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Effect of slope positions on selected chemical properties of Pseudogley in the vineyard

Utjecaj položaja na obronku na odabrana kemijska svojstva pseudogleja u vinogradu

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ABSTRACT

The study aimed to determine the effect of different slope positions on selected chemical properties of Pseudogley in the vineyard. The study was conducted in Zagreb, central Croatia. A total of 15 top-soil samples (0-30 cm) were collected from a hilltop, backslope, and footslope and analysed for pH, hydrolytic acidity (Hy), soil organic carbon (SOC) content, P_2O_5, K_2O, and potentially toxic elements (As, Cu, Ni, Pb, and Zn). A slight increase in mean pH value from the hilltop to the footslope and a decrease in Hy were observed, although differences were not statistically significant. The SOC content was low and uniform along the entire slope. A significantly higher concentration of P_2O_5 at the footslope compared to the hilltop was established (10.4 and 3.4 mg/100 g of soil, respectively). The K_2O concentration at the footslope (29.7 mg/100 g of soil) was significantly higher than at the backslope (21.2 mg/100 g of soil). The Cu, Pb, and Zn concentrations were significantly affected by slope positions in terms of download accumulation. The studied soil was contaminated by As, Ni, and Zn at the hilltop and the footslope and partly at the backslope, according to the Ordinance on the Protection of Agricultural Land from Pollution. The Cu concentrations exceeded the maximum allowed concentrations only on the backslope and footslope. The minor differences in studied soil properties between slope positions can be attributed to a short length, low and uneven inclination, and relatively short-term anthropogenic influence.

Keywords: nutrients, pH, pollution, potentially toxic elements

SAŽETAK

Cilj istraživanja bio je utvrditi utjecaj različitog položaja na obronku na odabrana kemijska svojstva pseudogleja u vinogradu. Istraživanje je provedeno u Zagrebu, centralna Hrvatska. Ukupno je uzorkovano 15 uzoraka površinskog horizonta tla (0-30 cm) sa gornjeg, srednjeg i donjeg dijela obronka i analizirano na pH, hidrolitski aciditet (Hy), sadržaj organskog ugljika tla, P_2O_5, K_2O i potencijalno toksične elemente (As, Cu, Ni, Pb i Zn). Uočeno je blago povećanje prosječne pH vrijednosti i snižavanje Hy od vrha prema dnu obronka, iako razlike nisu bile statistički opravdane. Sadržaj organskog ugljika je bio nizak i uniforman duž cijelog obronka. Ustanovljene su signifikantno više koncentracije P_2O_5 na dnu u usporedbi s vrhom obronka (10.4 i 3.4 mg/100 g tla). Koncentracije K_2O bile su značajno više na dnu (29.7 mg/100 g tla) u odnosu na sredinu obronka (21.2 mg/100 g tla). Koncentracije Cu, Pb i Zn bile su pod značajnim utjecajem položaja na obronku u smislu nakupljanja na dnu. Istraživano tlo bilo je onečišćeno s As, Ni i Zn na vrhu i dnu, te djelomično na sredini obronka prema Pravilniku o zaštiti poljoprivrednog zemljišta od onečišćenja. Koncentracije bakra prešle su maksimalno dozvoljene koncentracije samo na sredini i dnu padine. Male razlike u istraživanim svojstvima tla između dijelova obronka mogu se pripisati kratkoj dužini obronka, malom i neujednačenom nagibu te relativno kratkotrajnom antropogenom utjecaju.

Ključne riječi: hraniva, onečišćenje, pH, potencijalno toksični elementi

INTRODUCTION

Relief is one of the five crucial soil-forming factors, and it affects soil formation by slope, elevation, and aspect (Jenny, 1941). An increase in elevation led to changes in climatic conditions and vegetation types, while the aspect mainly influences the reception of solar energy and therefore soil temperature. The slope is a key factor that governs the redistribution of precipitation water and erosion processes (Cerdan et al., 2010; Shi et al., 2012). Soil water erosion causes the downward movement of soil particles (Rienzi et al., 2013; Ding and Huang, 2017), soil organic matter (Khan et al., 2013; Switoniak et al., 2015; Ibadulah et al., 2017), macronutrients (Ruiz Colmenero et al., 2011; Farsang et al., 2012; Babcsanyi et al., 2021; Lopez Vicente et al., 2022), and trace elements (Ribolzi et al., 2002; Fernandez Calvino et al., 2012; Jurišić et al., 2012; Pham et al., 2022).

Pseudogley (Stagnosol according to the IUSS Working group of WRB, 2015) is the second most frequent soil type in Croatia, mainly widespread in the Pannonian region (Bogunović et al., 1998). It is characterized by a vertical texture contrast and a periodic stagnation of precipitation water on/in the poorly permeable subsoil horizon (Rubinić et al., 2015). The top-soil horizons of Pseudogleys are dominated by silt fraction and unstable soil aggregates susceptible to erosion (Husnjak, 2014). Since around 55% of Croatian Pseudogleys are found in agroecosystems (Husnjak et al., 2011), anthropogenic activities influence erosion rates (Poesen, 2018). Croatia has around 22,000 ha of vineyards (FAO, 2021), most of which are on slopes. Intensive agrotechnical practices (e.g., tillage), lack of plant cover, and rows oriented downhill further increase the erosion process in soils under vineyards. Therefore, vineyards are one of the most erosion-prone agricultural lands in Europe (Cerdan et al., 2010), and the study of erosion processes in vineyard soil deserves particular attention (Prosdocimi et al., 2016).

