PhD DISSERTATION

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UNIVERSITY OF SZEGED

DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCES

SZEGED

2022

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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Szeged, 2022

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List of abbreviations

API: Plasticity Index according to Arany

BCR: the Community Bureau of Reference three-step sequential extraction procedure proposed by the Standards, Measurements and Testing Programme (SM&T, formerly BCR) of the European Commission

Cf: Contamination factor

EF: Enrichment factor

Ei: Ecological risk factor

ERI: Ecological risk index

ER: Enrichment ratio

HI: Hazard index

HQ: Hazard quotient

PLI: Pollution load index

PTE: Potentially toxic element

SOM: Soil organic matter

XRD: X-Ray Diffraction

1. Introduction

Viticulture is an important agricultural practice, especially in Europe, which still comprises the largest and oldest wine-growing area in the world (Fraga et al., 2012). Although most of the agricultural land in Europe can be considered adequately safe for food production (Tóth et al., 2016), one of mankind's greatest challenges is providing sustainable crop yields without damaging and polluting the environment. 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 (Komárek et al., 2010; Preston et al., 2016). 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, topography, climate, and lithology are the most important factors for soil erosion and the spatial distribution of macro- and micronutrients (Chevigny et al., 2014; Czigány et al., 2020). Then, 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 (He et al., 2004; Ribolzi et al., 2002). Indeed, PTEs can be significantly relocated in the topsoils of sloping vineyards accumulating in low energy zones of the landscape. The elevated PTEs contents in sediments can raise perilous environmental issues (Fernández-Calviño et al., 2012, 2008; Pham et al., 2021).

However, 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 (Arenas-Lago et al., 2014; Fernández-Calviño et al., 2012; Rinklebe and Shaheen, 2014; Szolnoki and Farsang, 2013). Moreover, the bioavailability of PTEs has been used as a useful tool for evaluating the environmental pollution risk and toxicity to crops (Borgese et al., 2013; Nunes et al., 2014; Violante et al., 2010). The geochemical fractions and mobility of PTEs in soils and sediments, as well as their bioavailability and toxicity to plants and other organisms are strongly governed by soil and sediment solids (such as organic matter, silt and clay constituents, iron and aluminum oxy-hydroxides) to which the PTEs are bound (Arenas-Lago et al., 2014; Bacon and Davidson, 2008; Brun et al., 2001; Szolnoki and Farsang, 2013). Therefore, determination of the geochemical distribution of PTEs is appropriate to assess their potential mobility and contamination status in soils and sediments. Moreover, health and ecological risks associated with the accumulation of PTEs have occurred and become an environmental burden (Arfaeinia et al., 2019;

Milićević et al., 2018; Mirzaei et al., 2019). In particular, high-metal hotspots within vineyards may ultimately result in toxicity to newly planted vines and soil biota, and therefore spatial variability in soil-bound metal content should be included in environmental risk assessments. Furthermore, to our knowledge, the relationships between soil properties and the vertical distribution of the different PTE fractions have not been studied in soil profiles for vineyards. The accumulation 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 (Antoniadis and Alloway, 2003, McBride, 1995; Richards et al., 1998; Torri and Corrêa, 2012) and then pose a potential risk of toxicity to plants, especially in the rhizosphere. 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, part of the UNESCO World Cultural Heritage List (Nyizsalovszki and Fórián 2007). The vineyards are situated at the hillslopes of the Tokaj Mountains, a member of the inner Carpathian volcanic range. Lately, innovative processes, changes in cultivation techniques, and socio-economic transformations have significantly transformed the landscape that also affected the soil environment in Tokaj-Hegyalja (Nyizsalovszki and Fórián 2007; Novák et al., 2014). 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 wine region (northeastern Hungary) in relation to the pedological characteristics of the soils, viticultural practices, and soil erosion. In addition, my dissertation evaluates and clarifies the risks associated with the target PTEs for human health (for workers, children, and adults) and for the environment.

2. Objectives

My research focused on measuring and evaluating the total, bioavailable and geochemical fractions of Zn, Pb, Co, Ni, Cr, Cu, Mn, Ba, and Sr in the topsoils, subsoils, and eroded sediments of the vineyards. The specific goals of this study were:

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

(2) Determining the contamination levels, accumulation patterns, enrichment characteristics, and spatial distribution of target PTEs (Zn, Pb, Co, Ni, Cr, Cu, Mn, Ba, and Sr) in vineyard topsoils, subsoils, and eroded sediments. The enrichment factors for PTEs with a calculation of pedologic enrichment factor and contamination factor based on Fe (as a reference element) and reference soil (local forests) were used in my research, respectively. Thence, I 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.

(3) 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.

(4) 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.

(5) Calculating the human health risk and the ecological risk of target PTEs accumulated through different viticultural practices.

3. Literature overview

3.1. Impact of viticulture on the pedological characteristics of vineyard soils

Agricultural production is influenced by natural drivers such as soil, topography, climate, and landscape (Li and Zhou, 2015; Schaller et al., 2018). These factors play a key role in cultivation culture and product quality, especially in sustainable agriculture (Schaller et al., 2018). However, the dramatic change in agricultural practices over time is one of the main drivers of environmental degradation, especially through its impact on soil resources and the ecological system. Many agricultural practices result in alteration of soil attributes that lead to soil dysfunction and ultimately degradation of soil resources (Zalidis et al., 2002). Moreover, soil is an open system characterized by properties that are interconnected both within boundaries and functionally. Sustainability, while multidimensional, focuses on the quality of soil resources, the relationships between their use and management, and the environment (Larson and Pierce, 1994). Therefore, research on the impact of agricultural practices on soil environment should be included in environmental risk assessments. On the other hand, agriculture alters the natural cycle of nutrients in the soil. Intensive cultivation and harvesting of crops can negatively affect the ability of soils to supply nutrients to plants. Soil amendments, chemical fertilizers, and fungicides are usually required to maintain soil fertility for adequate crop yields. These factors directly affect soil properties and the environment. Therefore, agricultural management can determine the fate of soils and thus the sustainability of human society and the Earth system, because agriculture sets the pace of processes that contribute to the degradation of biodiversity and soil quality (Bruun et al., 2013; García-Díaz et al., 2017).

Viticulture is an important practice that plays a key economic activity in many regions worldwide. Especially, the significant role of viticulture in Europe is largely acknowledged (Fraga et al., 2012). Vineyards represent one of the most extensive of the agroecosystems which cover the southern sloped mountainous and hilly areas of temperate climate regions (Stanchi et al., 2013). The term ‘‘terroir’’, which is the combined effect of several local factors (such as local rocks, topography, climate, soil, and landscape), has a substantial role in determining the grape quality and wine sensory properties (Czigány et al., 2020; Ferretti, 2019; Qi et al., 2019). Vine growth is strongly affected by soils and the terroir effect. Wine organoleptic quality might vary considerably depending on soil chemical and physical properties (Stanchi et al., 2013). On the contrary, viticulture can exert an impact on soil characteristics such as pH, SOM, soil texture, and other soil chemical properties, particularly in the sloping vineyard. In addition, the impact of viticulture on erosion risk is exacerbated by improper management practises such as tillage, low organic matter content, biomass removal, and a limited percentage of soil cover (Prosdocimi et al., 2016). The amount of nutrients available to plants is closely related to the soil chemical properties. The mobility and availability of nutrients is influenced by soil pH (Dhaliwal et al., 2019). In addition, the soil pH reaction has also a significant impact on fertilization efficiency. Therefore, changes in soil pH should be taken into account in managing grapevine nutrition. The management practice in vineyards can cause soil acidification or alkalinization mostly due to different types of fertilizers, fungicides (elemental sulfur containing), and organic waste and manure applications. For example, ammonium-based fertilisers tend to be more acidifying, whereas nitrate based fertilisers tend to raise the soil pH. In general, farming practices are widely known to exert strong control over soil organic content because they affect both input and turnover rates of SOM. Most vineyard soils are considered as highly degraded in terms of loss of organic carbon as a result increasing erosion and diminution of nutrient contents (Coll et al., 2011; Martínez-Casasnovas and Concepción Ramos, 2009). Indeed, intensive viticulture without any erosion control practice reduces soil fertility and depletes SOM stocks. Soil erosion processes in vineyards, beyond surface runoff and sediment transport, have a strong effect on soil organic carbon loss and redistribution along the slope (Novara et al., 2018). Erosion can be considered one of the most widespread human induced causes of land degradation, impacting crop yields, threatening the soil system and raising ecological risks via the transport of pollutant-rich sediment particles. In addition, erosion leads to loss of nutrients, lower soil water holding capacity, decrease thickness of the soil layer that is most useful for plant growth, and reduction in soil fertility and biodiversity (García-Díaz et al., 2017). The use of fertilizers and passes by heavy machinery leads to noteworthy reductions in vineyard sustainability due to increases in soil pollution, soil compaction, and soil erosion rates (Cerdà et al., 2017).

Although soil erosion by water is a natural process generally in balance with natural soil formation due to weathering, human activities significantly increase the extent of soil erosion beyond the equilibrium level and cause various hazardous environmental effects. Soil organic matter content, which is closely related to soil quality and vegetation productivity, contributes to soil properties by improving soil structure and water retention, increasing cation exchange capacity, and providing nutrients to plants through mineralization (Bruun et al., 2013). Therefore, SOM loss probably leads to the leaching of fine soil particles which is rich in organic carbon.

Furthermore, soils are unstable and easily broken by slaking and mechanical disturbance (Martínez-Casasnovas and Concepción Ramos, 2009; Xiao et al., 2017). This exerts a negative influence on soil structure and erodibility. Indeed, cultivation on the sloping and poor soil fertility areas are highly susceptible to erosion with most precipitation lost as runoff and soil structure decline, then leads to a low resistance to erosion. For this reason, the application of organic waste or compost can be beneficial for soil conservation. Organic farming and cover crops claim to reduce disturbance intensity of agricultural practices on the environment, and enrich the soil with organic matter materials (Coll et al., 2011; Gattullo et al., 2020). Compost and organic material application can also improve the physical properties of a soil, such as soil porosity, structure and water holding capacity (Ouédraogo et al., 2001; Ramos and Martínez-Casasnovas, 2006). Organic viticulture started to spread at the end of the 20th century simultaneously with the development of contemporary analytical methods for analyzing food quality, research on food impact on human health and environmental awareness (Milićević et al., 2020). Organic farming is present in almost all of European countries, and the largest areas of organic vineyards are located in Italy, Spain, and France. Although the agrochemical application is strictly controlled and dosed by the guidelines of organic farming, environmental concerns have been raised over the years.

3.2. Accumulation of potentially toxic elements in vineyard soils

Agricultural activities with the long-term use of agrochemicals are known as a primary source of toxic elements and other pollutants in cultivated soils, generating permanent pollution of large areas (Chen et al., 2015; Li et al., 2015). Moreover, elements in soil exceeding the limit values can cause risk for crop growth, environment or humans, and can also exhibit toxicological characteristics and thus in this study, are named as potentially toxic elements (PTEs). Contamination of soil with PTEs is a major environmental issue at a global scale (Doumett et al., 2008; Rai et al., 2019). Potentially toxic elements, unlike organic chemicals (Pempkowiak, 1991) can accumulate and contaminate the soil environment for a long period of time that may also affect agricultural production in the long term. The accumulation of PTEs in agricultural soils and vineyard soils is probably not unexpected issue (He et al., 2004; Islam et al., 2015; Mirzaei et al., 2019; Ribolzi et al., 2002). Particularly, in the vineyards, soil pollution with PTEs from the continuous use of cupric fungicides and fertilizers is a predominant issue (Preston et al., 2016). The intensive use of fertilizers and copper-based fungicides has resulted in PTEs enrichment in the vineyard soils (Brunetto et al., 2016; Milićević et al., 2018; Mirzaei et al., 2019). With the long-term use of chemical fertilizers, fungicides, and organic byproducts, viticulture can exert a considerable risk of soil contamination that may also ultimately impact product quality (Mirzaei et al., 2019; Preston et al., 2016). In addition, the intensive application of copper-based fungicides in vineyards in Europe, mainly as Bordeaux mixture ($Ca(OH)_2 + CuSO_4$), since the end of the 19th century has resulted in a long-term accumulation of Cu in vineyard soils (especially in the upper layers) (Brunetto et al., 2016; Fernández-Calviño et al., 2008), reaching concentrations that are far higher as compared to the trace amounts that are required for healthy plant growth and, in some circumstances, even exceeding the limits imposed in the EU for agricultural soils (Komarek et al., 2010). Bordeaux mixture and, more recently, Cu oxychloride (Blitox, Coppesan), are used to prevent and treat fungal diseases such as downy mildew (*Plasmopara viticola*). Besides Cu-containing fungicidal and bactericidal sprays, substantial Cu addition to soils can occur from the addition of mineral- and organic-fertilizers, including organic residues (e.g. cattle manure and organic composts) (Brunetto et al., 2014; Xiaorong et al., 2007). Fertilizers supply non-negligible quantities of PTEs, such as Cu, Zn, and Ni, that are essential micronutrients for plant growth. Yet, their increased contents in the cultivated soils may reach toxicity thresholds, exceeding the optimal range for plants and soil microorganisms (Dhaliwal et al., 2019). The intensive use of fertilizers and copper-based fungicides have already induced superabundance of PTEs (such as Cu, Zn, Cd, Pb, Cr, Ni, Hg, and As) in many vineyard soils (Chen et al., 2015; Liang et al., 2015; Mirzaei et al., 2019). Therefore, with the long-term use of chemical fertilizers, fungicides, pesticides, and organic byproducts such as animal manure, viticulture can induce a considerable risk of soil pollution, particularly by PTEs. Potentially toxic elements enrichment in vineyard topsoils (Farsang, Barta 2004; Farsang et al., 2012) is of particular concern due to the repeated use of metal-based pesticides and fertilizers, especially through the accumulation of Cu and Zn (Brunetto et al., 2014, 2016; Komárek et al., 2010; Patinha et al., 2018). On the other hand, the distribution and mobility of PTEs with regard to soil profile at different soil depths should be taken into account. The downward movement of PTEs within the soil profile occurring in a prolonged period of time can result in their substantial redistribution and their available fraction in the subsoil (Antoniadis & Alloway, 2003; McBride, 1995; Richards et al., 1998; Torri & Corrêa, 2012), then pose a potential risk of toxicity to plants, especially in the rhizosphere area.

3.3. Impact of soil erosion on potentially toxic element distribution in sloping 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 (He et al., 2004; Ribolzi et al., 2002). In addition, the soil lost through erosion, especially in steep area such as sloping vineyards, has raised environmental concerns (Martínez-Casasnovas & Ramos, 2009; Koulouri & Giourga, 2007). The contamination by PTEs of neighbouring freshwater ecosystems is often inevitable due to leaching and wash-off (Brunetto et al., 2014; Mirlean et al., 2007; Patinha et al., 2018). Indeed, vineyards are primarily cultivated on steep slopes, and high Cu fluxes can be transported downslope and eventually off-site by surface runoff, in which metals are predominantly bound to soil particles (El Azzi et al., 2013; Babcsányi et al., 2016).

Throughout the world, soil water erosion on cultivated lands represents a severe threat to soil resources and has received much concern, due to both the increase of problems caused by the erosion itself and the significant environmental consequences (Fernández-Calviño et al., 2012; Prosdocimi et al., 2016; Quinton and Catt, 2007). Erosion has been also indicated as one of the major threats that affect agricultural soils (Biddoccu et al., 2016). Among the cultivated lands, vineyards located on steep slopes merit a particular attention. Vineyards use to reach the highest soil and water losses due to the lack of vegetation cover (Novara et al., 2011). Indeed, hilly vineyards are easily subject to soil erosion, depending not only on soil characteristics, climate, and slope, but also on the soil management system, and have the highest measured soil losses compared to rainfed cereals, olives, eucalyptus plantation, or scrubland (Biddoccu et al., 2016; Kosmas et al., 1997; Novara et al., 2011). Erosion leads to loss of nutrients, lower soil water holding capacity, decrease thickness of the soil layer that is most useful for plant growth, and reduction in soil fertility and biodiversity (García-Díaz et al., 2017). Topography is recognized to be one of the most significant factors affecting soil water erosion and the transport of sediments (Prosdocimi et al., 2016). Moreover, the amount of organic matter is closely related to the formation of aggregates which are a key factor in soil erodibility. Therefore, organic matter loss causes soil aggregates to break down easily and increases soil erodibility (Novara et al., 2011, 2018). The joint occurrence of hilly topography, low organic matter inputs, high rainfall intensities, and continuous tillage on bare soils enhances the soil water erosion processes. Moreover, the impact of vineyard cultivation on erosion risk is exacerbated by improper management such as soil tillage, low organic matter contents, biomass removal, and limited percentage of soil cover (Prosdocimi et al., 2016). Tillage or weed control with herbicides usually used in vineyards leave the bare soil exposed to rainfall and runoff during whole or part of the year (Biddoccu et al., 2020; Novara et al., 2011). As a result, in the sloping vineyard, soil erosion and agricultural practices drive the spatial distribution of macro-and micronutrients in the soil (Chevigny et al., 2014; Czigány et al., 2020). The spatial distribution of the fertilizer- and pesticide-derived PTEs in vineyard soils is also affected (Manaljav et al., 2021). Soil erosion and redeposition of PTE-rich sediment particles increase the risk of contamination of non-target environments (He et al., 2004; Ribolzi et al., 2002). Indeed, vineyard soils undergo wash-off during intense rainfall events, especially in steep areas, which may raise environmental and ecological concerns locally (in the soil) and off-site when reaching vulnerable aquatic environments (Martnez-Casasnovas & Ramos, 2006; Koulouri & Giourga, 2007). In vineyards subject to erosion, PTEs can be significantly relocated and accumulated in low-energy zones of the landscape. Therefore, in the sloping vineyard, soil erosion plays a key role in the transport of PTEs associated with sediment particles (Pham et al., 2021; Ribolzi et al., 2002), then exert an impact on their geochemical phase distribution in the vineyard soils and eroded sediments. The soil lost through erosion and the elevated concentration of PTEs in sediments can raise perilous environmental issues, explaining the predominant impact of PTEs export into the environment, especially for sloping areas (Martínez-Casasnovas & Ramos, 2006; Pham et al., 2021; Quinton and Catt, 2007). As the slope increases, the surface washout becomes the dominant factor, and the sediment transport is more intensive. The accumulation of PTEs in vineyard soils may increase their potential for export into the environment (Ribolzi et al., 2002). Hence, the impact of soil erosion on the distribution and transport of PTEs should be carefully examined and evaluated based on assessing both the total and the bioavailable PTE contents, and the geochemical distribution of PTEs in the soil and eroded sediments in vineyards. In some previous works related to the vineyard soil (Liang et al., 2015; Milićević et al., 2018; Mirlean et al., 2007; Mirzaei et al., 2019; Romíc et al., 2004), the PTEs selected in our work (Zn, Pb, Co, Ni, Cr, and Cu) were indicated as potential soil pollutants with ecological risk concerns. Nevertheless, most studies concerning PTE contamination and risk in vineyards are based on the analysis of total and available PTE content or on PTE fractionation of a small number of soil samples, obtaining only a scatter view of this issue. In addition, studies of PTE accumulation, distribution, and fractionation in vineyards with pH-contrasted soils and under different farming practices are scarce. Therefore, Zn, Pb, Co, Ni, Cr, and Cu, and such elements include Mn, Ba, and Sr, which are rarely studied, especially in the assessment of PTE-associated geochemical fractions, will be taken into account in my research in the soil and eroded sediment of two sloping vineyards of the Tokaj Nagy Hill, a part of the Tokaj-Hegyalja Wine Region (northeastern Hungary). In addition, examining the spatial distribution of the soil-bound PTE contents can allow for the identification of contamination hotspots within the sloping vineyards, potentially displaying hazardous concentration levels.

3.4. Copper accumulation in vineyards soils

In particular, Cu pollution in vineyard soils is a common challenge in conventional and organic farming as vine growers hardly have any efficient alternative to Cu substances for protecting plants against the occurrence of fungal diseases, including downy mildew (*Plasmopara viticola)* (Brunetto et al. 2016). Although Cu is an essential element for plants as playing key roles in several biochemical and physiological processes connected to plant growth and development (Yruela, 2005), Cu can exert toxic effects on plants, especially when its bioavailable concentration exceeds a standard limit (Ambrosini et al., 2015) leading to severely impaired their productivity (Brunetto et al., 2016). For instance, in acidic soils, Cu toxicity, besides affecting grapevine plants growth and productivity, can also worsen the quality and the nutritional value of the products (Brunetto et al., 2016; Komárek et al., 2010). The distribution of Cu between solid phase and soil solution depends on precipitation/dissolution, adsorption/desorption and redox reactions (Brunetto et al., 2016). In the soil solution, the complexation may occur with either inorganic anionic binders or organic molecules. Meanwhile, in the solid phase, Cu can be sorbed through mechanisms such as ion exchange (nonspecific adsorption), specific adsorption and complexation with soil organic matter (Alloway, 1995). Non-specific adsorption is weak and unstable. This type of adsorption weakly affects the availability of Cu. In this type of sorption, Cu can retain its internal hydration sphere and a high degree of rotational mobility on exchange sites (Brunetto et al., 2016). Copper-available fraction for plants strongly depends on mineral and organic forms in the soil and on biogeochemical cycles (Fernández-Calviño et al., 2008; Komárek et al., 2010). Due to the high affinity of Cu for soil colloids and especially SOM, Cu is rated a low-mobile element in near-neutral soils. In contrast, with more alkaline soils, while free Cu^{2+} solubility is exceedingly low, soluble complexes of Cu (hydroxy-, carbonate-, and OM-complexes) may form, thus increasing the total soil fraction of mobile Cu (Brunetto et al., 2016). A survey on 21 calcareous agricultural soils from Western Iran with a pH ranging from 6.8 to 7.9 showed that, on average, about 56% of Cu remained in the residual fraction after sequential extractions while about 20% was associated to SOM (Khanlari and Jalali, 2008). The (hydr)oxides or hydroxy-carbonates Cu-forms are the most abundant fractions of Cu in these conditions (McBride, 1995). Moreover, Fernandez-Calvino et al. (2009) investigated soils from 170 vineyards in Spain treated for long time with Cu-based fungicides (possessing a pH between 4.9 and 6.6) and found that Cu was present mainly in less mobile fractions, with about 48% bound to SOM, 15% associated to amorphous inorganic materials, 12% to crystalline Fe and Al oxides, and 23% as residual. The spread of high Cu contents in vineyard soils leads to a serious environmental issue due to their non-biodegradable nature and long-term biological half-lives (Fernandez-Calvino et al., 2009). The Cu contained in topsoils is susceptible both to water erosion and leaching down to deeper horizons (Ribolzi et al., 2002) and hence it can affect negatively aquatic organisms. On the other hand, Cu is rather stable in soils and its availability depends on the characteristics of the binder (particularly organic matter, Fe, Al, and Mn minerals and (hydr)oxides), carbonate content and soil pH (Brunetto et al., 2014; Fernandez-Calvino et al., 2009). Copper adsorption in soil occurs primarily in the most avid binding sites, especially SOM, and the remaining is redistributed into fractions that are held with less energy and that consequently exhibit a higher availability and mobility in the soil profile (Brunetto et al., 2016). With a survey on published references on over the world about the Cu accumulation in the vineyard upper soil layers, Komárek et al. (2010) revealed that Cu contents in superficial horizons can exceed 200 mg/kg and the highest Cu contents are present in the uppermost layers of soil profiles. These value exceed the warning and critical legislative limits valid in most countries around the world. For example, the pollution limit value of Cu content of 75 mg/kg for soils and sediments is figured in Hungarian standards (Joint Decree No. 6/2009, 2009). In a paper by Toth et al. (2016) on the concentration of heavy metals in agricultural soils of the European Union, a threshold of 100 mg/kg was indicated for Cu, with lower and higher guideline values set at 150 mg/kg and 200 mg/kg, respectively.

The presence of high Cu concentrations may adversely affect soil microorganisms, which are critical to the long-term sustainability of soil ecosystems because they control the decomposition of organic matter and thus the net fluxes and amounts of carbon and nutrients in the soil through decomposition, mineralization, and immobilization processes. Elevated metal concentrations in soils negatively affect the sustainability of agroecosystems. Earthworm populations are sensitive to tillage and Cu/Zn pesticide residues and are therefore useful and reliable bioindicators of agroecosystem stability in viticulture (Komárek et al., 2010). Belotti (1998) set the critical Cu concentration in soils (above which populations of several earthworm species are negatively affected) at 33 mg/kg, a level easily reached in most vineyards (Table 1).

