



THE IMPACT OF SOIL EROSION ON THE SPATIAL DISTRIBUTION OF SOIL CHARACTERISTICS AND POTENTIALLY TOXIC ELEMENT CONTENTS IN A SLOPING VINEYARD IN TÁLLYA, NE HUNGARY

Samdandorj Manaljav^{1,2}, Andrea Farsang², Károly Barta², Zalán Tobak², Szabolcs Juhász², Péter Balling³, Izabella Babcsányi^{2*}

¹Institute of Geography-Geoecology, Mongolian Academy of Science, Erkhuu str. 11th khoroolol, Sukhbaatar district, Ulaanbaatar, Mongolia

²Department of Geoinformatics, Physical and Environmental Geography, University of Szeged, Egyetem u. 2-6, 6722 Szeged, Hungary

³Research Institute for Viticulture and Oenology, Tokaj, Könyves Kálmán u. 54., Tarcsl, Hungary, HU-3915

*Corresponding author, email: babcsani@geo.u-szeged.hu

Research article, received 25 February 2021, accepted 23 April 2021

Abstract

Soil erosion is a main problem in sloping vineyards, which can dramatically affect soil quality and fertility. The present study aimed to evaluate the spatial patterns of selected physico-chemical soil characteristics and the soil's potentially toxic element (PTE) contents in the context of erosion. The study was conducted in a 0.4 ha vineyard plot on a steep slope in Tállya, part of the wine-growing region of Tokaj-Hegyalja (Hungary). A total of 20 topsoil samples (0-10 cm) were collected and analysed for PTEs (B, Co, Ba, Sr, Mn, Ni, Cr, Pb, Zn, and Cu), soil pH (deionized water and KCl solution), particle-size distribution, soil organic matter (SOM), (nitrate+nitrite)-N, P₂O₅, and carbonate content. Among the selected PTEs, only Cu (125±27 mg/kg) exceeds the Hungarian standards set for soils and sediments (75 mg/kg) due to the long-term use of Cu-based pesticides in the vineyard. Examined PTEs are negatively correlated with the sand content of the topsoil, except for Mn, while the significant positive relationship with the clay content shows the role of clay in retaining PTEs in soil. SOM seems to play a minor role in binding PTEs, as Cu is the only element for which a significant correlation with the SOM content can be detected. The spatial distribution maps prepared by inverse distance weighting (IDW) and lognormal kriging (LK) methods show higher PTE contents at the summit and the shoulder of the hillslope and lower contents at the backslope and the footslope zones. The low slope gradients (0-5 degree) and the high contents of the coarse fraction (> 35%) likely protect the soil at the summit and the hillslope's shoulder from excessive erosion-induced losses. While the raising PTE contents at the toeslope are likely due to the deposition of fine soil particles (silt and clay). The highest SOM contents at the summit and the toeslope areas, and increased contents of the coarse fraction at the backslope, confirm the effects of soil erosion on the spatial distribution patterns of main soil quality indicators. Overall, the LK outperformed the IDW method in predicting the soil parameters in unsampled areas.

Keywords: PTEs, soil organic matter, soil erosion, Tokaj, geostatistics, interpolation

INTRODUCTION

Viticulture is known to affect soil quality significantly, both its physical and chemical properties. Soil is one of the most important factors in viticulture, because its physico-chemical properties (e.g. pH, particle-size distribution, soil organic matter and N-, P- macronutrient contents) determine the nutrient supply for the growth of the vine. In general, vineyard soils tend to be poor in macronutrients and organic matter contents, and a general decrease in soil pH is often observed in older vineyards (Patinha et al., 2018). Past and present soil management in a vineyard, especially tillage in the vine inter-rows, is responsible for the degradation of the soil's physical characteristics that may have dramatic effects on its nutritional element contents (Biddoccu et al., 2016). Surface and subsoil hydraulic conductivity is highly affected by different soil management practices in vineyards (Bordoni et al., 2019). For example, tractor

traffic has a considerable impact on the spatial distribution of the soil's water infiltration capacity and compaction, resulting in more surface runoff generation and enhanced soil erosion (Biddoccu et al., 2016; Capello et al., 2019). The rock fragment content and its spatial variability are also influenced by soil erosion and cultivation patterns in vineyard topsoils (Follain et al., 2012). Besides these fundamental characteristics of the soil, some specific soil components are also affected by viticultural practices and soil erosion dynamics.

Contamination of agricultural soils with potentially toxic elements (PTEs) may raise human health concerns due to their ability to integrate the human food chain. PTEs often show increased concentrations in agricultural soils due to the long-term use of chemical fertilizers and pesticides (Solgi et al., 2016). Biosolid applications may also increase PTE contents in agricultural soils, including Pb, Ni, Zn, Cu, Cd, Cr, and even contents of some rarely assessed PTEs, such as Ba (Ippolito and Barbarick, 2006,

Torri and Corrêa, 2012). However, PTE accumulation in the topsoil of biosolid-amended arable lands is not always detectable (Ladányi et al., 2020). Elevated contents of Cd, Cu and Zn have been observed in Chinese agricultural soils due to repeated treatments with chemical fertilizers and manure (Lu et al., 2012; Sun et al., 2013), additionally, Pb also accumulated in agricultural soils of the European Mediterranean region (Micó et al., 2006). In vineyard soils, Cu and Zn are often observed at elevated concentrations due to the repeated use of Cu- and Zn-based agrochemicals (Rodríguez Martín et al., 2006, Dos Santos et al., 2013). In Europe, Cu-based fungicides have been intensively used since the end of the 19th century to control fungal diseases. High Cu contents can accumulate in the topsoil of vineyards and surrounding areas, which may raise ecotoxicological concerns (Milićević et al., 2017, Ungureanu et al., 2017, Patinha et al., 2018). Additionally, the foliar applications of micronutrient fertilizers containing Fe, Mn, B, Cu, Zn and Mo are part of viticultural practices. Therefore, PTE concentrations in conventionally managed vineyard soils should be carefully assessed and the eventual PTE accumulation in the topsoil evidenced. On the other hand, soil erosion influenced by various agronomic practices can also considerably impact the spatial patterns of PTE soil contents.

Vineyards are often planted on steep slopes, thus they are prone to intensive soil erosion, enhancing the mobility of PTEs (Rodríguez Martín et al., 2007, Dos Santos et al., 2013). According to model forecasts, fewer but more intense rainfall events are likely to occur in Hungary during the 21st century (Mezősi and Bata, 2016). As rainfall intensity is a key triggering factor of soil erosion, its probable increase in the future can have dramatic effects on soil erosion rates, which will certainly impact soil quality. The spatial variability of topsoil PTEs

may be affected by soil erosion processes and anthropogenic inputs. Given that some PTEs are also essential micronutrients for plants, their soil contents are an indicator of soil fertility too. Also, key soil properties, such as soil organic matter content, particle size distribution, and soil pH, are required to explain the distribution of PTEs. Overall, there is an increasing need to understand the impact of soil erosion on the spatial distribution of essential physico-chemical properties and PTE contents in cultivated soils (Rodríguez Martín et al., 2006; Solgi et al., 2016).

Predictive soil mapping has been efficient for assessing the spatial variability of soil properties at the field scale (Scull et al., 2003). However, few studies focused on mapping and explaining the spatial distribution of soil characteristics and PTEs in vineyards at a plot scale. Yet, this information is necessary to monitor soil quality changes as a consequence of soil erosion. The key objectives of this study are: (I) to identify relationships between soil properties and PTE contents, (II) to map the spatial distribution of essential soil characteristics and specific PTE contents in a vineyard's topsoil; and (III) to assess the accuracy of the applied interpolation models.