A combination of natural and anthropogenic factors that govern erosion in vineyards result in changes in physical and chemical soil properties at particular slope positions. A hilltop is usually depleted in soil organic matter and macro- and micronutrients, while a footslope contains an increased content due to the accumulation of eroded particles (Kisić et al., 2002). In addition, base washout downhill affects pH values, so the pH-dependent bioavailability of nutrients and potentially toxic elements (PTEs) on different parts of the slope differs (Khan et al., 2013). Furthermore, accumulated organic matter on the footslope affects the retention and accumulation of some PTEs in the soil. For example, the complexation of Cu with soil organic matter is one of the most efficient mechanisms of its retention in soil (Romić et al., 2014). Therefore, elevated concentrations of some physiologically available nutrients (e.g., phosphorus) (Ruiz Colmenero et al., 2011; Lopez Vicente et al., 2022) and PTEs at footslope (Ribolzi et al., 2002; Fernandez Calvino et al., 2012) are commonly observed. However, some studies (Kenderessy and Lieskovsky, 2014; Filipović et al., 2022) reported uneven spatial variability of soil properties along the variable slope inclination.

Viticulture requires the use of mineral fertilizers and plant protection products, containing PTEs (e.g., Cu, Zn, and As). The excessive accumulation of these elements in soil may generate environmental problems (Fernandez Calvino et al., 2008). Soil pollution by PTEs in vineyard soils has been observed in many studies. For example, Komarek et al. (2010), in an extensive review paper, reported that Cu concentrations in the top-soil horizons of vineyard soils throughout the world often exceed 200 mg/kg, which is above the legislative limits valid in the EU. Elevated Zn concentrations in vineyard soils were stated by Weingerl and Kerin (2000), Vitanović et al. (2008), and Fernandez Calvino et al. (2012). Romić and Romić (2002) reported elevated concentrations of Pb in agricultural land in the urban environment of the town of Zagreb.

This study has been performed in a sloping vineyard on Pseudogley, located in Zagreb, that represents typical vineyard soil for continental Croatia. We hypothesized that different slope positions affect soil chemical properties due to erosion. Knowing the differences in particular soil chemical properties is important for adequate soil management.

The general aim of the study was to determine the effect of different slope positions on selected chemical properties of Pseudogley in vineyards. The specific goals of the study were to: (i) determine selected chemical properties of top-soil samples from the hilltop, backslope, and footslope positions of the vineyard; and (ii) compare analysed soil properties among different slope positions. The supplementary goal was to evaluate soil contamination by potentially toxic elements (PTEs) in different slope positions of the vineyard.

MATERIAL AND METHODS

Experimental site

The study was performed in 2022 in a sloped vineyard located in Zagreb, central Croatia (45°51'24'' N, 16°00'22''), (Figure 1). The vineyard is 11 years old on a hillslope with southwest exposure, intercropped with grass. Rows are oriented along the slope with a spacing of 1.2 m between vines. The experimental plot (slope) is separated into three segments: hilltop, backslope, and footslope, (Figure 1). The slope between the hilltop and backslope is 12%, and between the backslope and footslope is 16%. The total length of the investigated slope is 100 m.

The study area belongs to a temperate continental climate zone that can be classified as a moderately warm humid climate with hot summers (Cfb) according to the Köppen classification (Šegota and Filipčić, 2003). According to the IUSS Working Group of WRB (2015), the soil type is Dystric Luvic Stagnosol, characterized by Apg-Btg-Cg horizons (Filipović et al., 2022). The illuvial Btg horizon acts as a barrier for the percolation of precipitation water that periodically stagnates on/in this horizon. Parent material is a loess derivate thoroughly altered by pseudogleization (Rubinić et al., 2018). According to the Croatian soil classification (Škorić et al., 1985), the soil type in the study area is Pseudogley.