Table 1. Copper concentration in upper layers of vineyard soils as published in literature

Country	Depth (cm)	mg Cu/kg	Method used	Reference
Spain	0 - 5	42 - 583	$HNO_3 + HCl + HF$	Fernández-Calviño et al. (2008a)
Spain	0 - 20	79 - 130	$HNO_3 + HCl + HF$	Fernández-Calviño et al. (2008b)
Spain	0 - 20	55 - 112	$HNO_3 + HCl + HF$	Fernández-Calviño et al. (2009)
France	0 - 25	55 - 115	$HClO_4 + HCl + HF$	Ribolzi et al. (2002)
Croatia	0 - 10	30 - 700	$HNO_3 + HCl$	Romić et al. (2004)
Brazil	0 - 5	37 - 3216	$HNO_3 + HClO_4 + HF$	Mirlean et al. (2007)
Iran	0 - 20	0.06 - 100	$HNO_3 + HClO_4 + HF$	Mirzaei et al. (2019)

The threshold for Cu concentrations at which changes in enzyme activities became apparent were 150-200 mg total Cu/kg and 60-80 mg bioavailable Cu/kg (Fernández-Calviño et al., 2010). However, in vineyard soils, Cu toxicity limits are not easily definable and, in principle, could be set at higher values than in other Cu-contaminated soils (Brunetto et al., 2016). For this reason, a deeper understanding of Cu dynamics in soil, particularly considering studies of Cu accumulation, distribution and fractionation can represent a prerequisite for the development of agronomic strategies aimed at limiting soil Cu-availability.

3.5. Enrichment characteristics, bioavailability, and geochemical distribution of potentially toxic elements in vineyard soils and eroded sediments

Potentially toxic elements in soils and sediments may exist in different chemical forms or ways of binding (Rauret, 1998). Therefore, 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 (Arenas-Lago et al., 2014; Fernández-Calviño et al., 2012; Rinklebe & Shaheen, 2014; Szolnoki and Farsang, 2013). Although total PTE content in the soil by itself does not provide enough information on the potential dangers and risks (Szolnoki and Farsang, 2013), by calculating PTE enrichment factor (EF), the prevailing natural or anthropogenic character of PTEs can be unveiled (Fernández-Calviño et al., 2012; Liao et al., 2017; Loska et al., 2004; Preston et al., 2016; Szolnoki and Farsang, 2013). The PTEs in the soils originate from natural (geogenic) sources based on the mineralogical and geochemical composition of parent material (lithogenic origin) and soil-forming processes (pedogenic origin) or can derive from various anthropogenic sources. The mobility and plant availability of PTEs depend on their origin, since plants do not readily take up lithogenic PTEs dominantly linked to primary minerals (Szolnoki et al., 2013). By contrast, anthropogenic PTEs are mostly very mobile and readily accessible by plants (Kabata-Pendias, 2004). Several studies suggested that PTE availability depends mostly on the soil environment, such as soil pH, soil texture, and SOM content (Alibrahim and Williams 2016; Takáč et al., 2009; Violante et al., 2010). Meanwhile, types of farming (conventional and organic agriculture) and the age of the vineyard can also be considered as dominant factors generating changes in pedological properties and PTE pollution status of the soil. Specific accumulation patterns and bioavailability of PTEs have been assessed in previous studies for evaluating the contamination level, the environmental pollution risk, and the toxicity of PTEs to crops in conventional vineyards (Borgese et al., 2013; Liu et al., 2005; Nunes et al., 2014; Sipos 2004; Violante et al., 2010). However, organic vineyards have been rarely targeted in those studies. Therefore, further research on PTEs and the associated ecological risk is also necessary to supply information on the sustainability of current organic farming practices in vineyards. The enrichment factor (EF) has been widely used to assess the enrichment of PTEs in soils and sediments, decipher their prevailing sources and prove the anthropogenic interferences with natural element cycles (Farsang et al., 2009; Preston et al., 2016; Reimann and Caritat, 2005; Szolnoki et al., 2013). Additionally, the EF is a useful tool to evaluate the enrichment or depletion of a given element relative to a reference material and to a reference element (Duplay et al., 2014). The use of a selected reference element (usually Al, Li, Sc, Ti, Zr, and Fe) is advisable to standardize the contents of the PTEs (Duplay et al., 2014; Preston et al., 2016; Reimann and Caritat, 2005; Szolnoki et al., 2013). The reference element is assumed to have negligible human sources. The enrichment of PTEs in the soil surface can be evaluated using EFs based on their contents in the upper soil layer and the reference soil horizon (Farsang et al., 2009). Moreover, the increased concentration of PTEs in the eroded sediments shows an obvious increase in the pollution level and the ecological and environmental risk of these elements due to soil erosion (Fernández-Calviño et al., 2012, 2008; Pham et al., 2021). Therefore, the PTE enrichment in the eroded sediment should be considered in comparison with the vineyard topsoil. Accordingly, the enrichment ratio (ER) is calculated by dividing the PTE content in the sediment by that in the topsoil of the vineyards (Boy & Ramos, 2002; Zhang et al., 2004; Farsang et al., 2012).

Potentially toxic elements are exhibited in different geochemical fractions, which also may significantly affect their behaviour in the soils and eroded sediments (Arenas-Lago et al., 2014). Different geochemical associations of PTEs present distinct effects on their mobility and bioavailability. In addition, to evaluate the ecotoxicological risks of PTEs in such materials, it is first of all necessary to predict the bioavailability of PTEs for the plants. Therefore, the bioavailability and geochemical fractionation of PTEs are appropriate factors to assess their potential mobility and polution level in soils and sediments. Investing of total PTE contents in soils represents the first measure of caution related to pollution and food safety control, while mobility and bioavailability of PTEs in soil-eroded sediment system should be a further step in understanding the toxicity of PTEs to crops, potentially ecological risk, their transportations, and it could also improve farming management practices. Research on mobility and bioavailability of PTEs in soils has attracted attention worldwide in the last few decades (Pelfrêne et al., 2012). Single extraction procedures are one-step extraction procedures, recommended for studying the mobility (Santos et al., 2010) and bioavailability of elements in soils (Milićević et al., 2018, 2020). The single extraction procedures most applied are simple procedures and those with Na_2-EDTA, NH_4NO_3, $CaCl_2$, and deionized H_2O as extractants (Milićević et al., 2018), giving information on the assessment of the labile elements in soils. According to the available literature, there are not many researches that compare all the mentioned single extraction procedures with pseudo-total digestion for assessing the bioavailability of PTEs in the soil. However, studies, which two or three single extraction procedures were compared, were performed. For example, aqua regia and Na_2-EDTA procedures were normally applied in studies for determining an environmental risk assessment, while 0.05 mol/l Na_2-EDTA procedure was presented in studies as an agent that by the complexation process simulate the uptake of available element fraction from the soil (Alibrahim & Williams, 2016). Weak salt solutions such as $CaCl_2$ and NH_4NO_3 probably can be used as extractants for elements presented in the exchangeable phase and the water-soluble phase (Pinto et al., 2015), and together with deionised H_2O as extractants, they were usually applied in soil–plant uptake studies. Meanwhile, $CaCl_2$ and NH_4NO_3 are determined as unbuffered mild extractants and can extract the exchangeable fraction of the elements (Antoniadis et al., 2017a; Pueyo et al., 2004). Aqua regia and 0.01 mol/l $CaCl_2$ also were used to determine soil fertility (Pueyo et al., 2004). In particular, Milićević et al. (2018) (in conventional vineyard), 2020 (in organic vineyard) assessed the bioavailability of PTEs in the vineyard soil for predicting their influence on plants and comparing to the pseudo-total PTE contents by simultaneously testing different single extraction procedures (CH_3COOH, Na_2-EDTA,, $CaCl_2$, NH_4NO_3 and deionised H_2O). Accordingly, the complexing agent, Na_2-EDTA,, point out as the most appropriate and selective extractant for extracting the elements from the vineyard soils (Al, As, Ca, Cd, Co, Cu, Fe, K, Mn, Pb, V, Sr and Zn). The chelating agent Na_2-EDTA, has proven to be effective in removing metal bound to Fe/Mn oxide surfaces isolating the elements with which it usually builds very stable complexes (Inczédy, 1976; and Lo & Yang, 1999).

On the other hand, using fractionation methods based on sequential extractions, the PTEs distribution in the soil can be clarified in order to study their availability and possible toxicity (Bacon and Davidson, 2008). For example, the acid-soluble (easily mobilizable) form is considered as most bioavailable; reducible bounded to Fe/Mn oxides and oxidizable bounded to SOM may be potentially bioavailable, while the residue bounded to the soil matrix is not phytoavailable (Ma and Rao, 1997; Rinklebe and Shaheen, 2014). Therefore, determining the geochemical fractions of PTEs is appropriate to assess their potential mobility and pollution status in soils, and it is a key issue in many environmental studies (Duplay et al., 2014; Merkx et al. 2013). Sequential extraction procedure has been commonly used for studying PTE mobility and availability in soils and is a better approach to determine the geochemical fractionation of the PTEs (Ma and Rao, 1997; Rinklebe and Shaheen, 2014). Sequential extraction procedures were developed and used to extract the geochemical fractions of PTEs in soil in order to assess the distribution, mobilization, retention, and bioavailability of these elements to plants and to groundwater (Arenas-Lago et al., 2014; Bacon & Davidson, 2008; Merkx et al., 2013; Rinklebe & Shaheen, 2014; Szolnoki & Farsang, 2013). The Standards, Measurements and Testing Programme (SM&T, formerly BCR) of the European Commission has been widely used in metal fractionation for both soil and sediment. However, the main problem of the analytical results is highly dependent on the extraction procedures used. As a result, the improved BCR three step sequential extraction procedure was designed by Rauret et al., 1999 and then provided an optimised procedure to improve this situation (Achiba et al., 2010; Davidson et al., 2006; Nemati et al., 2011; Szolnoki & Farsang, 2013). The sequential extraction used allows the potential mobility and bioavailability of PTEs in soils to be assessed. Therefore, evaluation of the potential mobility of PTEs in vineyard soils and eroded sediments using a three-step sequential extraction technique should be included in contamination risk assessments. In some previous works related to the vineyard soil (Milićević et al., 2018; Mirzaei et al., 2020; Ribolzi et al., 2002), the PTEs selected in our research (Zn, Pb, Co, Ni, Cr, and Cu) were studied as common potentially soil pollutants. Besides, such elements include Mn, Ba, and Sr, which are rarely studied, especially in the assessment of PTE-associated geochemical fractions, will be taken into account.

3.6. Ecological and human health risks of potentially toxic elements in vineyards

Potentially toxic elements are receiving increasing attention due to a better understanding of their toxicological significance for the ecosystem, agriculture, and human health (Farsang et al., 2009). In addition, vineyards located close to residential areas can exert a considerable health risk when the soils display high PTE content. Determination of PTEs in vineyard soils is of great importance because elevated levels of these elements can have environmental and health impacts (soil contamination, inhibition of plant growth, health risk to workers and residents, etc.). The accumulation of PTEs can have various effects, either directly threatening natural soil functions or indirectly threatening the biosphere through bioaccumulation and uptake into the food chain. In addition, the constant use of chemical fertilizers, pesticides and fungicides in vineyards has led to the accumulation of PTEs in the soils and eroded sediments, which is a major ecological and toxicological burden. It is important to note that health assessment usually quantifies risks to human health and does not consider wildlife (Mirzaei et al., 2019), whereas ecological risk of heavy metals indicates the potential risk of these metals to the entire ecosystem and represents the overall risk of environmental pollution (Islam et al., 2015). Therefore, calculating ecological and health risk indices can provide a more comprehensive view of environmental pollution. In recent years, ecological risks associated with the accumulation of PTEs have emerged and become a serious issue. Ecological risk of PTEs calculated based on contamination factors and biological toxicity factors has been widely used for soil and sediment contamination studies (Arfaeinia et al., 2019; Hakanson, 1980; Milićević et al., 2018; Mirzaei et al., 2019). On the other hand, PTEs can have serious health consequences (poisoning, respiratory illnesses, even carcinogenic diseases) for workers in the fields who are chronically exposed to these elements from the soil and directly during agrochemical spray treatments (Milićević et al., 2018). Potentially toxic elements in soil can also affect human health through inhalation of dust, ingestion of soil, or skin contact. There are several models that can be used to calculate human health risk assessment based on measured contaminant concentrations in soil samples. The risk assessment most commonly used in soil studies (Farsang et al., 2009; Li et al., 2015; Mirzaei et al., 2019; Rinklebe et al., 2019) is from USEPA guidance for human health risk assessments. In the study of the risk associated with PTEs, the quotient of health risk and average daily intake for oral intake was used.

4. Material and methods

4.1. Study area

The study sites are two vineyards, a 0.4 ha plot near Tállya and a 1.8 ha plot in the outskirts of Tokaj both located in the Tokaj-Hegyalja wine region (northeastern Hungary) (Fig 1A). The vineyards are situated at the hillslopes of the Tokaj Mountains. The interplay between the volcanic base rocks, the loess cover of variable thickness of the Tokaj Hill, the surrounding alluvial plains, as well as the landscape topography create the diversity of soils in the region (Lóczy, 2015; Nyizsalovszki and Fórián, 2007; Zelenka et al., 2012; Szepesi et al., 2018). The climate of the area is humid continental, characterized by cold winters and warm summers. The mean annual precipitation varies between 590 and 610 mm, with a clear maximum value (360 mm falls) in the summer months (Dövényi et al., 2010). The mean and the maximum rainfall intensity during the year of study (2019) were 1.3 mm/h and 27.8 mm/h. The mean annual temperature is 8.5 °C at the summit and reaches almost 10 °C at the base of the Tokaj Nagy Hill (Novák et al., 2014). Although the vineyards of Tállya and Tokaj belong both to the Tokaj-Hegyalja region, the soil-forming processes, soil characteristics, and cultural practices of the two sites considerably differ.

In Tállya, vineyard soils developed on rhyolit and rhyiolite tuff, fine-grained, extrusive igneous rocks. The andesite of the subvolcanic body in Tállya was intruded into loose pumiceous rhyolite tuff in two phases based on the observations of two kinds of pyroxene andesite (Zelenka et al., 2012). The vineyard's slope shape displays a slight curving at the upper part and sharply increasing steepness at the middle (Fig 1A). The mean slope of the plot is 18^{o}, and a marked inflection point is situated at the middle of the 146 m long slope. 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 backslope is the linear or transitional part of the slope between convex and concave (Fig 1A). Conventional grape growing was set up a long time ago (supposedly more than 100 years ago) in Tállya. The Bordeaux mixture was applied in 2019 (the year of study) in a dose of 2.5-3 kg/ha/year (in May, June, and July), representing a yearly Cu dose of 0.5-0.6 kg/ha. The Bordeaux mixture was complemented with a foliar micronutrient fertilizer application 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%). A synthetic insecticide (deltamethrin) was also sprayed in the vineyard.

The soil is regularly ploughed and no cover crops are sown in the vine inter-rows for soil protection.

The second site of study is situated at the southeastern foothill of the Tokaj Nagy Hill, the easternmost part of Hungary's inner Carpathian volcanic range (Lóczy, 2015). The late Miocene pyroxene dacite lava flows and subordinate pyroxene dacite tuffs, mainly represented by the Amadévár Andesite and Tarcal Dacite Formations (Novák et al., 2014; Zelenka et al., 2004), constitute the primary parent materials with geochemical characteristics typical of subduction- related magmas (Harangi and Lenkey, 2007). The Tokaj Nagy Hill is surrounded by alluvial plains formed from the deposits of the Bodrog, Tisza, and Takta rivers. Its andesite cone is mantled by loess deposits with a downslope increasing thickness (ranging from a few centimeters to 20 meters), except for the summit zone (Kerényi, 1994; Lóczy, 2015; Novák et al., 2014). The vineyards surrounding Tokaj are situated mainly on these loess deposits. The soil in the vineyard is a Calcaric Regosol (Siltic, Ochric) according to the World Reference Base for Soil Resources (2014). The soil in the vineyard is weakly developed due to the intense soil erosion that prevents the formation of apparent diagnostic horizons. The mean slope of the plot is 8°, and the investigated slope section is of 270 m in length. Before its replantation in 1993, no viticulture was practised at the site from the 1950s. A mixture of grass and herbaceous plants cover the vine inter-rows for limiting soil erosion. The soil is tilled (0-20 cm) biannually in the inter-rows to reduce soil compaction and increase their infiltration capacity; meanwhile, tillage is done twice a year underneath the vine rows. Mowing is used to control weed and no herbicides are used. The vineyard is managed according to the guidelines of organic farming. The local farmers used in the past fresh cattle manure to fertilize vineyards at a dose of 0.3t/ha every 3 - 4 years. However, for the last 10 years, cattle manure pellets have replaced fresh manure. To protect grape plants, Cu-based fungicides are repeatedly used in a typical dose of 4 kg/ha/year (metallic Cu), supplemented with sulfur-containing pesticides and foliar fertilizers containing macro- and micronutrients. We suppose that most of the Cu-pesticide applications have taken place over the past 28 years since replanting the vineyard in 1993. In addition, there is a nearby open-pit quarry (Binét quarry) in the research area situated at ~500 m from the experimental site (Fig 1D). The dacite stone quarry was abandoned in the 1980s. The waste soil, rock, and dust in mining processes can be reached and stored in surrounding areas after removal, resulting in significant levels of potentially toxic substances nearby the open-pit quarry.

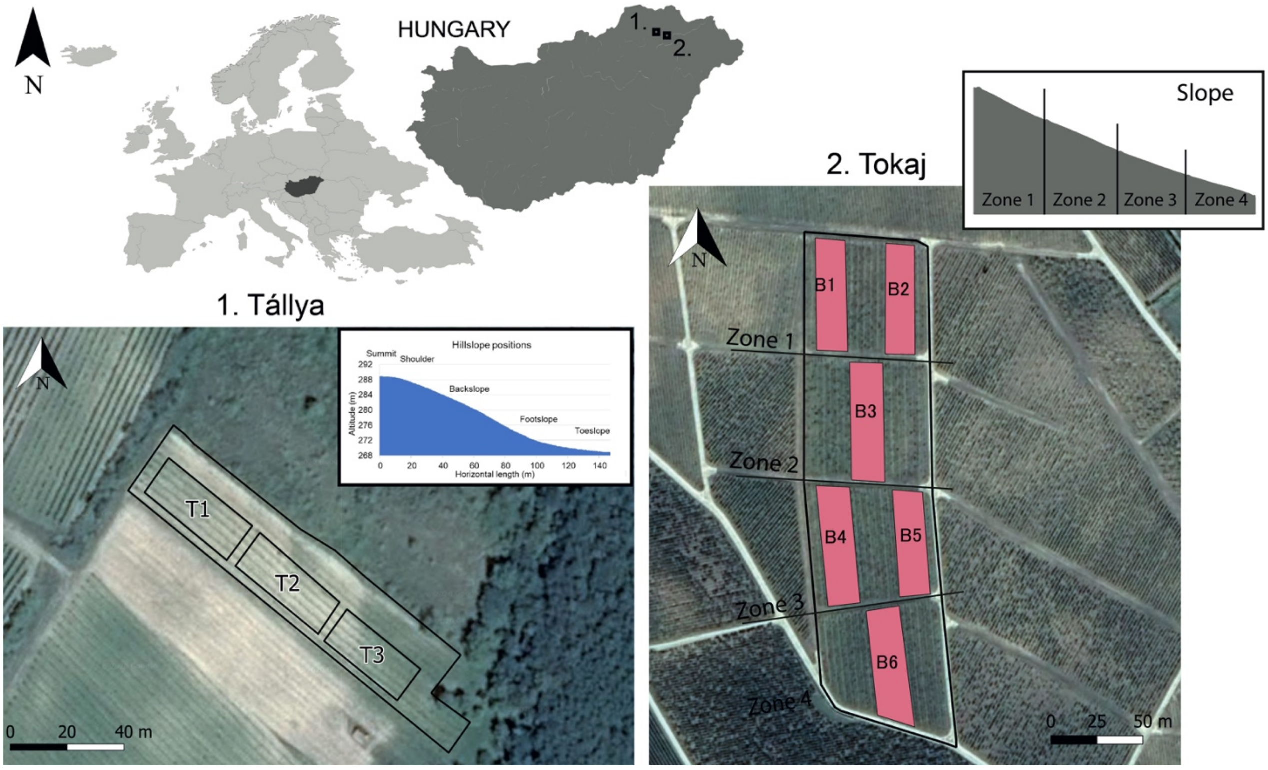

Fig 1A. Location of the two study vineyards: 1) Tállya, 2) Tokaj, both situated in the winegrowing region of Tokaj-Hegyalja (NE Hungary), the slope profiles of each site are also displayed. Sampling zones for composite sampling are marked with rectangles and are named T1-T3 for Tállya and B1-B6 for Tokaj

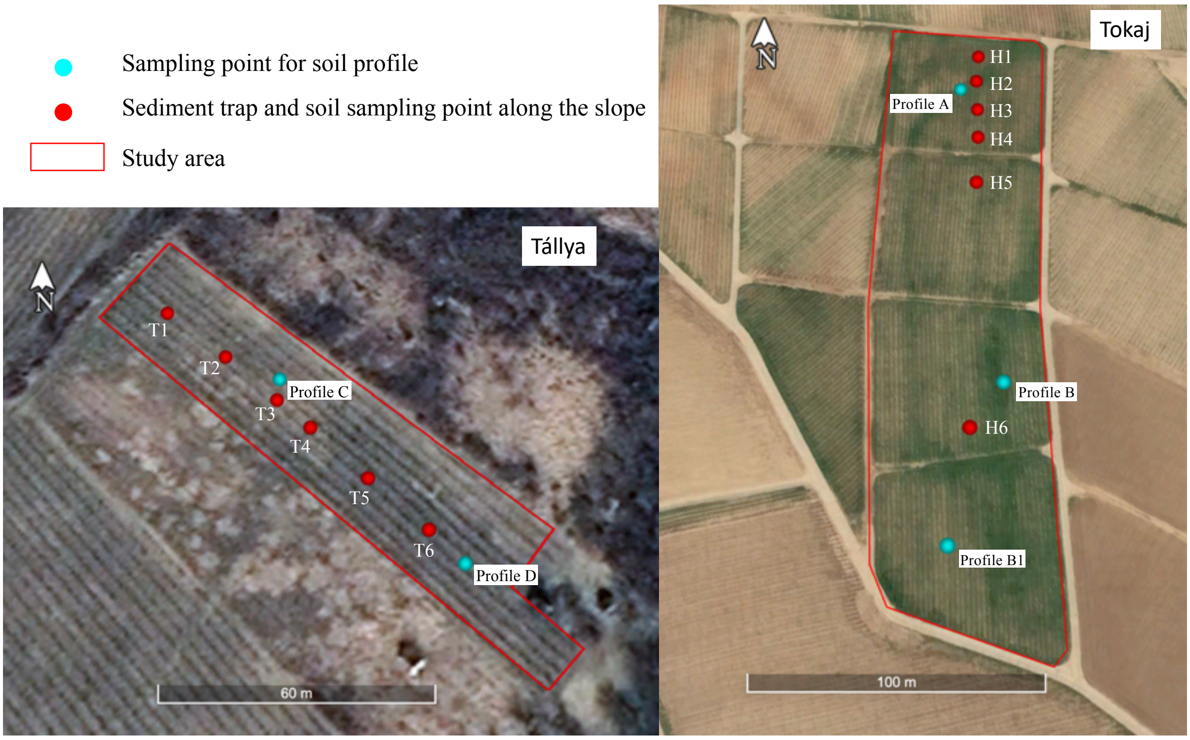

Fig 1B. Location of the soil profiles; and the position of sediment traps and soil sampling along the main slope

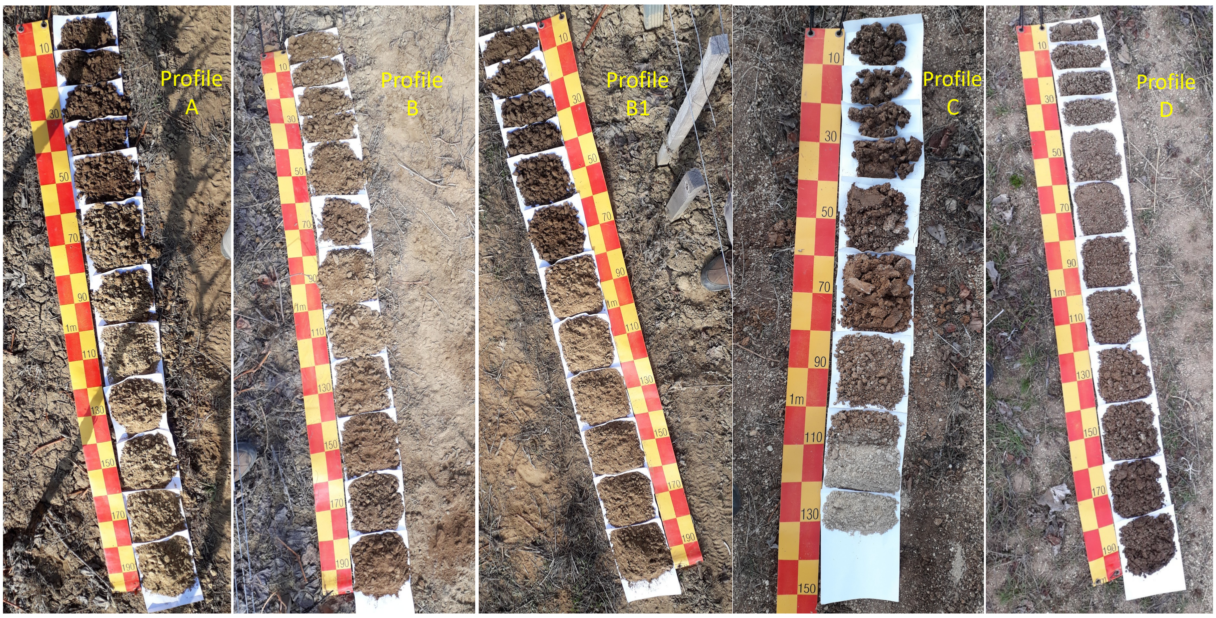

Fig 1C. The soil profiles: in Tokaj: profile A, B, and B1; in Tállya: profile C and D

