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GEOCHEMICAL DISTRIBUTION AND RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN THE SOIL AND ERODED SEDIMENT IN TWO SLOPING VINEYARDS (TOKAJ-HEGYALJA, HUNGARY)

PhD dissertation

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INTRODUCTION AND OBJECTIVES OF THE RESEARCH

Viticulture is an important agricultural practice, especially in Europe, which still comprises the largest and oldest wine-growing area in the world. In vineyards, long-term application of chemical fertilizers, fungicides, pesticides, and organic by-products such as animal manure poses a significant risk of soil contamination, particularly through the accumulation of potentially toxic elements (PTEs). Soil degradation due to contamination with PTEs and nutrient losses through water erosion can reduce soil quality and pose a significant ecological and toxicological concerns. In addition, the type of farming (conventional and organic) and the age of the vineyard can be considered as dominant factors that cause changes in soil pedological properties and pollution levels PTE. Remarkably, in hillside vineyards, the enrichment of PTEs in the soil may increase their potential for export into the non-target environment via water erosion, mainly as associated with sediment particles in low energy zones of the landscape. The elevated PTEs contents in sediments can raise perilous environmental issues. Furthermore, the downward movement of PTEs within the soil profile that occurs over an extended period of time may result in their significant redistribution and available fraction in the subsoil and then pose a potential risk of toxicity to plants, especially in the rhizosphere. The total PTE content is a poor predictor of the impact of contaminated soils or sediments and is insufficient for an adequate environmental risk assessment because the mobility of these elements depends on their binding forms. Therefore, determination of the bioavailability and geochemical distribution of PTEs is appropriate to assess their potential mobility and contamination status in soils and sediments.

Health and ecological risks associated with the accumulation of PTEs have occurred and become an environmental burden. In particular, high-metal hotspots within vineyards may ultimately result in toxicity to newly planted vines and soil biota. Therefore, further assessment of PTEs associated with health and environmental risks in vineyard soils is needed to provide information on the sustainability of current viticultural practices.

Tokaj-Hegyalja, is one of the historical wine-producing regions in northeastern Hungary. The vineyards are situated at the hillslopes of the Tokaj Mountains, a member of the inner Carpathian volcanic range. In addition to conventional farming, organic and ecological farming practices gain ground in the vineyards of the region exerting different effects on the soil environment, soil erosion dynamics, and PTE accumulation patterns. To date, no research has focused on assessing PTEs associated with ecological and health risks in Tokaj-Hegyalja vineyards. Therefore, I consider it is important to study the accumulation patterns, spatial distribution, bioavailability, and binding forms of Zn, Pb, Co, Ni, Cr, Cu, Mn, Ba, and Sr in the topsoil and subsoil of the vineyards and in the eroded sediments in the two sloping vineyards of the Tokaj-Hegyalja in relation to soil properties, viticultural practices, and soil erosion. The specific goals of this study are as follows:

- Evaluating the impacts of viticulture on soil pedological properties based on the local forest soil characteristics as the reference soil.

- Determining the contamination levels, accumulation patterns, enrichment characteristics, and spatial distribution of target PTEs in vineyard top- and subsoils, and eroded sediments. In addition, I also focused on decipherment the predominant sources of these elements (natural or anthropogenic) and their accumulation trends in the sloping landscape related to the physico-chemical soil properties, soil erosion, and terrain.

- Investigating the bioavailability and distribution of geochemical fractions of target PTEs in the vineyard soils (in vertical and horizontal directions) and eroded sediments. I aimed to ascertain different ways of soil- and sediment-bound PTEs, giving more information on PTE mobility, environmental risk, and toxicity to crops.

- Assessing the correlation between the basic soil properties (pH, SOM, carbonate content, and soil texture) and the contents of the target PTEs in the studied forms in the vineyard top- and subsoil to point out the role of soil properties in PTE binding.

- Calculating the human health risk (for workers, children, and adult residents) and the ecological risk of target PTEs in vineyard soils and eroded sediments to assess the risk under different viticultural practices.