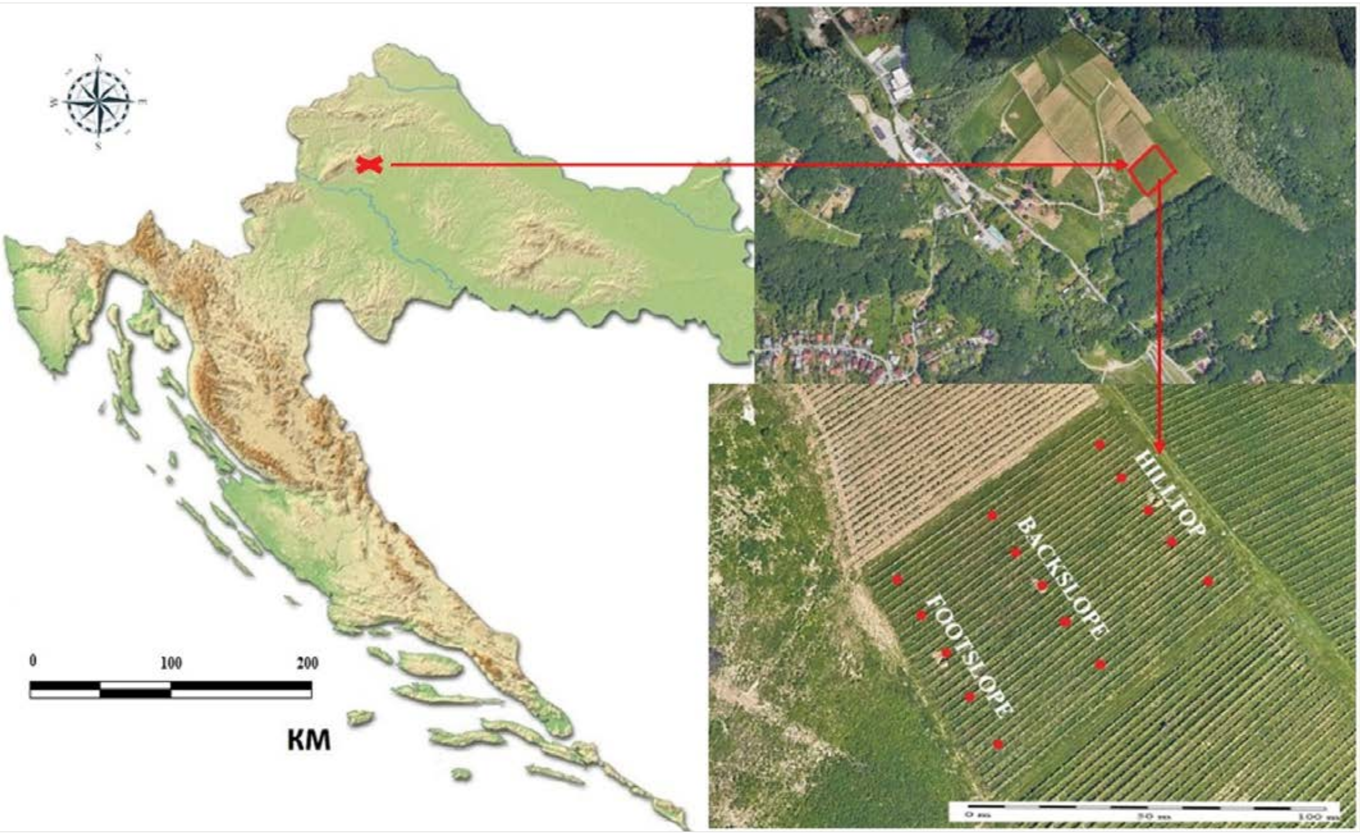

Figure 1. The position of the study area in Croatia and segments (hilltop, backslope and footslope) of the studied slope with sampling points

Soil sampling and laboratory analysis

A total of 15 top-soil samples (0-30 cm) were collected as composite samples in the intra-row area, out of which five were on the hilltop, five on the backslope, and five on the footslope (Figure 1).

The disturbed soil samples were air-dried, crushed, and sieved (2 mm mesh size) according to ISO 11464:2006. Soil pH was determined in a 1:5 (*v/v*) suspension of soil in water and soil in KCl solution (c = 1 mol/L) by the potentiometric method using a combined glass electrode (ISO 10390:2005). Humus content was detected by the volumetric method with previous digestion of the soil samples with $K_2Cr_2O_7$ (c = 0.4 mol/L), following the method of Tjurin (JDPZ, 1966). Soil organic carbon (SOC) content was obtained by dividing the humus content with the Van Bemmelen factor (1.724). Hydrolytic acidity (Hy) was determined by the titrimetric method using CH_3COONa solution (c = 1 mol/L) as an extractant and NaOH solution (c = 0.1 mol/L) for titration according to the Kappen method (JDPZ, 1966). Physiologically available phosphorus and potassium were extracted according to the Egner-Riehm-Domingo lactate-acetate method (Egner et al., 1960) and detected via spectrophotometry and flame spectrometry, respectively.

Total concentrations of PTEs (As, Cu, Ni, Pb, and Zn) were determined by the portable X-ray fluorescence method using the Vanta handheld XRF analyser C Series (Olympus, Waltham, MA, USA, 2019). The measurement was conducted according to the loose powder method (Takahashi, 2015), which involves a simple „point and shoot" technique. Each sample was measured in three repetitions, and each measurement time was 120 seconds. Data quality control was performed by an analysis of certified (SRM 2711) and reference soil (ISE 989) samples. The accuracy and precision of measurements were within the prescribed allowed values according to ISO 13196: 2015.

Statistical analysis

A one-way analysis of variance (ANOVA, F test) was used to test whether there are any significant differences between the means of selected soil properties at different slope positions. In cases where the ANOVA showed the existence of significant differences, a post hoc test (multiple comparison test) was performed. It was carried out to find out exactly which groups are different from each other. Statistical analysis was undertaken using MS Excel.

