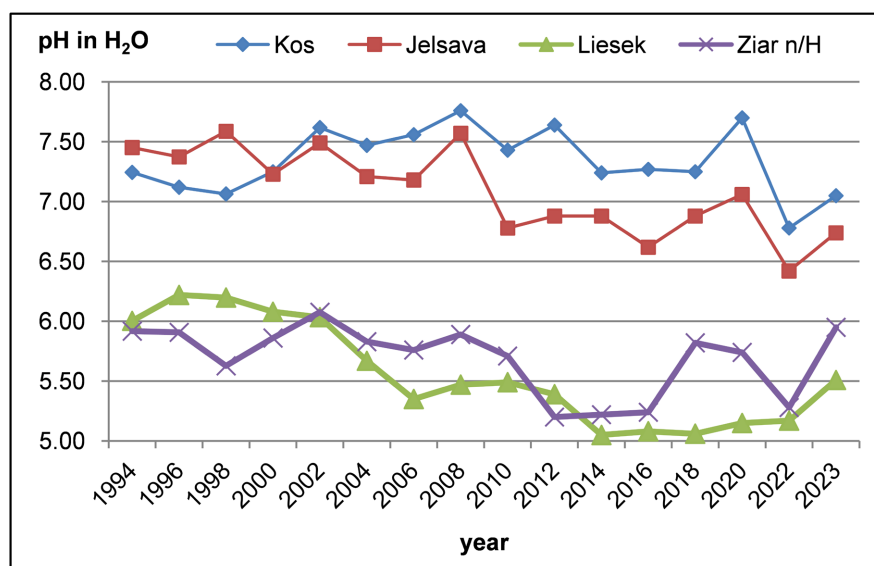


Figure 7. Development of pH value at key locality—Stagnosols.

Figure 8 shows the influence of land use. Development of soil pH reaction on the localities which are used as arable land (Jelsava and Kos) is different from the sites used as grassland (Liesek and Ziar n/Hronom). Stagnosols located in different climatic regions showed significant differences in pH values during the monitored period (statistically significant differences were between Jelsava and Kos, as well as between Liesek and Ziar n/hronom; see Table 3). The pH values of agricultural soils at the European scale follow climatic gradients (Fabian et al., 2014).

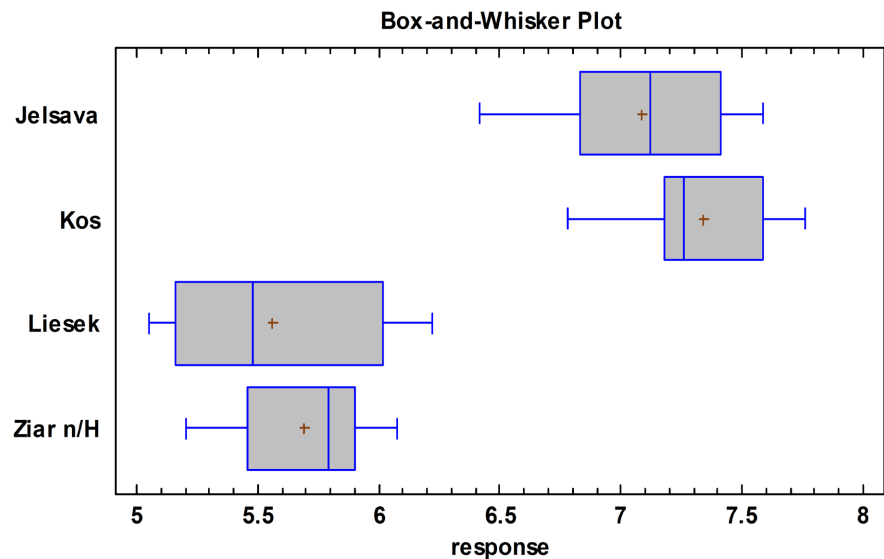


Figure 8. Box and Whisker plot (years 1994–2023) of pH value—Stagnosols.