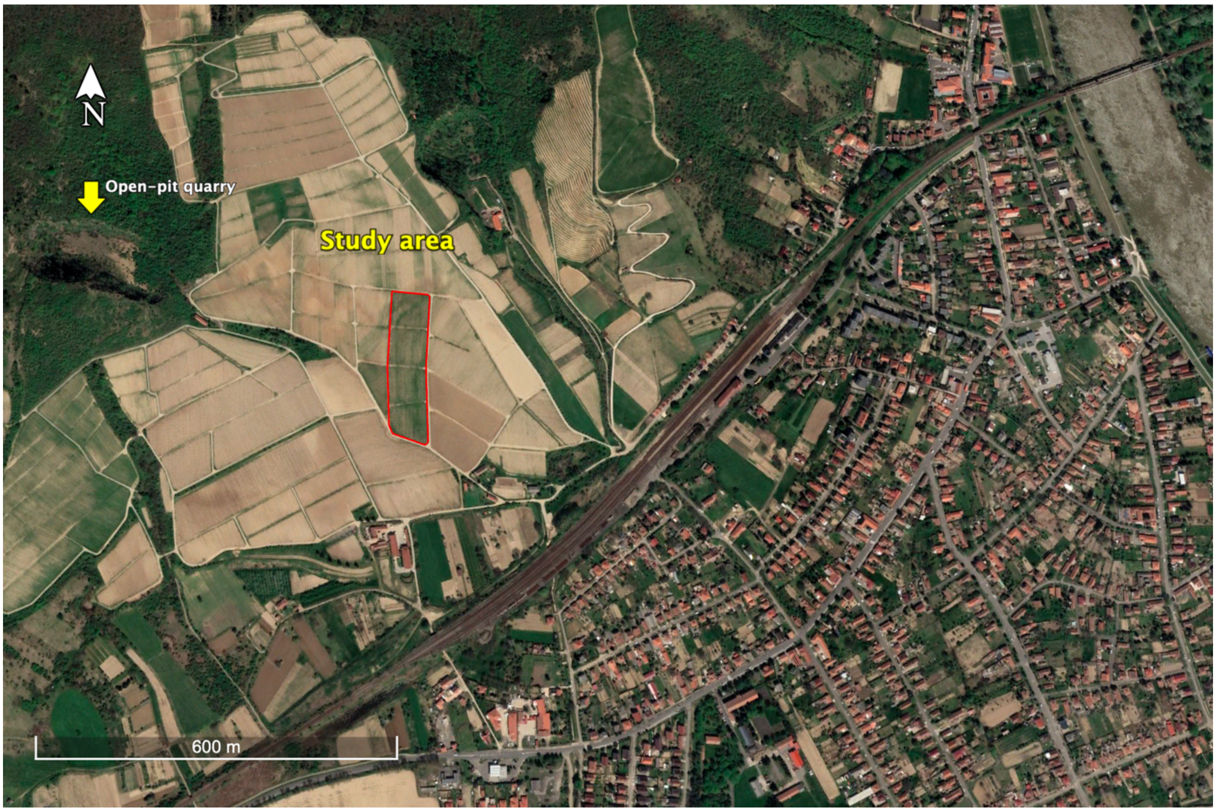

Fig 1D. The location of the study plot in Tokaj with the nearby residential area and the nearby open-pit quarry

4.2. Soil and sediment sampling

Composite topsoil samples (< 20 cm layers: 0-10 cm and 10-20 cm) were collected from the studied vineyards in March 2019 (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 (Fig 1A) with the help of a hand auger. The study plot in Tállya consists of nine grapevine rows. Composite samples were taken from three sampling zones (of ~ 1500 m^2) (Fig 1A). Two subsoil samples were collected from the 120-130 cm depth and the 180-200 cm depth considered respectively as the reference soils for sampling zones 1-2 and 3. Pathways separate the study plot in Tokaj into four zones perpendicular to the main slope, whose primary role is surface drainage and erosion control. Composite soil samples were collected from six sampling zones chosen by a zig-zag method. Each zone includes ten rows of vine plants and has an approximate area of 1200 m^2. Subsoil samples collected from boreholes at 180-200 cm depth are considered reference soils, suggesting that negligible quantities of agrochemical-derived PTEs reach those layers. 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 in Tállya (profile C and D) and 3 in Tokaj (profile A, B, and B1)) representing vineyard soils along the hillslope (Fig 1B, 1C), 35 soil samples were collected. In each profile, except for profile C (0-130 cm), 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). The soil in the vineyard is weakly developed due to the intense soil erosion that prevents the formation of apparent diagnostic horizons.

At the same time, sediment traps were deployed along the main slope for both vineyards (Fig 1B). Then, in May 2019, twelve eroded sediment samples from the traps were collected along with twelve topsoil samples (0-20 cm) near each trap (Fig 1B). During the sample collection period (one week), the average precipitation depth was 2.58 mm per rainfall event; the mean rainfall intensity was 1.55 mm/h and the maximum intensity was 5.5 mm/h. The total rainfall depth was 15.5 mm. Rainfall data are continuously recorded on-site within the area of the Hétszőlő vineyard using a rain gauge set up (Type BCU LITE2, Boeras Ltd., Hungary).

4.3. Sample treatment and 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 (SOM) were analyzed following Hungarian Standards (MSZ 21470–52, 1983; MSZ-08-0206-2, 1978; MSZ-08-0205, 1978). The soil pH was measured in deionized water with a soil/water ratio of 1:2.5 using a digital pH meter (Inolab pH 720) (MSZ-08-0206-2, 1978) (±0.05). 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 (Bojar et al., 2020). The determination of the soil texture based on the plasticity index values according to Arany (Arany Plasticity Index) was performed in accordance with the Hungarian Standard (MSZ-08-0205, 1978) (Table 2). Briefly, this index is calculated from the amount (cm^3) of deionized water added to an air-dry soil sample (100 g) until reaching the upper limit of its plasticity (Pham et al., 2021; Szolnoki and Farsang, 2013). The particle size distribution was determined by the pipette method following treatment with 0.1 M sodium pyrophosphate (MSZ-08-0205: 1978). After that, the soil texture is classified according to the United States Department of Agriculture (USDA) standard. 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 (Thermo Electron Corporation) in saturated soil samples (±10). The SOM content was determined by a UV-VIS spectrophotometer (a type Spectronic Helios-γ, Thermo Fisher Scientific), following H_2SO_4 -aided oxidation of the organic matter with 0.33 M $K_2Cr_2O_7$ (MSZ-21470-52, 1983) (±2%).

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. Then, approximately 0.5 g of oven-dried (at 105°C) sample material was precisely weighed into a PFA vessel, and 7 ml aqua regia (HNO_3/HCl=1:3) was added. All sample containers (tubes, vessels, volumetric flasks, etc.) were acid-washed and clean acids were applied (Normatom® for trace metal analysis, VWR Chemicals) for sample digestion and multi-element standard dilution. Samples were digested in a microwave oven (Anton Paar Multiwave 3000), as described elsewhere (Szolnoki and Farsang, 2013). Element concentrations in digested samples were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 7000 DV, PerkinElmer) (±10% uncertainty), using yttrium as an internal standard. For quality control purposes, a commercially available certified reference material (ERM®-CC141, a loam soil) was digested following the aforementioned method. The recoveries were consistent with the certified values, with the recovery percentages of: 92±2% (Zn), 87±1% (Pb), 88±0.2% (Co), 117±2% (Ni), 102±2% (Mn), 116±2% (Cr), and 104±3% (Cu). The procedural blank, and laboratory reference materials for soils were regularly checked. The sample treatment and PTE analyses were done in a laboratory accredited by the National Accreditation Body of Hungary (a member of the European Accreditation). For quality insurance, the laboratory regularly participates in interlaboratory comparisons.

Single extraction procedures are recommended for studying the mobile and bioavailable proportions of elements in soils (Milićević et al., 2018, 2020). The chelating agent Na_2EDTA has proven to be effective in isolating the elements with which it usually builds very stable complexes (Milićević et al., 2018). The 0.05 M Na_2-EDTA was presented in studies as an agent that simulates the uptake of available elements in various soils (Alibrahim & Williams, 2016). In the present study, the bioavailability of target PTEs (Zn, Pb, Co, Ni, Cr, Cu) was also determined by that agent (0.05 M Na_2-EDTA partially neutralized with NH_4^+) as described by Carter & Gregorich, 2007. For that, 1.0 g of soil was weighed in a 50 ml centrifuge tube and 25 ml of purified 0.05 M Na_2-EDTA was added. All centrifuge tubes and labware were acid-washed and rinsed with purified 0.05 M Na_2-EDTA followed by a complete ultrapure water rinse. Samples were shaken on an end-over-end shaker (Stuart SP3 Rotator) (at 15 rpm for 1 hour), centrifuged (at 2500 *g* for 20 min), filtered (at 0.45 µm), and then kept at 4^0C until ICP analysis. Prior to determining bioavailable PTE concentrations by ICP-OES, all samples were diluted 20-times with ultrapure water. Calibration standards were prepared in the same matrix as the diluted extract solution.

Table 2. Texture categories according to the Arany plasticity index, a measure of soil texture according to a standard method (MSZ-08-0205 1978)

Soil texture class	Arany Plasticity Index (ml d.w./100 g soil)
Coarse sand	<25
Sand	25-30
Sandy loam	30-38
Loam	38-42
Clayey loam	42-50
Clay	50-60
Heavy clay	>60

Modified Community Bureau of Reference (BCR) sequential extraction

Soil and sediment samples were extracted by the improved version of the BCR three-step sequential extraction procedure proposed by Rauret et al., 1999. The contents of target PTEs (Zn, Pb, Co, Ni, Ba, Mn, Cr, Cu, and Sr) in the extracts were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 7000 DV, PerkinElmer) (±10% uncertainty). All centrifuge tubes and labware were acid-washed (overnight) and then rinsed by ultrapure water before use. In the procedure, 1 g of sample material is placed into a 50 ml tube, exposed to reagents and shaken. The extractions were performed by shaking on an end-over-end shaker (Stuart SP3 Rotator), at a speed of 30 rpm and a room temperature of 22 ± 5^{0}C. The extraction steps were described below:

Step 1 - *Acid-soluble fraction* (F1)*:* 40 ml of acetic acid (0.11 mol/l) is added to 1g of sample material in a 50 ml centrifuge tube. Then the tube is shaken for 16 h at room temperature (overnight). The extract is separated from the solid residue by centrifugation at 2500 *g* for 25 min, filtered (at 0.45 μm), decanted the supernatant liquid in polyethylene container, and afterward kept at 4^{0}C prior to ICP analysis. The solid residue is washed by shaking with 20ml of distilled water for 15 min on the end-over-end shaker at a speed of 30 rpm and then centrifuged for 25 min at 2500 *g*, discarding the supernatant.

Step 2 - *Reducible fraction* (F2)*:* residue from step 1 is extracted with 40 ml of fresh 0.5 mol/l hydroxylamine hydrochloride solution (acidified to pH 1.5 with HNO_3) which is prepared on the same day the extraction is performed. The extraction procedure and the separation the extract from the solid residue are the same as described in step 1. Then wash the residue by adding 20ml of distilled water, shaking for 15 min on the end-over-end shaker at a speed of 30 rpm, centrifuging for 25 min at 2500 *g*, and discarding the supernatant.

Step 3 - *Oxidisable fraction* (F3): 10 ml of 8.8 mol/l hydrogen peroxide is added to the residue from step 2 in the centrifuge tube. The sample is digested for 1 hr at room temperature with occasional manual shaking, and continue the digestion for 1 hr at 85±2°C in a water-bath, then the volume of extract solution is reduced to less than 3 ml by further heating. Afterwards, an additional 10 ml of hydrogen peroxide is added to the moist residue, and digestion was continued for 1 hr at 85±2°C in a water bath, and then the volume is reduced to about 1 ml by continuing the heating. Finally, add 50 ml of 1 mol/l ammonium acetate solution (acidified to pH 2 with HNO_3) to the cool moist residue and shake on an end-over-end shaker for 16 hr (overnight). The extraction procedure and the separation are then repeated as described in step 1.

Residual (F4) is determined by aqua regia. Then, 0.5 g sample is weighed into a PFA vessel and 7 ml aqua regia (HNO_3/HCl=1:3) was added. Samples are digested in a microwave oven (Anton Paar Multiwave 3000) as described above for the PTE content determination. Concentrations of PTEs in digested samples are determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) as above, using yttrium as an internal standard.

4.4. 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 (Cheng et al., 2018; Farsang et al., 2009; Preston et al., 2016; Reimann and Caritat, 2005; Szolnoki et al., 2013). In this 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. The most common reference elements used in similar studies are Fe, Al, Ti, Li, Sc, and Zr (Duplay et al., 2014; Liu et al., 2005; Loska et al., 2004; Preston et al., 2016; Reimann and Caritat, 2005; Szolnoki et al., 2013). 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).

Potentially toxic elements are not considered enriched in the topsoil when EF values are around 1 or slightly below 1. In contrast, EFs greater than 1 indicate that PTEs are enriched in the soil surface either from geogenic or anthropogenic sources. EF values higher than 2 usually imply non-negligible anthropogenic input of PTEs into the soil (Facchinelli et al., 2001; Szolnoki et al., 2013).

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 were used (Farsang et al., 2012; Farsang and Barta, 2004; Fernández-Calviño et al., 2012) as follows:

$$ER = \frac{E_{sed}}{E_{soil}}$$

where $[E]_{sed}$ is the concentration of PTE in the eroded sediment and $[E]_{soil}$ is is the concentration of PTE in the topsoil.

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 (Antoniadis et al., 2017a, b; Mirzaei et al., 2019; Rinklebe et al., 2019). 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:

$$Cf = \frac{C_s}{C_{RefS}} \quad (1)$$

(Antoniadis et al., 2017a, b; Rinklebe et al., 2019)

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 (Hakanson, 1980; Islam et al., 2015): 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 (Islam et al., 2015; Mirzaei et al., 2019) following the equation 2:

$$\mathrm{PLI} = \sqrt[n]{\mathrm{Cf}_1 \times \mathrm{Cf}_2 \times \mathrm{Cf}_3 \times \ldots \times \mathrm{Cf}_n} \quad (2)$$

where Cf_l to Cf_n are the contamination factors of the first to the nth PTE in the vineyard soil/ sediment. The degree of contamination based on the PLI is described in 5 levels (Mirzaei et al., 2019): 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 ($3 < PLI$).

4.5. Ecological risk assessment

Hakanson (1980) first used the ecological risk factor to evaluate the ecological risk of pollutants in sediments. Thereafter, authors have widely included these indices in their studies investigating the environmental consequences of soil contamination (Arfaeinia et al., 2019; Islam et al., 2015; Mirzaei et al., 2019). 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:

$$\mathrm{Ei} = \mathrm{Cf_i} \times \mathrm{T_i} \tag{3}$$

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 in Luo et al., 2007, standard response coefficients (T_i) for the toxicity of the target PTEs are: Zn = 1, Pb = Co = Cu = 5, Ni = 6, and Cr = 2. These values were also used in my research.

The ecological risk index (ERI) is estimated according to Eq. 4 to evaluate the overall ecological risk of all studied PTEs (Islam et al., 2015; Mirzaei et al., 2020).

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

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

The ecological risk is grouped into 5 categories for the Eis and 4 for the ERI values (Chen et al., 2015; Islam et al., 2015; Liu et al., 2014):

$Ei < 40$: 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

4.6. 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 (Fig 1D). 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. Reference doses of PTEs were taken from the literature (Chen et al., 2015; Kamunda et al., 2016; Mirzaei et al., 2019; Rinklebe, et al. 2019). The RfD is the potentially toxic element dose, defined as the maximum allowable level of an element that will not pose any harmful effects on human health. Average daily intake (mg element/kg bodyweight/day) was calculated as follows (USEPA, 2001):

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

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:

$$\mathrm{HQ} = \mathrm{ADI/RfD}$$

where RfD is the oral reference dose 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 (Chen et al., 2015; Mirzaei et al, 2019; Rinklebe et al., 2019), and Co = 0.02 (Kamunda et al., 2016).

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

$$\mathrm{HI} = \sum \mathrm{HQ}$$

When the values of HQ and HI are higher than 1, an apparent probability of the occurrence of adverse health effects is indicated (USEPA, 2001), and HI < 1 shows that exposed persons are unlikely to experience dangerous health effects (Liang et al., 2015; Mirzaei et al., 2019).

4.7. 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.

5. Results and discussion

5.1. Soil properties of the studied vineyards

Table 3 summarizes data about the measured soil properties based on composite samples, such as soil pH (d.w), soil texture, salt content, carbonate, and soil organic matter (SOM) contents. According to the Arany Plasticity Index, topsoils in Tállya display a loam to sandy loam texture without any marked difference between the 0-10 cm and the 10-20 cm layers. The predominant soil texture in Tokaj is also sandy loam, only with a slightly lighter character compared to Tállya. Stone fragments are one of Tállya's soils' significant components and appear in a higher proportion at the middle section of the main slope. The top 0-10 cm soil layer contains an average of 48% of coarse fractions (>2 mm), and the underlying 10-20 cm layer displays 53%. Vineyard topsoils in Tállya are slightly acidic, with pH ranging from 6.12 to 6.67, while, in Tokaj, the soil pH is moderately alkaline (ranging from 7.96 to 8.10). In Tállya, the soil is poor in carbonates ($CaCO_3$). The generally higher carbonate contents characterizing the soil in Tokaj (varying from 1.65% to 6.26%) explain their moderately alkaline character and originate from loess parent material. The highest SOM content in Tállya is detected at the upper part of the hillslope (1.95%), which then decreases to 1.04% at the backslope zone. The re-raising SOM at the footslope suggests that the organic matter is transported downslope from the backslope zone. Signs of intense erosion at the backslope, such as the high coarse fraction and low SOM, clearly explain the uneven distribution of soil components. Likewise, in Tokaj, the redeposition of SOM-enrich material is observed from the zone 2 (1.26%) to zone 4 (1.46%), while the highest SOM content is examined at the top zone (zone 1) (1.67%). Generally, the downslope accumulation of organic matter can be indicated. There is no marked difference in the soil texture between topsoil samples along the hillslope. Therefore, the slope gradient may explain the high SOM content at the uppermost part of the studied vineyard. The main erosion-impacted part of the hill is situated at the zone 2, where the slope increases significantly.

The local forest soils in the two studied sites display a clayey loam texture (according to the Arany Plasticity Index). The observed difference in the soil texture between the vineyards and the forest soils can be explained by intense farming leading to serious soil erosion in the vineyards. Meanwhile, in Tállya, the topsoil in the local forest has a more pronounced acidic character (0-10 cm soil layer: 4.66 and 10-20 com soil layer: 4.70) compared to the vineyard topsoil.

Table 3. Basic soil parameters: Arany Plasticity Index (API) (-), total salt content (%), $pH_{d.w}$ (-), $CaCO_3$ (%), soil organic matter (SOM) content (%), major element contents and mineral composition determined in the topsoil and sediment samples collected from the studied vineyards in Tállya and Tokaj

		API	Salt (%)	pH (d.w)	$CaCO_3$ (%)	SOM (%)	Al*	Fe*	Mn***	Mg**	K**	Ca**
Tállya												
Vineyard	Mean	37	0.02	6.36	3.15	1.26	2.9	1.7	310	326	489	310
	Median	37	0.02	6.29	3.15	1.11	3.2	2.0	275	375	514	312
	Min	36	0.02	6.12	2.94	0.88	1.9	1.1	199	214	349	264
	Max	39	0.03	6.67	3.36	1.95	3.6	2.2	471	392	572	357
	SD	2	0.01	0.24	0.23	0.39	0.8	0.5	113	86	88	42
Local forest◆	1	48	0.01	4.66	3.78	8.01	1.7	0.9	533	121	186	132
	2	43	0.01	4.70	2.52	5.87	1.9	1.0	314	151	203	91
Sediment		-	-	-	1.60± 0.19	2.79± 0.70	-	-	-	-	-	-
Tokaj												
Vineyard	Mean	35	0.02	8.03	4.35	1.36	2.1	2.4	504	732	440	1654
	Median	35	0.02	8.02	4.98	1.40	2.1	2.4	503	750	440	1842
	Min	34	0.01	7.96	1.65	1.00	1.8	2.3	476	671	294	190
	Max	37	0.02	8.10	6.26	1.67	2.5	2.5	538	793	552	2097
	SD	1	0.00	0.04	1.46	0.20	0.2	0.1	14	47	65	498
Local forest◆	1	44	0.02	7.60	2.89	3.34	1.9	2.1	420	586	340	1244
	2	42	0.02	7.74	2.06	2.74	2.1	2.0	416	629	412	1594
Sediment		-	-	-	4.93± 0.72	3.14± 0.23	-	-	-	-	-	-

Mineral composition	Main components	Additional components
Tokaj		
B1 (0-10 cm)	q (60–70%), 10A (10–20%)	14A (5–10%), ab (5–10%), dol (ny), cal (ny), goe (ny), amp (ny), sm (ny)
B5 (0-10 cm)	q (60–70%), 10A (10–20%)	14A (5–10%), ab (5–10%), dol (ny), cal (ny), sm (ny)
B6 (0-10 cm)	q (~50%), 10A (30–40%)	14A (5–10%), ab (5–10%), dol (ny), cal (ny), kfp (ny)
H2 (soil)	q (~50%), 10A (20–30%)	14A (5–10%), ab (5–10%), dol (ny), cal (ny)
H6 (soil)	q (50–60%), 10A (~30%)	14A (5–10%), ab (ny), dol (ny), cal (ny), amp (ny)
H5 (sediment)	10A (40–50%), q (30–40%)	14A (~10%), ab (ny), dol (ny), cal (ny), kfp (ny)

Mineral composition	Main components	Additional components
Tállya		
T1 (0-10 cm)	q (50–60%), kfp (~30%)	10A (5–10%), 14A (ny), ab (ny), sm (ny), dol (ny), cal (ny), 7A (ny)
T2 (0-10 cm)	q (50–60%), kfp (~10%), ab (~10%)	10A (ny), sm (ny), dol (ny), cal (ny), 7A (ny)
T3 (0-10 cm)	q (50–60%), kfp (~10%), ab (~10%)	10A (ny), sm (ny), dol (ny), cal (ny)
T5 (soil)	q (50–60%), 10A (10–20%)	kfp (5–10%), ab (5–10%), 7A (ny), sm (ny)
T3 (sediment)	q (60–70%), ab (~10%)	10A (5–10%), 7A (ny), kfp (ny), sm (ny)

** Units are in weight percent (wt%), ** Units are in mg/100 g, *** Units are in mg/kg*
◆ Local forest: 1: 0-10 cm soil layer; 2: 10-20 cm soil layer

Abbreviations for mineral composition: q: quartz; 10A: 10Å-phase (illite/muscovite); 14A: 14Å-phase (chlorite/vermiculite); 7A: 7Å-phase (kaolinite); ab: albite; dol: dolomite; cal: calcite; amp: amphibole; kfp: potassic feldspars; sm: smectite; goe: goethite; ny: trace quantities

Vineyard topsoils in Tokaj are characterized by a moderately alkaline, while a shift towards neutral pH values can be observed in the local forest soils (0-10 cm soil layer: 7.60 and 10-20 cm soil layer: 7.74). The vineyard soil in Tállya displays an average increase of 1.6 unit in soil pH, whereas in Tokaj the difference is merely under 0.5 unit. The observed shift towards higher pH values in the cultivated soils can be explained by the presumed more intense leaching of base cations (Ca, Mg, K) in the forest topsoil (De Vries et al., 2021). Previous studies showed higher organic acid production in forest soils due to incomplete and slower mineralisation of the SOM (and high input of organic materials) leading to soil acidification (Moslehi et al., 2019). The local forest soils (uncultivated soils) have a high SOM content in Tállya: 8.01% in the 0-10 cm and 5.87% in the 10-20 cm layers, while the vineyard topsoil displays a low SOM content (<2%) that further decreases with depth. Similarly, in Tokaj, the SOM content of the local forest soil is slightly higher compared to the vineyard topsoil (0-10 cm soil layer: 3.34%; 10-20 cm soil layer: 2.74%) (Table 3). Overall, the relatively greater decrease in the SOM content at the vineyard in Tállya compared to Tokaj reveals that intensive viticulture without any erosion control practice, reduces soil fertility and depletes SOM stocks. However, the organic and an environmentally sounder farming could somewhat reduce the SOM decline in Tokaj by implementing erosion control, such as landscaping measures and cover crops, and using organic fertilizers.