METHODS AND MATERIALS

Study area and soil sampling

The field survey was carried out in a 0.4 ha vineyard plot at the foothills of the Tokaj Mountains (North-eastern Hungary), in Tállya, part of the historical wine-growing region of Tokaj-Hegyalja (Fig. 1). The vineyard's elevation ranges from 269 m to 291 m above sea level. The plot has nine grapevine rows parallel to the main slope; vine stocks are spaced 1 m from one another, while

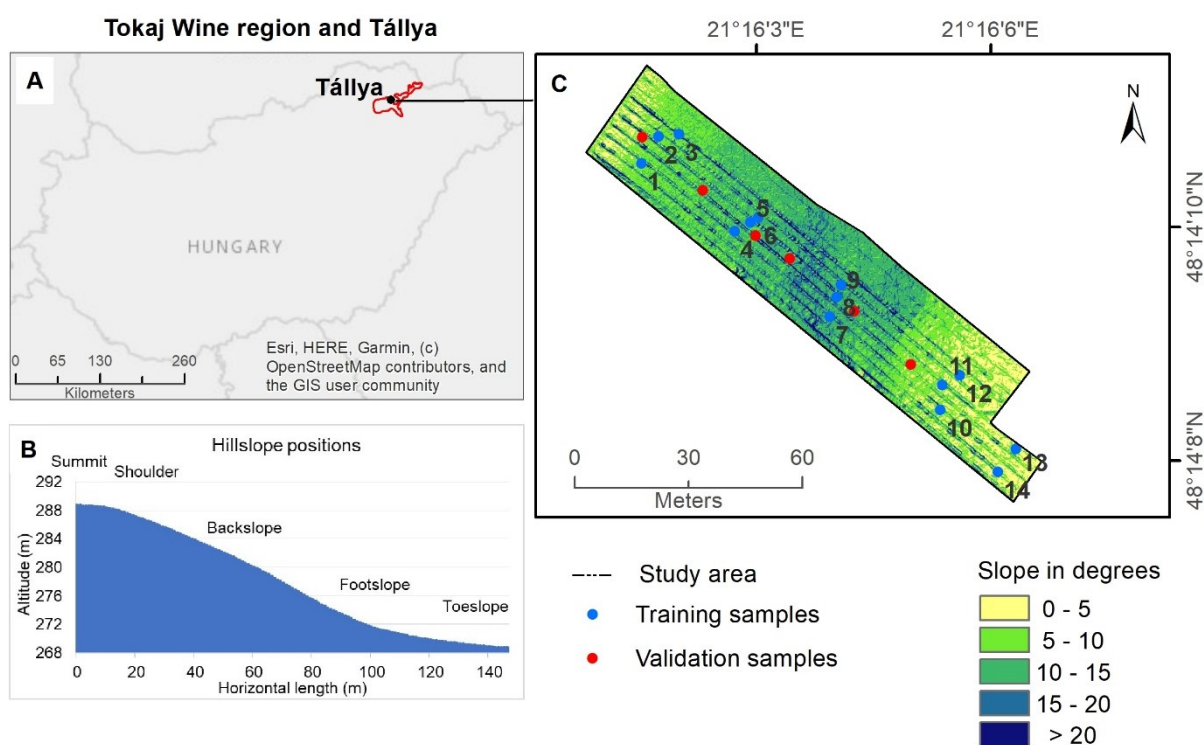


Fig. 1 A) The study area is a 0.4 ha vineyard plot near Tállya in the Tokaj wine region (NE Hungary). The slope profile (B) and slope map (C) were prepared based on the digital elevation model of the area. Sampling points are marked in blue for the training samples and red for the validation samples.

the inter-rows are 3.8 m wide. The total slope length is 130 m, and the mean slope is 18°. The soil type slightly varies along the transect. At the top of the hillslope, it belongs to the Skeletic Regosol (Loamic, Ochric) type, while at the backslope it shows Skeletic Leptosol (Loamic, Ochric) patterns, at the footslope the soil is Skeletic Colluvic Regosol (Loamic, Ochric) according to the World Reference Base for Soil Resources (2014). The soils in the area developed on a fine-grained extrusive igneous rock, rhyolite, and rhyolite tuff. Therefore, the soil has a weakly acidic character.

The vineyard is managed conventionally with regular uses of synthetic and inorganic pesticides, primarily Cu fungicides. The current application doses of the Bordeaux mixture amount to 2–2.5 kg/ha/year (applied three times a year in May, June, and July). The Bordeaux mixture was complemented with a foliar micronutrient fertilizer pulverized in a dose of 4–5 l/ha, containing Fe (3.2 m/v%), Mn (0.32 m/v%), Cu (0.15 m/v%), B (0.31 m/v%) and Mo (0.003 m/v%). The soil is regularly ploughed, and no cover crops are sown in the vine inter-rows for soil protection.

In May 2020, 14 point samples of topsoil (0–10 cm) were taken in the middle of the vine inter-rows based on random sampling (USDA, 2014) (Fig. 1). Additionally, six topsoil samples were collected in November 2019, which were used to check the interpolation methods' performance.

Aerial photography campaign using a DJI Phantom 4 drone and geodetic field measurements were performed to collect true colour images and elevation information. The digital elevation model (DEM) of the vineyard plot was prepared by stereo-photogrammetry described elsewhere (Szatmári et al., 2011). The slope map of the study area was generated from the DEM as its first derivative.

Soil analyses

All soil samples were air-dried at room temperature and passed through a 2 mm stainless steel sieve. The non-negligible coarse fraction (>2 mm) was systematically weighed. Soil organic matter was determined by oxidation with $K_2Cr_2O_7$ in the presence of sulphuric acid and the subsequent analysis of the reduced Cr^{3+} ions with a spectrophotometer (UNICAM Helios Gamma UV-VIS, Thermo Scientific) according to the Walkley Black method based Hungarian standards (MSZ 21470–52:1983). The carbonate content was measured by the volumetric method with a Scheibler calcimeter. Soil pH was determined by a pH-meter (Mettler Toledo FiveEasy) in a 1:2.5 ratio of soil: deionized water ($pH_{d.w.}$) and soil: 1 mol/L KCl (pH_{KCl}) (MSZ-08-0206-2:1978). Differences greater than one between the two pH values measured in the deionized water and the KCl solution

suggest a susceptibility of the soil to acidification (Rodrigo Comino et al., 2016). The pipette method was used to determine soil particle size distribution using pyrophosphate for dispersing soil aggregates (USDA, 2014). The plant-available macronutrient contents of P_2O_5 extracted using ammonium-lactate and (nitrate+nitrite)-N extracted with a KCl-solution according to standard procedures (MSZ20135:1999), were measured by a flow injection analysis (FIA) spectrometer (FIA STAR 5000, Foss).

Pseudototal PTE analyses

Digestion in aqua-regia allows for determining the so-called pseudototal element content because it does not dissolve the silicate matrix. Soil samples (<2 mm) were ground to a fine powder (<0.25 mm) in an agate ball mill and dried in an oven at 105°C for 24 h. Approximately 0.5 g of each ground soil sample was weighed into pre-cleaned PFA vessels using an analytical balance and digested in aqua regia (HCl: HNO_3 ratio of 3:1). All labware was acid-cleaned before use, and acids were for trace metal analysis (Normatom®, VWR Chemicals). The pseudototal digestion was performed in a laboratory microwave digestion system (Multiwave 3000, Anton Paar). After cooling, the digested samples were filtered into 50 ml volumetric flasks (acid-cleaned plastic flasks), and the volume was made up with ultrapure water (TKA MicroPure). The concentrations of selected PTEs (B, Co, Ba, Sr, Mn, Ni, Cr, Pb, Zn, and Cu) were then determined by an inductively coupled plasma optical emission spectrometer using yttrium as an internal standard (Optima 7000 DV, Perkin Elmer) ($\pm 5\%$). Calibration standards were freshly prepared in 2% HNO_3 by diluting ICP Multi-Element Standards (CPAchem). ERM®-CC141 certified reference material (a loam soil) was used for quality control for the pseudototal element analysis. The recoveries for the certified elements (based on two digested aliquots of the reference material and four ICP analyses) are presented in Table 1.