SAMPLES AND METHODS

Soil and sediment sampling

The study sites are two vineyards, a 0.4 ha plot near Tállya and a 1.8 ha plot in the outskirts of Tokaj. In March 2019, composite topsoil samples (< 20 cm layers: 0-10 cm and 10-20 cm) were collected from the studied vineyards (18 samples). Composite sampling was performed by mixing topsoil samples from the 0-10 cm and 10-20 cm layers taken from five points based on a two-way diagonal method. Soil samples were taken from the middle of grape inter-rows. Subsoil samples (borehole samples: 7 samples from 180-200 cm soil layer and 1 samples from 120-130 cm soil layer) were collected from the center of each sampling zone. Composite topsoil samples were also collected from local forested sites as background soil (not being impacted by vine-growing), both in Tállya and Tokaj from the 0-10 cm and 10-20 cm soil layers. From 5 profiles (2 profiles in Tállya and 3 profiles in Tokaj), 35 soil samples were collected. In each profile, samples were taken from all different observed pedogenetic horizons (0-10 cm; 10-20 cm; 20-30 cm; 30-40 cm; 60-80 cm; 120-140 cm; and 180-200 cm). Apart from collecting soil samples, at the same time, sediment traps were deployed along the main slope for both vineyards. Then, in May 2019, twelve eroded sediment samples from the traps were collected along with twelve topsoil samples (0-20 cm) near each trap.

Laboratory analyses

The collected soil samples were air-dried, while the eroded sediment samples were oven-dried at 80°C. All samples were disaggregated in a mortar with a pestle and then sieved to pass through a 2-mm sieve. The hygroscopic moisture of each sample was determined at 105°C in the oven for 24 hours (overnight). Basic soil parameters such as pH (d.w), carbonate content, soil texture, total salt content, and soil organic content were analyzed following Hungarian Standards. The soil pH was measured in deionized water with a soil/water ratio of 1 : 2.5 using a digital pH meter. The carbonate content (in percentage of dry matter weight, ±8%) was determined with a calcimeter according to the Scheibler method using 10% HCl solution for the reaction. The determination of the soil texture based on the plasticity index values according to Arany (Arany Plasticity Index) was performed. In addition, the particle size distribution was determined by the pipette method following treatment with 0.1 M sodium pyrophosphate. X-Ray Diffraction (XRD) also was used to identify the composition of minerals of the studied vineyard soils. The total salt content was analyzed by a conductivity meter type Orion 3-Star in saturated soil samples. The soil organic matter content was determined by a UV-VIS spectrophotometer, following H_2SO_4 (95%) -aided oxidation of the organic matter with 0.33 M $K_2Cr_2O_7$ (overnight).

For determining the PTE and major element contents (Zn, Pb, Co, Ni, Cr, Cu, and Al, Fe, Mn, Mg, K, Ca), samples were finely ground in an agate ball mill (for soil samples) or in a mortar with a pestle (for sediment samples) to pass through a 250 μm sieve. Samples were digested in a microwave oven with aqua regia, and then element concentrations in digested samples were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES), using yttrium as an internal standard.

The bioavailability of target PTEs (Zn, Pb, Co, Ni, Cr, Cu) was determined by the 0.05 M Na_2-EDTA. Meanwhile, to determine the geochemical fractions of target PTEs (Zn, Pb, Co, Ni, Cr, Cu, Mn, Ba, and Sr), soil and sediment samples were extracted by the improved version of the BCR three-step sequential extraction procedure. The contents of studied PTEs in the extracts were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES).

Enrichment factor and soil contamination indices

Enrichment factor (EF)

The EF has been widely used to assess the enrichment of metals in soils and sediments, decipher their prevailing sources and prove the anthropogenic interferences with natural element cycles. In my research, EF was applied to explore

PTE accumulation and determine whether the natural or anthropogenic sources are dominant in the studied vineyard topsoils. The EF was calculated based on a reference element assumed to have negligible human sources. Iron (Fe) was appointed the reference element in my research, with the subsoil horizon as the reference soil. The EF was determined as follows:

$$EF = \frac{[E]_{SH}/[Fe]_{SH}}{[E]_{RH}/[Fe]_{RH}}$$

where $[E]$ is the concentration of PTE in the topsoil (*SH*) (0-10 cm) and the reference horizon (*RH*) (the subsoil). EF values higher than 2 usually imply non-negligible anthropogenic input of PTEs into the soil.

Enrichment ratio (ER)

To compare the concentrations of the studied PTEs in the eroded sediments with those in the topsoils (<20 cm depth), enrichment ratios (ER = element content in the sediment over that in the topsoil) were used.

