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Potentially toxic elements (As, Cu, Pb and Zn) in former vineyard soils under olive groves and natural vegetation

Potencijalno toksični elementi (As, Cu, Pb and Zn) u bivšim vinogradarskim tlima pod maslinicima i prirodnom vegetacijom

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ABSTRACT

The study aimed to determine and compare concentrations of As, Cu, Pb, and Zn in former vineyard soils under olive groves and natural vegetation and to assess soil pollution in the studied area. The study was conducted in the Primošten municipality in Middle Dalmatia, Croatia, on Terra rossa soil. A total of 20 topsoil samples were taken, out of which 10 were from soils under natural vegetation (NV) and 10 from olive groves (OG). The total concentrations of As, Cu, Pb, and Zn were determined by using the pXRF method. Significantly higher Cu and Zn concentrations were determined in OG (199.3 and 138.0 mg/kg, respectively) compared to NV (51.8 and 118.1 mg/kg, respectively). Mean concentrations of As and Pb in NV (19.8 and 48.2 mg/kg, respectively) and OG (19.8 and 46.6 mg/kg, respectively) were not statistically different. The As, Cu, Pb, and Zn concentrations in NV were below maximum permissible concentrations (MPC) for agricultural land according to Croatian legislation (OG 71/19). However, the soils of OG were polluted by Cu and Zn. Enrichment factor (EF) pointed to minimal enrichment of soils under NV with As, Pb, and Zn, and minimal to moderate with Cu. Soils under OG were minimally enriched with As and Pb, minimally to moderately with Zn, and moderately to significantly with Cu. The obtained results pointed to more detailed studies of potentially toxic elements (PTE), especially Cu, in the study area.

Keywords: Dalmatia, soil pollution, enrichment factor, Terra rossa

SAŽETAK

Cilj istraživanja bio je utvrditi i usporediti koncentracije As, Cu, Pb i Zn u bivšim vinogradarskim tlima pod maslinicima i prirodnom vegetacijom, te procijeniti onečišćenje tla u istraživanom području. Istraživanje je provedeno na crvenicama u Hrvatskoj, u općini Primošten u Srednjoj Dalmaciji. Ukupno je uzeto 20 površinskih uzoraka, od čega 10 u tlima pod prirodnom vegetacijom (PV) i 10 iz maslinika (M). Ukupne koncentracije As, Cu, Pb i Zn kvantificirane su primjenom pXRF metode. Signifikantno više Cu i Zn koncentracije utvrđene su u M (199,3 odnosno 138,0 mg/kg) u usporedbi s PV (51,8 odnosno 118,1 mg/kg). Srednje koncentracije As i Pb u PV (19,8 odnosno 48,2 mg/kg) i M (19,8 odnosno 46,6 mg/kg) nisu bile statistički različite. Koncentracije As, Cu i Zn u PV bile su ispod maksimalno dozvoljenih koncentracija (MDK) za poljoprivredno zemljište prema hrvatskoj zakonskoj regulativi (NN 71/19). Međutim, tla maslinika bila su onečišćena sa Cu i Zn. Faktor obogaćenja (FO) uputio je na minimalno obogaćenje tla pod PV sa As, Pb i Zn, te minimalno do umjereno sa Cu. Tla pod M bila su minimalno obogaćena sa As i Pb, minimalno do umjereno sa Zn, te umjereno do značajno sa Cu. Dobiveni rezultati upućuju na detaljnije istraživanje potencijalno toksičnih elemenata (PTE), posebno bakra, u istraživanom području.

Ključne riječi: crvenica, Dalmacija, faktor obogaćenja, onečišćenje tla

INTRODUCTION

The concentration of potentially toxic elements (PTE) in soils depends on many natural and anthropogenic factors. Natural factors include parent material and weathering processes (Alloway, 2013), as well as soil type, topography, and erosion process (Valladares et al., 2009). Anthropogenic sources of PTE in soils are emissions from industrial areas, mining, smelting, and motor vehicles; application of fertilizers and fungicides; sewage sludge, and atmospheric deposition (Kabata Pendias and Mukherjee, 2007). The impact of agricultural production on soil pollution by PTE is a well-known problem recognized in many studies (Panagos et al., 2018; Avramidis et al., 2019; Ennaji et al., 2020; Shammi et al., 2021).

The most frequently reported and widely documented problem in the literature is elevated levels of Cu in permanent crops, especially vineyards (Komarek et al., 2010). Copper-based fungicides have been intensively used in Europe since the end of the 19th century to control vine fungal diseases, with their concentrations depending on agroecological conditions and vineyard management. These practices resulted in significant accumulation of Cu in vineyard soils due to its strong adsorption to soil colloids, especially humus (Parat et al., 2002). The impact of agricultural production on Cu concentrations in vineyard soil is clearly illustrated by the fact that average Cu levels in natural worldwide soil vary from 13 to 24 mg/kg (Kabata Pendias and Mukherjee, 2007), while Komarek et al. (2010) reported range 77-3200 mg/kg for vineyard soils around the world. Furthermore, modern olive production implies the application of copper-based fungicides, which also leads to the accumulation of Cu in soils under olive groves (Avramidis et al., 2019).