Data analyses

Descriptive statistical analyses (minimum, maximum, mean, median, standard deviation, skewness, and kurtosis) were used to describe the soil characteristics and PTEs. The coefficient of skewness is a measure of the symmetry of a distribution. For symmetric distributions, the coefficient of skewness should be close to zero and the kurtosis must be near 3. The mean is greater than the median for positively skewed distribution and vice versa for negatively skewed distribution. Pearson's correlation was used to define the relationships between soil characteristics and PTE contents. All statistical analyses were carried out using IBM SPSS Statistics 25.

Table 1 The recoveries of the pseudototal element (aqua regia extractable) contents in ERM®-CC141 certified reference material (n=4) and the PTE contents of the local forest topsoil used as a reference for calculating enrichment factors in the vineyard soil.

| | Unit | B* | Mn | Ni | Cr | Cu | Pb | Zn | Co | Ba* | Sr* |
|-------------------|-------|----|-------|-------|-------|-------|------|------|--------|-----|-----|
| Recovery | % | - | 102±2 | 117±2 | 116±2 | 104±3 | 87±1 | 92±2 | 88±0.2 | - | - |
| Local forest soil | mg/kg | 2 | 424 | 8 | 11 | 7 | 27 | 35 | 2 | 48 | 9 |

*The ERM®-CC141 is not certified for B, Ba and Sr.

Enrichment factors (EFs) were calculated to compare PTE contents observed in the vineyard topsoil with PTE background levels measured in a local forest topsoil (average of pseudototal PTE contents measured in 0–10 cm and 10–20 cm) (Table 1).

$$EF = \frac{\text{PTE(vineyard topsoil)}}{\text{PTE(reference soil)}} \quad (1)$$

The observed PTE contents were also compared with the median PTE concentration data collected in the framework of the Hungarian Soil Information and Monitoring System (SIMS) based on 842 topsoil sampling points (0–30 cm) on arable land nation-wide in Hungary (Csorba et al., 2014).

Geostatistical approaches

In geostatistics, variograms or semivariograms are applied to measure the spatial patterns of a known variable. Its main contribution in soil science has been predicting and mapping the spatial variability of soil attributes at unsampled locations (Goovaerts, 1999; Guo et al., 2001). Interpolation is a process of estimating the values at unsampled places based on known values at sampled locations. In this study, interpolation maps were created using ArcGIS 10.5 Geostatistical Analyst extension (ESRI, Redlands, CA). We set the nearest 2 to 8 neighbour values and a sector type of 4 for defining neighbourhood to interpolate a surface. The estimated standard errors of kriged values can be used to test the accuracy of the kriging results (Rodríguez Martín et al., 2006). Several geostatistical methods exist for modeling the spatial variability of data (Szatmári et al., 2015). However, ordinary kriging is a robust and one of the commonly used spatial interpolation methods to estimate the value of target variables at unsampled points using the weighted average of sampled neighbouring points in the area of interest. Ordinary kriging computes a weighted average of the data:

$$\hat{Z}(\mathbf{X}_0) = \sum_{i=1}^n \lambda_i(\mathbf{X}_0)Z(\mathbf{X}_i) \quad (2)$$

where, $\hat{Z}(\mathbf{X}_0)$ is the estimated value of the variable Z at any location \mathbf{x}_0 ; $Z(\mathbf{X}_i)$ is the measured data; $\lambda_i(\mathbf{X}_0)$ refers to the weight associated with the measured values, and n is the number of observations in a neighborhood.

Lognormal kriging (LK) is the ordinary kriging of the measured values' logarithms (Webster and Oliver, 2007). It is used for strongly positively skewed data that approximate a lognormal distribution, commonly the case with environmental data. For lognormal kriging the data should be transformed by the following equation:

$$y = \log_{10}Z \quad (3)$$

Inverse distance weighting (IDW) is more popular and based on inverse functions of distance in which the weights are defined by:

$$\lambda_i = 1/|x_i - x_0|^\beta \quad \beta > 0 \quad (4)$$

Data points near to the target point carry larger weights than those further away. The most popular choice of β is 2 so that the data are inversely weighted as the square of the distance. Its attractive feature is that the relative weights decrease rapidly as the distance increases, and so the interpolation is locally sensible. Furthermore, because the weights never become zero, there are no discontinuities. Its disadvantages are that the weighting function's choice is arbitrary, and there is no measure of error (Webster and Oliver, 2007).

Assessment of model performance

In this study, independent validation was used to evaluate and compare the performance of interpolation models. The root mean square error (RMSE) measures the difference between predicted values and observed values, while the mean absolute error (MAE) computes how far estimated values are away from measured values (Xie et al., 2011). The smaller MAE and RMSE values indicate the better-predicted values. The RMSE and the MAE were estimated using the predicted and observed values at each validation sampling location:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (P_i - O_i)^2} \quad (5)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |P_i - O_i| \quad (6)$$

where P_i , O_i are predicted (interpolated) and observed soil parameter values at location i , and n is the sample number.

RESULTS AND DISCUSSION

Soil characteristics and PTE concentrations in the vineyard topsoil

The descriptive statistics of the examined soil characteristics and PTE contents in the vineyard topsoil in Tállya are summarised in Table 2. Most soil properties had positively skewed distributions except for CaCO_3 , P_2O_5 , and clay content. But most of the PTEs had negatively skewed distributions except for the concentration data of Co and Sr. The examined vineyard soil is slightly acidic ($\text{pH}_{\text{d.w.}}$ (mean): 6.4). However, the soil has a potential acidity due to the greater than one difference between the two pH values (measured in d.w. and in the KCl solution). Mean concentration of the soil organic matter (SOM) content is $1.5 \pm 0.4\%$, indicating that the vineyard soil is poor in SOM. A poor SOM content is often observed in vineyards planted on steep slopes as a consequence of intense soil erosion and redeposition and/or off-site export of organic carbon with surface runoff (Novara et al., 2018). SOM can influence PTE (particularly cationic metals) sorption in soils, probably attributed to its high cation exchange capacity (Rodrigues et al., 2010). Hence it is essential to assess SOM variations in the vineyard topsoil. The topsoil has a low carbonate

Table 2 Descriptive statistics of selected soil parameters, macronutrient, and PTE contents in the topsoil of the vineyard in Tállya.

| | Unit | Vineyard topsoil (0-10 cm) | | | | | | |
|---------------------------------------|-------|----------------------------|-------|-------|--------|-------|----------|----------|
| | | Min | Max | Mean | Median | Std.D | Skewness | Kurtosis |
| SOM | % | 0.9 | 2.3 | 1.5 | 1.4 | 0.4 | 0.98 | 0.22 |
| CaCO ₃ | % | 0.4 | 2.0 | 1.3 | 1.6 | 0.5 | -0.96 | -0.35 |
| pH _{d.w.} | | 6.1 | 6.9 | 6.4 | 6.4 | 0.2 | 0.67 | -0.48 |
| pH _{KCl} | | 4.6 | 5.8 | 5.2 | 5.0 | 0.4 | 0.34 | -1.65 |
| (nitrate+nitrite)-N | mg/kg | <0.1 | 2.5 | 0.8 | 0.6 | 0.8 | 1.06 | -0.07 |
| P ₂ O ₅ [mg/kg] | mg/kg | 107.9 | 299.4 | 196.6 | 200.1 | 55.7 | 0.02 | -0.64 |
| Coarse fraction (> 2mm) | % | 31 | 48 | 40 | 40 | 5 | -0.11 | -0.82 |
| Sand (0.05 - 2 mm) | % | 32 | 60 | 41 | 39 | 9 | 0.93 | 0.00 |
| Silt (0.002 - 0.05 mm) | % | 21 | 35 | 27 | 26 | 4 | 0.42 | 0.04 |
| Clay (<0.002 mm) | % | 19 | 40 | 31 | 34 | 7 | -0.53 | -1.36 |
| B | mg/kg | 6 | 13 | 10 | 10 | 2 | -0.27 | -1.32 |
| Mn | mg/kg | 199 | 607 | 351 | 355 | 102 | 0.84 | 2.19 |
| Ni | mg/kg | 10 | 23 | 17 | 19 | 4 | -0.36 | -1.19 |
| Cr | mg/kg | 14 | 35 | 25 | 26 | 7 | -0.22 | -1.49 |
| Cu | mg/kg | 88 | 184 | 125 | 127 | 27 | 0.44 | 0.25 |
| Pb | mg/kg | 10 | 17 | 14 | 14 | 2 | -0.13 | -0.98 |
| Zn | mg/kg | 32 | 64 | 44 | 45 | 8 | 0.68 | 1.53 |
| Co | mg/kg | 5 | 8 | 7 | 6 | 1 | 0.05 | -1.84 |
| Ba | mg/kg | 63 | 136 | 101 | 102 | 25 | -0.10 | -1.65 |
| Sr | mg/kg | 19 | 42 | 30 | 28 | 7 | 0.34 | -1.16 |