The statistics of measured characteristics of the soil profiles (0-200 cm, with five examined soil layers) in the two studied vineyards such as pH, particle size distribution (PSD), carbonate and SOM contents are presented in Table 4. The vineyards display contrasted soils in the two studied vineyard. In general, soil properties in both vineyards did not differ significantly between the top- and subsoil layers, except for SOM content and particle size distribution. In general, a decrease in SOM content is observed along the soil profile from the soil surface to the deepest sampling layer (180-200 cm).

The soil texture of both top- and subsoil in the vineyard in Tokaj is silt loam according to the PSD, with a high silt content in the whole soil profile (more than 60%) characteristic of loess soils (Table 4). Soils in Tállya are characterized by a higher clay content compared to those in Tokaj. Vineyard soils in Tállya display a clayey to sandy loam texture with a finer soil texture indicated in the upper part of the hillslope. In Tokaj, the mineral composition of soil showed a homogeneous in the soil samples. Accordingly, quartz was the main mineral composing the vineyard soil (50-70%), followed by illite/muscovite (10A) (20-40%) and chlorite/vermiculite (14A) (5-10%) phyllosilicates, with minor quantities of albite, dolomite, calcite, and potassic feldspars (Table 3). In Tállya, the vineyard soil displayed differences in the chemical composition of the mineral between the soil samples taken in the top and bottom of the hillslope (Table 3B). On the upper slope, quartz (50-60%) and potassium feldspars (~30%) were the main minerals found in the soils, along with illite/muscovite (10A) (5-10%) and a small amount of chlorite/vermiculite (14A), albite, smectite, dolomite, and kaolinite. Meanwhile, on the lower slope, the soil contained quartz (50-60%), illite/muscovite (10A) (10-20%), albite (~10%), and potassium feldspars (~10%), with minor quantities of kaolinite.

Table 4. Soil parameters for topsoils (from soil sampling points along the hillslope) and soil profiles in the two studied vineyards

Soil depth (cm)	SOM (%)	pH (d.w.)	$CaCO_3$ (%)	Clay %	Silt %	Sand %	Soil texture *	API*
Tokaj - Profile A								
0-20	1.74	7.95	4.19	15.20	60.73	24.07	Silt Loam	34
20-40	1.08	8.01	4.19	22.31	65.16	12.53	Silt Loam	33
60-80	0.57	8.38	5.41	23.20	68.98	7.82	Silt Loam	35
120-140	0.37	8.52	6.24	20.10	72.33	7.57	Silt Loam	33
180-200	0.51	8.21	5.44	14.43	74.61	10.96	Silt Loam	34
Tokaj - Profile B								
0-20	0.88	8.24	4.74	16.94	68.41	14.65	Silt Loam	34
20-40	0.57	8.37	3.95	18.88	67.68	13.44	Silt Loam	34
60-80	1.41	8.23	4.57	15.31	59.84	24.85	Silt Loam	35
120-140	1.35	7.98	4.57	15.63	65.43	18.94	Silt Loam	35
180-200	1.32	7.85	3.77	23.36	68.64	8.00	Silt Loam	35
Tokaj - Profile B1								
0-20	1.90	7.94	4.19	-	-	-	-	37
20-40	1.44	8.00	4.19	-	-	-	-	34
60-80	1.40	8.14	3.33	-	-	-	-	34
120-140	0.93	8.34	4.57	-	-	-	-	36
180-200	0.82	8.14	5.02	-	-	-	-	36

Soil depth (cm)	SOM (%)	pH (d.w.)	$CaCO_3$ (%)	Clay %	Silt %	Sand %	Soil texture *	API*
Tállya - Profile C								
0-20	1.19	6.17	2.94	33.57	33.57	32.86	Clay Loam	42
20-40	0.58	6.18	2.28	41.78	23.87	34.35	Clay	44
60-80	0.30	5.11	1.66	41.18	24.32	34.50	Clay	44
120-140	0.83	6.28	3.36	17.39	22.19	60.42	Sandy Loam	40
Tállya - Profile D								
0-20	1.32	6.54	3.36	12.59	24.86	62.55	Sandy Loam	35
20-40	0.65	6.35	1.66	19.32	25.86	54.82	Sandy Loam	34
60-80	0.58	6.80	2.07	19.52	24.62	55.86	Sandy Loam	31
120-140	0.37	6.80	2.07	25.39	27.71	46.90	Loam	35
180-200	0.66	6.58	2.10	23.26	32.16	44.58	Loam	27

** Classification of soil texture was according to USDA*

**API: Arany Plasticity Index; SOM: Soil organic matter*

5.2. Total contents of PTEs in the studied vineyard soils

The soil-bound PTE contents at the vineyards in Tállya and Tokaj are summarized in Fig 2. In Tállya , the PTEs apart from Pb (13.0±1.6 mg/kg in the vineyard and 30.9 mg/kg in the local forest), showed higher contents in the vineyard (Zn: 42.3±6.2 mg/kg, Co: 6.0±1.7 mg/kg; Ni: 13.1±3.5 mg/kg; Cr: 22.5±6.9 mg/kg, and Cu: 111.4±32.1 mg/kg) compared to the local forest soil (Zn: 35.4 mg/kg, Co: 2.3 mg/kg; Ni: 5.3 mg/kg; Cr: 9.5 mg/kg, and Cu: 7.2 mg/kg) (Fig 2). In Tokaj, the contents of Zn (57.8±2.8 mg/kg), Ni (46.9±14.2 mg/kg), Cr (78.9±31.0 mg/kg), and Cu (48.1±5.3 mg/kg) in the vineyard topsoil were higher than in the local forest soil (Zn: 54.6 mg/kg, Pb: 14.4 mg/kg; Co: 9.0 mg/kg; Ni: 28.5 mg/kg; Cr: 31.5 mg/kg, and Cu: 24.1 mg/kg), while Pb (9.8±0.6 mg/kg) and Co (8.8±0.4 mg/kg) showed opposite trends. Although the observed Pb contents in both control sites were higher than in the vineyards, evaluating Pb contents is necessary due to health risk concerns (especially for children) (Rinklebe, et al. 2019; Tirima et al. 2016). So far, Co has received little attention, and it has rarely been assessed in vineyards, especially for evaluating Co-related environmental and health risks. Therefore, Co is also included in the present study.

The mean content of Cu in Tállya (111.4 mg/kg) exceeded the pollution limit value (B) (75 mg/kg) for soils and sediments figuring in Hungarian standards (Joint Decree No. 6/2009, 2009). Due to the long-term and repeated use of Cu-based fungicides, Cu contamination can be considered a major environmental concern in vineyards. Old vineyards (such as the vineyard in Tállya) are particularly affected. Even though the background content of Cu in Tállya was lower than that in Tokaj, twice as high concentrations were observed in the topsoil (Cu-fungicides have been used for more than 100 years in Europe). The presumably shorter period of Cu-fungicide applications in Tokaj can be a plausible reason as most of the agrochemical derived Cu took place during the past 28 years, starting from the re-planting of the vineyard in 1993. Copper pollution in vineyard soils is a common challenge in conventional and organic farming as vine growers hardly have any efficient alternative to Cu substances for protecting vine plants against the infection by *Plasmopara Viticola* (Brunetto et al. 2016). Moreover, the average Cu contents (111.4 mg/kg (Tállya) and 48.1 mg/kg (Tokaj)) detected in the vineyard topsoil in both vineyards are higher compared to (for Tállya) and comparable with those in vineyards within the 25 member states of the European Union (49.26 mg/kg) and noticeably higher compared to the overall average Cu concentration of 16.85 mg/kg in European soils (Ballabio et al., 2018). High anthropogenic Cu contents in the soil may raise ecotoxicological concerns therefore determining the easily soluble proportions of the total Cu is a prerequisite for assessing the environmental impact of Cu-based fungicide use (Komárek et al. 2010).

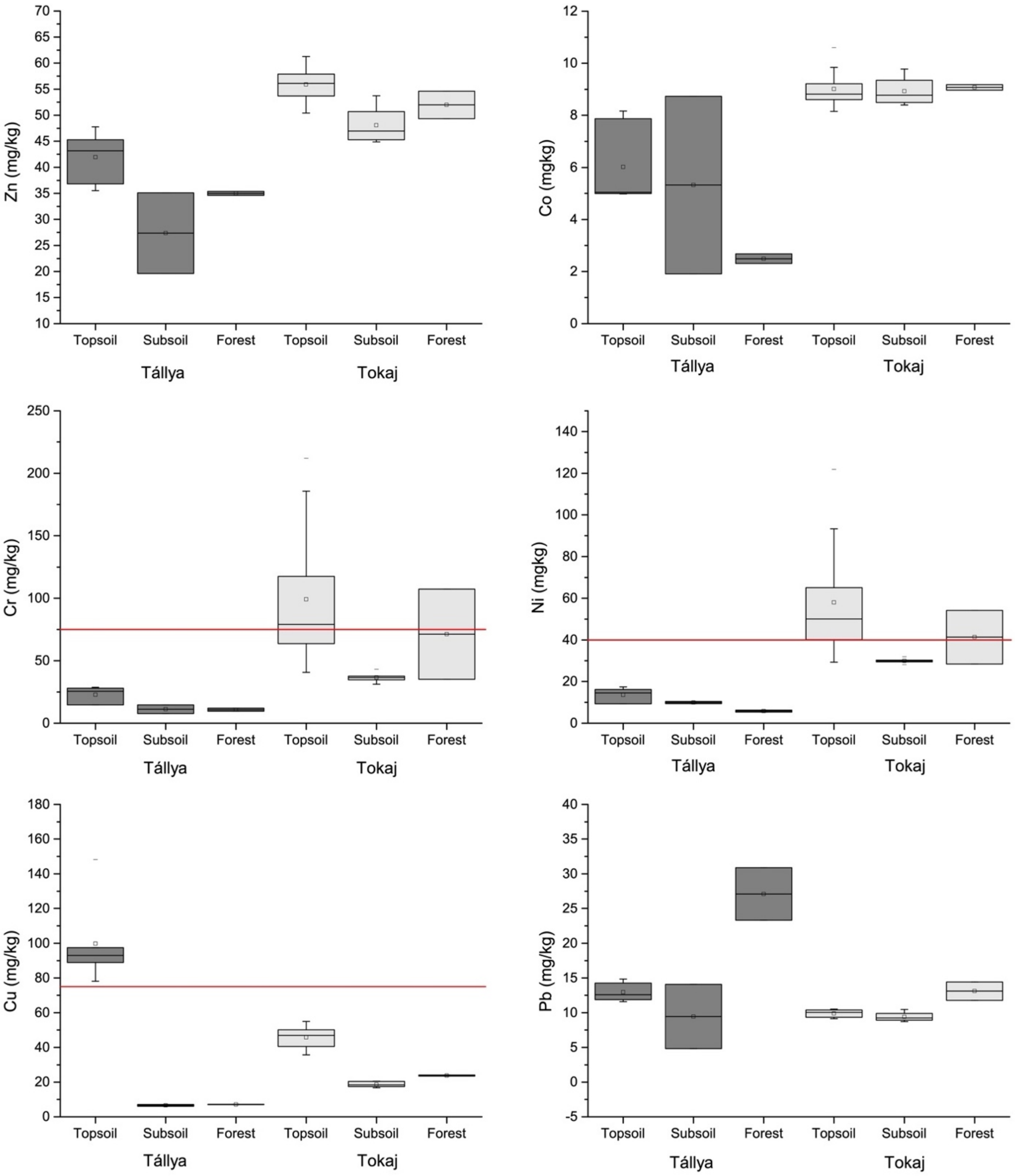

Fig 2. Concentrations (mg/kg) of PTEs measured in the top- (0-10 cm and 10-20 cm) and subsoil samples in the vineyards at Tállya and Tokaj and the local forest soils. The pollution limit values (B) of the Hungarian standards (Joint Decree No. 6/2009, 2009) for the PTEs are indicated by the horizontal red line (Zn: 200 mg/kg, Pb: 100 mg/kg, Co: 30 mg/kg, Ni: 40 mg/kg, Cr: 75 mg/kg, and Cu: 75 mg/kg).

Although the observed Zn contents did not exceed the Hungarian standards (Joint Decree No. 6/2009, 2009), assessing its accumulation tendencies is important due to the frequent use of fertilizers containing Zn (as Zn is an essential micronutrient for plants). Zinc is often used in fertilizers, in particular in those, spread directly on the plants during the growing season (30 g/ha/year used in Tokaj). In both vineyards, the higher Zn contents in the vineyard topsoil compared to the subsoil and the local forest soils imply a moderate enrichment of Zn from fertilizer applications. While in Tállya, the vineyard topsoil overall contains low levels of Ni and Cr, the markedly higher Ni and Cr levels observed in Tokaj exceed the pollution limit values (B) (Joint Decree No. 6/2009, 2009). These similarly high contents of Ni and Cr in both the forest and vineyard topsoils suggest that additional local sources (such as the dacite base rock and the abandoned quarry), other than pesticides and manure treatments, should be considered. In addition, a strong correlation was found for Ni and Cr (R = 0.99) (Table 5), indicating their common origins and behaviour in the investigated soils at Tokaj. Indeed, the soil samples from the local forest have been taken near the edges of the abandoned dacite stone quarry, supporting the idea of the bedrock's influence and the elevated local geochemical background for Ni and Cr. In addition, the repeated applications of fresh manure, manure compost and, more recently, manure pellets can also exert impact on Ni and Cr enrichment in the vineyard topsoil. Indeed, it has been previously suggested that such organic amendments can add significant amounts of PTEs, such as Zn, Cr, Ni, and Cu (Gong et al. 2019; Wuana and Okieimen 2011). High concentrations of Cr and Ni in vineyard topsoils may eventually pose a potential risk of toxicity, especially when re-planting young vine plants (Romić et al. 2004, Lago-Vila et al. 2015). Hence, their bioavailable proportions should be evaluated.

On the other hand, besides the vineyard's age and farming practices, the relief, and soil properties such as soil texture, pH, SOM content, and other soil constituents may also impact total and bioavailable PTEs in the soil. The significant correlation between SOM and total Cu (R = 0.88) in Tállya pointed out the role of organic matter in Cu binding. The high molecular weight and insoluble fractions of organic matter can retain significant Cu in the soil (Brunetto et al. 2016). Meanwhile, Zn, Ni, and Cr showed a significant positive relationship with total Al and Fe, and the Arany Plasticity Index (API) (Table 5), revealing their association with fine soil fractions and the inorganic colloids, such as clay minerals and Fe/Mn oxyhydroxides, contained in those fine-grained fractions (Fernández-Calviño et al. 2012; Scheniost 2005). The aqua regia extractant is ideal to release elements trapped in Mn and Fe oxides and oxyhydroxides.

This solution is also suitable to dissolve PTEs from their strong bonds, probably by total or partial dissolution of Mn-oxides (due to its better ability to dissolve Mn-oxides than Fe/Al oxides) (Pavlíčková et al. 2003). Meanwhile, aqua regia is unable to dissolve silicates and Al oxides (Niskavawara et al. 1997; Lymperopoulou et al. 2017). Also in Tállya, the negative correlation between the soil pH and Zn, Ni, and Cr contents, may indicate a higher environmental risk prevailing at lower pH.

In Tokaj, the relationship between Zn and Pb contents and total Mn also indicates their association with oxides of Mn (bounded and/or occluded). Our extraction results of Mn recovered in the reducible fraction accounting for more than 50% of the total Mn in both studied vineyards, indicate that Mn oxides are the predominant form of the soil-bound Mn (Fig 9 & 10). Iron/Mn oxides in the soil may exhibit a high surface area, with reactive surface sites which strongly bind and tightly sorb metals such as Cu, Pb, Zn, Ni, Co, Cd (Scheniost, 2005). Conversely, a negative correlation was observed between total Al and Co, Ni, and Cr contents suggesting that low Al- and high Ca-containing (due to a positive relationship with Ca) soil constituents (such as pyroxene, amphibole, and apatite) may carry the soil-bound Ni and Cr in Tokaj (Table 5). Indeed, in Tokaj, the Ca content is anticorrelated with Al contents. In addition, negative relationships of Co, Ni, and Cr with the slope steepness imply that terrain plays an essential role in their spatial distribution, showing the possible impacts of soil erosion and redeposition processes. Generally, Cu showed a less significant correlation with soil properties in the vineyard at Tokaj.

Table 5. Spearman's rank correlation matrix between soil properties, slope, and total PTE data in vineyard soils in Tállya and Tokaj

	Zn	Pb	Co	Ni	Cr	Cu	Al	Fe	Mn	Ca	SOM*	API*	CaCO$_3$	Mean slope (degree)	pH
Tállya															
Zn	1.00	0.42	0.52	0.88*	0.92**	0.45	0.88*	0.91*	0.24	0.84*	0.18	0.93**	-0.17	-0.23	-0.90*
Pb	0.42	1.00	0.92**	0.53	0.49	0.72	0.10	0.45	0.91*	-0.08	0.59	0.10	-0.31	-0.93**	-0.59
Co	0.52	0.92**	1.00	0.74	0.68	0.54	0.28	0.64	0.95**	0.03	0.48	0.19	0.05	-0.93**	-0.74
Ni	0.88*	0.53	0.74	1.00	0.99**	0.23	0.84*	0.98**	0.51	0.64	0.04	0.67	0.14	-0.44	-0.98**
Cr	0.92**	0.49	0.68	0.99**	1.00	0.26	0.89*	0.99**	0.43	0.73	0.04	0.74	0.06	-0.36	-0.99**
Cu	0.45	0.72	0.54	0.23	0.26	1.00	0.05	0.22	0.50	0.11	0.88*	0.37	-0.63	-0.59	-0.34
Al	0.88*	0.10	0.28	0.84*	0.89*	0.05	1.00	0.92*	0.00	0.94**	-0.20	0.84*	0.00	0.08	-0.85*
Fe	0.91*	0.45	0.64	0.98**	0.99**	0.22	0.92*	1.00	0.39	0.75	0.00	0.75	0.06	-0.32	-.986**
Mn	0.24	0.91*	0.95**	0.51	0.43	0.50	0.00	0.39	1.00	-0.26	0.55	-0.10	0.08	-0.99**	-0.51
Ca	0.84*	-0.08	0.03	0.64	0.73	0.11	0.94**	0.75	-0.26	1.00	-0.16	0.92**	-0.17	0.30	-0.67
SOM*	0.18	0.59	0.48	0.04	0.04	0.88*	-0.20	0.00	0.55	-0.16	1.00	0.12	-0.31	-0.63	-0.12
API*	0.93**	0.10	0.19	0.67	0.74	0.37	0.84*	0.75	-0.10	0.92**	0.12	1.00	-0.19	0.09	-0.69
CaCO$_3$	-0.17	-0.31	0.05	0.14	0.06	-0.63	0.00	0.06	0.08	-0.17	-0.31	-0.19	1.00	0.00	0.02
Mean slope (degree)	-0.23	-0.93**	-0.93**	-0.44	-0.36	-0.59	0.08	-0.32	-0.99**	0.30	-0.63	0.09	0.00	1.00	0.45
pH	-0.90*	-0.59	-0.74	-0.98**	-0.99**	-0.34	-0.85*	-0.99**	-0.51	-0.67	-0.12	-0.69	0.02	0.45	1.00

	Zn	Pb	Co	Ni	Cr	Cu	Al	Fe	Mn	Ca	SOM*	API*	CaCO$_3$	Mean slope (degree)	pH
Tokaj															
Zn	1.00	0.51	0.06	-0.12	-0.12	0.68^{*}	0.28	0.43	0.76^{**}	-0.10	0.47	-0.03	-0.05	-0.18	0.47
Pb	0.51	1.00	0.34	0.22	0.16	0.41	0.19	0.70^{*}	0.61^{*}	-0.37	0.39	0.38	0.32	0.14	0.39
Co	0.06	0.34	1.00	0.97^{**}	0.97^{**}	0.15	-0.60^{*}	0.42	0.35	0.58^{*}	-0.37	0.27	0.05	-0.69^{*}	-0.37
Ni	-0.12	0.22	0.97^{**}	1.00	0.99^{**}	0.11	-0.69^{*}	0.26	0.19	0.62^{*}	-0.44	0.35	0.10	-0.63^{*}	-0.44
Cr	-0.12	0.16	0.97^{**}	0.99^{**}	1.00	0.10	-0.67^{*}	0.25	0.19	0.64^{*}	-0.49	0.27	0.04	-0.68^{*}	-0.49
Cu	0.68^{*}	0.41	0.15	0.11	0.10	1.00	-0.20	0.05	0.42	0.05	0.26	0.19	0.36	-0.18	0.26
Al	0.28	0.19	-0.60^{*}	-0.69^{*}	-0.67^{*}	-0.20	1.00	0.21	0.19	-0.75^{**}	0.57	-0.19	-0.36	0.66^{*}	0.57
Fe	0.43	0.70^{*}	0.42	0.26	0.25	0.05	0.21	1.00	0.80^{**}	-0.18	0.25	0.22	-0.15	-0.15	0.24
Mn	0.76^{**}	0.61^{*}	0.35	0.19	0.19	0.42	0.19	0.80^{**}	1.00	0.08	0.31	0.26	0.02	-0.35	0.30
Ca	-0.10	-0.37	0.58^{*}	0.62^{*}	0.64^{*}	0.05	-0.75^{**}	-0.18	0.08	1.00	-0.61^{*}	0.15	0.16	-0.87^{**}	-0.61^{*}
SOM*	0.47	0.39	-0.37	-0.44	-0.49	0.26	0.57	0.25	0.31	-0.61^{*}	1.00	0.01	-0.20	0.52	1.00^{**}
API*	-0.03	0.38	0.27	0.35	0.27	0.19	-0.19	0.22	0.26	0.15	0.01	1.00	0.37	0.05	0.01
CaCO$_3$	-0.05	0.32	0.05	0.10	0.04	0.36	-0.36	-0.15	0.02	0.16	-0.20	0.37	1.00	-0.09	-0.20
Mean slope (degree)	-0.18	0.14	-0.69^{*}	-0.63^{*}	-0.68^{*}	-0.18	0.66^{*}	-0.15	-0.35	-0.87^{**}	0.52	0.05	-0.09	1.00	0.51
pH	0.47	0.39	-0.37	-0.44	-0.49	0.26	0.57	0.24	0.30	-0.61^{*}	1.00^{**}	0.01	-0.20	0.51	1.00

**API: Arany Plasticity Index; *SOM: Soil organic matter;* * *Significant at the level of* $p < 0.05$*;* ** *Significant at the level of* $p < 0.01$*.*

5.3. Enrichment characteristics of PTEs in the vineyard soils and eroded sediments

5.3.1. Enrichment of PTEs in the vineyard topsoils

The intensive use of agrochemicals such as fertilizers and copper-based fungicides has led to the accumulation of PTEs in vineyard soils, especially in the topsoil. Calculating enrichment factor (EF) based on Fe as a reference element may also allow deciphering the predominant natural or anthropogenic character of PTEs and their accumulation trends in the sloping landscape.