The enrichment of agricultural soils with other PTE, such as As (Alexakis et al., 2021; Kobza, 2021) and Zn (Park et al., 2011; Garcia-Navarro et al., 2021), was also documented in the literature. The elevated level of As in agricultural soils can be related to the application of mineral nitrogen and phosphate fertilizers (Kabata Pendias and Mukherjee, 2007). The contamination of vineyard soils with Zn Fernandez Calvino et al. (2012) attributed to mineral fertilizers containing zinc, while Komarek et al. (2010) highlighted pesticides as possible sources for Zn in vineyard soils. Pollution of agricultural soils with Pb was also recorded in some urban areas (Mao et al., 2014; Romić and Romić, 2002). The major source of Pb in the environment was vehicle emissions due to the use of tetraethyl lead gasoline (Kelepertzis et al., 2020), while in recent times, coal combustion and smelting emissions have become the main sources of Pb in soils (Ye et al., 2022).

An accumulation and elevated level of PTE in soils can cause environmental problems in terms of phytotoxic effects (Thalassinos et al., 2023) and adverse effects on microbiological activities (Markowicz et al., 2016). Therefore, control of PTE concentrations is necessary in agricultural soils, and the necessity of protecting soil from pollution is recognized not only at the national but also at the international level. The maximum permissible concentrations (MPC) of PTE in agricultural soils in Croatia are prescribed taking into account pH_{KCl} values (Official Gazette 71/19). However, there is no uniform legislation in EU countries regarding PTE concentrations in soil. Reimann et al. (2018) reported a wide range of Soil guideline values in EU countries that are highly variable in multiple aspects, starting from purpose, through derivation methods to terminology. These differences are associated with environmental variability across Europe, socio-cultural, political, regulatory, and scientific reasons, but the Finnish standard values (MEF, 2007) represent a good approximation of mean values from different national systems that have been widely applied (Carlon et al., 2007).

Apart from legislation, one of the most commonly used indices to assess soil pollution by anthropogenic impact is the enrichment factor (EF). The concept of EF was developed in the early seventies to speculate on the origin of elements in the atmosphere and was progressively applied to other environmental materials, such as soil (Reimann and de Caritat, 2005). The EF indicates possible sources of anthropogenic impact on soil pollution by comparing the concentration of the element in the observed soil sample with the concentration of the reference element in the soil. Many authors (Bourenanne et al., 2010; Sucharovà et al., 2012; Bern et al., 2019; Aytop et al., 2023) promoted the use of EF.

The abandonment of agricultural land significantly impacts ecosystem functioning (Valverde-Asenjo et al., 2020). It is followed by natural recolonization that affects soil properties depending on environmental conditions (de Santiago-Martin et al., 2016). Alteration of soil properties and the absence of fresh input in PTE in soil via agricultural practices (fertilization, application of pesticides) lead to changes in PTE concentrations in abandoned vineyard soils (Fernandez-Calvino et al., 2012). However, it is well-known that some PTE are retained in soil for a long time due to their strong binding and low mobility, e.g., Cu (Parat et al., 2002; Cerqueira et al., 2011; Avramidis et al., 2019) and Zn (Park et al., 2011; Fernandez Calvino et al., 2012; Garcia-Navarro et al., 2021). In addition to abandonment, vineyards are often converted to olive groves in the Mediterranean environment, resulting in changes in agricultural practices and their impacts on soil properties. Generally, the input of PTE in soils by fungicide is lower in olive groves compared to vineyards. It is illustrated for Cu by the large-scale study of European agricultural soils based on the LUCAS database that revealed a higher mean value of Cu concentrations (49.3 mg/kg) for vineyard soils in comparison to olive groves (33.5 mg/kg) (Ballabio et al., 2018).

It is important to gain knowledge on soil quality regarding PTE concentrations in former vineyard soils, especially in fragile Mediterranean environments, but such studies are scarce in Croatia (Miloš and Bensa, 2021). The study's objectives were to:

i) determine and compare the concentration of PTE (As, Cu, Pb, and Zn) in former vineyard soils under olive groves and natural vegetation, and

ii) assess soil pollution for selected PTE in the studied area.