RESULTS AND DISCUSSION

Basic soil chemical properties

The studied soil was strongly acidic to acidic at the hilltop and backslope (pH_{KCl} 4.34-4.93 and 4.17-5.18, respectively) and acidic at the footslope (pH_{KCl} 4.58-1.92, Table 1). The hydrolytic acidity (Hy) values varied from 8.3 to 14.3 cmol(+)/kg indicating the need for medium doses of materials for calcification on the whole experimental plot. The SOC content was low on all segments of an experimental plot (1.28–1.69%, Table 1). The studied soils were very poorly supplied with physiologically available phosphorus at the hilltop and backslope (mean values 3.4 and 3.6 mg P_2O_5/100 g of soil) and poorly at the footslope (mean value 10.4 mg P_2O_5/100 g of soil, Table 1). The content of K_2O was higher, pointing to a medium soil supply with physiologically active potassium in the whole experimental plot (Table 1).

Generally, the obtained results are in line with previous studies of Stagnosols in Croatia (Rastija et al., 2009; Rubinić et al., 2014; Rubinić et al., 2015; Magdić et al., 2022; Filipović et al., 2023), Serbia (Mrvić et al., 2007), Czech Republic (Vopravil et al., 2017) and Germany (Kemman et al., 2022). However, some differences in the particular properties of Stagnosols can be attributed to different parent materials, climatic conditions, and land management. For example, Rubinić et al. (2014) highlighted substantial differences in the chemical properties (pH, SOC, and CEC) of Pseudogleys in continental Croatia due to the precipitation gradient and the incomplete uniformity of the loess parent material.

Table 1. Descriptive statistics for basic chemical properties of the soil samples

Slope position	Statistical parameter	pH		Hy cmol(+)/kg	SOC %	P_2O_5	K_2O
		H_2O	KCl			mg/100 g of soil	
Hilltop	Min	6.02	4.34	10.8	1.28	2.7	17.0
	Max	6.35	4.93	13.3	1.61	4.1	26.5
	Mean	6.16	4.64	12.1	1.50	3.4	21.2
	SD	0.11	0.19	0.93	0.11	0.54	3.3
	CV	0.02	0.04	0.08	0.08	0.16	0.15
Backslope	Min	5.85	4.17	8.3	1.40	3.0	16.2
	Max	6.54	5.18	14.3	1.53	4.1	32.5
	Mean	6.28	4.81	10.3	1.46	3.6	24.0
	SD	0.24	0.36	2.15	0.06	0.47	5.20
	CV	0.04	0.07	0.21	0.04	0.13	0.22
Footslope	Min	6.03	4.58	9.3	1.40	5.5	24.0
	Max	6.35	4.92	11.5	1.69	14.0	33.0
	Mean	6.23	4.77	10.6	1.51	10.4	29.7
	SD	0.12	0.14	0.86	0.10	3.03	3.34
	CV	0.02	0.03	0.08	0.07	0.29	0.11

Min – minimum; Max – maximum; Med- median; SD – standard deviation; CV – coefficient of variation

Effect of slope position on basic soil chemical properties

The results of the one-way ANOVA for the basic chemical properties of the studied soils are shown in Table 2. Statistically significant differences in chemical properties between slope positions (hilltop, backslope, and footslope) of the studied soil (F_{exp} > F_{crit}) were established only for P_2O_5 and K_2O content ($P < 0.05$).

Although soil pH values did not show significant variation down the slope (Table 2), a slight increase from the hilltop to the footslope was observed. Mean values of pH_{H_20} and pH_{KCl} increased from the hilltop to the footslope (6.16-6.23 and 4.64-4.81, respectively), (Table 1). Many authors (Kisić et al., 2002; Jurišić et al., 2012; Ibadulah et al., 2017) reported significantly higher pH values at the bottom of the slope and attributed them to erosion and base washout. However, some authors, e.g., Khan et al. (2013), did not observe significant variation in pH values down the slope, although they noticed 2-3% higher pH values at the bottom of the slope. Minimal differences in the pH values between the hilltop and footslope in the current study can be ascribed to the relatively short length of the studied slope, and the low and discontinuous inclination.

Mean values of hydrolytic acidity followed pH values (inversely proportional) and slightly decreased from the hilltop to the footslope (12.1-10.6 cmol(+)/kg, Table 1). However, these differences were not statistically significant (Table 2). The minimal and statistically insignificant impact of slope on pH and Hy values was reported by Rubinić et al. (2015) for Pseudogley under vegetable production on slope lengths up to 50 m and inclinations of 12%. The authors attributed it to the discontinuous toposequence and inadequate length of the slope.

Table 2. One-way ANOVA for pH_{H_2O}, pH_{KCl}, Hy, SOC, P_2O_5 and K_2O

Source of variation	SS	df	MS	F_{exp}	*P* value	F_{crit}
			pH_{H_20}			
Between groups	0.034973	2	0.017487	0.496076	0.620871	3.885294
Within groups	0.423000	12	0.03525			
Total	0.457973	14				
			pH_{KCl}			
Between groups	0.07644	2	0.03822	0.50411	0.616283	3.885294
Within groups	0.90980	12	0.075817			
Total	0.98624	14				
			Hy			
Between groups	9.196	2	4.598	1.77392	0.211382	3.885294
Within groups	31.104	12	2.592			
Total	10.3	14				
			SOC			
Between groups	0.00652	2	0.00326	0.301666	0.745033	3.885294
Within groups	0.12968	12	0.010807			
Total	0.1362	14				
			P_2O_5			
Between groups	160.2639	2	80.13194	19.84525	0.000157	3.885294
Within groups	48.45408	12	4.03784			
Total	208.718	14				
			K_2O			
Between groups	185.7453	2	92.87267	4.55102	0.033817	3.885294
Within groups	244.884	12	20.407			
Total	430.6293	14				

SS – the sum of squares, df - degrees of freedom, MS - mean square.