Contamination factor (Cf)

Assessing the degree of contamination by a given PTE is performed by comparing the pollutant element concentration with unpolluted reference material as background concentration. Thence, in my study, Cf was calculated by dividing the content of an individual PTE in the vineyard soil/ sediment by its background concentration in the local forest as the reference soil. The equation is as follows:

$$\mathrm{Cf} = \frac{\mathrm{C_s}}{\mathrm{C}_{RefS}} \qquad (1)$$

where C_s is an element content (mg/kg); C_{RefS} is the reference concentration of the element in the local forest soil. The classification of the contamination factor is described in 4 levels: low contamination ($Cf < 1$); moderate contamination ($1 \leq Cf < 3$); considerable contamination ($3 \leq Cf < 6$); high contamination ($6 \leq Cf$).

Pollution load index (PLI)

The PLI was applied here for evaluating the overall pollution degree of soils and sediments considering all target PTEs. PLI (unitless) was calculated by multiplying the Cf of each element following the equation 2:

$$\mathrm{PLI} = \sqrt[n]{\mathrm{Cf_1} \times \mathrm{Cf_2} \times \mathrm{Cf_3} \times \ldots \times \mathrm{Cf_n}} \qquad (2)$$

where Cf_1 to Cf_n are the contamination factors of the first to the n^{th} PTE in the vineyard soil/ sediment. The degree of contamination based on the PLI is described in 5 levels: non pollution ($PLI = 0$); non to moderate pollution ($0 < PLI \leq 1$); moderate pollution ($1 < PLI \leq 2$); moderate to high pollution ($2 < PLI \leq 3$); high pollution ($3 < PLI$).

Ecological risk assessment

The *ecological risk factor (Ei)* is applied to assess the ecological risk of an individual metal according to the Hakanson ecological risk index, as follows:

$$\mathrm{Ei} = \mathrm{Cf_i} \times \mathrm{T_i} \quad (3)$$

where Cf_i is the single PTE contamination factor (calculated by Eq. 1) and T_i is the biological toxicity factor of an individual target PTE. Based on the recommendations, standard response coefficients (T_i) for the toxicity of the target PTEs are: Zn = 1, Pb = Co = Cu = 5, Ni = 6, and Cr = 2.

The *ecological risk index (ERI)* is estimated according to Eq. 4 to evaluate the overall ecological risk of all studied PTEs.

$$\mathrm{ERI} = \sum_{i=1}^{6} \mathrm{Ei}\ (i\text{=}1\text{-}6) \quad (4)$$

where Ei is the ecological risk factor for each individual PTE.

The ecological risk is grouped into 5 categories for the Eis and 4 for the ERI values: $Ei < 40$: Low ecological risk; $40 \leq Ei < 80$: Moderate ecological risk; $80 \leq Ei < 160$: Considerable ecological risk; $160 \leq Ei < 320$: High ecological risk; $320 < Ei$: Very high ecological risk; $ERI < 90$: Low risk; $90 \leq ERI < 190$: Moderate risk; $190 \leq ERI < 380$: Considerable risk; $380 \leq ERI$: High risk.

Human health risk assessment

My research evaluated the health risk associated with the total PTE contents primarily for outdoor workers in the two studied vineyards. In Tokaj, residential areas are located nearby the vineyards. Therefore, a resident scenario was also included for human health risk assessment considering children and adults. Accordingly, the hazard quotient (HQ) was determined as the ratio of the average daily intake (ADI) from ingestion of soil and a specific reference dose (RfD) of each PTE.

$$\mathrm{ADI} = \frac{\mathrm{C_n \times SIR \times EF \times ED}}{\mathrm{BW \times AT}} \times 10^{-6}$$

where C_n is the concentration of a PTE in the 0-10 cm soil layer (mg/kg); SIR is the soil ingestion rate: workers: 100; children: 200; adults: 100 mg/day; EF is the exposure frequency: (workers: 250; children: 350; adults: 350 days/year); ED is the exposure duration (workers: 25; children: 6; adults: 30 years); BW is the bodyweight (workers: 70; children: 15; adults: 70 kg); and AT is the averaging time (workers: 25 x 365 day/year = 9125 days, children: 2190 days; adults: 10950 days).

Then HQ (unitless) was calculated with the following formula:

$$HQ = ADI/RfD$$

where RfD is the oral reference dose (defined as the maximum allowable level of an element that will not pose any harmful effects on human health) of a PTE (unit is the same as for ADI): for Cr = 0.003, Cu = 0.04, Ni = 0.02, Pb = 0.0035, Zn = 0.3, and Co = 0.02.