MATERIAL AND METHODS

Study area

The study was conducted in the Primošten municipality in Middle Dalmatia, Croatia (Figure 1A). According to Köppen's classification, the study area has a Csa type of climate (Filipčić, 1998), which is characterized by dry and hot summers and mild, rainy winters. The study area is built of well-bedded limestones that alternate with dolomites or dolomitic limestones (Marinčić et al., 1973). It is characterized by typical karst geomorphology and a longstanding history of anthropogenic influence. A high density of terraces and rectangular dry stone enclosures known as “vlačice”, usually 6 x 3 (4) m, are distinctive features of this area (Miloš and Bensa, 2021). The regularity of the rectangular pattern can be related to the initial cultivation of vines and some socio-economic conditions, such as organized clearing of the land, but also the configuration of relief (Andlar et al., 2018). Organized land clearing and the formation of “vlačice” were conducted in the period 1947-1952 as a part of the project of vineyard establishment for the state vinery. After about 40 years (in the 1990s), the abandonment of vineyards began, and some of the old vines were replaced with olive trees. Therefore, part of these former vineyard soils is today overgrown with natural vegetation of different ages, and part is under currently productive olive groves. Given that this is privately owned land, data on the age of the olive trees and applied agrotechnical practices, unfortunately, are not available. According to the Basic Soil Map of Croatia at a scale of 1:50 000, section Šibenik 3 (Čolak and Martinović, 1974), the dominant soil type in the study area is Terra rossa or Leptic Chromic Cambisols (Clayic) according to the IUSS Working Group of WRB (2015). Particle size distribution reveals the domination of silt particles followed by clay particles in most studied soils. Mean values of sand, silt and clay are as follows: 3.4, 50.5, and 46.3 %. Terra rossa is silty-clayey to clayey soil developed over limestones and dolomites in the karst Mediterranean region and characterized by variable depth.

A) B)

Figure 1. The position of the study area in Croatia (A) and soil sampling locations (B) (locations of currently productive olive groves are symbolised by red circles, and abandoned land (natural vegetation) by green circles)

Soil sampling and laboratory analysis

A total of 20 topsoil samples (0-25 cm) were collected as composite samples in former vineyard soil, out of which 10 were from the currently productive private olive groves and 10 from abandoned land (Figure 1 B). The composite soil samples were taken by a pedological probe with a diameter of 80 mm. They consisted of 3 sub-samples taken at a distance of 1 m in a cross arrangement. The disturbed air-dried soil samples were prepared for laboratory analysis by grinding and sieving using a sieve with a 2 mm mesh size (ISO 11464:2006). Soil pH was measured using a combined glass electrode in a 1:5 (*v/v*) suspension of soil in water and soil in KCl solution (c=1 M) according to ISO 10390:2005. Carbonate content was determined by a modified volumetric method (ISO 10693:1995). The humus content was analysed following the method of Tjurin (JDPZ, 1966). The humus content was then divided by the Van Bemmelen factor (1.724) to calculate soil organic carbon (SOC). Physiologically available phosphorus and potassium were determined according to Egner-Riehm-Domingo lactate-acetate as the extraction solution (Egner et al., 1960). The total concentrations of PTE (As, Cu, Pb, and Zn) were determined by the portable X-ray fluorescence method using the Vanta handheld XRF analyser C Series (Olympus, Waltham, MA, USA, 2019) according to the loose powder method (Takahashi, 2015). The accuracy and precision of the analyses were controlled using certified (SRM 2711) and reference soil samples (ISE 989), and results were acceptable (accuracy: RPD < 5% and recovery 95 % -105 %; precision: RSD < 5%).

Soil pollution

According to Croatian legislation (Official Gazette 71/19), agricultural land is considered polluted when it contains more PTE than the maximum permissible concentrations (MPC) (mg/kg). The MPC of PTE in agricultural soils is prescribed taking into account pH_{KCl} values (Table 1).

Table 1. Maximum permissible concentrations (MPC) (mg/kg) of selected PTE in agricultural soils in Croatia (Official Gazette 71/19)

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

Since there is no uniform legal regulation for PTE concentrations in agricultural soils in EU countries, we used Finnish standard values (MEF, 2007) that have been widely applied as an approximation of mean values from different national systems (Carlon et al., 2007). This legislation sets different values, indicating the need for different actions if exceeded. The threshold value indicates the need for further assessment of the area, and the guideline value indicates the contamination level that represents ecological risk (Table 2).

Table 2. Threshold and guideline values for metals in soils (MEF, 2007)

Element	Threshold value	Guideline value
As	5	50
Cu	100	150
Pb	60	200
Zn	200	250

Additionally, the assessment of the ecological risk of exposure to PTE was based on the calculation of the enrichment factor (EF). The formula to calculate EF (Eq. 1) can be generalised from Zoeller et al. (1974) to be:

$$EF(El) = \frac{(El)sample/(X)\,sample}{(El)background/(X)\,background} \quad \text{Eq. (1)}$$

where "El" is the element under consideration, brackets indicate concentrations (mg/kg), "X" is the chosen reference element, and "sample" or "background" indicates which medium the concentration refers to. The reference element "X" is most often taken to be Al, Fe, or Mn (Reimann and de Caritat, 2005), and we used Al. In the current study, the background concentration of studied elements represented concentrations of elements determined in the area of Primošten (Table 3), Halamić and Miko (2009).