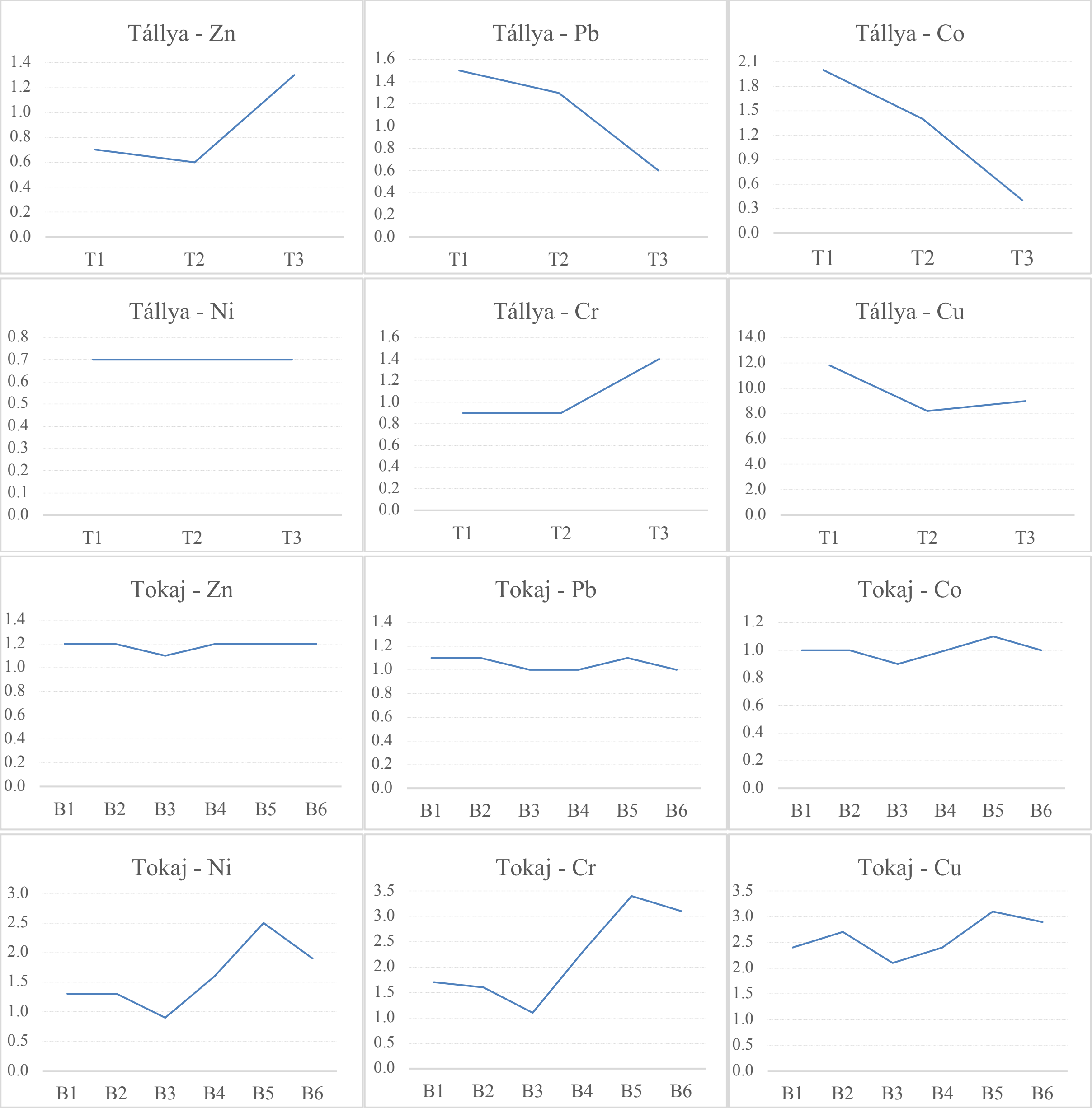

Fig 3. The spatial variations in the enrichment factors of the examined PTEs calculated using Fe as a reference element for the different sampling zones along the hillslope

In Tállya, the mean EFs for Zn and Ni were below 1, while EFs for Pb, Co, and Cr were slightly higher than unity. The mean Cu EF was 9.7, indicating significant enrichment in the surface soil layer. In Tokaj, the mean EFs for Zn, Pb, Co, and Ni were around 1, while Cr (2.2) and Cu (2.6) EFs were over 2, indicating their moderate enrichment in the topsoil. The anthropogenic origin of Cu is predominant in the vineyards. The higher EFs of Cu observed in Tállya (Fig 3) show the effect of its long-term use as Cu-fungicides in that old vineyard. In contrast, the prevailing geogenic origin of Pb, Co, and Cr can be concluded in Tállya and no significant enrichment of Ni and Zn can be noticed. Likewise, Pb, and Co are mainly of geogenic origin in Tokaj, while a moderate enrichment of Ni and Cr cannot be excluded due to local sources, such as the open pit quarry. Although the observed EF levels of Zn indicate a slight enrichment of this element in the topsoil of vineyards. Treatments with Zn-containing fertilizers are regularly done in the vineyard, spreading an annual Zn dose of approximately 30 g/ha. Alkaline soils are often devoid of adequate Zn levels (Fernández-Calviño et al., 2012); hence, foliar fertilizers are commonly used for preventing Zn deficiency in crops. The frequent use of fertilizers containing Zn may increase its toxicity and accumulation in the soil. In addition, 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. 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 (Fig 2), indicating their local source.

In Tállya, Pb, Co, and Cu tend to get enriched at the top of the hillslope in the summit zone, while in Tokaj a pronounced downslope enrichment can be highlighted (Fig 3). Due to the complex slope shape of the vineyard in Tállya, EF (Cu) reaches the highest value at the top (the summit) and decreases to its lower value at the steepest backslope area (T2), before re-rising at the footslope (Fig 3). The higher EFs for Zn and Cr at the bottom of the slope also indicate their erosion-impacted spatial distribution pattern. Indeed, 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 (Manaljav et al. 2021). In contrast, the EFs of Cu in Tokaj reach their highest values at the footslope (Fig 3). In line with the negative correlations between PTEs and the mean slope gradients of the sampling zones, a general trend of downslope accumulation of PTEs can be noticed, especially for Co, Ni, Cr, and Cu (Fig 3). Hence, the terrain plays a significant role in the accumulation and enrichment patterns of PTEs in the topsoil, showing the impact of erosion in the re-distribution of PTEs within the sloping landscape.

5.3.2. Enrichment of PTEs in the eroded sediments

Enrichment ratios (ER) were applied to assess PTE enrichment in eroded sediments compared to the vineyard topsoil along the hillslope (<20 cm depth) (Fig 4 & 5). In Tállya, there was slight difference between the mean of PTE total content in the topsoil compared to that in the eroded sediment in Tállya. The ER levels of around 1 were determined with equal values for all PTEs (Zn: ER = 1.17, Pb: ER = 1.12, Co: ER = 1.25, Ni: ER = 1.05, Cr: ER = 1.18, and Cu: ER = 1.16). Similar to the accumulation of PTEs in the topsoil, the complex slope shape of the vineyard at Tállya could also explain a slight tendency to enrich PTEs in the sediments. Accordingly, the terrain and high coarse fraction content likely protect the soil from excessive erosion-related losses in the summit zone. Hence, PTEs associated with the fine soil fraction were less affected by sediment transported by runoff.

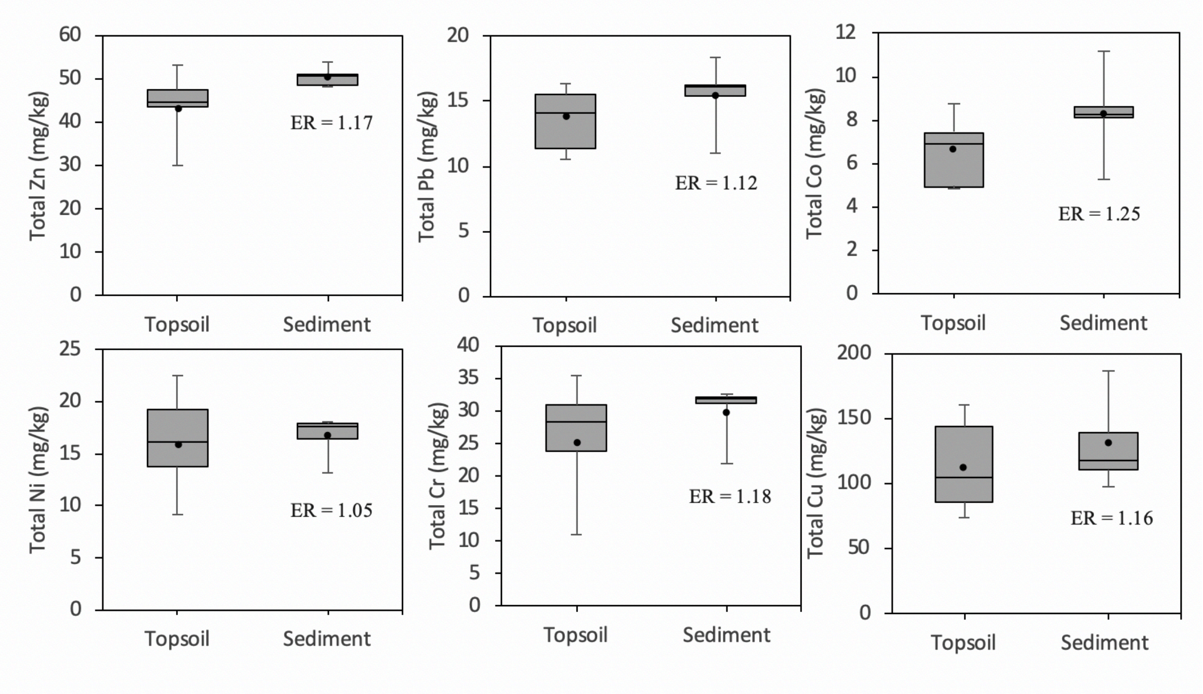

Fig 4. Total concentration of PTEs in the topsoils (along the hillslope) and eroded sediments in Tállya. ER stands for the average of enrichment ratios (ER) in sediments compared to the topsoil.

In Tokaj, the PTEs tented to show increased contents in eroded sediments. Zinc (ER = 1.35), Pb (ER = 1.30), Co (ER = 1.32), Ni (ER = 1.27), and Cr (ER = 1.25) exhibited significantly higher contents in the sediments compared to the vineyard topsoil. The total concentration of Cu in the eroded sediments ranging between 148.1 and 211.5 mg/kg was substantially greater than its topsoil levels (range: 36.5 - 70.0 mg/kg). Accordingly, the highest ER was also observed for Cu (3.36). Elevated concentrations of PTEs are often detected in sediments moved by rainfall-runoff in sloping vineyards (Devi et al., 2018; Komárek et al., 2010). The preferential association of PTEs with the organic-rich sediments (3.14±0.23%) can explain their enrichment (Table 3A). Erosion and subsequent sedimentation of organic-rich suspended material and the post-deposition association of PTEs with organic-rich deposits within the low-energy zones of the terrain may be an important process driving the heterogeneous distribution of such elements in the topsoil (Rinklebe and Shaheen, 2014; Rinklebe et al., 2019). In addition, the eroded sediments are suggested to be enriched in silt-sized particles and depleted in coarser particles (Fernández-Calviño et al., 2008). Such fine-grained particles are generally considered an important contributor to the accumulation of PTEs in soils and sediments. The high contents of Cu in sediments indicated that an appreciable part of anthropogenic Cu from treatments with organic amendments (fresh cattle manure, cattle manure pellets) and Cu-based fungicides might be moved and eventually exported off-site during rainfall-runoff events, as earlier observed in vineyard areas (Babcsányi et al., 2016; Besnard et al., 2001; Fernández-Calviño et al., 2008; Ribolzi et al., 2002). Therefore, a plausible risk of the translocation of PTE-polluted soil from this vineyard into adjacent areas and surface water environments raises ecological risk concerns.

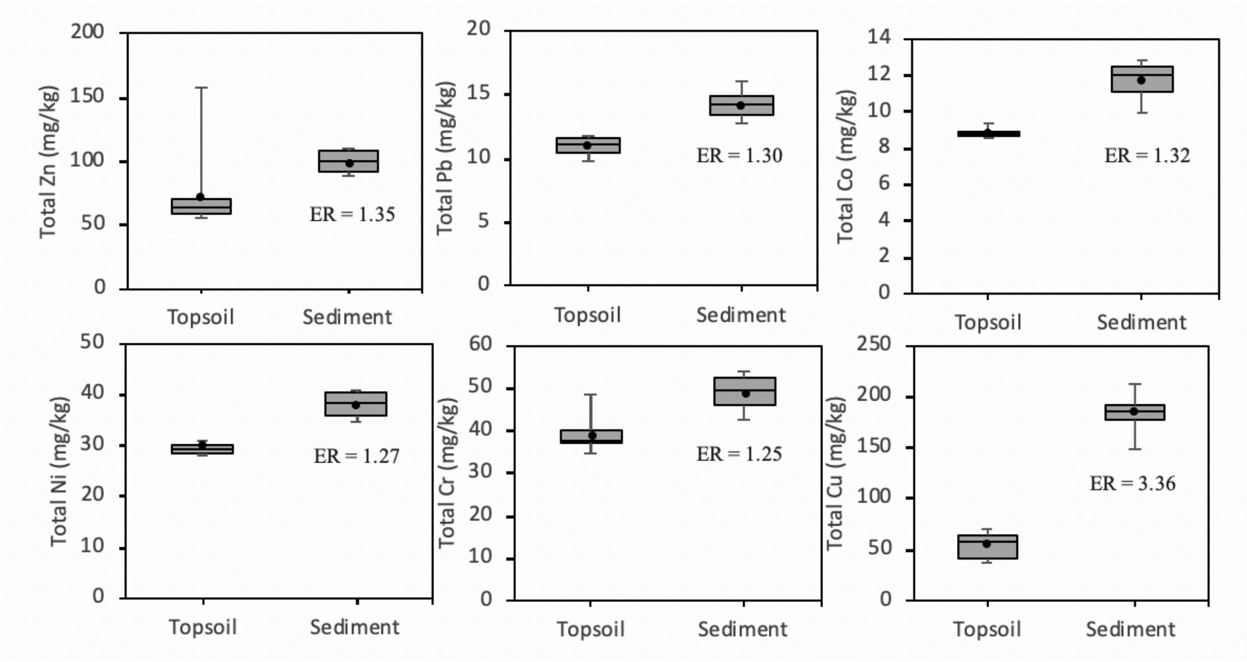

Fig 5. Total concentration of PTEs in the topsoils (along the hillslope) and eroded sediments in Tokaj. ER stands for the average of enrichment ratios (ER) in sediments compared to the topsoil.

5.4. Bioavailable contents of PTEs in the vineyard soils and eroded sediments

5.4.1. Bioavailable contents of PTEs in the vineyard topsoil and forest topsoil

The total PTE content is insufficient for an adequate environmental risk assessment because the mobility of these elements depends on their binding forms (Fernández-Calviño et al., 2012; Rinklebe & Shaheen, 2014; Szolnoki & Farsang, 2013). Meanwhile, the bioavailability of PTEs has been used as a useful tool for evaluating the environmental pollution risk and toxicity to crops (Borgese et al., 2013; Nunes et al., 2014; Violante et al., 2010).

Based on the EDTA extracted PTE contents (marked with X_E), Zn, Ni, and Cr showed low mobility in both vineyards (Fig 6). Bioavailable proportions of Pb reached almost 50% of its total contents both in the vineyard and the forest topsoils, with slightly higher Pb_E in Tállya. This can be explained by the high retention capacity of manganese oxides for Pb and the high affinity of Pb for Fe oxides in the soil (Arenas-Lago et al. 2014), which can be extracted with the applied EDTA (Lo & Yang, 1999). In the current study, Pb shows the greatest affinity for Mn oxides in both vineyards. Ni_E and Cr_E are not considerably tailored by their total concentrations. Even though the total contents of Ni and Cr in Tokaj are markedly higher compared to Tállya (Fig 6), there is no significant difference between their bioavailable proportions. Bioavailability ratios of Cr in both studied sites are less than 1%, indicating its almost immobile character and a strong binding to the soil (Table 6). Despite differences in the total Cu contents between the two vineyards, the bioavailability ratios in Tállya (48-49%) are only slightly higher than those in Tokaj (39-49%) (Fig 6). Similarly, high bioavailability ratios of Pb and Co in both vineyard soils and uncultivated soils indicate their lability in the soils (Table 6). The Zn_E contents are less than 10 mg/kg (Fig 6). However, its slight increase in the uppermost soil layer, may indicate the input of some soluble Zn via foliar fertilizers' use.

Table 6. Average of bioavailable ratio* (%) of target PTEs in the topsoils

Sampling site	Depth (cm)	Zn	Pb	Co	Ni	Cr	Cu
Tállya	0-10	5.9	48.7	51.6	5.9	0.8	49.1
	10-20	3.8	47.5	53.0	5.5	0.7	47.6
The local forest in Tállya	0-10	11.5	50.7	33.8	0.0	2.7	13.7
	10-20	9.3	65.0	28.1	0.0	1.8	20.5
Tokaj	0-10	10.8	44.9	40.2	5.5	0.4	48.5
	10-20	6.8	41.3	34.4	3.3	0.2	39.4
The local forest in Tokaj	0-10	2.6	48.8	33.6	7.1	0.0	23.2
	10-20	0.0	51.6	34.7	4.3	0.2	20.1

*[*Average of Bioavailable Ratio (%) = Average of (bioavailable PTE fraction/ total PTE concentration in soil) × 100 (Alibrahim & Williams, 2016]*

There is a significant difference between the bioavailable proportions of Zn and Cu in the vineyard soil and the local forest soil (Fig 6). 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. As expected, with a strong accumulation of Cu in the vineyard topsoil, Cu can be sorbed through mechanisms such as ion exchange (non-specific adsorption), specific adsorption and complexation with soil organic matter in the solid phase (Brunetto et al. 2016; Kabata-

Pendias 2004). The weak and unstable non-specific adsorption directly affects the availability of Cu (Brunetto et al. 2016). Although there is no noticeable difference between the total content of Zn in the vineyard soil and the local forest soil, significantly high proportions of bioavailable Zn is observed in the vineyard topsoil in Tokaj. Meanwhile, higher bioavailabilable ratio of Zn in the local forest soil in Tállya with lower total contents of Zn suggest that Zn bioavailability probably depends on local soil attributes, while anthropogenic inputs play a minor role.

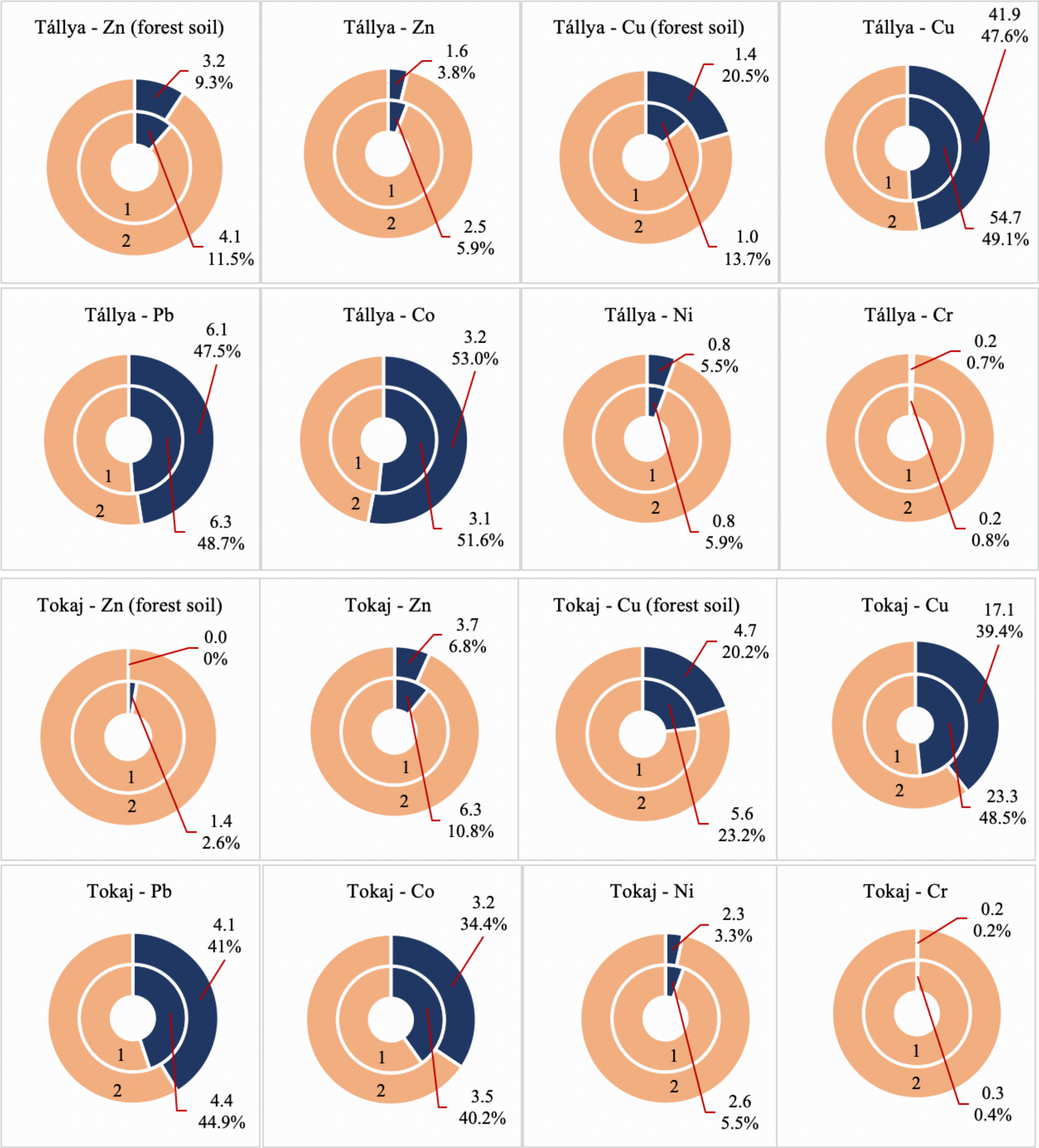

Fig 6. Average concentrations of bioavailable PTEs (mg/kg) and bioavailable ratio (%) in vineyard soils and forest soils (diagram 1: 0-10 cm, diagram 2: 10-20 cm) in Tállya and Tokaj.

The quantity of PTEs extracted by EDTA can be highly dependent on soil mineral phases and their respective total contents (Brunetto et al., 2014; Duplay et al., 2014; Fernández-Calviño et al., 2012). In Tállya, the SOM content strongly influenced the EDTA extracted contents of Cu showing a positive correlation (Table 7). A positive correlation with the SOM content and Cu_E may be driven by the soil pH of the studied vineyard soils. Indeed, the alkaline pH in former researches promoted organic matter solubilization and hence the release of complexed Cu from soils (Brunetto et al., 2016; Fernández-Calviño et al., 2008). Significant correlation between total Mn contents and PTEs (except for Cu) may indicate their association with the reactive surface sites of Mn oxides (Table 7). Indeed, the extractant Na_2-EDTA has proven to be effective in removing metal bound to Fe/Mn oxide surfaces (Lo & Yang, 1999). A negative relationship between Ni_E and Co_E and the mean slope implies that terrain may also alter the solubility of some PTEs. On the other hand, soil properties, such as the Arany Plasticity Index (soil texture), carbonate content, and soil pH seem to play a minor role in shaping the bioavailability of the studied PTEs.

Table 7. Spearman's correlation matrix between soil properties, relief, and bioavailable PTE contents in the vineyard topsoil in Tállya and Tokaj (with composite soil samples)

	Fe_E	Mn_E	SOM*	API*	$CaCO_3$	Mean slope (degree)	pH
Tállya							
Zn_E	0.20	0.36	0.70	-0.20	-0.50	-0.16	0.52
Pb_E	0.46	0.81	0.73	-0.27	-0.53	-0.68	0.12
Co_E	0.53	0.99^{**}	0.64	-0.30	-0.02	-0.95^{**}	-0.18
Ni_E	0.38	0.91^{*}	0.50	-0.21	-0.12	-0.96^{**}	-0.43
Cr_E	0.30	0.94^{**}	0.59	-0.61	0.00	-0.77	0.22
Cu_E	0.39	0.57	0.89^{*}	0.04	-0.62	-0.50	0.07
Tokaj							
Zn_E	0.02	0.72^{**}	0.57	-0.02	-0.24	0.28	-0.23
Pb_E	-0.04	0.70^{*}	0.51	0.54	-0.11	0.42	-0.57
Co_E	0.38	0.95^{**}	0.46	0.31	-0.29	0.35	-0.33
Ni_E	0.63^{*}	0.79^{**}	0.34	0.22	-0.12	-0.09	-0.33
Cr_E	0.37	0.78^{**}	0.33	0.46	-0.10	-0.10	-0.20
Cu_E	-0.11	0.51	0.53	0.22	0.12	0.25	-0.27

**API: Arany Plasticity Index; *SOM: Soil organic matter;*

* *Significant at the level of* $p < 0.05$; ** *Significant at the level of* $p < 0.01$.

5.4.2. Bioavailable contents of PTEs in the vineyard soils and eroded sediments

In this section, the bioavailability of PTEs in the vineyard soils and eroded sediments is evaluated and compared using topsoil samples collected along the hillslope adjacent to the traps and sediment samples. In addition, topsoil (0 - 20 cm) and subsoil samples (>20 cm) collected in the soil profiles (0-200 cm) were also used.