content (CaCO₃) ranging from 0.4 to 2.0%. The ammonium-lactate soluble P₂O₅ content ranges from 107.9 to 299.4 mg/kg, while the KCl- soluble (nitrate+nitrite)-N content is low in the soil, varying from undetectable to 2.5 mg/kg. The vineyard soil in Tállya is characterised by a high proportion of the coarse fraction (>2 mm): 31–48%. Such important proportions of the coarse fraction embedded in the topsoil greatly impact soil erosion losses (Gong et al., 2018). The soils belong to the clay loam, sandy clay loam, loam textural categories depending on the hillslope position. The mean sand (0.05–2 mm), silt (0.002–0.05 mm), and clay (<0.002 mm) fractions are respectively 41%, 27%, and 31%.

The high standard deviations for Mn (102 mg/kg), Cu (27 mg/kg), and Ba (25 mg/kg) indicate a marked heterogeneous spatial distribution in the topsoil of the vineyard plot. Compared to the local forest topsoil we can observe increased PTE concentration levels in the cultivated soil, except for Mn and Pb. The median EFs range from 1.3 (for Zn) to 17.9 (for Cu) (Table 3). The calculated EFs (with the forest soil as a reference) indicate low enrichment for Zn (1.3), Co (2.4), Ni (2.5), Ba (2.1), and Cr (2.3), more significant accumulation for B (3.8), Sr (3.1) and a marked Cu pollution of the vineyard soil (17.9). Copper contents also exceed the Hungarian environmental quality standards set for soils and sediments (Joint Decree No. 6/2009. (IV. 14) KvVM-EüM-FVM). The EFs calculated taking the Hungarian

arable soils as a reference show lower or no PTE concentration increase in the vineyard soil. Only B (EF: 1.6) and Cu (EF: 8.5) are considerably enriched in the vineyard topsoil in Tállya compared with the Hungarian arable soils. Altogether, these observations suggest that grape growing and more precisely, the related use of agrochemicals in vineyards significantly enriches the soil in PTEs. Only Pb and Mn contents are higher in the local forest topsoil underlining their geogenic origin. Compared to arable soils, the elevated concentration levels of Cu and B are attributed to plant protection practices specific to vineyards (and orchards). Copper-based fungicides (such as the Bordeaux mixture) are frequently applied to combat the fungal infections of grapevine, and micronutrient-rich fertilizers (with high B contents) are also regularly used in vineyards. Boron accumulation in cultivated soils has rarely been evidenced so far. However, EFs clearly demonstrate a moderate B accumulation in the vineyard soil due to current grape fertilizing methods.

Relationships between the soil PTE contents and the soil characteristics

The Pearson's correlation coefficients (*r*) between soil properties and PTE concentrations in the vineyard topsoil samples are summarised in Table 4. According to correlation analysis, a strong positive relationship was

Table 3 Median enrichment factors (EFs) of target PTEs compared to the PTE levels of a local forest topsoil and the Hungarian Soil Information and Monitoring System (SIMS) dataset. Median PTE contents of arable land (based on 842 sampling points) (Csorba et al., 2014) are compared with the topsoil PTE contents of the studied vineyard

| | B | Mn | Ni | Cr | Cu | Pb | Zn | Co | Ba | Sr |
|-------------------|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|
| EF (local forest) | 3.8 | 0.8 | 2.5 | 2.3 | 17.9 | 0.5 | 1.3 | 2.4 | 2.1 | 3.1 |
| EF (SIMS) | 1.6 | - | 0.9 | 1.0 | 8.5 | 0.8 | 0.8 | 0.7 | - | - |

Table 4 Pearson's correlation matrix between examined soil characteristics and PTEs. The bold numbers denote statistically significant correlation coefficients (with p -value<0.05).

| | SOM | CaCO ₃ | pH _{d.w.} | pH _{KCl} | (nitrate+nitrite)-N | P ₂ O ₅ | Coarse f. | Sand | Silt | Clay |
|-------------------------------|---------------|-------------------|--------------------|-------------------|---------------------|-------------------------------|-----------|----------------|------|------|
| SOM | 1 | | | | | | | | | |
| CaCO ₃ | -0.25 | 1 | | | | | | | | |
| pH _{d.w.} | -0.01 | -0.14 | 1 | | | | | | | |
| pH _{KCl} | 0.30 | -0.15 | 0.89** | 1 | | | | | | |
| (nitrate+nitrite)-N | -0.45 | 0.23 | 0.10 | 0.30 | 1 | | | | | |
| P ₂ O ₅ | 0.52 | 0.26 | -0.24 | 0.05 | 0.19 | 1 | | | | |
| Coarse fraction | -0.43 | 0.22 | -0.44 | -0.64* | -0.22 | -0.30 | 1 | | | |
| Sand | -0.31 | -0.07 | 0.67** | 0.65* | 0.40 | -0.45 | -0.08 | 1 | | |
| Silt | 0.84** | -0.05 | -0.28 | -0.03 | -0.30 | 0.61* | -0.32 | -0.60* | 1 | |
| Clay | -0.06 | 0.11 | -0.68** | -0.79** | -0.33 | 0.23 | 0.27 | -0.91** | 0.21 | 1 |

| | B | Mn | Ni | Cu | Cr | Pb | Zn | Co | Ba | Sr |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| SOM | 0.11 | 0.22 | 0.06 | 0.56* | 0.05 | 0.14 | 0.14 | 0.17 | 0.07 | 0.31 |
| CaCO ₃ | 0.2 | 0.40 | 0.17 | 0.09 | 0.21 | 0.34 | 0.10 | 0.39 | 0.27 | 0.32 |
| pH _{d.w.} | -0.71** | -0.67** | -0.76** | -0.48 | -0.78** | -0.80** | -0.59* | -0.87** | -0.82** | -0.71** |
| pH _{KCl} | -0.74** | -0.51 | -0.78** | -0.30 | -0.78** | -0.75** | -0.51 | -0.74** | -0.79** | -0.54* |
| (nitrate+nitrite)-N | -0.22 | 0.05 | -0.25 | -0.16 | -0.23 | -0.13 | -0.13 | -0.08 | -0.18 | -0.06 |
| P ₂ O ₅ | 0.41 | 0.37 | 0.36 | 0.80** | 0.43 | 0.22 | 0.50 | 0.58* | 0.45 | 0.74* |
| Coarse fraction | 0.17 | 0.33 | 0.18 | -0.13 | 0.22 | 0.46 | -0.13 | 0.31 | 0.23 | -0.00 |
| Sand | -0.92** | -0.46 | -0.93** | -0.83** | -0.93** | -0.63* | -0.82** | -0.79** | -0.91** | -0.88** |
| Silt | 0.29 | 0.38 | 0.33 | 0.76** | 0.33 | 0.34 | 0.32 | 0.47 | 0.37 | 0.61* |
| Clay | 0.97** | 0.36 | 0.97** | 0.62* | 0.96** | 0.60* | 0.83** | 0.71** | 0.93** | 0.76** |

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed).

detected between the SOM content and the silt content ($r = 0.84$) of the samples, suggesting that particulate organic matter is mainly associated with the silt size fraction. Similarly, Parat et al. (2002) recovered the highest proportions of the soil organic carbon content in the silt fraction of Burgundy vineyard loam soils. The ammonium-lactate soluble P₂O₅ concentration presented a positive relationship with SOM ($r = 0.52$) and clay ($r = 0.61$) contents, implying that available P pools are present at higher concentrations in organic- and clay-rich topsoil samples. On the contrary, a strong negative correlation was found between the clay and the sand ($r = -0.91$) contents indicating the size sorting effect of soil erosion that produces high sand and low clay and vice versa containing topsoils at distinct areas of the hillslope. Correlation of the soil clay content with both pH values (measured in d.w. ($r = -0.68$) and the KCl solution ($r = -0.79$)) infer the role of exchangeable H⁺ and hydroxy-Al ions adsorbed on clay minerals in determining soil (potential) acidity.