The mean values of SOC content were uniform throughout the hilltop, backslope, and footslope (1.50, 1.46, and 1.51%, respectively), (Table 1) and no statistically significant differences were observed (Table 2). Many studies reported more pronounced differences in SOC content between slope positions. In the study of Khan et al. (2013), the bottom slope position had 25 and 65% higher SOC content than the mid and top slope positions, respectively. Ibadulah et al. (2017) found 41% higher SOC content on the bottom slope compared to the top slope. Switoniak et al. (2015) established a twofold increase in SOC in the footslope position of different soil types under vineyards in Slovakia due to accelerated erosion and the accumulation of humus colluvial material. Magdić et al. (2022) also reported a statistically significant increase in SOC content from 1.04 to 1.66% in the topsoil of

Stagnosol under vineyard in continental Croatia. However, Rubinić et al. (2015) did not determine the effect of slope position on SOC content in sloping Stagnosol under forest. Molina et al. (2019) also did not notice differences in SOC content between slope positions along the slope under grassland and forest. It can be assumed that grass cover in the studied soil under the vineyard in the current study reduced the loss of soil organic matter by erosion, as proven in studies by Lopez Vicente et al. (2020) and Telak et al. (2021). In addition, relatively low inclination and short slope length may be the reasons for the subtle differences, as already mentioned. Also, it should be mentioned that this is a young vineyard planted 11 years ago when deep tillage (0-50 cm) was carried out. Due to the deep tillage, the surface and underlying soil layers were mixed, which can cause atypical soil properties at some slope positions. Eleven years might not be enough time for the development of noticeable changes in SOC content at various slope positions.

Given that ANOVA showed statistically significant differences in P_2O_5 concentrations between slope positions of the studied soil (Table 2), a post hoc test was applied. The results of multiple comparison tests revealed a significantly higher mean value of P_2O_5 on the footslope compared to the hilltop and backslope (Table 3). The difference between the hilltop and backslope was not statistically significant.

Table 3. Multiple comparison post hoc test for the significant differences between slope position in the P_2O_5 concentration (mg/100 g of soil)

Slope position	Mean value	Differences between mean values	
Hilltop (H)	3.4	H - B	- 0.2
Backslope (B)	3.6	B – F	**- 6.8***
Footslope (F)	10.4	F - H	**7.0***

* difference is significant at $P < 0.05$; LSD = 2.77

Many authors (Ruiz Colmenero et al., 2011; Farsang et al., 2012; Khan et al., 2013; Lopez Vicente et al., 2022) observed an increasing trend of P_2O_5 concentration from the top to bottom slope due to downward movement with runoff water. Negligible differences among concentrations of physiologically available phosphorus in hilltop and backslope (3.43 and 3.56 mg P_2O_5 /100 g of soil, Table 3) in the current study can be explained by the lower inclination between these two segments (12%). Higher inclination (16%) between the backslope and footslope resulted in accelerated washout erosion and the accumulation of significantly higher P_2O_5 concentrations at the footslope position. It is in accordance with the study of Filipović et al. (2023), conducted at a sloping vineyard with an uneven inclination along the slope. Khan et al. (2013) highlighted that a higher pH in eroded material also contributes to the higher physiological availability of phosphorus in the footslope.

Slope position also significantly affected concentrations of physiologically available potassium (Table 2). However, a statistically significant difference ($P < 0.05$) was established only between the hilltop and footslope positions (21.2 and 29.7 mg K_2O/100 g of soil, respectively), (Table 4). The highest mean concentration of K_2O at the footslope position (29.7 mg/100 g of soil, Table 4) pointed to the accumulation of physiologically available potassium in eroded soil material. Soil erosion by water gradually leads to the selective distribution of nutrients: depletion in the upper parts of the slope and accumulation in the zone of erosional drift sedimentation (Kisić et al., 2002). Many studies (Gomez et al., 2011; Babcsanyi et al., 2021; Lopez Vicente et al., 2022) confirmed the significant impact of water erosion on the loss of physiologically available potassium in the upper part of the slope. Lopez Vicente et al. (2022) highlighted differences in selectivity during the erosional and sediment delivery processes involved in the transfer of eroded material. A greater amount of coarser materials (poorer in nutrient content) may be transported during high-intensity rain events, while finer materials (richer in nutrients) may be delivered during low-intensity rain events. Dugan et al. (2022) highlighted the effect of tillage and grass cover on K_2O losses by erosion. The authors reported significantly lower potassium losses in grass-covered treatments in comparison to tilled and herbicide treatments in sloping vineyards. Therefore, relatively small differences in K_2O concentrations between slope positions in the current study can be attributed to grass cover that reduces erosion.