We observe a development towards acidification at the Istebné location until 2018 (Figure 9), which was used primarily for the cultivation of clover grass mixtures. Since 2019, it has been used as arable land. Cambisols are developed on heterogeneous substrates, which subsequently also determines their different resistance to acidification. In Cambisols developed on flysch, the dominant activity is the buffering system of silicates and exchangeable cations, in Cambisols developed on acidic substrates, the dominant activity is the buffering system of silicates, exchangeable cations and aluminum. Acid buffering system cannot maintain the soil pH within the prescribed ranges in most circumstances (Zhu et al., 2018). The instability of the buffering system is manifested by significant fluctuations in soil reaction values at the Krompachy location (grassland). A balanced course of soil reaction values that oscillates around the equilibrium value can be observed in the case of the Sihla location (grassland), where the equilibrium value of the soil reaction already falls into a strongly acidic area and no further acidification occurs. On a European scale, Müller et al. (2022) observed a lower pH of the topsoil for grasslands, which is related to a higher content of acidifying humic acids. Liming of acidic soils is one of the effective soil management strategies to achieve and maintain soil pH within specified ranges and the main substrate used in EU countries is calcium carbonate (Leblanc et al., 2016; Müller et al., 2022).

Cambisols (Figure 10), the most widespread soil type in Slovakia, are developed on different types of substrates, which primarily determines their different buffering capacity and thus their susceptibility to acidification (Demo et al., 1998). The state and development of the buffering function in relation to acidification is indicated by the value of the soil reaction and the active buffering system in the context of the acidification load. Figure 10 also shows the impact of land use. The development of the soil reaction at the Istebné locality (a locality developed on a flysch substrate with dominant buffering systems of silicates and exchangeable

cations), which is used as arable land, is different from the sites of Cambisols (developed on acidic substrates) that are used as grasslands (the Raková, Sihla, Krompachy). Since the P-value (Kruskal-Wallis test) is less than 0.05, there is a statistically significant difference amongst the medians at the 95.0% confidence level.

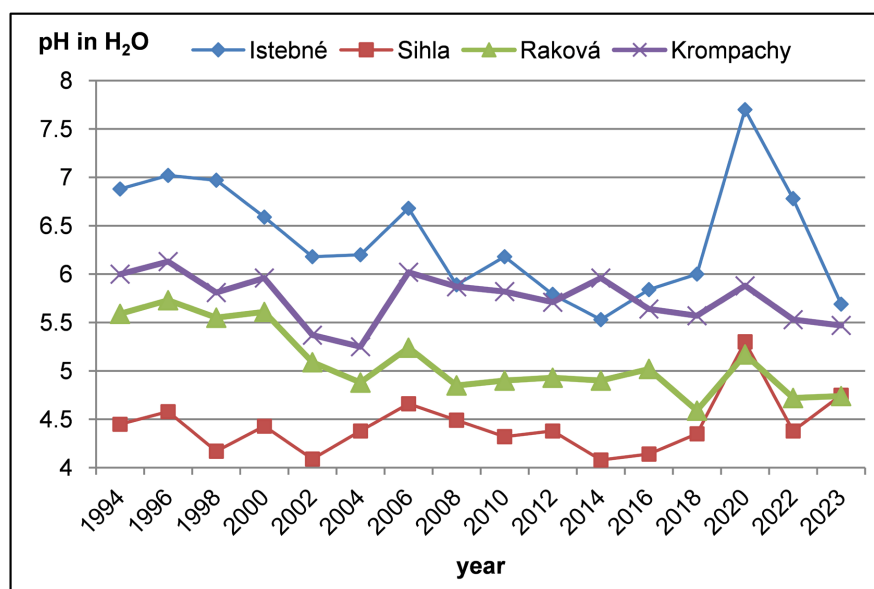


Figure 9. Development of pH value at key locality—Cambisols.