Table 3. Background concentrations of Al, As, Cu, Pb and Zn (mg/kg) in soils (Halamić and Miko, 2009)

Al	As	Pb	Cu	Zn
78900	24	47	60	144

For the interpretation of EF, we used the criteria given by Sutherland (2000), shown in Table 4.

Table 4. Categories of EF (Sutherland, 2000)

EF	Soil enrichment
< 2	Minimal
2-5	Moderate
5-20	Significant
20-40	Very high
> 40	Extremely high

Statistical analysis

Obtained data on basic chemical soil properties and PTE concentrations were processed at the level of descriptive statistics (minimum, maximum, mean, standard deviation, skewness). A statistical comparison of analysed PTE concentrations between the olive groves and abandoned land under natural vegetation was carried out using a one-way analysis of variance (ANOVA). The statistical analysis was performed with MS Excel.

RESULTS AND DISCUSSION

Basic soil chemical properties

Studied soils under natural vegetation (NV) and olive groves (OG) have slightly acidic to neutral reactions, with an average neutral (pH_{KCl} 7.04 and 6.80, respectively; Table 5). It is in agreement with literature data for Terra rossa soils reported in Croatia (Peh et al., 2003; Miloš and Bensa, 2021), Spain (Delgado et al., 2003; Conde et al., 2007), and Italy (Vingiani et al., 2018). In the soils under olive groves, pH values varied in a wider range (6.00-7.21) compared to soils under natural vegetation (6.82-7.18) (Table 5). Furthermore, data distribution for pH_{KCl} in soils under olive groves is highly negatively skewed (-1.23). These results can be attributed to the different fertilization in olive groves, since the application of organic (Roussos et al., 2017) and mineral fertilizers (Jordão et al., 2010) can affect the pH in soils of olive groves. The mean values of total carbonate content in NV and OG (6.75 and 8.41%, respectively; Table 5) pointed to weakly calcareous soils. A comparable range of $CaCO_3$ content was observed in some studies of Terra rossa of Middle Dalmatia (Miloš and Maleš, 1998; Miloš and Bensa, 2020), and authors linked it to the process of colluviation.

The SOC content was higher in soil under NV than in OG (mean values 4.57 and 4.05, respectively) and varied in a narrower range (Table 5). Averagely lower SOC content in soils under olive groves can be attributed to the soil tillage that enhances the mineralization of organic matter (Haddaway et al., 2017; Hashimi et al., 2022). However, these differences were not so pronounced since organic fertilization can compensate for this loss and increase SOC content (Mbarek et al., 2020).

The soils under NV were poorly supplied with physiologically available phosphorus (mean value 41.5 mg/kg) and moderately with available potassium (mean value 337.9 mg/kg) (Table 5). The skewness coefficient for P_2O_5 and K_2O (0.13 and -0.08, respectively) pointed to symmetrical data distribution. Uniformly low P_2O_5 and moderately K_2O concentrations are in line with the study of Miloš and Bensa (2020), which reported similar data for the Terra rossa of Dalmatia under natural vegetation. The authors pointed out that it is typical for all soil derived from limestones and dolomites.

However, soils of OG contained much higher concentrations of P_2O_5 (162.8-410.5 mg/kg) and K_2O (355-1124.4 mg/kg, respectively) (Table 5). The skewness coefficient for K_2O of -1.08 pointed to a negatively skewed data distribution. Elevated concentrations of P_2O_5 and K_2O can be attributed to the mineral fertilization of olive groves, as proven in the study of Bensa et al. (2023). The study area in the current study includes several olive groves in private ownership, and data on agrotechnical measures, including fertilization, unfortunately, are not available. Generally, soils under OG are richly supplied with physiologically available phosphorus and potassium (mean values 276.1 and 839.6 mg/kg) (Table 5). However, a wide range of P_2O_5 and especially K_2O concentrations indicates different doses of applied fertilizers.

Table 5. Descriptive statistics for basic chemical properties of the studied soil samples

Land use type	Soil property	Min	Max	Mean	SD	Skew
Natural vegetation (NV)	pH_{H_2O}	7.27	7.73	7.55	0.69	-0.78
	pH_{KCl}	6.82	7.18	7.04	0.12	-0.69
	$CaCO_3$ (%)	1.10	19.3	6.75	7.48	1.03
	SOC (%)	3.32	5.66	4.57	0.82	-0.49
	P_2O_5 (mg/kg)	12.1	74.2	41.5	22.1	0.13
	K_2O (mg/kg)	285	386	337.9	33.6	-0.08
Olive groves (OG)	pH_{H_2O}	6.88	7.79	7.42	0.26	-0.63
	pH_{KCl}	6.00	7.21	6.80	0.37	-1.23
	$CaCO_3$ (%)	1.10	29.0	8.41	9.87	1.64
	SOC (%)	2.35	5.38	4.05	0.85	-0.47
	P_2O_5 (mg/kg)	162.8	410.5	276.1	79.2	0.31
	K_2O (mg/kg)	355.0	1124.4	839.6	225.9	-1.08

Effect of land use type on PTE concentrations in soil

Descriptive statistics for PTE concentrations in the studied soils under natural vegetation and olive groves are presented in Table 6. A one-way analysis of variance was used to examine the effect of land use type on concentrations of PTE in the studied soil (Table 7). Statistically significant differences (P<0.05) between soils under natural vegetation and olive groves were established for Cu and Zn, while As and Pb concentrations did not significantly differ.