Table 4. Multiple comparison post hoc test for the significant differences between slope position in the K_2O concentration (mg/100 g of soil)

Slope position	Mean value	Differences between mean values	
Hilltop (H)	21.2	H - B	-2.80
Backslope (B)	24.0	B – F	-5.70
Footslope (F)	29.7	F - H	**8.50***

* difference is significant at $P < 0.05$; LSD = 6.22

Potentially toxic elements (PTE) in soil

A descriptive statistic for PTE concentrations in studied soil samples for the entire experimental plot is presented in Table 5. Median values of As, Cu, and Zn concentrations (20, 57, and 96 mg/kg, respectively), were higher than median values for Croatia (12.0, 25.4, and 88 mg/kg, respectively) according to the Geochemical Atlas of Croatia (Halamić and Miko, 2009). It is typical for vineyard soils and can be attributed to the frequent use of fertilizers and pesticides containing the mentioned elements (Komarek et al., 2010; Fernandez Calvino et al., 2012; Jimenez Ballesta et al., 2023).

The mean value of copper concentrations (55.7 mg/kg, Table 5) was higher than the mean value for European vineyard soil (49.3 mg/kg) reported by Ballabio et al. (2018). However, it was lower than the mean values for vineyard soils in France (91.3 mg/kg) and Italy (71.9 mg/kg) reported by Panagos et al. (2018). The maximum zinc concentration (101 mg/kg) (Table 5) was lower than the maximum values in the vineyard soil of north Spain (149 mg/kg) reported by Fernandez Calvino et al. (2012) and Slovenia (147 mg/kg) (Weingerl and Kerin, 2000). The maximum arsenic concentration (25 mg/kg, Table 5) was much lower than the maximum value of 108.4 mg/kg reported by Jimenez Ballesta et al. (2023) for vineyard soils in Spain. The median values of nickel and lead concentrations (42 and 26 mg/kg, respectively) (Table 5) were below the median values for Croatia (47.5 and 33 mg/kg, respectively) (Halamić and Miko, 2009). Nevertheless, the median values of Ni and Pb concentration were higher than the median values for agricultural soils in Europe (18 and 22.6 mg/kg, respectively) (Salminen et al., 2005). Romić and Romić (2002) established elevated levels ofnickel and lead in the topsoils of agricultural soils in the urban area of Zagreb and attributed them to anthropogenic sources such as the combustion of fuels along roads.

Effect of slope position on potentially toxic elements (PTEs) in soil

A one-way analysis of variance was used to examine the effect of slope position on concentrations of PTEs in the studied soil (Table 6).

Table 5. Descriptive statistics for PTE concentrations (mg/kg) in studied soil samples

Statistical parametar	As	Cu	Ni	Pb	Zn
Min	17	44	32	17	93
Max	25	67	50	30	101
Mean	19.8	55.7	41.8	26.3	97.1
Median	20.0	57.0	42.0	26.0	96.0
SD	1.97	6.39	5.44	3.63	2.75
CV	0.10	0.11	0.13	0.14	0.03

Min – minimum; Max – maximum; SD – standard deviation; CV – coefficient of variation

Table 6. One-way ANOVA for As, Cu, Ni, Pb, and Zn concentrations in the studied soil

Source of variation	SS	df	MS	F_{exp}	*P* - value	F_{crit}
			As			
Between groups	12.4	2	6.2	1.617391	0.23882	3.885294
Within groups	46.0	12	3.8333			
Total	58.4	14				
			Cu			
Between groups	294.933	2	147.4667	**5.557789**	**0.019573**	**3.885294**
Within groups	318.4	12	26.5333			
Total	613.33	14				
			Ni			
Between groups	55.6	2	27.8	0.858025	0.448449	3.885294
Within groups	388.8	12	32.4			
Total	444.4	14				
			Pb			
Between groups	138.133	2	69.06667	**14**	**0.000729**	**3.885294**
Within groups	59.2	12	4.9333			
Total	197.333	14				
			Zn			
Between groups	56.9333	2	28.4667	**6.014085**	**0.015515**	**3.885294**
Within groups	56.8	12	4.7333			
Total	113.733	14				

SS – the sum of squares, df - degrees of freedom, MS - mean square.

Statistically significant differences (P < 0.05) in PTE concentrations between slope positions (hilltop, backslope, and footslope) of the studied soil were established for copper, lead, and zinc concentrations. The slope position had no significant effects on the distribution of arsenic and nickel in the studied soil.

To compare the mean values in the copper, lead, and zinc concentrations among slope positions, the post-hoc test was applied. The backslope and footslope had significantly higher concentrations of copper and lead than the hilltop, while the zinc concentration was significantly higher only on the footslope (Table 7).