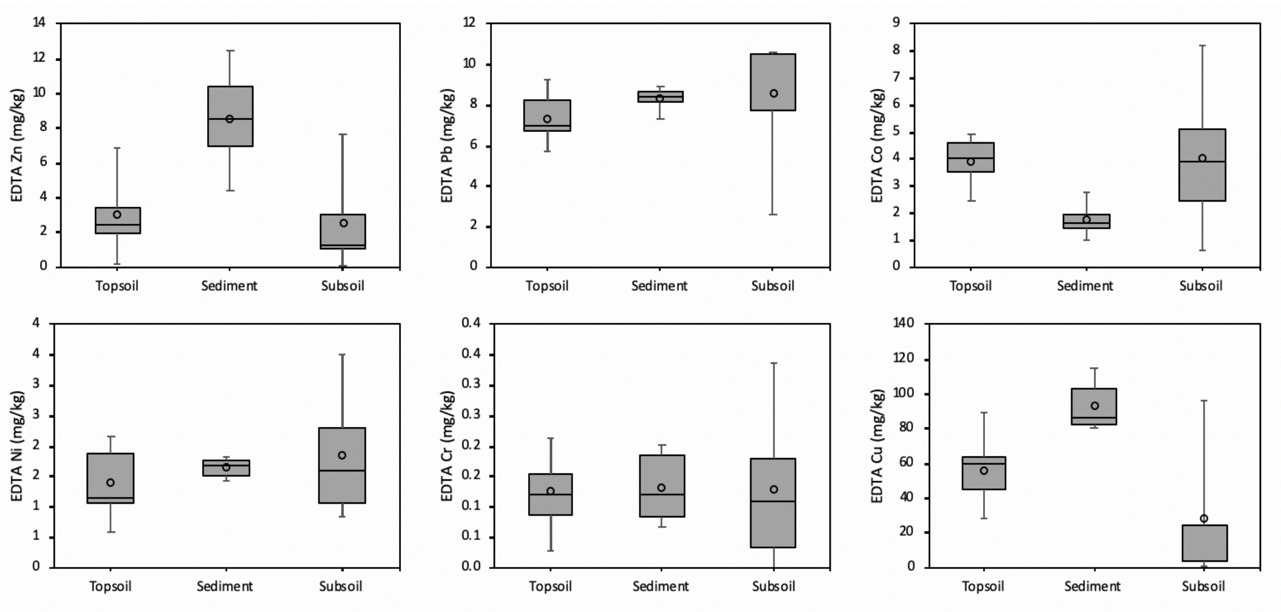

Fig 7. Bioavailable contents of the target PTEs (mg/kg) in the top- (0-20 cm), subsoil (>20 cm), and the eroded sediments in the studied vineyard in Tállya.

In Tállya, the contents of Pb, Ni, and Cr extracted with EDTA (marked with X_E) have shown no significant difference between vineyard soils and sediments (Fig 7). However, the bioavailable content of Co in the eroded sediment was obviously lower than that in the vineyard top- and subsoil. In contract, higher Zn and Cu bioavailable contents were observed in the eroded sediments compared to the vineyard soils. In Tokaj, typically, the EDTA extracted PTE contents in the sediments were higher than those in the vineyard top- and subsoil, except for Co and Ni (Fig 8). Copper showed substantial lability in the eroded sediments compared to the vineyard soils (Fig 8). In addition, the important proportions of bioavailable Cu in the topsoil, sediment, and subsoil (with bioavailable ratios of 51.4%, 73.2%, and 51.6%, respectively in Tállya and 46.8%, 65.0%, and 35.9%, respectively in Tokaj) indicated its weak binding (Table 8). At the same time, EDTA salt was formerly found to overestimate Cu_E content, especially in eroded sediments with a high organic matter content, due to its capability of dissolving high molecular weight organic compounds and of sequestering the Cu from the organic matter binding sites (McBride et al., 1998). Similarly, high bioavailability ratios of Pb and Co in the vineyard soil and sediment indicated their lability, particularly in the sediments (64.8% in Tokaj) and subsoil (57% in Tállya) for Pb; and in the top- (60.9% in Tállya) and subsoil for Co

(67.6% in Tállya and 45.8% in Tokaj) (Table 8). Therefore, assessment of Pb associated ecological risk is also required for vineyards (especially for children) (Rinklebe et al,. 2019; Tirima et al., 2016). Cobalt has received so far little attention in assessing PTE-associated ecological risks, yet Co is broadly considered as an element in the high-risk category (Barrio-Parra et al., 2017). Mean EDTA contents of Co and Ni in the subsoil were higher than those in the sediment in both vineyards (in Tállya: Co: 4.0 vs 1.7 mg/kg and Ni: 1.8 vs 1.6 mg/kg; in Tokaj: Co: 4.1 vs 2.6 mg/kg and Ni: 4.4 vs 2.6 mg/kg), indicating the mobilization of particles bearing less bioavailable Ni and Co. The Cr_E content in the sediments was higher than that in the top- and subsoil, which contrasted its lower total content in the sediment. Overall, bioavailability ratios of Ni and Cr in both vineyard soil and sediments were low, accounting for less than 13% and 1%, respectively (Table 8).

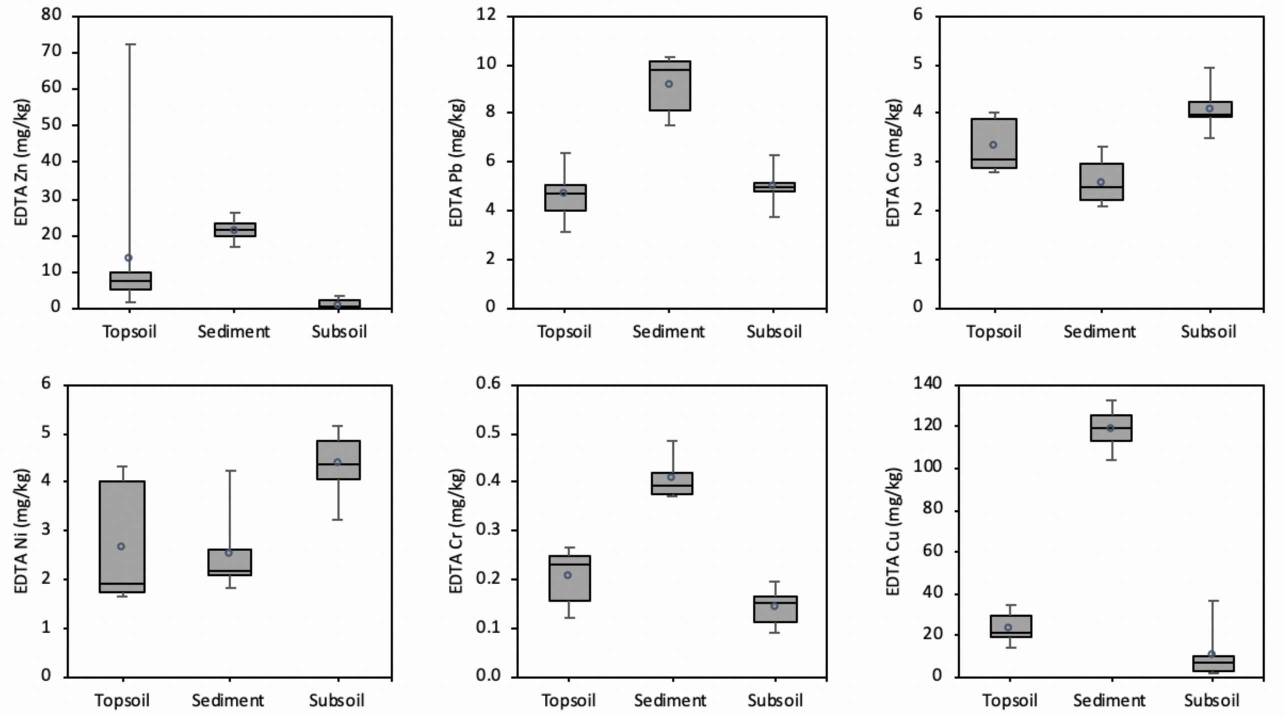

Fig 8. Bioavailable contents of the target PTEs (mg/kg) in the top- (0-20 cm), subsoil (>20 cm), and the eroded sediments in the studied vineyard in Tokaj.

In Tokaj, the Zn_E contents in the topsoil showed agreat range of variation (range 1.9 - 72.3 mg/kg) and represented on average 16.9% of the total Zn. Meanwhile, in Tállya, the bioavailable content of Zn in the topsoil was low and varied from 0.2 mg/kg to 6.9 mg/kg. Bioavailable fractions of Zn were either not detected or negligible in the subsoil. A higher mean Zn_E content was found in the sediment (8.6 mg/kg and 21.6 mg/kg) compared to the vineyard topsoil (3.0 mg/kg and 13.4 mg/kg in Tállya and Tokaj, respectively), the former accounting for 15.5% and 21.7% of the total Zn contents in Tállya and Tokaj, respectively (Table 8). Zinc was reported as an element presenting low mobility in alkaline soils, mainly bound to and incorporated into minerals (Brunetto et al., 2014; Duplay et al., 2014).

Likewise, Zn in eroded sediments showed similar geochemical partitioning mainly detected in the residual and organically-bound fractions (Fernández-Calviño et al., 2012). The significantly higher proportion of the bioavailable proportions of Zn and Cu in the eroded sediments compared to the vineyard soils can be explained by the higher content of organic matter and fine soil particles (clay and silt) in the eroded sediments.

Table 8. Average of bioavailability ratio* (%) of target PTEs in the top- (0-20 cm), subsoil (>20 cm), and sediments

	Zn	Pb	Co	Ni	Cr	Cu
Tállya						
Topsoil (0-20 cm)	6.8	54.4	60.9	9.3	0.5	51.4
Sediment	15.5	53.9	20.7	9.6	0.4	73.2
Subsoil (>20 cm)	6.8	57.9	67.6	12.1	0.7	51.6
Tokaj						
Topsoil (0-20 cm)	16.9	37.9	32.9	5.8	0.7	46.8
Sediment	21.7	64.8	22.2	6.8	0.8	65.0
Subsoil (>20 cm)	7.0	53.0	45.8	10.3	0.2	35.9

*[*Bioavailable Ratio (%) = (Bioavailable PTE fraction/ total PTE concentration in sample material) × 100 (Alibrahim & Williams, 2016)]*

5.5. Distribution of PTEs in the different geochemical fractions in the vineyard soils and eroded sediments

5.5.1. Distribution of PTEs in the different geochemical fractions in the vineyard soils

To determine the distribution of PTEs in the different soil geochemical fractions, the improved three-step sequential BCR extraction procedure was applied in my research. Accordingly, the acid-soluble and easily mobilised PTEs are extracted in the first extraction step (F1). This fraction also contains PTEs bound to carbonates. The potentially toxic elements in the first fraction are therefore the most mobile and can be easily taken up by the plants (Kazi et al., 2005; Ure et al., 1993). In the second extraction step (reducible fraction) (F2), the PTEs bound to iron and manganese oxyhydroxides are released. The PTEs in this fraction can be mobilised when the soil state changes from oxic to anoxic. In the third extraction step (F3), the PTEs bound to organic material and sulphides are extracted. The analytical results of the target PTEs (Zn, Pb, Co, Ni, Ba, Mn, Cr, Cu, and Sr) fractionation achieved in my study are presented in Fig 9, 10, & 11. In which, the average percentage of each fraction is calculated in total PTE content (the sum of all extracted fractions (F1+F2+F3+F4)). The BCR extraction experiment results show that the proportions of target PTEs in the four extracted soil fractions have the same dominant ranks in the examined soil layers in both vineyards. In addition, except for Co, Cu, Sr, these rank orders are similar in both vineyards. The content and percentage of PTEs bound to the different soil fractions in the two studied sites are described below.

The majority of the Cr was in the residual soil fraction (95% of the total in Tokaj vineyard soil and 95% in Tállya) (Fig 9 & 10). The proportion of Cr in the remaining soil fractions accounted for 5% of the total content, indicating its strong bond and low mobility in the studied vineyard soil.

For all soil profiles, the soil residual fraction contains the highest proportion of Zn (average of 84% in Tokaj and 82% in Tállya, Fig 11) indicating that Zn is strongly bound to the soil particles (Arenas-Lago et al., 2014; Brunetto et al., 2014). Indeed, the content of Zn in this last fraction is significantly correlated with the silt content (Table 9). The concentration of Zn in the first three extracts (F1, F2, F3) is lower than 3%, 13%, 0% in Tokaj (Fig 10), and 4%, 12%, 1% in Tállya (Fig 9), respectively revealing a relatively low Zn bioaccessibility and Zn deficiency risk for grapevines. In addition, the higher proportions of Zn in residual geochemical fractions in the deeper soil layers may be explained by the higher contents of fine particles (clay and silt) in the vineyard subsoil.

Based on the contents of Pb in different soil fractions, most of the Pb is associated with the reducible fraction and the residual fraction of the soil (Fig 11). The proportion of total Pb associated with the reducible soil fraction is the highest, reaching 68% in Tállya and 63% in Tokaj (Fig 9 & 10). Meanwhile, the amount of total Pb in the residual fraction is 36% in Tokaj and 30% in Tállya. In agreement with the findings of various studies, the comparatively high proportion of these two forms of Pb was explored by the high retention capacity of manganese oxides for Pb and the high affinity of Pb for Fe oxides, thus providing a long-term sink for Pb (Arenas-Lago et al., 2014; Covelo et al., 2007; Vega et al., 2010). In addition, Pb in the reducible fraction showed the positive affinity in clay minerals and negative correlation with sand contents (Table 9). Hence, it can be indicated that the accumulation of clay minerals and iron oxides significantly influence the sorption properties of Pb. Cobalt was one of the most immobility elements (Co, Pb, and Cr) in Tokaj with the percentage of acid-soluble fraction of 2% (Fig 10). Meanwhile, in Tállya, Co was the third highest mobility element with 11% of Co exhibiting in the first extracted fraction. Especially, in the 0-20 cm soil layer, the percentage of Co in the F1 extracted fraction can reach 18% on average, indicating lability in the Tállya vineyard topsoils (Fig 9). Similar to Pb, Co in the acid-soluble fraction also showed a positive correlation with sand and a negative correlation with silt. In addition, a positive correlation was also observed between Pb fraction F1, F2 and F3 and sand in Table 9. At the same time, these two elements and sand showed a negative correlation with pH and carbonate content, which may explain that the easily mobilizable fractions of Pb and Co are strongly determined by the soil solution (influenced by soil pH). In addition, the negative relationship between soil pH and both Pb and Co in the most mobile fraction is an indication that there may be a higher risk of pollution at a lower pH. A negative correlation of the soil pH and the Co content in the fraction F1 revealed that a higher soil pH exhibited lower mobility of Co (Jović et al., 2017). This may explain the significantly different impact of soil pH on the mobility of Co in the two vineyards, with a higher percentage of the acid-soluble Co fraction detected in the acidic topsoil in Tállya.

Nickel was also an immobile element in both studied vineyards with the most mobile fraction percents and contents less than 5% (Fig 11) and 3 mg/kg, respectively. Most of the Ni was associated with the residual soil fraction (79% in Tokaj and 74% in Tállya), indicating that residual Ni as the dominant fraction (Davidson et al., 2006; Lu et al., 2007). The proportion of Ni in the F2 fraction was the same for the two vineyard with 12%. The contribution of Ni related to the organic matter and sulfides accounted for 7% and 9% of the total content in Tokaj and Tállya, respectively (Fig 11). In addition, there is no marked difference in the percenntage of Ni in extracted fractions between sampled soil layers along the soil profiles in both vineyards (Fig 9 & 10). These calculated contributions further confirmed the strong and stable soil-binding of Ni in the soil. In fact, there was a significant positive relationship between Ni and silt content (Table 9), illustrating its association with fine soil fractions.

Manganese, generally known to be a less toxic element in agricultural soils (with no allowable limit in soils) (Mng'ong'o et al., 2021), was the most abundant metal in the studied soils based on the sum of all extracted forms of PTEs (the highest value was below 600 mg/kg). There was no significant difference between the total concentration of Mn in the topsoil compared to that in the subsoil in Tokaj. However, in Tállya, a remarkably higher Mn content was found in the subsoil compared to the topsoil. This indicates that the Mn is of geogenic origin and no evidence of Mn accumulation by viticulture in the studied vineyard topsoils. However, as an essential micronutrient element for plants, the determination of the fractionation of Mn in the soil profile can evaluate the transformation and biovailable fraction of this element. The geochemistry distribution of Mn in soils is very complex due to the several oxidation states of Mn (in several crystalline or pseudocrystalline states, the oxides can form coprecipitates with Fe oxides) (Davidson et al., 2006). The distribution pattern of Mn in the soil fractions shows no significant difference with the soil depth in either vineyard (Fig 9 &10). The proportion of Mn associated with the reducible soil fraction was the highest, accounting for more than 50% of the total Mn in both vineyards (Fig 11). This indicates that, as expected, the Mn is strongly associated with reducible material since manganese oxyhydroxides are a major target of the hydroxylammonium chloride reagent (Davidson et al., 2006). The amount of

Mn associated with the organic matter fraction (2% in Tokaj and 3% in Tállya vineyard soil) is lower than the amount associated with the acid-soluble fraction of the soils (16% in Tokaj and 19% in Tállya vineyard soil) (Fig 9 & 10). The large amounts of Mn in the acid-soluble fraction, the reducible fraction, and the residual fraction indicate a connection with organic matter and the low stability of the Mn complexes with organic material (Kabata-Pendias, 2010). In addition, the considerable proportion of Mn in the reducible fraction and the residual fraction seemed to indicate a significant relationship with soil properties (Walna et al., 2010) such as pH, carbonates, and silt, as evidenced by a positive correlation between these factors and the Mn content in both fractions (Table 9).

The distribution of Cu fractions showed that the residual fraction (63%) and the reducible fraction (44%) dominated in the soils of the vineyards in Tokaj and Tállya, respectively (Fig 11). Although the portions of Cu found in the acid-soluble fraction and the oxidisable fraction in the vineyard soil in Tokaj was lower than those in Tállya, the rank-order of these fractions displayed an similar trend. Accordingly, in Tokaj, the proportion of Cu in the acid-soluble fraction and the oxidisable fraction was 3% and 1% of the total content, respectively. In Tállya vineyard soil, these values were 10% and 4%, respectively (Fig 11). Eventhough Cu has a high affinity for organic matter (a significant positive relationship was observed between Cu in all extracted fractions and organic matter, Table 9), the Cu fraction associated with organic matter and sulfide fraction had the lowest content. This fact can be attributed to the soluble complexes formed between soil organic matter and Cu, which is more present in the acid-soluble fraction than in the organic matter fraction (Arenas-Lago et al., 2014). 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) (Fig 9). 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 (Fig 10)). The first two extracted fractions (F1 & F2) displayed a high capacity for Cu sorption and were the most likely to bind Cu in a non-exchangeable form (Cerqueira et al., 2011; Vega et al., 2010).

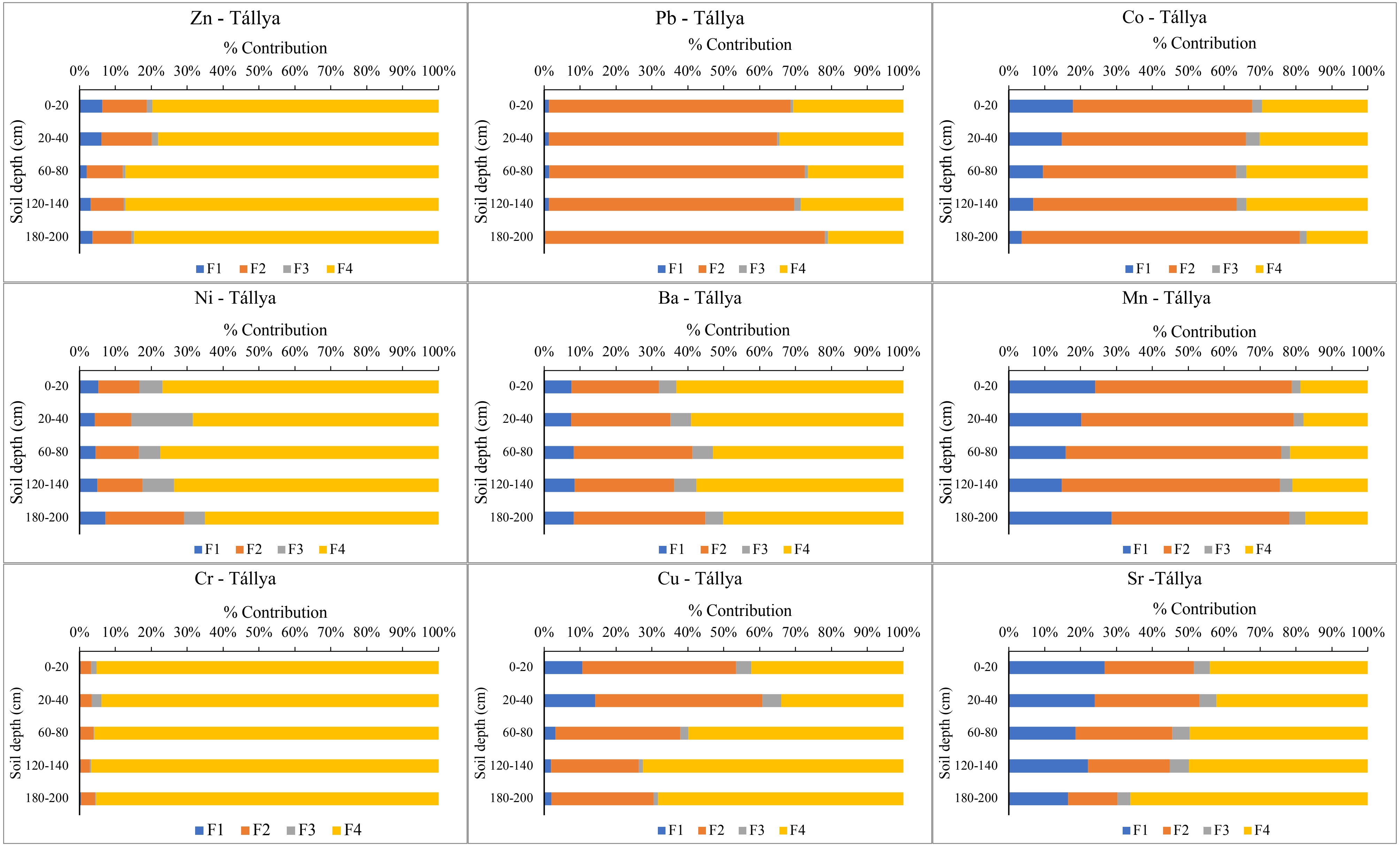

Fig 9. Contribution (%) of PTEs in four BCR extracted fractions in different soil depths in the Tállya vineyard (*F1: Acid-soluble fraction. F2: Reducible fraction. F3: Oxidisable fraction. F4: Residual fraction*)

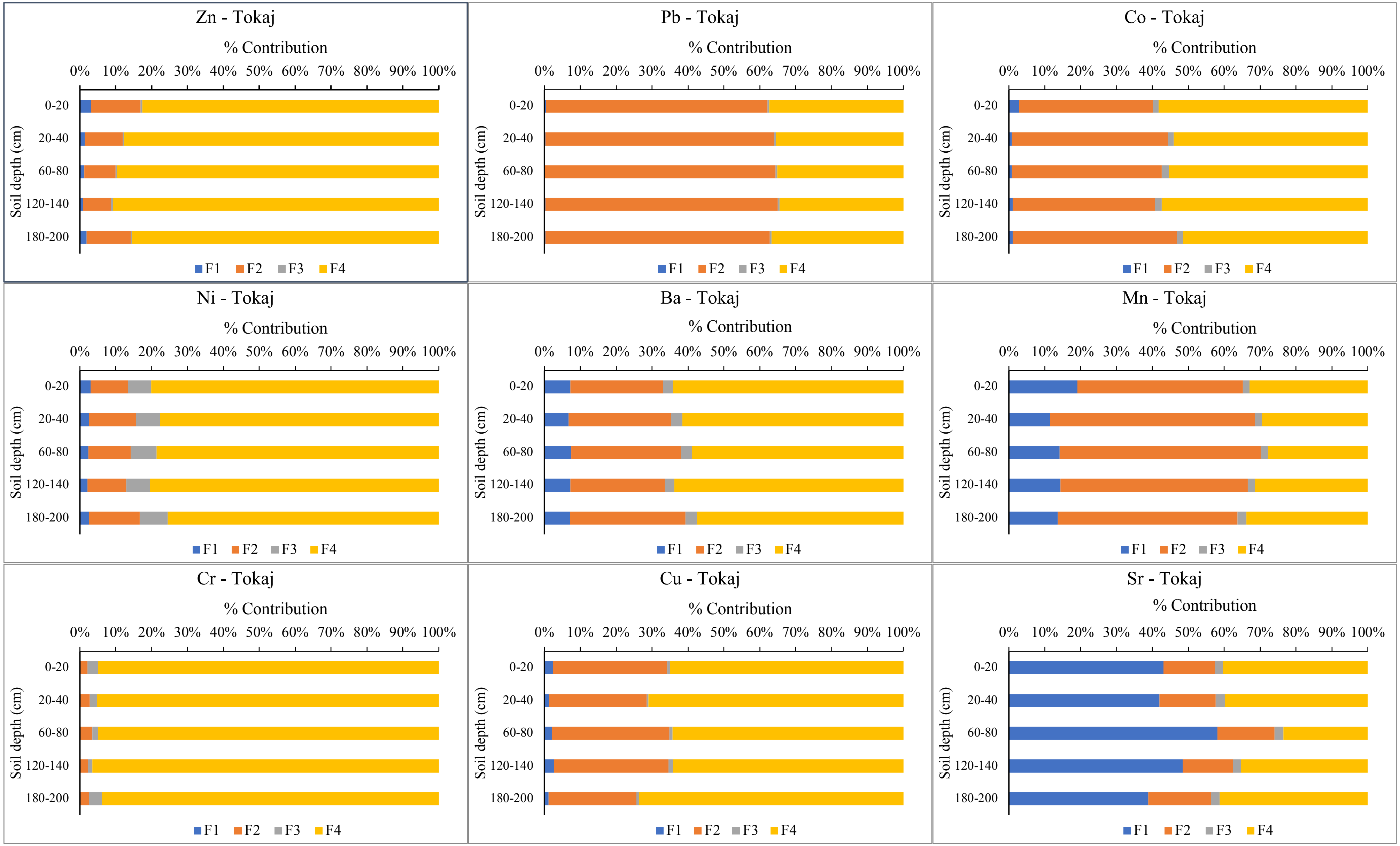

Fig 10. Contribution (%) of PTEs in four BCR extracted fractions in different soil depths in the Tokaj vineyard
(*F1: Acid-soluble fraction. F2: Reducible fraction. F3: Oxidisable fraction. F4: Residual fraction*)