Median values of As concentration in soils under NV and OG (19.2 and 19.4 mg/kg, respectively) (Table 6), exceeded median values for coastal Croatia and the whole Croatia (18 and 12 mg/kg, respectively) according to the Geochemical Atlas of Croatia (Halamić and Miko, 2009). Furthermore, median As concentrations in the current study were above the median value for Europe of 7 mg/kg according to the Atlas of Europe (Salminen et al., 2005). The obtained results are similar to the study of Alexakis et al. (2021), which reported a mean value of As concentrations of 19.8 mg/kg for 102 samples from soils under agricultural land use in Greece. According to Kabata Pendias and Mukherjee (2007), the use of fertilizers, including nitrogen and phosphate, may be a major source of As in agricultural soils. Perčin et al. (2023) reported As content in the range 2.8-8.0 mg/kg in six NPK and NP formulations of commercial complex fertilizers from Croatia. Elevated As concentrations in all studied soils can be explained by the fact that these are former vineyard soils that were fertilized for a long time. Maximum As concentration of 25.5 mg/kg (Table 6) was measured in soil under olive groves that are currently being fertilized. Although differences in As concentrations between NV and OG soil exist (Table 6), they are not statistically significant (Table 7).

Table 6. Descriptive statistics for PTE concentrations (mg/kg) in the studied soil samples

Land use type	Element	Min	Max	Mean	Median	SD	Skew
Natural vegetation (NV)	As	16.1	23.9	19.8	19.2	2.62	0.19
	Cu	36.1	83.9	51.8	60.1	16.9	0.04
	Pb	43.5	52.0	48.2	49.0	2.83	-0.47
	Zn	104.5	130.5	118.1	121.0	7.83	-0.37
Olive groves (OG)	As	14.0	25.5	19.8	19.4	3.61	0.09
	Cu	106.1	303.4	199.3	195.3	61.5	0.37
	Pb	31.5	56.0	46.6	47.3	6.62	-0.94
	Zn	110.0	201.5	138.0	131.5	23.6	2.05

Table 7. Summary statistics of the one-way ANOVA for PTE concentrations in the studied soils

PTE	SS	df	F_{exp}	P value	F_{crit}
As	0.008487	1	0.00077	0.978168	4.413873
Cu	**100111.4**	**1**	**44.27518**	**3.04E-06**	**4.413873**
Pb	12.8	1	0.444359	0.513481	4.413873
Zn	**1980.05**	**1**	**5.772367**	**0.027282**	**4.413873**

SS – the sum of squares, df – degrees of freedom

Cu concentration in soils under NV ranged from 36.1 to 83.9 mg/kg, while in soils under OG, higher values (106.1-303.4 mg/kg) were recorded (Table 6). The mean value of Cu concentration in soils under OG (199.3 mg/kg) is much higher in comparison to the mean value of Cu concentration in olive groves of some Mediterranean countries, e.g., Italy (41.2 mg/kg), Greece (31.5 mg/kg), and Portugal (17.8 mg/kg) (Panagos et al., 2018). The differences in Cu concentrations may be even more pronounced on the regional/local level as illustrated by mean values of Cu concentrations for Spanish regions Castilla, Andalusia, and Catalonia of 9.5, 35.6, and 65.3 mg/kg, respectively (Panagos et al., 2018). These differences reflect natural conditions (geology, soil type) and anthropogenic impact (application of Cu- based fungicides). Elevated Cu concentrations in soil can be related to its complexation with organic matter (Parat et al., 2002) and adsorption to soil colloids (clay and Fe and Al oxides) (Cerqueira et al., 2011). Miloš and Bensa (2021) pointed out a wide range of Cu concentrations in Terra rossa soils under olive groves in Middle Dalmatia (33.8-250.0 mg/kg) and linked it to long-lasting application of Cu-based fungicides in different doses and to the fact that the growing area of olives and vines overlaps. Avramidis et al. (2019) reported an even wider range (58.4-671.3 mg/kg) for soils under olive groves in Greece with a mean value of 286.2 mg/kg that is higher than the mean value for OG soil in the current study (199.3 mg/kg) (Table 6). Significantly higher Cu concentrations in soils under olive groves in comparison to soils under natural vegetation (Table 7) are expected due to the long-lasting application of Cu-based fungicides.