Table 7. Multiple comparison post hoc test for the significant differences between slope position in the Cu, Pb, and Zn concentrations (mg/kg) in the studied soil

Slope position	Mean values, mg/kg		
	Cu	Pb	Zn
Hilltop (H)	50.4 ^{b}	22.2 ^{b}	96.4 ^{b}
Backslope (B)	60.0 ^{a}	29.4 ^{a}	95.2 ^{b}
Footslope (F)	59.6 ^{a}	27.4 ^{a}	99.8 ^{a}
LSD	7.09	3.06	2.99

The same letters in the columns indicate there is no significant difference between the means of groups (P < 0.05)

Numerous studies from Croatia (Jurišić et al., 2012; Poljak et al., 2021), France (Ribolzi et al., 2002), Spain (Fernandez Calvino et al., 2008), and Hungary (Pham et al., 2022) noted a significant increase in Cu concentrations in soils under vineyards at the footslope position. Ribolzi et al. (2002) highlighted two to four times higher Cu concentrations in the suspended matter than the Cu concentrations in the top-soil horizon. The authors attributed it to the preferential mobilization of fine particles in the first few centimetres of soil, which are the richest part of the top-soil horizon. Romić et al. (2014) emphasized that the redistribution of material suspended by erosion depends on the relief, shape, and length of the slope.

The study of spatial variability of trace metals in agricultural soils in the wider Zagreb City area revealed elevated zinc concentrations in vineyards and orchards at footslope positions due to the accumulation of eroded material (Romić and Romić, 2002). Fernandez Calvino et al. (2012) also observed the accumulation of zinc in sediments resulting from erosive events in vineyards in northwest Spain.

The lead concentrations in all slope positions in the current study (Table 5) were below the median value for Croatia of 33 mg/kg (Halamić and Miko, 2009). However, Marin et al. (2016) reported elevated values of Pb concentrations in the vineyards of Spain (up to 65 mg/kg) with considerable variations. The authors emphasized the integrated effects of topography and anthropogenic impact as the main reasons for these variations. A general trend of downslope accumulation of lead and copper was also noticed by Pham et al. (2022) in vineyards in northeastern Hungary.

Soil contamination by PTEs

The Ordinance on the protection of agricultural land from pollution (Official Gazette 71/19) defines the maximum admissible concentrations (MAC) of PTEs in agricultural soils in Croatia, taking into account pH_{KCl} values (Table 8). The pH_{KCl} values in all soil samples at the hilltop and footslope positions were below 5, while at the backslope position, pH_{KCl} exceeded 5 in some samples (Table 1).

Table 8. Maximum admissible concentrations (MAC) (mg/kg) of PTEs in agricultural soils in Croatia (Official Gazette 71/19)

Element	pH_{KCl}		
	< 5	5-6	> 6
As	15	25	30
Cu	60	90	120
Ni	30	50	75
Pb	50	100	150
Zn	60	150	200

According to the mentioned Ordinance (Official Gazette 71/19), the studied soil was contaminated by arsenic, nickel, and zinc at the hilltop and footslope, while at the backslope position, two samples with higher pH (B4 and B5) had concentrations below MAC (Figures 2-4).

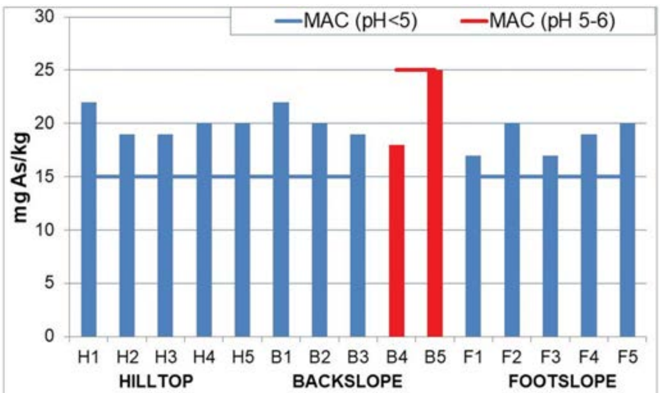

Figure 2. Concentrations of As and MAC

Elevated As and Ni concentrations in the wider Zagreb area are noted in a geochemical map of Croatia (Halamić and Miko, 2009). It can be attributed to the parent material of soil enriched by these elements. In addition, pesticides and mineral fertilizers can be anthropogenic sources for arsenic in soil (Jimenez Ballesta et al., 2023), as well as fuel combustion in urban areas for nickel (Romić and Romić, 2002).

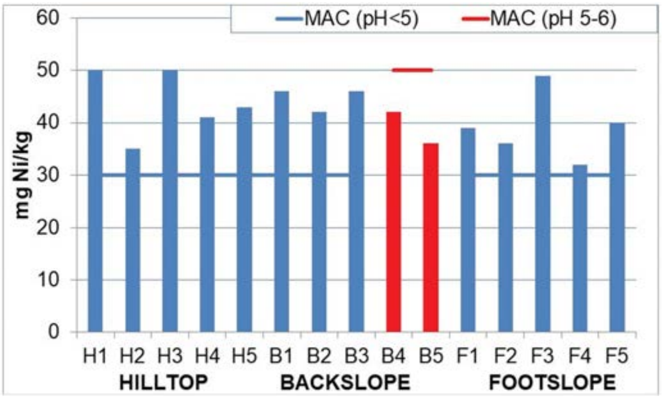

Figure 3. Concentrations of Ni and MAC

Contamination of vineyard soils by zinc was reported by many authors (Xue et al., 2003; Fernandez Calvino et al., 2012; Beygi and Jalali, 2019). Elevated Zn concentrations in agricultural soils may be related to the application of pesticides (Komarek et al., 2010) and mineral fertilizers containing zinc (Fernandez Calvino et al., 2012). In addition, isolated high Zn concentrations in soils in the wider study area were observed by Halamić and Miko (2009). The authors attributed it to the result of natural ore occurrences.