The sum of all HQ values of each target PTE is the Hazard Index (HI):

$$HI = \sum HQ$$

When the values of HQ and HI are higher than 1, an apparent probability of the occurrence of adverse health effects is indicated, and HI < 1 shows that exposed persons are unlikely to experience dangerous health effects.

Statistical analysis

Maps of the study sites were designed using the QGIS software (version 3.4). Spearman rank-order correlation analysis determined the relationships between PTEs, relief, and soil properties. The significance level was considered at $p < 0.05$ and $p < 0.01$. In addition, one-way analysis of variance (ANOVA) was used to compare means of soil parameters between top- and subsoil layers at the level of $p < 0.05$. The statistical analyses were performed with the SPSS version 20.

SUMMARY OF RESULTS

1. Impact of viticultural on soil envrionment

Viticulture can exert an impact on soil characteristics such as pH, soil organic matter, soil texture, and other soil chemical properties, particularly in the sloping vineyard. Indeed, the results obtained from my research indicate that viticulture affects soil fertility principally because of increasing soil pH and decreasing humus content. Intensive conventional viticulture in the vineyard with no cover crops in the alleys (in Tállya) can make a strong decline of soil organic matter. Meanwhile, organic farming with implementing erosion control and using organic fertilizers (in Tokaj) can reduce remarkably soil organic matter depletion and optimize soil buffer's pH changes making the soil pH more stable. In addition, terrain exerts a significant impact on distribution of soil componets such as soil organic matter, fine particle, and coarse fraction. The slope gradient and the main erosion-impacted part of the hill play an important role in erosion-induced losses and redeposition of soil components in different hillslope positions.

2. Accumulation and enrichment characteristics of potentially toxic elements in the vineyard soil

The studied sites display contrasted soils: a slightly acidic soil derived from a magmatic rock (rhyolite) in a more than 100-year-old conventional vineyard near Tállya and a moderately alkaline soil developed on loess in a young organic vineyard near Tokaj. Our results indicate that although the Cu content in the uncultivated soil in Tállya was lower than the local background in Tokaj, three times higher Cu concentrations were observed in the conventional vineyard compared to the younger organic vineyard. The long history of Cu-fungicides applications resulted in a more pronounced accumulations of Cu in the older conventional vineyard, exceeding the Hungarian environmental quality standards (Joint Decree No. 6/2009. (IV. 14) KvVM-EüM-FVM). With Fe as a reference element, an average enrichment factor of 2.6 in the 28-year-old organic vineyard in Tokaj and 9.7 in the old vineyard in Tállya further confirmed the importance of the duration of Cu applications in vineyards. In the more recently re-planted vineyard in Tokaj, Ni and Cr levels were over the pollution limit value, while Cu was observed below that limit. High contents of Ni and Cr in the vineyard and forest soil and their apparent enrichment in the topsoil in Tokaj suggest that they probably originate from both local sources (such as the dacite base rock) and organic amendment applications. The higher Cu and Zn contents in the vineyard topsoil compared to the subsoil and the local uncultivated soils imply their anthropogenic origin in both vineyards (with a moderate enrichment of Zn from regular foliar fertilizer applications). For the other PTEs (Pb, Co, Ni, and Cr), there is no difference between the contents in the vineyard topsoil and the local forest soil, indicating their local source. Apart from Ni and Cr, the considered PTEs accumulate principally in the top 10 cm in both vineyards. Terrain played a key role in the enrichment patterns of PTEs in the topsoil. In general, in Tállya, PTEs tend to get enriched at the top of the hillslope in the summit zone, while in Tokaj a pronounced downslope enrichment can be highlighted due to soil erosion processes. Meanwhile, along with the complex slope shape of the vineyard in Tállya, the low slope gradients (0-5 degrees) and the high contents of the coarse fraction probably protect the soil from excessive erosion-induced losses at the summit zone.