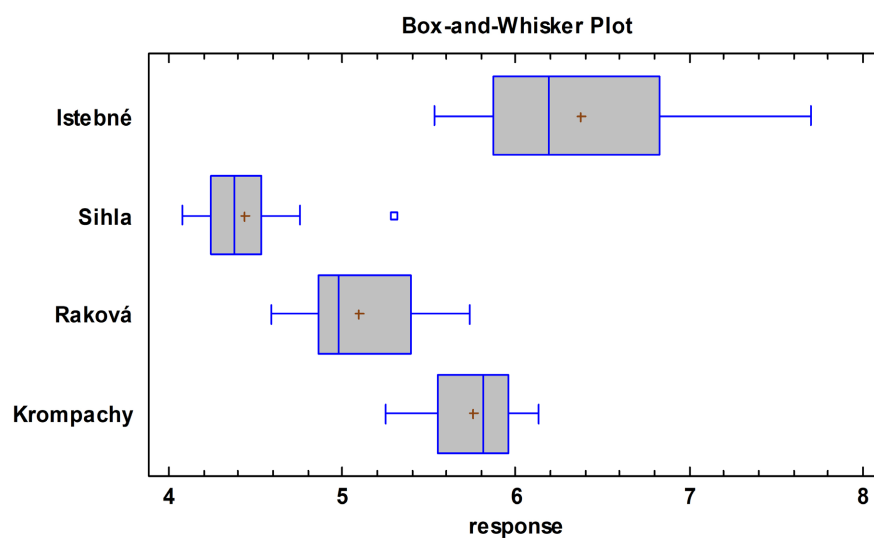


Figure 10. Box and Whisket plot (years 1994-2023) of pH value at key localities—Cambisols.

Dendrogram (**Figure 11**) compares the similarity between the development of the pH value of localities representing the main soil types found in different climatic regions. The comparison of model locations showed the most significant differences in soil pH value development between soil types, followed by land use (arable land, grassland); climatic areas have a smaller influence.

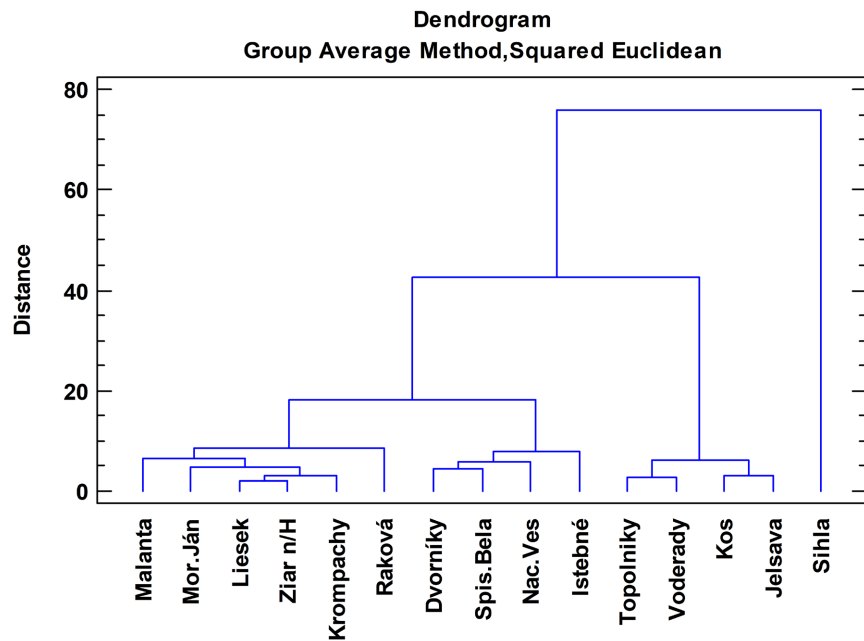


Figure 11. Cluster analysis: dendrogram.

4. Conclusion

The goal of efficient use of natural resources is to ensure that the use of natural resources and the related impact on the environment, i.e. on the quality of the soil, does not exceed the carrying capacity. Changes in soil reaction values (comparison of 1994 and 2023) at 15 key locations showed an unfavorable trend, resulting in a decrease in soil reaction values at up to 13 locations. The most significant negative changes (reduction of soil reaction values) are in the pseudogley group and in the cambizem group. When limiting agrotechnical measures aimed at optimizing soil reaction values, in the case of cambizems and pseudogleys used as arable soils, we can assume a slow decrease in soil reaction on naturally more acidic substrates. Similar tendencies were also noted in the case of soils developed on non-carbonate substrates. Acidification trends in soils with a soil reaction value in the weakly acidic region can prospectively be reflected in the deterioration of the hygienic state of the environment in the increased penetration of various pollutants, especially inorganic pollutants and aluminum, into the food chain. The comparison of model locations showed the most significant differences in soil pH value development between soil types, followed by land use (arable land, grassland). Climatic areas have a smaller influence.

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the area”.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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