Significant correlation between SOM and silt contents with Cu ($r = 0.56$ for SOM - Cu and $r = 0.76$ for silt - Cu) suggests that the silt-bound particulate organic matter and organo-mineral complexes govern Cu binding in the vineyard soil. Former studies performed in high-Cu vineyard soils also emphasised the importance of the particulate organic matter in the sorption of pesticide-derived Cu (Besnard et al., 2001, Parat et al., 2002, Duplay et al., 2014). The closest relationship apparently exists between Cu and ammonium-lactate soluble P₂O₅ contents ($r = 0.80$).

Previous findings proposed that phosphate played a role in enhancing the adsorption of Cu (and Pb) to soil mineral phases, such as iron (hydr)oxides through the formation of ternary complexes (Tiberg et al., 2013). Soil pH and sand content showed negative correlation with the examined PTEs (except for the pairs of pH and Cu, sand and Mn). The clay content that markedly affects the soil pH (as previously shown) is also anticorrelated to the sand content. This can explain the negative relationship between PTE concentrations and sand content. Indeed, the PTE contents (except Mn) are significantly and strongly correlated with the clay-sized fraction in the topsoil. Clay-sized fractions are known carriers of PTEs in soils owing to their important metal retaining capacities and specific (organo-)mineral composition (Micó et al., 2006). Therefore, clay minerals and clay mineral-organic matter complexes that primarily constitute the clay fractions (Babcsányi et al., 2016) are proposed to be the main binding phases for B ($r = 0.97$), Ni ($r = 0.97$), Cr ($r = 0.96$), Zn ($r = 0.83$), Co ($r = 0.71$), Ba ($r = 0.93$) and Sr ($r = 0.76$) (significance at $p < 0.01$). A less significant correlation (significance at $p < 0.05$) in the case of Cu ($r = 0.62$) and Pb ($r = 0.60$) with the clay-sized fraction presumes that additional soil constituents intervene in their binding in the soil, such as the silt-bound SOM in the case of Cu.

In contrast, Mn lacks any statistically significant relationship with the clay-sized fraction and soil characteristics involved in the study (except for pH_{d.w.}). This dissimilarity of Mn from the other target PTEs

may stem from the predominantly natural (geogenic) origin of Mn in the studied soil supported by the low (<1) EF (Mn) compared to the local background (Table 3.). This means that Mn mainly enters the soil by weathering of the parent material rhyolite containing an average of 600 mg/kg Mn according to Gilkes and McKenzie (1988). Moreover, Mn's behaviour in soils is complex. Mn is likely to exist in the form of precipitated manganic (oxy)hydroxides in soils with a reaction above pH 6.0, an insoluble form of Mn (Bradl, 2004).

As shown in Table 5, most of the analysed PTEs are strongly correlated with each other. The Mn, Pb, and Cu contents show weaker relations with the other selected PTEs, which may be explained by diverse sources and/or geochemical behaviour in the studied soils, as discussed above.

Spatial distribution of the topsoil characteristics and PTE contents (B, Mn, Ni, Cr, Pb, Cu, Zn, Co, Ba, Sr) in the vineyard topsoil

In this study, root mean square error (RMSE) and mean absolute error (MAE) were used to evaluate inverse distance weighting (IDW) and lognormal kriging (LK) interpolations' performance (summarised in Table 6). IDW generates smoother surfaces than LK, which may decrease its performance. Meanwhile, the LK method tends to underestimate the higher values and overestimate the lower values. The results indicate that LK shows an overall better performance to predict most of the examined soil parameters, except for pH_{d.w.}, sand, and SOM contents. IDW tends to compute higher prediction errors as weighting values increase. The LK outperformed the IDW method for predictions made for P₂O₅, CaCO₃,

Table 5 Pearson's correlation matrix among PTEs. The bold numbers denote statistically significant correlation coefficients (with p-value<0.05).

| | B | Mn | Ni | Cu | Cr | Pb | Zn | Co | Ba | Sr |
|----|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|----|
| B | 1 | | | | | | | | | |
| Mn | 0.42 | 1 | | | | | | | | |
| Ni | 0.99** | 0.46 | 1 | | | | | | | |
| Cu | 0.72** | 0.34 | 0.69** | 1 | | | | | | |
| Cr | 0.99** | 0.50 | 0.99** | 0.73** | 1 | | | | | |
| Pb | 0.62* | 0.74** | 0.69** | 0.44 | 0.71** | 1 | | | | |
| Zn | 0.90** | 0.28 | 0.89** | 0.72** | 0.88** | 0.43 | 1 | | | |
| Co | 0.81** | 0.73** | 0.83** | 0.72** | 0.87** | 0.84** | 0.69** | 1 | | |
| Ba | 0.97** | 0.60* | 0.98** | 0.71** | 0.99** | 0.76** | 0.85** | 0.91** | 1 | |
| Sr | 0.87** | 0.59* | 0.87** | 0.90** | 0.89** | 0.67** | 0.83** | 0.90** | 0.91** | 1 |

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed).

Table 6 Performance of inverse distance weighting (IDW) and lognormal kriging (LK) for predicting soil characteristics and PTE contents in the vineyard topsoil. The smallest prediction errors are highlighted in bold. RMSE stands for root mean square error. MAE stands for mean absolute error.

| Soil properties | Unit | RMSE | | MAE | |
|-------------------------------|-------|--------------|--------------|-------------|--------------|
| | | IDW | LK | IDW | LK |
| pH _{d.w.} | | 0.38 | 0.39 | 0.34 | 0.36 |
| pH _{KCl} | | 0.56 | 0.56 | 0.34 | 0.34 |
| (nitrate+nitrite)-N | mg/kg | 0.64 | 0.65 | 0.51 | 0.46 |
| P ₂ O ₅ | % | 59.97 | 55.83 | 52.30 | 49.09 |
| SOM | % | 0.42 | 0.44 | 0.38 | 0.42 |
| CaCO ₃ | % | 0.50 | 0.47 | 0.47 | 0.42 |
| Clay | % | 3.15 | 3.03 | 2.79 | 2.42 |
| Silt | % | 3.32 | 3.30 | 2.69 | 2.67 |
| Sand | % | 4.31 | 5.22 | 3.58 | 4.53 |
| Coarse fraction | % | 11.91 | 11.86 | 11.42 | 11.20 |
| PTEs | | | | | |
| Zn | mg/kg | 3.66 | 3.63 | 3.30 | 3.17 |
| Pb | mg/kg | 1.47 | 1.53 | 1.30 | 1.20 |
| Ni | mg/kg | 1.62 | 1.44 | 1.29 | 1.16 |
| Cr | mg/kg | 1.48 | 1.13 | 1.17 | 0.85 |
| Cu | mg/kg | 23.51 | 23.76 | 15.93 | 15.88 |
| Co | mg/kg | 0.60 | 0.58 | 0.58 | 0.52 |
| B | mg/kg | 1.76 | 1.72 | 1.55 | 1.55 |

clay, silt, and coarse fractions. Furthermore, LK also showed smaller prediction errors than IDW for mapping the PTE contents except for Cu and Pb. As previously observed, the local minimum and maximum values are likely to be respectively overestimated and underestimated by LK, while the predicted local minimum and maximum values by IDW are similar to the measured ones (Xie et al., 2011). In the following, some maps for the selected soil properties and the B, Cu and Zn contents prepared by LK are displayed (Fig. 2).