Table 9. Spearman's correlation matrix between soil properties and PTE fractions data

Fraction	Element	SOM*	pH	$CaCO_3$%	Clay %	Silt %	Sand %
F1 *(Acid-soluble fraction)*	Zn	0.73^{**}	ns	ns	ns	ns	ns
	Pb	ns	-0.81^{**}	-0.77^{**}	ns	-0.64^{**}	0.65^{**}
	Co	ns	-0.73^{**}	-0.70^{**}	ns	-0.47^{*}	0.59^{**}
	Ni	0.66^{**}	ns	ns	-0.48^{*}	ns	ns
	Ba	0.47^{*}	0.41^{*}	0.50^{**}	ns	0.55^{**}	-0.42^{*}
	Mn	ns	ns	ns	-0.63^{**}	0.39^{*}	ns
	Cr	ns	ns	ns	ns	ns	ns
	Cu	0.60^{**}	ns	ns	ns	ns	ns
	Sr	ns	0.84^{**}	0.81^{**}	-0.45^{*}	0.79^{**}	-0.75^{**}
F2 *(Reducible fraction)*	Zn	0.65^{**}	ns	ns	ns	0.51^{**}	ns
	Pb	ns	-0.73^{**}	-0.71^{**}	0.52^{**}	-0.45^{*}	0.49^{*}
	Co	ns	ns	ns	ns	ns	ns
	Ni	ns	0.70^{**}	0.73^{**}	ns	0.65^{**}	-0.69^{**}
	Ba	ns	ns	ns	ns	ns	-0.43^{*}
	Mn	ns	0.60^{**}	0.58^{**}	ns	0.50^{**}	-0.45^{*}
	Cr	ns	ns	ns	0.42^{*}	ns	-0.39^{*}
	Cu	0.68^{**}	ns	ns	ns	ns	ns
	Sr	ns	ns	ns	ns	ns	ns
F3 *(Oxidisable fraction)*	Zn	0.43^{*}	ns	ns	ns	ns	ns
	Pb	ns	-0.59^{**}	-0.62^{**}	0.48^{*}	-0.62^{**}	0.50^{**}
	Co	ns	ns	ns	0.60^{**}	ns	ns
	Ni	ns	0.52^{**}	0.65^{**}	ns	0.55^{**}	-0.60^{**}
	Ba	ns	-0.78^{**}	-0.74^{**}	0.62^{**}	-0.55^{**}	0.46^{*}
	Mn	ns	ns	ns	ns	ns	ns
	Cr	0.53^{**}	ns	0.42^{*}	ns	0.51^{**}	ns
	Cu	0.60^{**}	-0.41^{*}	-0.40^{*}	ns	ns	ns
	Sr	ns	ns	ns	ns	ns	ns
F4 *(Residual fraction*)	Zn	ns	0.66^{**}	0.77^{**}	ns	0.75^{**}	-0.70^{**}
	Pb	ns	ns	ns	ns	ns	ns
	Co	ns	0.74^{**}	0.80^{**}	ns	0.71^{**}	-0.70^{**}
	Ni	ns	0.72^{**}	0.82^{**}	ns	0.70^{**}	-0.71^{**}
	Ba	ns	ns	0.48^{*}	ns	0.53^{**}	-0.56^{**}
	Mn	ns	0.66^{**}	0.72^{**}	-0.41^{*}	0.76^{**}	-0.63^{**}
	Cr	ns	0.52^{**}	0.69^{**}	ns	0.60^{**}	-0.61^{**}
	Cu	0.67^{**}	ns	ns	ns	ns	ns
	Sr	ns	0.45^{*}	0.60^{**}	ns	0.60^{**}	-0.48^{*}
Soil properties	SOM	1.00	ns	ns	ns	ns	ns
	pH	ns	1.00	0.84^{**}	-0.58^{**}	0.64^{**}	-0.62^{**}
	$CaCO_3$%	ns	0.84^{**}	1.00	-0.57^{**}	0.65^{**}	-0.59^{**}
	Clay %	ns	-0.58^{**}	-0.57^{**}	1.00	ns	ns
	Silt %	ns	0.64^{**}	0.65^{**}	ns	1.00	-0.87^{**}
	Sand %	ns	-0.62^{**}	-0.59^{**}	ns	-0.87^{**}	1.00

**SOM: Soil organic matter content, ns: not significant*

** Significant at the level of $p < 0.05$; ** Significant at the level of $p < 0.01$.*

Such elements as Ba and Sr have received little attention as compared to other more often-studied PTEs (Zn, Pb, Co, Ni, Mn, Cr, and Cu). Hence, the lability and mobilization of these elements have been studied in this research, then the assessment of PTE-associated contamination and environmental risk can be more comprehensive.

Although a higher Ba content was found in the vineyard soil in Tokaj than in the vineyard soil in Tálllya, in general no significant difference was found in the proportions of Ba in the extracted soil fractions in both vineyards. The geochemical distribution of Ba showed that the percentage of each fraction was uniform in all sampled soil layers of the soil profile in both studied sites (Fig 9 & 10). In addition, Ba was most strongly associated with the residual fraction (Tokaj: 62% and Tállya: 59%) and the reducible fraction (28% in both studied sites) (Fig 11). The Ba proportions associated with the F1 and F3 fractions were less than 8% and 5%, respectively in both vineyards. Barium dominated in the residual fraction, which is highly immobile and corresponds to the lithogenic origin of this metal. Indeed, Ba is known to be rather immobile in soils, probably due to the fact that it is immobilized by precipitation with sulfate and/or carbonate and/or by fixation to silicate clays with high-charge, and that Ba is geochemically associated with feldspars and biotites (Carbonell et all., 1999; Sungur et al., 2019).

The observed Sr concentration did not exceed the toxicity threshold of 150 mg/kg (Pendias and Pendias, 2000) in both vineyards. Relatively high percentages of Sr in the acid-soluble fraction in both vineyards indicated their high solubility and bioavailability (Fig 11). However, there was two times as high the acid-soluble fraction percentage of Sr of it total content in the vineyard soil in Tokaj (46%) as in Tállya (24%), indicating that the soil geochemical fractions of Sr are strongly influenced by soil characteristics. Strontium in the F1 fraction showed a strong positive relationship with $CaCO_3$ and pH (Table 9). The soil pH was reported to be an important factor in the speciation and stability of metals associated with carbonates. For Sr, carbonates were completely leached at soil pH of ≥ 6.0, (Wang et al., 2015). In addition, the precipitation of carbonates with Sr, which easily removed from the soil solution phase (Hodkin et al., 2016), can be explained the positive correlation of Sr and carbonates and the highest percentage of Sr in the first fraction, especially in Tokaj. In Tokaj, the proportion of Sr in the residual fraction is the second highest with 36%, followed by the reducible fraction (15%) and the oxidisable fraction (2%). In Tállya, on the other hand, the highest ratio of 45% was detected for the Sr in the residual fraction, succeeded by the reducible fraction, the acid-soluble fraction, and the oxidisable fraction accounting for 27%, 24%, and 4% of the total Sr content, respectively.

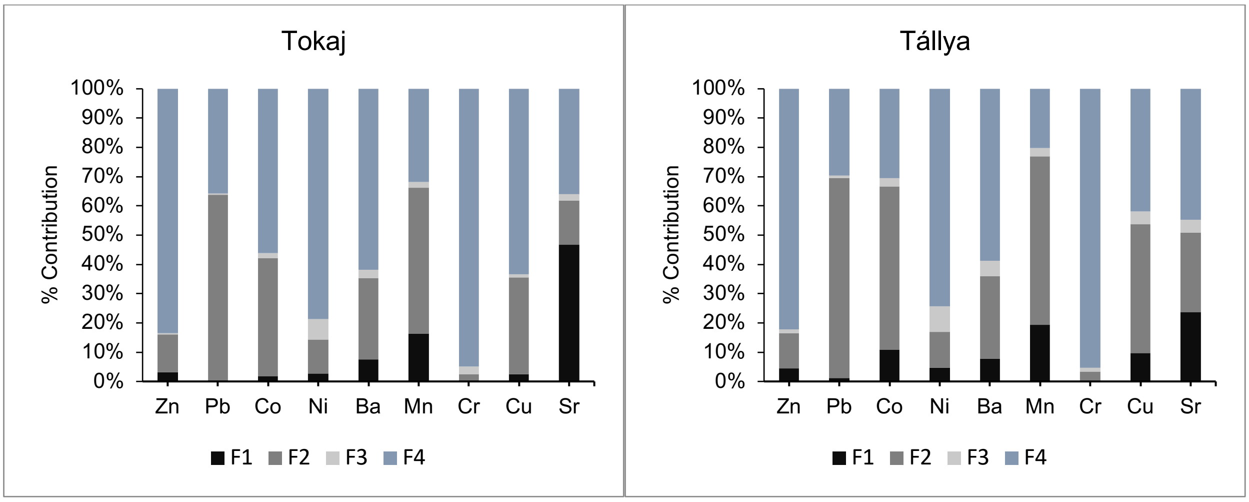

Fig 11. Average percentages for fractionation of target PTEs in all soil layers of the two studied vineyards

(*F1: Acid-soluble fraction. F2: Reducible fraction. F3: Oxidisable fraction. F4: Residual fraction*)

In summary, the residual fraction of the studied soils contained the highest proportion of PTEs, except for Sr, Co and Cu in Tálly, and Pb and Mn. In this context, most Sr was associated with the acid-soluble soil fraction in the Tokaj vineyard, while Co, Cu, Pb, and Mn showed the greatest affinity for the reducible fraction (bound to iron and manganese oxyhydroxides) in both vineyards. 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) (Matong et al., 2016; Nemati et al., 2011), which then become available for uptake by living organisms. Therefore, the risk of PTEs in this fraction should be included in environmental assessment. Contrary, the contents and propotion of PTEs associated with the organic component were the lowest values, indicating weak binding of PTEs to soil organic compounds, despite their high affinity and sorption capacity for metals (Arenas-Lago et al., 2014). Likewise, the acid-soluble fraction of target PTEs in both vineyards showed low PTE-binding capacity and less than 11% of the sum of all PTE forms, apart from Sr and Mn. However, even though the percentages of Zn, Pb, Co, Ni, Cr, and Cu in the acid-soluble fraction were lower than those of Sr and Mn, their environmental and ecological risks should be considered because these PTE can pose a potential risk of toxicity to crops even at low concentrations. Furthemore, the relatively high levels of Mn and Sr in the acid-soluble and reducible fractions in the soil in both studied vineyards revealed their high solubility and bioavailability (Hodkin et al., 2016). In general, 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 increasing their bioavailability.

Indeed, except for Pb and Cu, the residual fraction of the studied PTEs was strongly related to the soil parameters (the soil pH, $CaCO_3$, and soil particles) (Table 9). 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. The soil pH significantly affects the stability of PTEs associated with carbonate, often in metastable and polymorphic forms. Hence, it was suggested that soil acidification resulted in carbonate loss (Wang et al., 2015). As expected, in the present study, a higher carbonate content is detected in the Tokaj with a higher soil pH. As a result, PTEs bound to carbonates can be released into the soil solution phase when the soil is acidified, increasing their activities and bioavailability. The silt content showed a significant correlation with all investigated PTEs in the residual fraction, except for Pb and Cu (Table 9), indicating a strong binding of these PTEs to the soil mineral phase.

5.5.2. Distribution of PTEs in the different geochemical fractions in vineyard topsoils and eroded sediments

The distribution of PTEs in the geochemical fractions of the topsoil and sediment samples taken along the hillslope is displayed in Fig 12 for both studied sites.

With regard to comparison between the two vineyards, 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. 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. Accordingly, a higher percentage of the acid-soluble fraction of these PTEs was determined in the eroded sediments in Tokaj, indicating an increased mobility of these elements in the sediment. The Mn percentage in the reducible fraction was significantly higher in Tállya than in Tokaj. In contrast, the proportion of Sr associated with the acid-soluble fraction in the topsoil and sediment was remarkably higher in Tokaj than in Tállya (Fig 12). In the first two extracted fractions (F1 and F2 fraction), the contribution of Zn in the sum of all fractions in the vineyard soils and sediments was noticed and higher in Tokaj than in Tállya. As for Cu, higher mobility was observed in the topsoil in Tállya with 8% of the F1 fraction, however, the highest percentage of the F1 fraction was reported for Cu in the sediment in Tokaj. These differences can be mainly explained by the impact of organic matter content and particle size. The PTEs tend to occur in the acid-soluble fraction in the soluble complexes with organic material (Arenas-Lago et al., 2014). Indeed, the analytical results of the organic matter contents in the topsoils and sediments along the hillslope showed the highest values in the eroded sediments in Tokaj (average 3.14%). In addition, grain size distribution plays an important role in the release of the PTEs into the soil solution. Since a higher content of fine particles was observed in the sediments, the potential PTE contents bound to iron and manganese oxyhydroxides can be explored. Indeed, the XRD results in Tokaj revealed a significant presence of quartz (60 - 70%) and merely 10 - 20% illite/muscovite in the topsoil, while the major amount of illite/muscovite (40 - 50%) was found in the eroded sediments. The predominant presence of illite/muscovite in the sediments suggested a close relationship with the chelation of PTEs in the oxidation zone (Hasan et al., 2008). Accordingly, in Tokaj, all investigated PTEs (except Sr) dominated in the acid-soluble fraction and the reducible fraction of the eroded sediment compared to the topsoil (Fig 12). Meanwhile, in Tállya, the fractionation of PTEs showed no significant difference between the vineyard topsoil and the eroded sediment. This can be explained by the similar major constituents of quartz (~60%), albite (~10%), and illite/muscovite (~10%) in the two studied medium in Tállya vineyard. However, the lower contribution of illite/muscovite may result in a lower proportion of PTEs in the acid-soluble fraction and the reducible fraction in the eroded sediments and topsoils of the Tállya vineyard compared to the Tokaj vineyard.

As for Cu in Tokaj, in addition to significant Cu enrichment, a greater proportion of Cu were observed in the acid-soluble (10%) and reducible (53%) fractions in the eroded sediment compared to the vineyard topsoil (4% and 40%, respectively). Whereas, no significant difference in the Cu percent in the oxidisable fraction was found between the sediments (3%) and the topsoils (1%). In line with the proportion of Cu in the three first extracted fractions, the most Cu was associated with the residual fraction of the topsoil (55%), meanwhile its value in the eroded sediment was the second highest fraction, 33%. Copper was dominant in the acid-soluble fraction and the reducible fraction in the eroded sediment, indicating its high lability and bioavailability. Hence, in Tokaj, the environmental risk of Cu prevailing in the sediments can be apparently indicated.

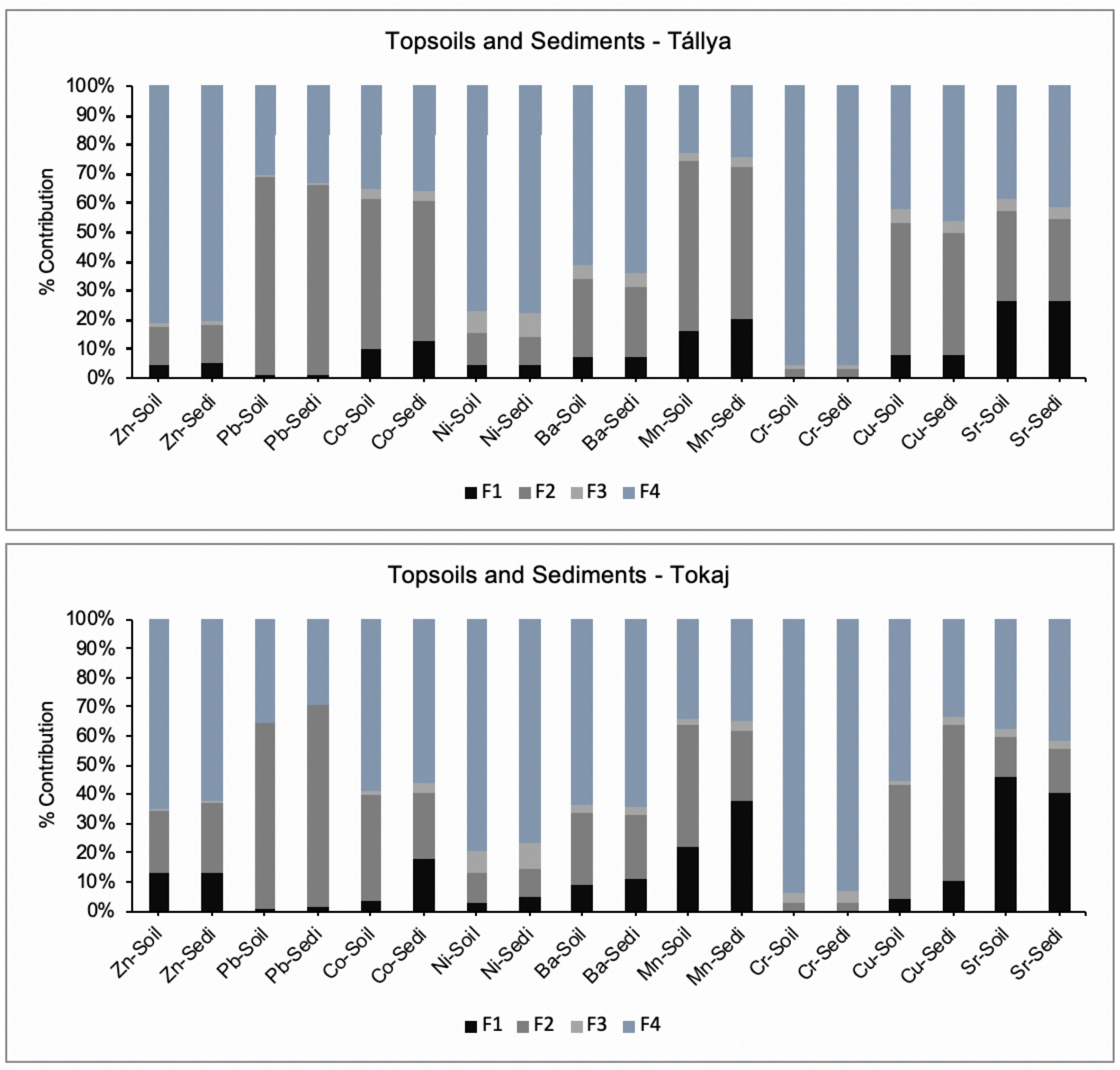

Fig 12. The relative percentage of target PTEs from the sum content in each fraction of the studied topsoils and eroded sediments along the hillslope. (*F1: Acid-soluble fraction. F2: Reducible fraction. F3: Oxidisable fraction. F4: Residual fraction*)

5.6. Soil contamination indices and ecological risk assessment in Tállya

5.6.1. Soil contamination indices of PTEs in soils and sediments in Tállya

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.

In Tállya, the Cf values for Pb were below 1 in both soils and sediments, while Cfs for remaining PTE in the eroded sediment were slightly higher than those in the vineyard soils (Fig 13). This is accodance with the slight enrichment of PTEs in the sediment compared to the vineyard topsoils (Fig 4). The median Cf in the topsoils and sediments for Zn (1.3 and 1.4, respectively), and in the subsoils for Co (2.9), Ni (2.4), Cr (1.7), and Cu (1.9) imply a moderate contamination level. Meanwhile, considerable contamination was observed for Co (3.0 and 3.58), Ni (3.0 and 3.3), and Cr (3.0 and 3.3) in the vineyard topsoils and eroded sediments (Fig 13). The highest Cfs for Cu (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.

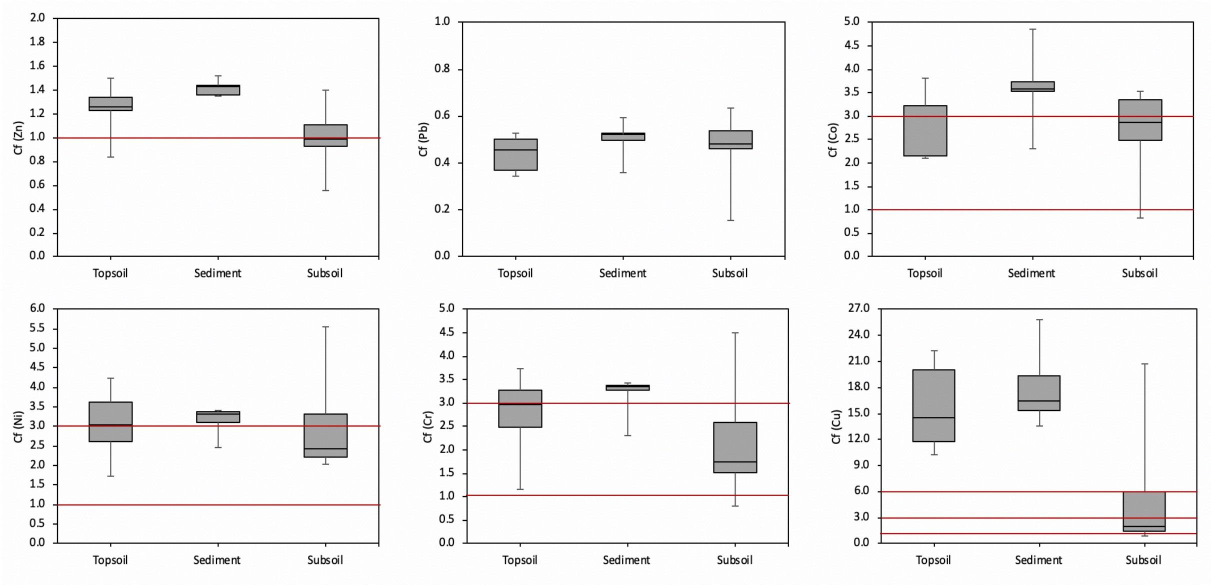

Fig 13. Contamination factor (Cf) of PTEs in the vineyard top- (0-20 cm) and subsoil (>20 cm) and sediments in Tállya. The added red lines highlight Cf = 1, above which contamination is identified; Cf = 3, above which considerable contamination is identified; Cf = 6, above which high contamination is identified.

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 with the median PLI value varies from 1.62 (in the subsoils) to 2.77 (in the eroded sediments). Meanwhile, the PLI for the vineyards based on the bioavailable PTEs concentrations is below 1.00 (Fig 14), classifying in no pollution status.

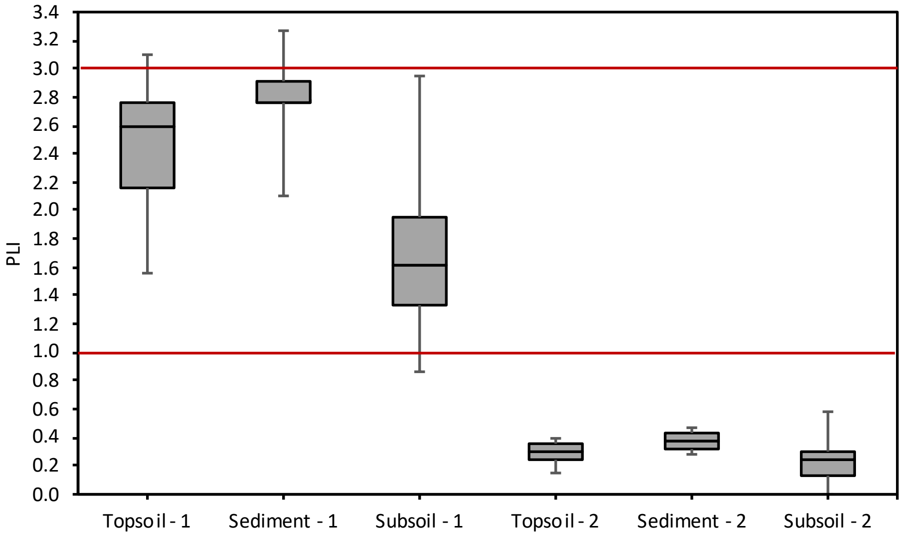

Fig 14. The pollution load index (PLI) of the vineyard top- (0-20 cm), subsoil (>20 cm), and sediments in Tállya (1 – calculated with the total PTEs; 2 – calculated with EDTA extracted PTEs). The red line displays PLI = 1, above which pollution is identified.