Soils under NV and OG had similar mean values of Pb concentration (48.2 and 46.6 mg/kg; Table 6) that were not significantly different (Table 7). It was expected since agricultural production does not contribute to lead enrichment in soil. Furthermore, the studied soils were exposed to relatively uniform atmospheric pollution due to the small distance between sampling locations. However, Pb concentration in soils under NV varied in a narrower range (43.5-52.0 mg/kg) and data distribution was symmetrical (skew -0.47), while Pb concentrations in OG soils varied in a wider range (31.5-56.0 mg/kg) and data distribution was moderately left skewed (skew -0.94) (Table 6). Established median values of Pb in NV and OG (49.0 and 47.3 mg/kg; Table 6) are comparable to the median value for coastal Croatia (48.7 mg/kg) according to the Geochemical Atlas of Croatia (Halamić and Miko, 2009) but higher compared to the median value for southern Europe of 20.0 mg/kg, (Reimann et al., 2012). These higher Pb concentrations in the whole study area in the current study can be regarded as anomalies related to geology. Similar elevated Pb background values were observed by Reimann et al. (2012) in the karst area of southern Slovenia.

Soils under OG had significantly higher mean values of Zn concentrations compared to soils under NV (138.0 and 118.1 mg/kg; Tables 6 and 7). Also, the maximum Zn concentration in OG was higher than in NV (201.5 and 130.5 mg/kg, respectively) (Table 6). Higher Zn concentrations in soils of olive groves can be explained by the application of mineral fertilizers (Fernandez Calvino et al., 2012) and pesticides containing zinc (Komarek et al., 2010). Mean values of Zn content in multi-element compound fertilizers (NPK formulations) and single nitrogen fertilizers usually used in Croatia (112.9 and 4.28 mg/kg) (Perčin et al., 2023) indicate different Zn inputs in agricultural soils via mineral fertilization. Many studies (Vitanović et al., 2008; Park et al., 2011; Fernandez Calvino et al., 2012; Garcia-Navarro et al., 2021) reported elevated Zn concentrations in agricultural soils in comparison to non-agricultural. In addition, the median value of Zn in soils under natural vegetation (121.0 mg/kg) is higher than the median value for coastal Croatia of 108 mg/kg (Halamić and Miko, 2009). A possible explanation for these concentrations is that these are former vineyard soils that were fertilized and treated with pesticides for over 50 years.

Assessment of soil pollution by PTE

The As concentrations in all soil samples were below the maximum permissible concentrations (MPC) of 30 mg/kg in agricultural soils according to Croatian legislation (OG 71/19) (Figure 2A).