Our results confirmed that terrain significantly impact the spatial variability of soil characteristics at the plot scale. Contrasting spatial patterns of soil texture can be delineated along the hillslope. The upper slope sections display higher proportions of clay and, accordingly, lower sand contents. Meanwhile, at the lower half of the hillslope, high sand contents coincide with reduced clay contents. The silt and the concomitantly varying SOM contents are found in higher concentrations at the summit and the shoulder positions of upslope areas. At the same time, a reraising trend can be observed at the toeslope zone. By contrast, in Mediterranean hillslope vineyards, the highest silt and total organic carbon contents were detected at the middle of a hillslope (Rodrigo Comino et al., 2016). The differences of the landscape topography and the soil characteristics may explain the observed differences. Indeed, the vineyard soil in Tállya is characterised by high contents of the coarse fraction (>30%), which is supposed to impact soil erosion dynamics significantly. Indeed, the slope steepness and the proportions of the coarse fraction in soil are found to determine soil loss rates. At mild slope gradients (at 5°), the high contents of the coarse fraction in the form of embedded rock fragments increase water infiltration rates, thus reducing overland flow. By contrast, at higher than 10° gradients, the coarse fraction seemingly enhances runoff generation and sediment transport (Gong et al., 2018). We can reasonably suppose that the coarse fraction protects the soil from excessive soil loss at the summit and the hillslope's shoulder, displaying <10° gradients (Fig. 1). The main erosion-impacted zone is situated at the backslope, where high slope gradients prevail. The highest contents of the coarse fraction are observed at the backslope section, further confirming intense losses of the fine earth (< 2 mm). Similarly, Rodrigo Comino et al. (2017) reported that the highest rock fragment contents (77%) were found at the hillslope's shoulder in a Spanish vineyard. Soil erosion induces particle size sorting according to the dominating sediment transport processes. Sediments moved during interrill erosion, transport predominantly fine soil particles (<0.05 mm) suspended in runoff, while rill development during intense rainfall displaces coarser soil fractions (fine sand, sand) (Shi et al., 2012).

Similar observations have been made in another sloping vineyard (Nagy-Eged Hill, Hungary), where grape rows were oriented parallel to the main slope and bare areas between rows enabled the downhill transport and the accumulation of both the fine fraction and the gravel eroded from uphill areas (Nagy et al., 2012). The accumulation of sand in the footslope zone of the vineyard in Tállya, together with reraising silt contents further

downhill in the toeslope area, suggest that sediment grain-sorting also occurs during its deposition. The displaced coarse (sand, fine sand) soil fractions are preferentially deposited right at the footslope. The fine fractions of silt and clay are transported farther downslope, increasing the silt content in the toeslope zone.

In general, the spatial distribution maps of Cu, Zn and B show that higher concentrations are found in upslope areas, while markedly lower concentrations prevail in the backslope and footslope areas. Spatial distribution of B, Pb, and Co present lower variability in the plot. Meanwhile, Zn, Sr, and Cr show moderate spatial variability, and Mn, Co, and Ba demonstrate high spatial variability. Their similar spatial distribution further supports the intimate association of PTEs with the clay-sized fraction. The spatial trends reveal that the higher concentrations of PTEs at the summit and the shoulder of the hillslope are associated with the low slope gradients (0-5 degree) and the high contents of the coarse fraction (that protects the soil from excessive erosion-induced losses). While the reraising PTE concentrations mostly at the toeslope are likely due to the deposition of fine soil particles, mainly silt and to a minor extent clay, the main vectors of PTEs during sediment transport.

CONCLUSION

We have demonstrated that grape growing and, more precisely, the related use of agrochemicals significantly enriches the potentially toxic element (PTE) content of soils, except for lead (Pb) and manganese (Mn). The slightly acidic vineyard soil in Tállya (Hungary) bears higher boron (B), nickel (Ni), chrome (Cr), copper (Cu), zinc (Zn), cobalt (Co), barium (Ba) and strontium (Sr) contents compared to the local forest soil. The vineyard soil accumulated Cu and – to a smaller extent – B in excess, considering median contents of these elements in Hungarian arable soils as a reference. The latter is attributed to plant protection practices specific to vineyards, including frequent applications of Cu-based fungicides (such as the Bordeaux mixture) and micronutrient-rich fertilizers (with high B contents). Anthropogenic B accumulation due to farming practices in vineyard soils within a low geochemical B area has rarely been evidenced so far.

The examined soil's clay content strongly correlated with the bulk pseudototal PTE contents of B, Ni, Cr, Zn, Co, Ba and Sr. Indeed, clay-sized fractions are known carriers of PTEs owing to their high metal(loid) sorbing capacities. Presumably, these PTEs are adsorbed primarily to clay minerals and clay mineral-organic matter complexes. A less significant correlation (significance at $p < 0.05$) in the case of Cu and Pb with the clay content presumes that additional constituents intervene in their retention in the vineyard soil in Tállya. In the case of Cu, the silt-bound soil organic matter (SOM) is also a plausible sorbing material. Manganese (Mn) has geogenic origin in the vineyard soil primarily. The lack of significant correlation with the soil characteristics (but $pH_{d,w}$) underlines the contrasting behaviour of Mn in the vineyard soil compared with the other PTEs involved in the study.