3. Enrichment characteristics of potential toxic elements in the eroded sediments

In my research, enrichment ratios (ER) were applied to assess PTE enrichment in eroded sediments compared to the vineyard topsoil along the hillslope (<20 cm depth). The target PTEs tented to show increased concentrations in eroded sediments, with the highest ER (3.36) observed for Cu in the Tokaj vineyard. In Tokaj, the target PTEs tented to enrich significantly in the eroded sediments. This revealed a preferential movement of PTE-rich soil particles by overland flow. Copper exhibited higher contents in the sediments (148.1 - 211.5 mg/kg) compared to those in the vineyard topsoil along the hillslope (range: 36.5 - 70.0 mg/kg). Conversely, in Tállya, there was no significant difference between the mean of PTE total content in the topsoil compared to that in the eroded sediment, indicating a slight tendency to enrich PTEs in the sediments. The terrain and the high content of coarse fractions may explain this behaviour, as these factors probably protect the soil from excessive erosion-related losses in the summit zone. Then, the PTEs were less affected by sediments transported by runoff with the fine soil fraction.

4. Bioavailability of potentially toxic elements in vineyard soils and eroded sediments

Based on the EDTA extracted PTE contents, Zn, Ni, and Cr showed low mobility in both vineyards. Bioavailable proportions of Pb and Co can reach almost 50% of its total contents both in the vineyard and the forest topsoils, with slightly higher bioavailable Pb and Co in Tállya, indicating their lability in the soils. In both vineyards, the markedly higher percentages of bioavailable Cu in the topsoil compared to the local forest soils suggest that the anthropogenic source can be a factor of variation for the bioavailability of Cu. In accord with the total contents, bioavailable Cu (reaching 50% at the top of the hillslope in Tállya) represents a plausible risk of toxicity to grapevines and soil biota. Despite the substantially higher contents of Ni and Cr observed in Tokaj, no significant difference was noticed in their bioavailable proportions in both sites. Their bioavailable proportions were generally below 1%.

On the other hand, the examined PTEs demonstrated higher bioavailable contents in the eroded sediments than the top- and subsoil in both vineyards, except Co and Ni. However, bioavailability ratios of Ni and Cr in both vineyard soil and sediments were low. There is a significant difference between the bioavailable fractions of Zn and Cu in the vineyard soils and the local forest soils, with a higher bioavailable proportion found in the vineyard soils. In contrast, a significantly higher proportion of bioavailable Cu and Zn was found in the eroded sediments.

5. Correlation between the basic soil properties (pH, soil organic matter content, carbonate content, and soil texture) and the contents of potentially toxic elements (total and biovailability)

The studied PTE accumulation and bioavailability can present very different behavior in the uppermost soil layers depending on the different soil conditions. Data of corelation analysis revealed that oxide minerals of Fe, Mn, and Al, total Ca content, soil pH, and soil organic matter content showed a significant correlation with the total contents of the target PTEs, meanwhile, the bioavailability of PTE was largely influenced by Mn oxides and soil organic matter (particularly for Cu).

6. Geochemical distribution of potentially toxic elements in vineyard soils and eroded sediments

The improved three-step sequential BCR extraction procedure was applied in my research to evaluate the distribution of Zn, Pb, Co, Ni, Cr, Cu, Mn, Ba, and Sr in the different geochemical fractions of soils and sediments from the two sloping vineyards. By studying the distribution of PTEs between different phases, their bioavailability and toxicity can be ascertained. Generally, the proportion of the most mobile fraction (acid-soluble fraction) tends to decrease with increasing soil depth. The results for all soil profiles showed that in Tokaj, major portions of Zn (84%), Co (56%), Ni (79%), Ba (62%), Cr (95%) and Cu (63%) mostly existed in the residual fraction, whereas, Pb (63%) and Mn (50%) were dominating in the reducible fraction. In the vineyard soil in Tállya, Sr (45%), Zn (82%), Ni (74%), Ba (59%), and Cr (95%) was mainly associated with the residual fraction, meanwhile, most of the Pb (68%), Co (56%), Mn (58%), and Cu (44%) was exhibited in the reducible fraction. Potentially toxic elements in the reducible fraction may be more labile and released to the environment when soils are subjected to changes in redox potential that result in the decomposition of the oxides or hydroxides (under highly acidic or reducing conditions). Therefore, although the highest contents of target PTEs were observed in the reducible and residual fractions with limited mobility, environmental concerns cannot be ruled out, as the change in soil conditions may cause the PTEs to shift to the mobile fraction, thereby becoming available for uptake by living organisms. The content of PTEs in the fourth extracted fraction was significantly correlated with soil pH, $CaCO_3$ content, and silt content, while it was largely influenced by sand content with a negative correlation.