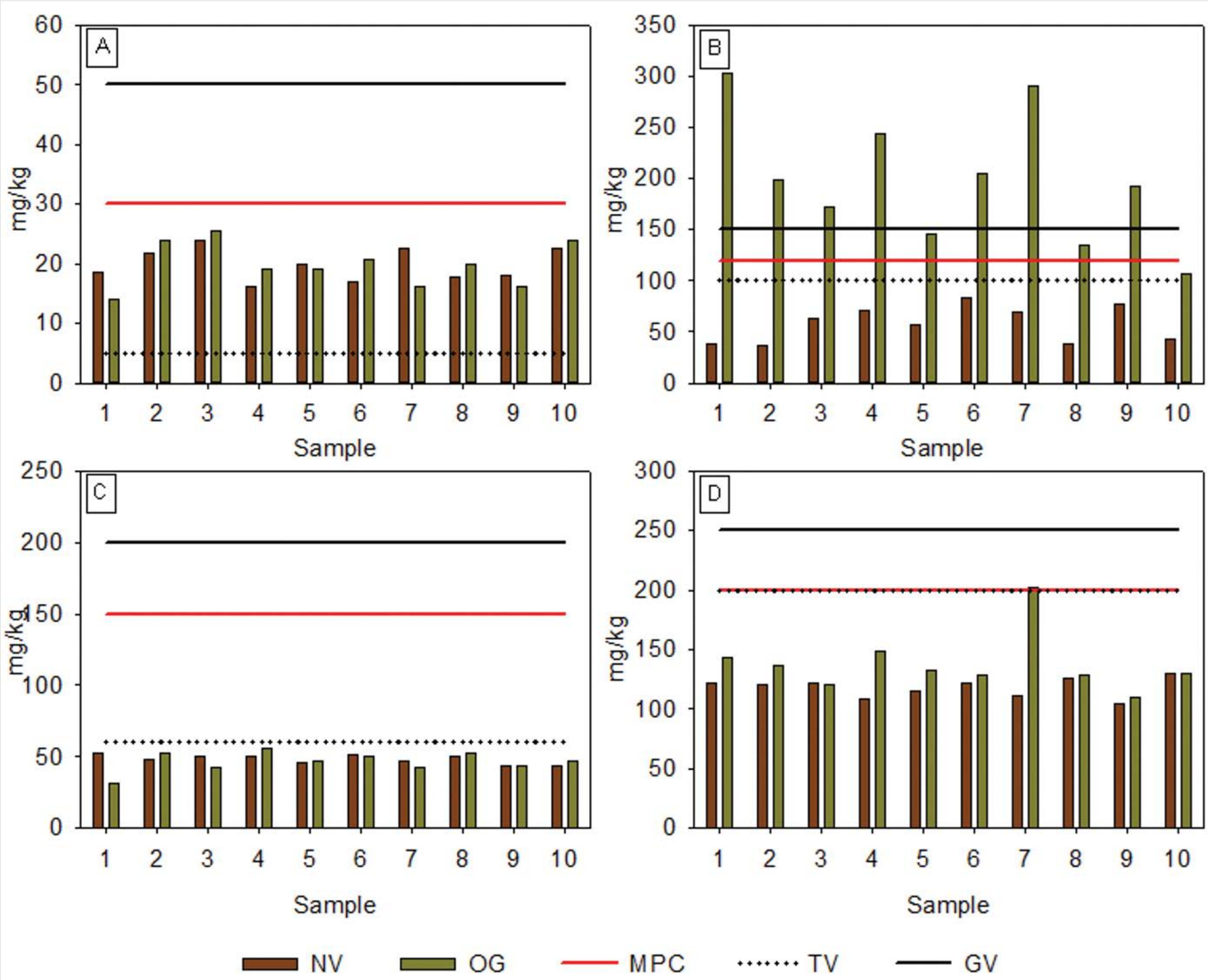

Figure 2. Concentrations of PTE in studied soils under natural vegetation (NV) and olive groves (OG), and MPC (OG, 71/19), threshold value (TV) and guideline value (GV) (MEF, 2007) for A) As, B) Cu, C) Pb and D) Zn

However, these concentrations were above threshold values that indicate the need for further assessment of the area, but there is no indication of contamination levels that represent ecological risk (MEF, 2007).

In 9 of 10 soil samples of OG Cu concentrations exceeded the MPC of 120 mg/kg (OG 71/19), while in all samples of NV were below it (Figure 2B). According to Finnish standard values (MEF, 2007), Cu concentration in 7 samples from OG (> 150 mg/kg) indicates a contamination level that represents an ecological risk, while for the remaining 3 samples, only further assessment of the area is needed (Figure 2B).

The Pb concentrations were below MPC (OG, 71/19), as well as threshold and guideline values (MEF, 2007) in all studied soil samples (Figure 2C).

Only one sample of OG Zn concentration (201.5 mg/kg) exceeded MPC (OG, 71/19), while all other samples from OG and NV had Zn concentrations below the MPC of 200 mg/kg (Figure 2D). In addition, there is no indication of ecological risk for all studied soils, but Zn concentration in one sample from OG indicates a need for further assessment of the area.

A commonly used metric to assess the impact of human activity on an element's presence in soil relative to its average natural abundance is the enrichment factor (EF) (Blaser et al., 2000; Singh et al., 2010; Sucharovà et al., 2012; Bern et al., 2019; Aytop et al., 2023). Results of the calculation of EF for the studied elements are presented in Figure 3 A-D.

The EF for As and Pb in soils under both land use types revealed minimal soil enrichment. The EF for As in soils under NV and OG ranged from 0.94-1.49 and 0.94-1.14, respectively (Figure 3A). Long-term application of mineral fertilizers may be the reason for this enrichment of former vineyard soils, since these fertilizers may contain As (Kabata Pendias and Mukherjee, 2007; Perčin et al., 2023). Low mean values of EF for Pb in NV and OG (1.07 and 1.00, respectively) (Figure 3C), were expected since agricultural production does not contribute to lead enrichment in soil.

Soils of NV were minimally enriched with Cu on average, although EF showed minimal to moderate enrichment (0.96 - 2.39) (Figure 3B). However, soils of OG were moderately (EF 2.22- 4.75) to significantly enriched with Cu (EF 5.13 – 11.35), on average moderately (EF 5.75) (Figure 3B).