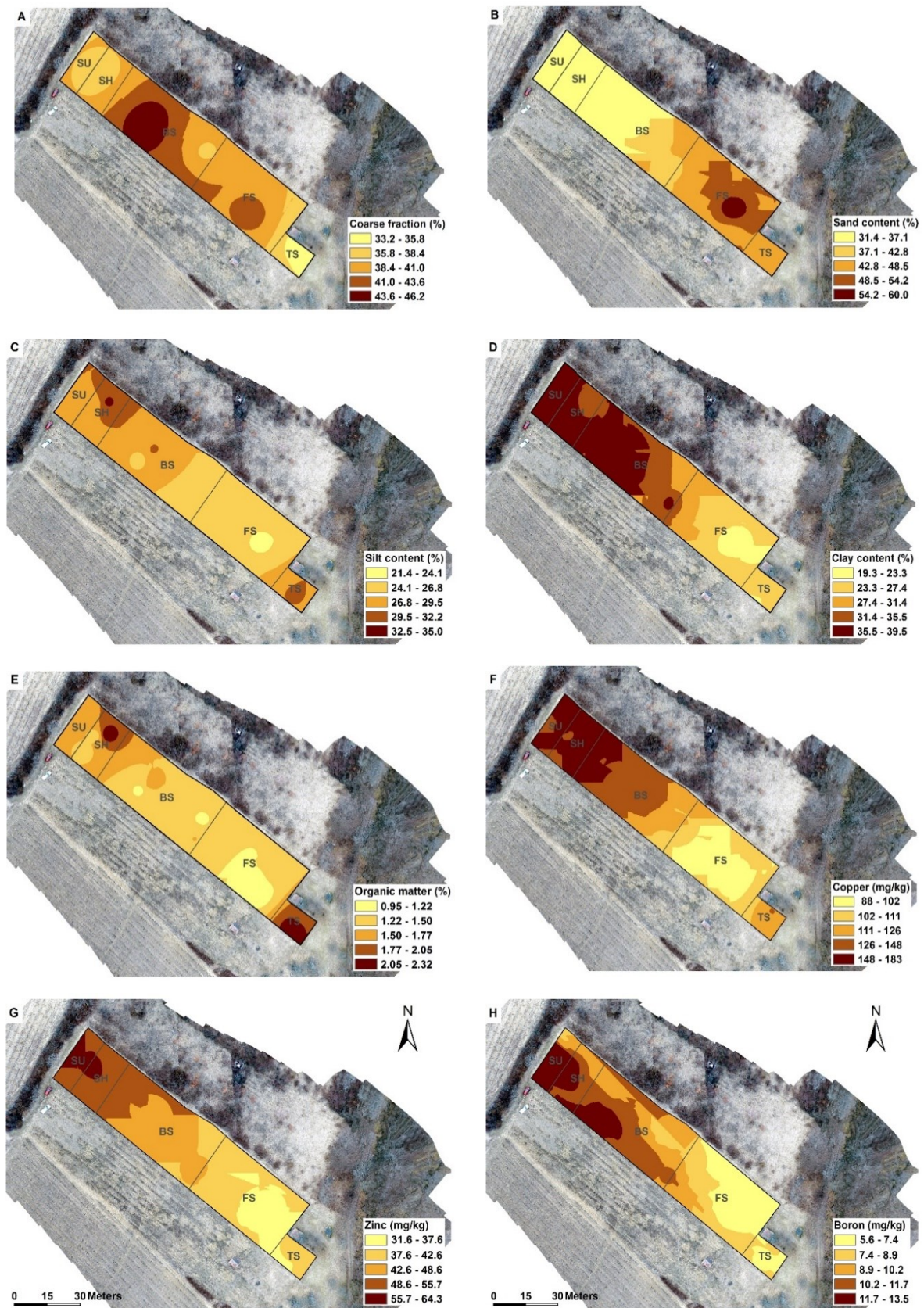


Fig. 2 Interpolated maps showing the spatial distribution of the topsoil contents of the (A) coarse fraction, (B) sand, (C) silt, (D) clay, (E) organic matter, (F) Cu, (G) Zn and (H) B predicted by lognormal kriging. Pixel values were reclassified using equal intervals, which divides the range of data values into equal-sized subranges. Hillside positions are also displayed on the maps: SU (summit), SH (shoulder), BS (backslope), FS (footslope), TS (toeslope).

The LK outperformed the IDW method for predicting the majority of soil parameters. The spatial distribution maps show higher contents of PTEs at the summit and the hillslope's shoulder, while lower ranges prevail at the footslope zone. The soil samples from the summit and the toeslope zones have the highest contents of SOM, while increased contents of the coarse fraction are found at the backslope. These observations confirm that soil erosion and sediment transport processes govern the redistribution of different particle-size soil fractions, associated soil constituents and PTEs within the vineyard.

A better understanding of the impact of soil erosion on the spatial patterns of soil quality will advance our knowledge of erosion and sedimentation processes, which in turn will improve erosion modelling.

ACKNOWLEDGMENTS

I. Babcsányi is grateful for the financial support of the Premium Postdoctoral Research Program of the Hungarian Academy of Sciences. The authors wish to thank István Fekete and Amanda Kiss for assisting in sample treatment and laboratory analyses of samples. The authors are grateful to the local vine-growers of Tállya for allowing our field survey and sharing information on the agrichemicals' use and soil management.

References

- Babcsányi, I., Chabaux, F., Granet, M., Meite, F., Payraudeau, S., Duplay, J., Imfeld, G. 2016. Copper in soil fractions and runoff in a vineyard catchment: Insights from copper stable isotopes. *Science of The Total Environment* 557-558, 154–162. DOI: 10.1016/j.scitotenv.2016.03.037
- Besnard, E., Chenu, C., Robert, M. 2001. Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils. *Environmental Pollution* 112 (3), 329–337. DOI: 10.1016/S0269-7491(00)00151-2
- Biddoccu, M., Ferraris, S., Opsi, F., Cavallo, E. 2016. Long-term monitoring of soil management effects on runoff and soil erosion in sloping vineyards in Alto Monferrato (North-West Italy). *Soil and Tillage Research* 155, 176–189. DOI: 10.1016/j.still.2015.07.005
- Bordoni, M., Vercesi, A., Maerker, M., Ganimede, C., Reguzzi, M.C., Capelli, E., Wei, X., Mazzoni, E., Simoni, S., Gagnarli, E., Meisina, C. 2019. Effects of vineyard soil management on the characteristics of soils and roots in the lower Oltrepò Apennines (Lombardy, Italy). *Science of The Total Environment* 693, 133390. DOI: 10.1016/j.scitotenv.2019.07.196
- Bradl, H.K. 2004. Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science* 277(1), 1–18. <https://doi.org/10.1016/j.jcis.2004.04.005>
- Capello, G., Biddoccu, M., Ferraris, S., Cavallo, E. 2019. Effects of tractor passes on hydrological and soil erosion processes in tilled and grassed vineyards. *Water (Switzerland)* 11, 10352. DOI: 10.3390/w11102118
- Csorba, S., Úveges, J., Makó, A. 2014. Relationship between soil properties and potentially toxic element content based on the dataset of the Soil Information and Monitoring System in Hungary. *Central European Geology* 57 (3), 253–263. DOI: 10.1556/ceugeol.57.2014.3.2
- Dos Santos, G.C.G., Valladares, G.S., Abreu, C.A., De Camargo, O.A., Grego, C.R. 2013. Assessment of copper and zinc in soils of a vineyard region in the state of São Paulo, Brazil. *Applied and Environmental Soil Science* 2013, 790795. DOI: 10.1155/2013/790795
- Duplay, J., Semhi, K., Errais, E., Imfeld, G., Babcsányi, I., Perrone, T. 2014. Copper, zinc, lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France): The impact of cultural practices. *Geoderma* 230-231, 318–328. DOI: 10.1016/j.geoderma.2014.04.022
- Follain, S., Ciampalini, R., Crabit, A., Coulouma, G., Garnier, F. 2012. Effects of redistribution processes on rock fragment variability within a vineyard topsoil in Mediterranean France. *Geomorphology* 175-176, 45–53. DOI: 10.1016/j.geomorph.2012.06.017
- Gilkes, R.J., McKenzie, R.M. 1988. Geochemistry and Mineralogy of Manganese in Soils. Manganese in Soils and Plants: Proceedings of the International Symposium on 'Manganese in Soils and Plants' held at the Waite Agricultural Research Institute, The University of Adelaide, Glen Osmond, South Australia, Dordrecht, Springer Netherlands: 23-35.
- Gong, T., Zhu, Y., Shao, M. 2018. Effect of embedded-rock fragments on slope soil erosion during rainfall events under simulated laboratory conditions. *Journal of Hydrology* 563, 811–817. DOI: 10.1016/j.jhydrol.2018.06.054
- Goovaerts, P. 1999. Geostatistics in soil science: State-of-the-art and perspectives. *Geoderma* 89, 1–45. DOI: 10.1016/S0016-7061(98)00078-0
- Guo, X., Fu, B., Ma, K., Chen, L., Wang, J. 2001. Spatio-temporal variability of soil nutrients in the Zunhua plain, northern China. *Physical Geography* 22, 343–360. DOI: 10.1080/02723646.2001.10642748
- Ippolito, J.A., Barbarick, K.A. 2006. Biosolids Affect Soil Barium in a Dryland Wheat Agroecosystem. *Journal of Environmental Quality* 35 (6), 2333–2341. DOI: 10.2134/jeq2006.0076
- Joint Decree No. 6/2009. (IV. 14) KvVM-EüM-FVM of the Ministers of Environmental Protection and Water Management, Public Health, Agriculture and Regional Development on the Limit Values Necessary to Protect the Quality of Geological Medium and the Groundwater and on Measurement of Pollution.
- Ladányi, Z., Csányi, K., Farsang, A., Perei, K., Bodor, A., Kézér, A., Barta, K., Babcsányi, I. 2020. Impact of Low-Dose Municipal Sewage Sludge Compost Treatments on the Nutrient and the Heavy Metal Contents in a Chernozem Topsoil Near Újkígyós, Hungary: A 5-Year Comparison. *Journal of Environmental Geography* 13 (1-2), 25–30. DOI: 10.2478/jengeo-2020-0003
- Lu, A., Wang, J., Qin, X., Wang, K., Han, P., Zhang, S. 2012. Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Science of the Total Environment* 425, 66–74. DOI: 10.1016/j.scitotenv.2012.03.003
- Mezősi, G., Bata, T. 2016. Estimation of the Changes in the Rainfall Erosivity in Hungary. *Journal of Environmental Geography* 9 (3-4), 43–48. DOI: 10.1515/jengeo-2016-0011
- Micó, C., Recatalá, L., Peris, M., Sánchez, J. 2006. Assessing heavy metal sources in agricultural soils of a European Mediterranean area by multivariate analysis. *Chemosphere* 65, 863–872. DOI: 10.1016/j.chemosphere.2006.03.016
- Miličević, T., Relić, D., Škrivanj, S., Tešić, Ž., Popović, A. 2017. Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion. *Chemosphere* 171, 284–293. DOI: 10.1016/j.chemosphere.2016.12.090
- MSZ-08-0206-2, 1978. Evaluation of Some Chemical Properties of the Soil. Laboratory Tests. (pH Value, Phenolphthaleine Alkalinity Expressed in Soda, All Water Soluble Salts, Hydrolite (y1-Value) and Exchanging Acidity (y2-Value)). Hungarian Standard Association, Budapest (in Hungarian).
- MSZ 21470-52, 1983. Environmental Protection. Testing of Soils. Determination of Organic Matter. Hungarian Standard Association, Budapest (in Hungarian).
- MSZ 20135:1999 Determination of the Soluble Nutrient Element Content of the Soil. Hungarian Standard Association, Budapest (in Hungarian).
- Nagy, R., Zsófi, Z., Papp, I., Földvári, M., Kerényi, A., Szabó, S. 2012. Evaluation of the relationship between soil erosion and the mineral composition of the soil: A case study from a cool climate wine region of Hungary. *Carpathian Journal of Earth and Environmental Sciences* 7, 223–230.
- Novara, A., Pisciotto, A., Minacapilli, M., Maltese, A., Capodici, F., Cerdà, A., Gristina, L. 2018. The impact of soil erosion on soil fertility and vine vigor. A multidisciplinary approach based on