5.6.2. Ecological risk assessment of PTEs in soils and sediments in Tállya

Former studies identified the Ecological Risk Index (ERI) as one of the most performant indices for assessing the overall ecological risk in soils and sediments (Arfaeinia et al., 2019; Liu et al., 2014; Luo et al., 2007).

The ecological risk factor (Ei) of an individual PTE summarised in Table 10 indicated that the total Cu in the topsoil and eroded sediments represent a moderate ecological risk and considerable ecological risk, respectively. 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 old conventional vineyard. The highest contributor to the ERI were Cu (Ei (average): 77.8 in the topsoil and 90.5 in the sediment), constituting more than 65% of the total ecological risk. Although the Ei and ERI values of PTEs calculated by the bioavailability of PTEs were significantly lower than those based on total PTEs and below the ecological risk thresholds, the disparity was noticeable for the bioavailable fraction of Cu in the eroded sediment with its maximum Ei of 64.5 (exceeding the threshold and accounting for 90% of the ERI). This indicates the high lability and bioavailability of Cu in the eroded sediments, increasing the ecological risk of this element in Tállya. Most of ERI is associated with the bioavailable Cu reaching its Ei of 38.6 (accounting for 77% of the ERI) in the topsoil and 19.3 (accounting for 61% of the ERI) in the subsoil.

Table 10. The average values of the ecological risk indices for target PTEs in the vineyard top- (0-20 cm) and subsoil (> 20 cm) and eroded sediments (EDTA extracted PTE contents are marked with X_E) in Tállya. Ei stands for the ecological risk factor, while ERI is the ecological risk index.

	Ei (Topsoil)	Ei (Sediment)	Ei (Subsoil)
Pseudo-total metals			
Zn	1.2	1.4	1.0
Pb	2.2	2.5	2.3
Co	14.4	18.0	13.7
Ni	17.9	18.8	18.1
Cr	5.3	6.3	4.4
Cu	77.8	90.5	27.3
ERI	118.9	137.5	66.8
EDTA extracted metals			
Zn_E	0.1	0.2	0.1
Pb_E	1.2	1.3	1.4
Co_E	8.4	3.7	8.8
Ni_E	1.6	1.9	2.1
Cr_E	0.0	0.0	0.0
Cu_E	38.6	64.5	19.3
ERI_E	49.9	71.7	31.6

5.7. Soil contamination indices and ecological risk assessment in Tokaj

5.7.1. Soil contamination indices of PTEs in soils and sediments in Tokaj

In Tokaj, the PTE-based contamination factors (Cfs) in the sediment were higher than those in the vineyard soil, except for Ni and Cr (Fig 15). The median Cfs in the sediments for Zn (1.8), Co (1.3), Ni (1.4), and Cr (1.4) imply a moderate contamination level. The high Cfs for Cu (ranging from 6.2 to 8.8) indicate high contamination and signicant enrichment of Cu compared to the local forest soil. In general, moderate contamination was observed for all examined PTEs in the vineyard top- and subsoil, except for Pb.

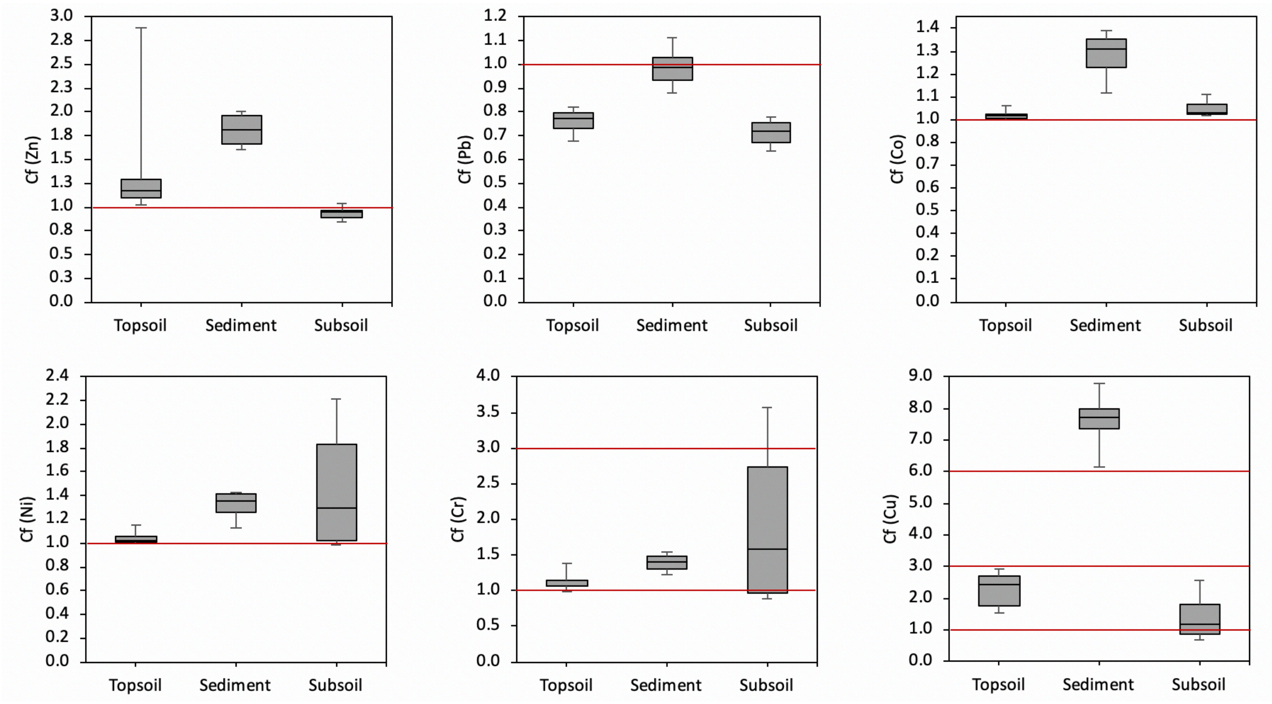

Fig 15. Contamination factor (Cf) of PTEs in the vineyard top- (0-20 cm) and subsoil (>20 cm) and sediments in Tokaj. The added red lines highlight Cf = 1, above which contamination is identified; Cf = 3, above which considerable contamination is identified; Cf = 6, above which high contamination is identified.

The calculated contamination indices showed that Cu, Zn, Ni, and Cr predominantly accumulated in the studied vineyard soils and were significantly enriched in the eroded sediments, causing an elevated pollution risk, in particular, for Cu. The Pollution load index (PLI) encompassing all individual Cf values varied from 1.01 to 1.42 and from 0.84 to 1.39 for vineyard top- and subsoils, respectively, classifying the vineyard soils in no to moderate pollution status. Meanwhile, the higher PLI for the eroded sediments, ranging from 1.55 to 1.98 (Fig 16), belong to the moderate pollution category. Significant contamination is detected when the PLI value exceeds 1 (Rinklebe et al., 2019), demonstrating that both studied vineyard soils and sediments represent a multi-element contamination case.

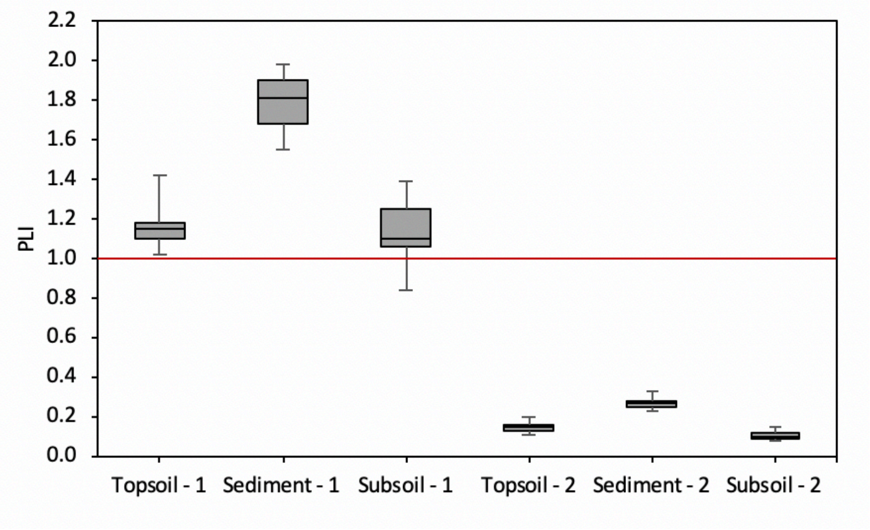

Fig 16. The pollution load index (PLI) of the vineyard top- (0-20 cm), subsoil (>20 cm), and sediments in Tokaj (1 – calculated with the total PTEs; 2 – calculated with EDTA extracted PTEs). The red line displays PLI = 1, above which pollution is identified.

5.7.2. Ecological risk assessment of PTEs in soils and sediments in Tokaj

Based on the ecological risk indices (Ei) summarised in Table 11, in Tokaj, the soil and eroded sediments represent a low ecological risk. Indeed, all calculated values are below the ecological risk factor thresholds of 40 for Ei and 90 for ERI. The ecological risk indices showed no elevated ecological risk in the studied organic vineyard, meanwhile, Mirzaei and co-workers (2019) reported the range of ERI (for Cu, Zn, Pb, Cr, and Cd) in 38 long-term fertilized vineyards from 5.30 to 468.09, indicating considerable ecological risk with 6 vineyards representing a moderate risk and 3 vineyards a high risk. Considering bioavailable PTE contents for the ecological risk assessment (Table 11), which depict an even more realistic estimation of environmental threats, the calculated indices are lower and show a negligible risk.

As expected from the Ei data for the target PTE, the two highest contributors to the ERI were Cu (Ei (average): 11.3 in the topsoil, 38.0 in the sediment, and 7.0 in the subsoil), followed by Ni (6.2 in the topsoil, 7.9 in the sediment, and 8.7 in the subsoil). The relative contribution to the overall ecological risk of the other examined PTEs was negligible. The highest values of Ei were assessed for Cu, especially in eroded sediments (Ei (total Cu) = 38.0, accounting for 61.3% of the total ecological risk). Similar to Tállya, the disparity was noticeable for the bioavailable fraction of Cu in the vineyard soil and sediment in Tokaj. However, the opposite trend was observed with higher contribution of Cu bioavailibilty in the sediment. The figures for bioavailable Cu contribution to the ERI in eroded sediments reached its maximum Ei of 24.6 and made up 82% of the total ecological risk. The latter revealed the prevailing influence of bioavailable Cu in the overall ecological risk represented by the six target PTEs in the vineyard soil. In addition, the most noticeable difference between the distribution percentage of total and bioavailable Cu relative to the total ERI indicated an apparent increase in the ecological risk prevailing in the sediments, especially for the EDTA extracted fractions.

Table 11. The average values of the ecological risk indices for target PTEs in the vineyard top- (0-20 cm) and subsoil (> 20 cm) and eroded sediments (EDTA extracted PTE contents are marked with X_E) in Tokaj. Ei stands for the ecological risk factor, while ERI is the ecological risk index.

	Ei (Topsoil)	Ei (Sediment)	Ei (Subsoil)
Pseudo-total metals			
Zn	1.3	1.8	0.9
Pb	3.8	4.9	3.6
Co	4.9	6.5	5.1
Ni	6.2	7.9	8.7
Cr	2.2	2.8	3.8
Cu	11.3	38.0	7.0
ERI	29.8	62.0	29.2
EDTA extracted metals			
Zn_E	0.2	0.4	0.0
Pb_E	1.6	3.2	1.7
Co_E	1.9	1.4	2.3
Ni_E	0.6	0.5	0.9
Cr_E	0.0	0.0	0.0
Cu_E	4.9	24.6	2.2
ERI_E	9.2	30.2	7.1

5.8. Human health risk assessment of PTEs in soils and sediments in both vineyards

The calculated hazard quotient (HQ) accounting for the health risk associated with the "soil-to-human" exposure of the studied PTEs were either negligible or moderate. The mean HQ for total Cr of 0.34 (unitless) for children based on the topsoil Cr content of the vineyard in Tokaj shows a higher risk compared to other PTEs. There was a remarkable difference between HQ values for children, workers and adults. Generally, the HQs for workers, adults and children were in the order of Cr > Pb > Ni > Cu > Co > Zn in Tokaj; and Cr > Pb > Cu > Ni > Co > Zn for workers in Tállya (Fig 17). The HQ assessment results in Tállya are in good agreement with the findings of

Mirzaei et al (2019), who estimated similar HQ for Cr, Pb, Cu, and Zn in vineyard soils. In Tokaj, due to the high total concentration of Ni in the topsoil, the HQ (Ni) exceeds the health risks associated with Cu (Fig 17). No significant non-carcinogenic risk was revealed in our study, similarly to anterior research on potential human health risks related to PTEs in vineyard soils by Mirzaei et al. (2019) and Liang et al. (2015) for adults and children, and Milićević et al. (2018) for workers.

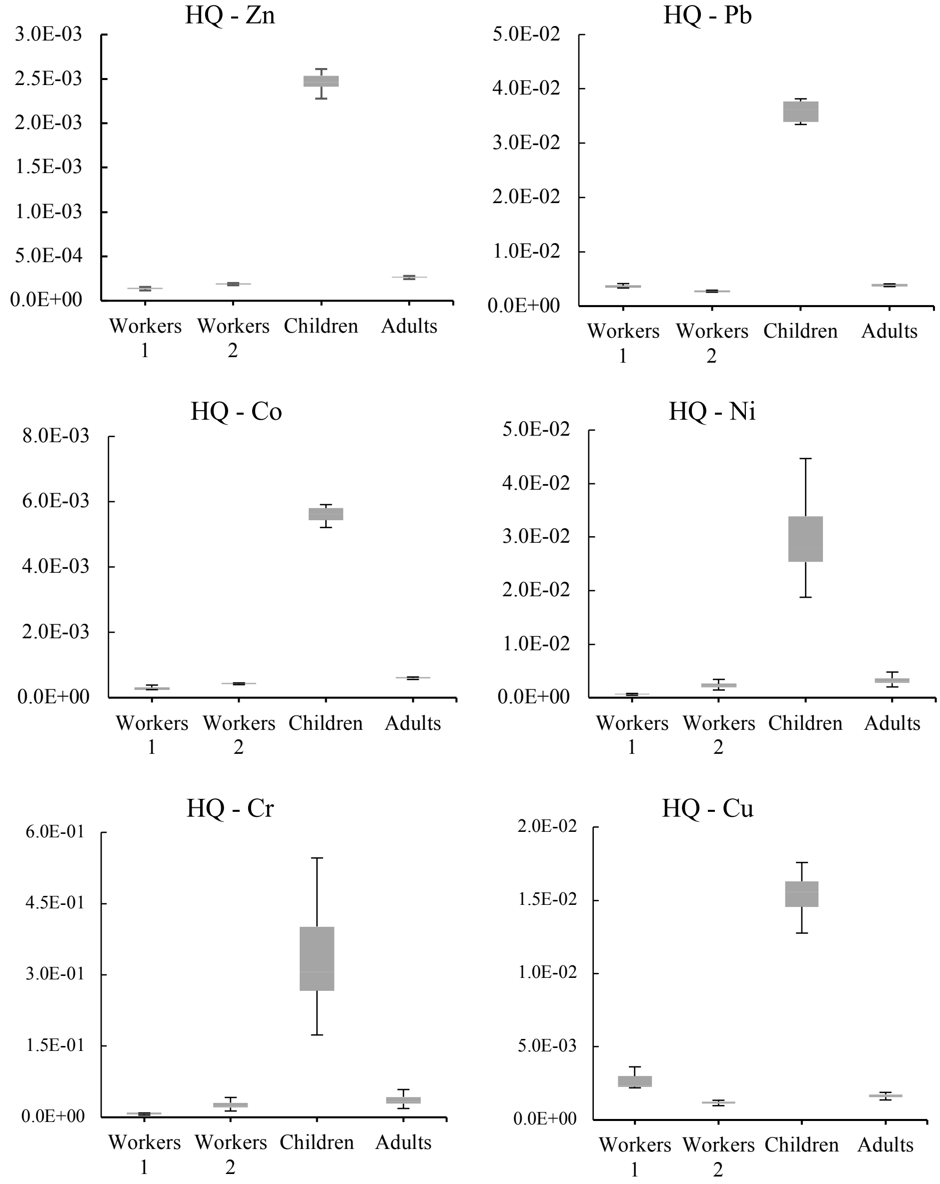

Fig 17. Hazard quotient (HQ) of the health risk assessment of target PTEs in the studied vineyards for workers (1 – in Tállya; 2 – in Tokaj); children and adults for Tokaj

Indeed, the calculated hazard index (HI) values for all groups considered (children, adults and workers) and throughout the study areas were less than unity (Fig 18). Therefore, no elevated health risks were detected. However, in Tokaj, considering overall health risks, the mean HI for children (0.43) was more than 9 times higher than for adults (0.046). Despite the substantially higher contents of Cu observed in Tállya, the mean HI for workers in Tállya (0.015) was half of calculated mean HI for workers in Tokaj (0.033) (Fig 18). Higher contents of PTEs can explain the latter (apart from Pb and Cu) observed in Tokaj compared to Tállya. In a previous study, Mirzaei and co-workers (2020) reported a maximum HI of 0.062 in a vineyard topsoil (0-20 cm) for Cu, Cd, Cr, Pb, and Zn, a score inferior to the highest HI of 0.65 in Tokaj (Fig 18). The difference is likely due to the significantly higher concentration of Cr in the Tokaj vineyard. Hence, the high Cr content observed in Tokaj originating from local sources and manure applications considerably increased the overall human health risks of the soil-bound PTEs.

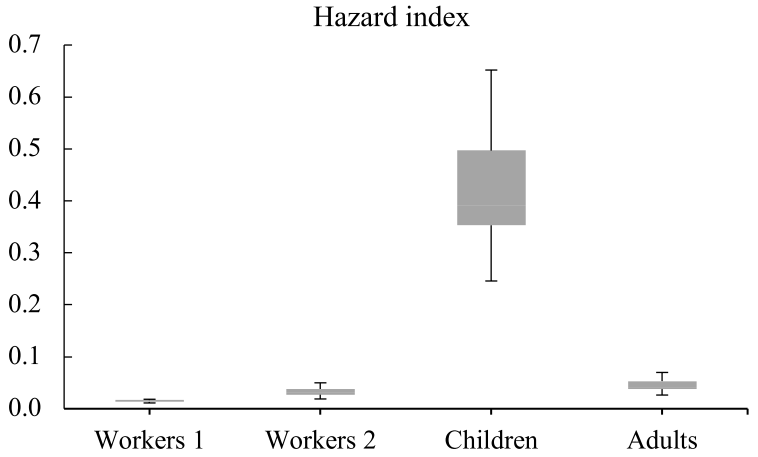

Fig 18. Hazard index (HI) of the health risk assessment of target PTEs in the two studied vineyards for workers (1 – in Tállya; 2 – in Tokaj); children and adults for the Tokaj vineyard

As expected from the individual HQs based on total PTE contents in Tokaj, the highest distribution percentage relative to the total HI is associated with Cr, reaching up to 79.0%, followed by Pb (8.4 %), Ni (7.0%), and Cu (3.6%). The relative contribution of the rest merely accounted for the remaining 2.0% of the total risk (Fig 19). Similarly to Tokaj, Cr displayed the highest distribution percentage (with 49.7%) in the vineyard topsoil of Tállya, succeeded by Pb (24.6%) and Cu (18.5%). The higher total Cu content due to the long-term use of Cu pesticides in the older vineyard in Tállya led to a higher contribution of Cu to the total HI, against 3.6% in Tokaj. Chromium and Pb were reported to represent the highest risk in similar studies concerning PTE-related health risks in vineyard soils (Mirzaei et al. 2019; Milićević et al. 2018).

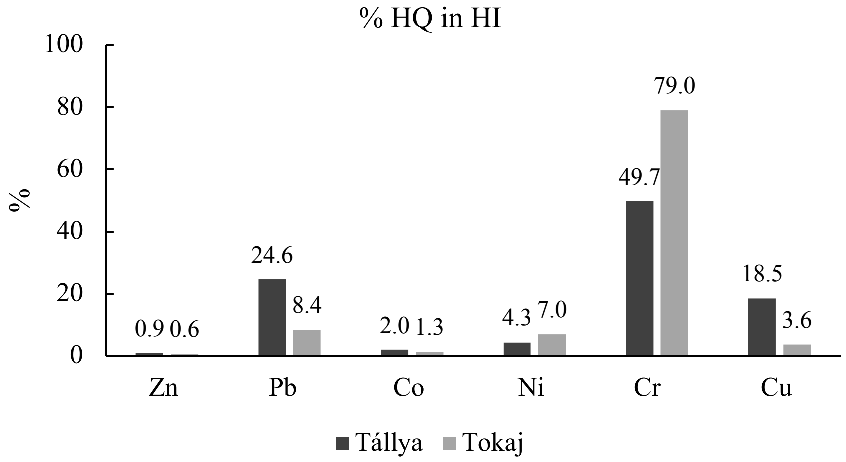

Fig 19. Contribution percentage of target PTEs to the hazard index (HI) related to vineyard soils. Note that percentages are the same among the various studied groups (children, adults and workers alike)

6. Conclusions

Viticulture exerts a significant impact on the soil environment. It changes specific soil properties and results in the accumulation of potentially toxic elements (PTEs) through farming practices. The soil management also induces enhanced soil erosion in the vineyards, which in turn impacts PTE accumulation patterns. Our results indicate that the studied PTEs (Zn, Pb, Co, Ni, Cr, and Cu) showed higher contents in the organic vineyard compared to the conventional one, except for Cu and Pb. 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. Copper was the major pollutant in the older conventional and the younger organic vineyards too, due to the repeated treatments of vine plants with Cu-based pesticides. Apart from Ni and Cr, the considered PTEs accumulate principally in the top 10 cm in both vineyards. The studied PTEs accumulation depended on the different soil conditions and vineyard management. In addition, terrain played an essential role in the enrichment patterns of PTEs in the topsoil. In Tállya, an inversed pattern was observed with predominant enrichment of PTEs at the top of the hillslope. Conversely, the target PTEs showed higher contents at the footslope in Tokaj, confirming the downslope relocation of PTE-rich sediments due to soil erosion processes.

Generally, the target PTEs tented to show increased concentrations in eroded sediments. 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. In contrast, in Tokaj, the target PTEs tented to enrich significantly in the eroded sediments. The examined PTEs demonstrated higher bioavailable contents in the eroded sediments than the top- and subsoil in both vineyards, except Co and Ni. A significantly higher proportion of bioavailable Cu and Zn was found in the eroded sediments, which can be attributed to the higher content of organic matter and fine soil particles (clay and silt) in the sediments compared to the vineyard soils.

The results of the improved three-step sequential BCR extraction procedure for all soil profiles showed that in Tokaj, major portions of Zn, Co, Ni, Ba, Cr and Cu mostly existed in the residual soil fraction, whereas, Pb and Mn were dominating in the reducible soil fraction. In Tállya, Sr, Zn, Ni, Ba, and Cr was mainly associated with the residual fraction, meanwhile, most of the Pb, Co, Mn, and Cu was exhibited in the reducible fraction. The amount of investigated PTEs in the soil fractions are largely influenced by soil pH, $CaCO_3$, and silt content. As for topsoils and sediments, there was no significant difference between the proportions of Pb, Ni, Ba, and Cr in the extracted fractions in accordance with each medium in comparison between the two vineyards. Meanwhile, the differences between the other PTEs 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. These differences can be mainly explained by the impact of organic matter content and particle distribution.

The PTE-based contamination factors (Cfs) showed significant Cu pollution compared to the reference neighboring forest soils in both sites. The calculated pollution load index (PLI) based on the total PTEs contents showed a moderate to a high pollution for the soils and sediments in the Tállya 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 thresholds of 40. The ERI calculated for topsoils and sediments showed an overall moderate risk in the old conventional vineyard. In Tokaj, 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. Ecological risk assessment of PTEs showed a low risk (ERI < 90) in the organic vineyard.

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 in both vineyards, accounting for 49.7% (in Tállya) and 79.0% (in Tokaj) of the calculated HIs.

7. Summary

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.

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.

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.

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.

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).

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.

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.

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. 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.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisors, Prof. Dr. Farsang Andrea and Dr. Babcsányi Izabella for the academic and personal support, who taught, encouraged and helped me during the last four years. I would especially like to thank my colleagues at the Department of Geoinformatics, Physical and Environmental Geography for their support and amazing study environment.

I would also like to thank the vine growers of Tállya and the Hétszőlő vineyard in Tokaj for allowing our field survey and sharing information about the used agrichemicals and soil management.

I would like to thank the Tempus Public Foundation (TPF) – Stipendium Hungaricum program for the support of my PhD scholarship. I would also like to thank the financial support from the Premium Postdoctoral Research Program of the Hungarian Academy of Sciences, OTKA 1K 116981 and the 'Thematic Network for the Sustainable Use of Resources – RING2017' (program code: EFOP-3.6.2-16-201700010) projects.

Finally, I am grateful to my family and my friends who always believed in me and supported me all these years, without their support, I would not have stayed strong to finish my study.

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