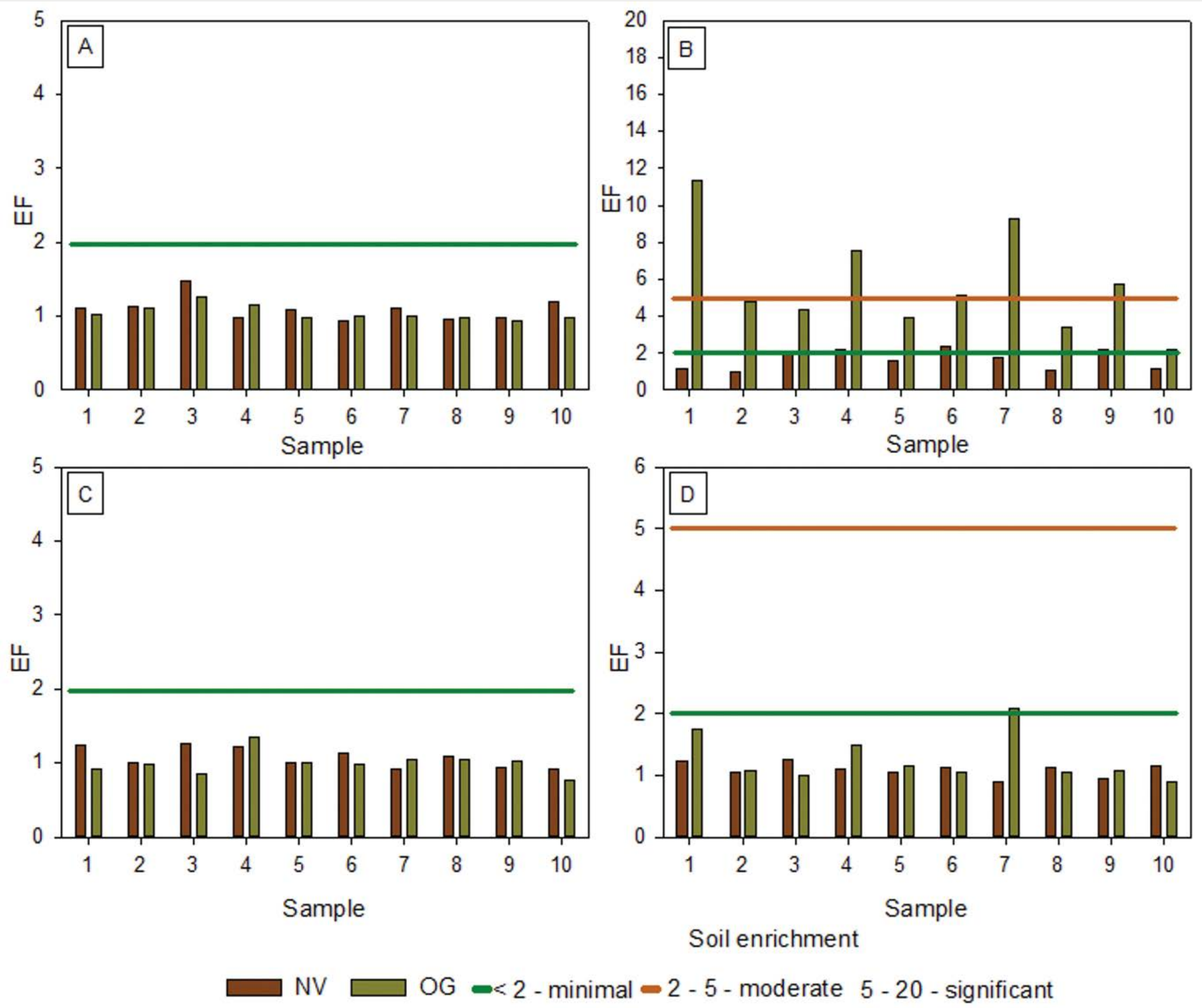

Figure 3. Enrichment factor for As (A), Cu (B), Pb (C) and Zn (D) in studied soils

Copper enrichment of vineyard soils is a well-known problem reported in many studies (e.g., Komarek et al., 2010). Many authors (Vavoluidou et al. 2005; Avramdis et al., 2005; Panagos et al., 2018) have also proven enrichment of olive grove soils due to the application of Cu-based fungicides. Vavoulidou et al. (2005) highlighted the importance of balance between input from agricultural chemicals and output by slow leaching from the neutral and alkaline soils.

The EF values for Zn in soils under NV (0.90-1.26) revealed minimal enrichment with Zn (Figure 3D). In soils under OG, a slightly wider range of EF (0.89-2.09) was established. Only one sample from soils under OG displayed moderate enrichment (EF 2.09), while all others belonged to minimally enriched soils with Zn. A similar range of EF values (0.66-2.63) was established by Loska et al. (2005) for agricultural soils in Poland. Authors reported that only 0.5% of soils were moderately enriched with Zn while all others were minimally enriched or depleted with Zn. Authors attributed low Zn concentrations in the studied soil to the acidic reaction that enhances Zn leaching. The impact of environmental conditions, especially pH values, on the solubility and mobility of elements was emphasized by Reimann and de Caritat (2000).

CONCLUSION

Analysis of PTE concentrations in former vineyard soil under different land use types revealed significantly higher Cu and Zn concentrations in soils of currently productive olive groves compared to soils overgrown with natural vegetation. That can be attributed to the use of plant protective agents in olive groves. Concentrations of As and Pb were not statistically different between the soils of OG and NV. The concentrations of studied PTE in former vineyard soils overgrown with natural vegetation were below the MPC according to Croatian legislation (OG 71/19). However, soils of olive groves were polluted with Zn and Cu. The EF showed minimal enrichment of soils under NV with As, Pb, and Zn, and minimal to moderate with Cu. Soils under OG also displayed minimal enrichment with As and Pb, but minimal to moderate with Zn, and moderate to significant with Cu. The obtained results indicate the need for further, more detailed studies of PTE, especially Cu, in the study area.

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