There was no significant difference between the proportions of extracted fractions of Pb, Ni, Ba, and Cr in the topsoil and the eroded sediment in accordance with each medium in comparison between the two vineyards. Meanwhile, the differences between the other PTEs (Zn, Co, Mn, Cu, and Sr) were mainly observed in the acid-soluble fraction and the reducible fraction with a higher percentage of the former in the sediments in Tokaj, indicating increased mobility of these elements in the sediment. The contribution of Zn in the first two extracted fractions (acid-soluble and reducible fraction) in the vineyard soils and sediments was noticed and higher in Tokaj than in Tállya. These differences can be mainly explained by the impact of organic matter content and particle distribution. Since a higher content of fine particles was observed in the sediments, the potential contents of PTEs bound to iron and manganese oxyhydroxides can be explored.

Along the soil depth, most of the Cu is associated with the reducible fraction of the upper soil layers in Tállya, ranging from 44% (in the 0-20 cm soil layer) to 46% (in the 20-40 cm soil layer). In addition, the higher proportion of Cu in the most mobile fraction (acid-soluble fraction) in the uppermost soil (11% in the 0-20 cm soil layer and 14% in the 20-40 cm soil layer) in Tállya and its strong enrichment in the topsoi may represent a considerably higher risk in Tállya compared to Tokaj (with 2% and 1% in the acid-soluble fraction in the 0-20 cm and 20-40 cm soil layers, respectively). On the other hand, Cu was dominant in the acid-soluble fraction and the reducible fraction in the eroded sediment in Tokaj, revealing its high lability and bioavailability as well as an elevated environmental risk.

7. Soil contamination indices and ecological risk assessment

Contamination factor (Cf) of target PTEs (Zn, Pb, Co, Ni, Cr, and Cu) in the vineyard top- (0-20 cm) and subsoil (>20 cm) and sediments based on their background concentrations (in the local forest as the reference materia) were used to assess the degree of contamination by a given PTE. The PTE-based contamination factors (Cfs) showed significant Cu pollution compared to the reference neighboring forest soils in both sites.

The highest Cfs for Cu observed in Tállya (ranging from 10.2 to 22.2 in the topsoils and 13.5 to 25.9 in the sediments) indicate high contamination status and strong enrichment of Cu compared to the local forest soil. The calculated pollution load index (PLI) based on the total PTEs contents showed that moderate to high pollution is indicated for the vineyards and sediments in this old conventional vineyard with the median PLI value varies from 1.62 (in the subsoils) to 2.77 (in the eroded sediments). As expected, the total Cu in the topsoil and eroded sediments has the highest contribution (more than 65%) to the ecological risk index (ERI) and represent a moderate ecological risk and considerable ecological risk, respectively via the ecological risk factor (Ei), meanwhile, all calculated Ei values for other PTEs are below the ecological risk factor thresholds of 40. However, the ERI calculated for topsoils and sediments showed an overall moderate risk in the Tállya vineyard. Moreover, the Ei (65.4) of bioavailable Cu in the eroded sediment exceeding the ecological risk factor threshold and accounting for 90% of the ERI (calculated for bioavailable PTEs) indicates its high mobile and lability in the sediment.

In Tokaj, ecological risk assessment based on the total and bioavailable contents of PTEs showed a low risk (ERI < 90) in the organic vineyard. Copper was also the dominating risk factor regardless of its forms (total and bioavailability) in the entire ecological risk. In addition, similarly to in Tállya, the high bioavailable Cu contents in eroded sediments accounted for up to 82% of the total ecological risk by all examined PTEs. The latter revealed an apparent risk induced by the high lability of Cu in the runoff-transported sediments, which is expected to increase over time with the repeated use of Cu-based agrochemicals. The median pollution load indices of 1.15, 1.81, and 1.10 for the topsoil, the sediments, and the subsoil, respectively, demonstrate a moderate multi-element contamination case in the organic vineyard.

The increased environmental risk due to the continuous use of copper-based fungicides and the subsequent accumulation of Cu in vineyard soils should be monitored, especially in old vineyards.