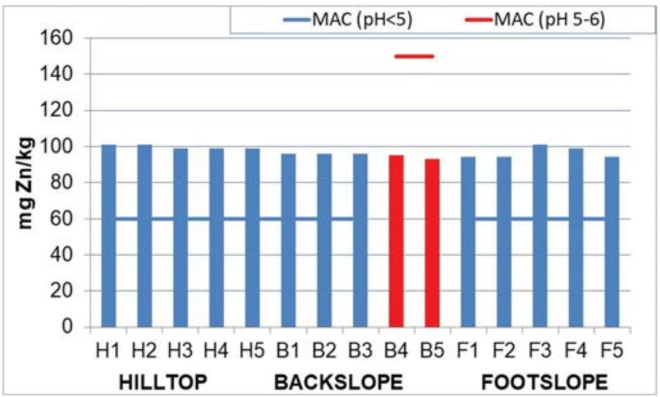

Figure 4. Concentrations of Zn and MAC

The Cu concentrations exceeded MAC at the backslope (samples B1 and B2) and footslope positions (samples F1, F3, and F4) (Figure 5). Contamination of vineyard soils by copper is a well-known problem proven in many studies, as summarized in a review paper by Komarek et al. (2010). The authors emphasized that the extensive use of copper-based fungicides has resulted in copper contamination of the majority of the studied vineyard soils.

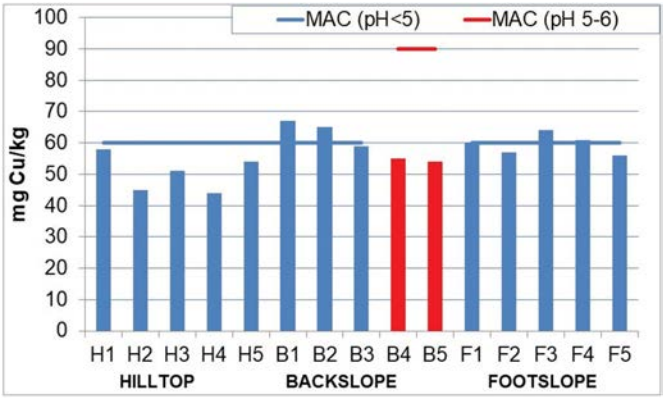

Figure 5. Concentrations of Cu and MAC

This is especially true for acidic soils affected by intensive erosion. In contrast to the Cu concentrations reported by Komarek et al. (2010), which frequently surpass 200 mg/kg, the Cu concentrations in the current study were substantially lower (44-67 mg/kg, Table 5). It can be explained by the fact that the vineyard in the current study is young (11 years old). Namely, higher Cu concentrations were often observed in older vineyards compared to younger ones (Rusjan et al., 2006) due to longer periods of copper accumulation in soil.

The Pb concentrations (17-30 mg/kg, Table 5) were far below MAC in the entire experimental plot (Figure 6).

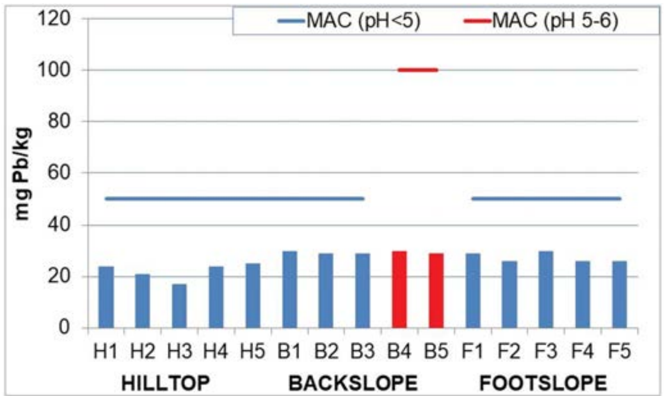

Figure 6. Concentrations of Pb and MAC

CONCLUSIONS

The slope position of the studied soil in the vineyard significantly influenced concentrations of physiologically available phosphorus and potassium, copper, lead, and zinc. Higher concentrations of the mentioned elements were recorded at the footslope compared to the hilltop and/or backslope. Soil reaction, hydrolytic acidity, and SOC content were not significantly affected by slope position. However, a slight increase in pH values and a decrease in hydrolytic acidity were observed from the top to the bottom of the slope. The studied soil was contaminated by arsenic, nickel, and zinc at the hilltop and footslope and partly at the backslope. The Cu concentrations exceeded maximum admissible concentrations (Official Gazzete, 71/19) only on the backslope and footslope, indicating the accumulation of copper originating from plant protection agents. The short length, low and uneven inclination of the slope and short-term anthropogenic influence resulted in minor differences in the studied soil properties between slope positions.

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