- field, laboratory and remote sensing approaches. *Science of The Total Environment* 622–623, 474–480. DOI: 10.1016/j.scitotenv.2017.11.272
- Parat, C., Chaussod, R., Lévêque, J., Dousset, S., Andreux, F. 2002. The relationship between copper accumulated in vineyard calcareous soils and soil organic matter and iron. *European Journal of Soil Sciences* 53 (4), 663–670. DOI: 10.1046/j.1365-2389.2002.00478.x
- Patinha, C., Durães, N., Dias, A.C., Pato, P., Fonseca, R., Janeiro, A., Barriga, F., Reis, A.P., Duarte, A., Ferreira da Silva, E., Sousa, A.J., Cachada, A. 2018. Long-term application of the organic and inorganic pesticides in vineyards: Environmental record of past use. *Applied Geochemistry* 88, 226–238. DOI: 10.1016/j.apgeochem.2017.05.014
- Rodrigo Comino, J., Ruiz Sinoga, J.D., Senciales González, J.M., Guerra-Merchán, A., Seeger, M., Ries, J.B. 2016. High variability of soil erosion and hydrological processes in Mediterranean hillslope vineyards (Montes de Málaga, Spain). *Catena* 145, 274–284. DOI: 10.1016/j.catena.2016.06.012
- Rodrigo Comino, J., Senciales, J.M., Ramos, M.C., Martínez-Casasnovas, J.A., Lasanta, T., Brevik, E.C., Ries, J.B., Ruiz Sinoga, J.D. 2017. Understanding soil erosion processes in Mediterranean sloping vineyards (Montes de Málaga, Spain). *Geoderma* 296, 47–59. DOI: 10.1016/j.geoderma.2017.02.021
- Rodrigues, S.M., Henriques, B., da Silva, E.F., Pereira, M.E., Duarte, A.C., Römkens, P.F.A.M. 2010. Evaluation of an approach for the characterization of reactive and available pools of twenty potentially toxic elements in soils: Part I – The role of key soil properties in the variation of contaminants' reactivity. *Chemosphere* 81 (11), 1549–1559. DOI: 10.1016/j.chemosphere.2010.07.026
- Rodríguez Martín, J.A., Arias, M.L., Grau Corbí, J.M. 2006. Heavy metals contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geochemical methods to study spatial variations. *Environmental Pollution* 144 (3), 1001–1012. DOI: 10.1016/j.envpol.2006.01.045
- Rodríguez Martín, J.A., Vázquez De La Cueva, A., Grau Corbí, J.M., López Arias, M. 2007. Factors controlling the spatial variability of copper in topsoils of the northeastern region of the Iberian Peninsula, Spain. *Water, Air, & Soil Pollution* 186: 311–321. <https://doi.org/10.1007/s11270-007-9487-9>
- Scull, P., Franklin, J., Chadwick, O.A., McArthur, D. 2003. Predictive soil mapping: A review. *Progress in Physical Geography: Earth and Environment* 27 (2), 171–197. DOI: 10.1191/0309133303pp366ra
- Shi, Z.H., Fang, N.F., Wu, F.Z., Wang, L., Yue, B.J., Wu, G.L. 2012. Soil erosion processes and sediment sorting associated with transport mechanisms on steep slopes. *Journal of Hydrology* 454–455, 123–130. DOI: 10.1016/j.jhydrol.2012.06.004
- Solgi, E., Solgi, M., Rodríguez Martín, J.A. 2016. Spatial variability of heavy metal concentrations in vineyard soils on Malayer Plains (Iran). *Environmental Forensics* 17 (1), 87–96. DOI: 10.1080/15275922.2015.1133728
- Sun, C., Liu, J., Wang, Y., Sun, L., Yu, H. 2013. Multivariate and geostatistical analyses of the spatial distribution and sources of heavy metals in agricultural soil in Dehui, Northeast China. *Chemosphere* 92, 517–523. DOI: 10.1016/j.chemosphere.2013.02.063
- Szatmári, G., Barta, K., Farsang, A., Pásztor, L. 2015. Testing a sequential stochastic simulation method based on regression kriging in a catchment area in Southern Hungary. *Geologia Croatica* 68 (3), 273–283. DOI: 10.4154/GC.2015.21
- Szatmári, J., Tobak, Z., Van Leeuwen, B., Dolleschall, J. 2011. Data acquisition for inland excess water mapping and modelling using artificial neural networks. *Földrajzi Közlemények* 135 (4), 351–363.
- Tiberg, C., Sjöstedt, C., Persson, I., Gustafsson, J.P. 2013. Phosphate effects on copper(II) and lead(II) sorption to ferrihydrite. *Geochimica et Cosmochimica Acta* 120, 140–157. DOI: 10.1016/j.gca.2013.06.012
- Torri, S.I., Corréa, R.S. 2012. Downward Movement of Potentially Toxic Elements in Biosolids Amended Soils. *Applied and Environmental Soil Science* 2012, 145724. DOI: 10.1155/2012/145724
- Ungureanu, T., Iancu, G.O., Pintilei, M., Chicoş, M.M. 2017. Spatial distribution and geochemistry of heavy metals in soils: A case study from the NE area of Vaslui county, Romania. *Journal of Geochemical Exploration* 176, 20–32. DOI: 10.1016/j.gexplo.2016.08.012
- Webster, R., Oliver, M.A. 2007. *Geostatistics for Environmental Scientists*. Second ed. John Wiley & Sons. DOI: 10.2136/vzj2002.3210
- World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.
- USDA, 2014. *Soil Survey Field and Laboratory Methods Manual*. United States Dep. Agric. Nat. Resour. Conserv. Serv. 487. DOI: 10.13140/RG.2.1.3803.8889
- Xie, Y., Chen, T. Bin, Lei, M., Yang, J., Guo, Q.J., Song, B., Zhou, X.Y. 2011. Spatial distribution of soil heavy metal pollution estimated by different interpolation methods: Accuracy and uncertainty analysis. *Chemosphere* 82, 468–476. DOI: 10.1016/j.chemosphere.2010.09.053