8. Human health risk assessment

The PTE-related health risk assessment showed no elevated health risk (Hazard index, HI<1) for children, adults and workers. The overall health risk related to all target PTEs in Tokaj (0.43) was more than 9 times higher for children than adults (0.046). The health risk related to Cr contents was the predominant risk factor for human health in both vineyards, accounting for 49.7% (in Tállya) and 79.0% (in Tokaj) of the calculated HIs. Chromium is indicated in the present study that it probably originates from both local sources (in both vineyards) and organic amendment applications (in the organic vineyard in Tokaj). Therefore, it can be considered that even though organic farming has been applied, potentially human health risks can be observed and the main risk factor is not always the most pollutant in environment.

Overall, the contents of target PTEs in the soil mainly depend on the vineyard age (particularly for Cu), farming practices, and terrain (due to erosion-impacted spatial distribution patterns). Meanwhile, the bioavailability and geochemical distribution of PTEs largely depends on the soil properties. Copper was the major pollutant in the older conventional and the younger organic vineyards too. The target PTEs tented to enrich in the eroded sediments, increasing ecological risk (particularly in the old conventional vineyard). The results of the present research indicate the fact that different viticultural practices and sloping terrain induce different effects on the pedological characteristics of vineyard soils, soil environment and can pose important environmental and toxicological concerns. In addition, the further accumulation of PTEs, especially in high-metal hotspots within the vineyards may ultimately cause toxicity to re-planted grapevines, soil biota, and in the longer term, farmers and residents living in the surrounding areas. Hence the spatial variability of soil-bound metal contents should be included in environmental and health risk assessments. Therefore, I strongly believe that my doctoral research is appropriate for vineyard winegrowers as a useful guide and for scientific research as a good example as well as further studies of the geochemistry of soils (in relation to the depth profiles of mobile elements) and the sorption of potentially toxic elements in soils and sediments.

LIST OF PUBLICATIONS RELATED TO THE THESIS

1. **Pham, N.T.H.,** Babcsányi, I. & Farsang, A (2021). Ecological risk and enrichment of potentially toxic elements in the soil and eroded sediment in an organic vineyard (Tokaj Nagy Hill, Hungary). Environ Geochem Health. (IF: 4,609 (2020)) https://doi.org/10.1007/s10653-021-01076-w

2. **Pham, N.T.H.,** Babcsányi, I., Balling, P. & Farsang, A (2022). Accumulation patterns and health risk assessment of potentially toxic elements in the topsoil of two sloping vineyards (Tokaj-Hegyalja, Hungary). J Soils Sediments. (IF: 3,308 (2020)) (in press)

3. Babcsányi, I., **Pham, N.T.H.,** Fekete, I., Farsang, A. (2022). The Spatial Distribution of Copper and Zinc in Vineyard Soils (in Tokaj, Hungary) as Impacted by Soil Erosion (Book Chapter). In: , et al. New Prospects in Environmental Geosciences and Hydrogeosciences. CAJG 2019. Advances in Science, Technology & Innovation. Springer, Cham. https://doi.org/10.1007/978-3-030-72543-3_47

4. **Pham, N.T.H.,** Babcsányi, I., and Farsang, A. (2022). Sequential extraction based environmental risk assessment of potentially toxic elements in the topsoil of two sloping vineyards (Tokaj-Hegyalja, Hungary), EGU General Assembly 2022, Vienna, Austria, 23–27 May 2022, EGU22-3829, https://doi.org/10.5194/egusphere-egu22-3829, 2022.

5. **Pham, N.T.H.,** Babcsányi, I., and Farsang, A. (2021). Accumulation and bioavailability of copper in the vineyard topsoil: Impact of the long-term application of pesticides and copper-fungicides in a conventional vineyard. The 9th International Plant Protection Symposium at University of Debrecen, October 13-14.

6. Babcsányi, I., Kovács, F., Juhász, S., Balling, P., **Pham Thi Ha, N.,** Tobak, Z., and Farsang, A. (2021). Assessing the impact of soil erosion on plant vigor (NDVI) and the spatial patterns of soil-bound Cu, Zn and B micro- and N, P macronutrients in a sloping vineyard (Tokaj, Hungary), EGU General Assembly 2021, online, 19–30 Apr 2021, EGU21-8445, https://doi.org/10.5194/egusphere-egu21-8445, 2021.

7. **Pham, N.T.H.,** Babcsányi, I., and Farsang, A. (2020). Soil contamination and ecological risk of heavy metals in alkaline vineyard soil, The EGU General Assembly, in Vienna (Austria) on 3-8 May, 2020, https://doi.org/10.5194/egusphere-egu2020-1587

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