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Cd, Cu, Pb and Zn in terraced soil on flysch deposits of Kaštela Bay coastal area, Croatia

Cd, Cu, Pb i Zn u terasiranim tlima na flišnim naslagama obalnog područja Kaštelanskog zaljeva, Hrvatska

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ABSTRACT

The aims of this study were: (i) to determine concentrations of heavy metals (HMs): Cd, Cu, Pb and Zn in terraced soils on flysch deposits of Kaštela Bay coastal area, Croatia, (ii) to define their possible sources and (iii) to compare concentrations of HMs among different land use types: olive groves, vineyards and abandoned agricultural land (grassland). In a total of 26 topsoil samples (0-25 cm) were analysed for pH, carbonates, organic carbon, K_2O, P_2O_5, texture and concentrations of the HMs. The elements were extracted with aqua regia and determined by inductively coupled plasma - optical emission spectrometry (ICP-OES). The following mean values of Cd, Cu, Pb and Zn concentrations were 0.39, 46.5, 15.8 and 51.4 mg/kg, respectively. The principal component analysis (PCA) and the correlation matrix (CM) revealed weak relationship of HMs with soil properties and strong similarity among Cd, Pb and Zn concentrations indicating its common origin, controlled by different anthropogenic activity. The Cu poorly correlated with all other metals that point to its different origin - application of copper-based fungicide. The mean concentrations of Cd, Pb and Zn in vineyards, olive groves and grasslands were not statistically significant different in relation to land use types. The Cu concentrations in vineyards were significantly higher compared to other land use types.

Keywords: agriculture, heavy metals, land use, pollution

SAŽETAK

Ciljevi ovog istraživanja bili su: (i) utvrditi koncentracije teških metala: Cd,Cu, Pb i Zn u terasiranim tlima na flišnim naslagama obalnog područja Kaštelanskog zaljeva, Hrvatska, (ii) utvrditi njihove moguće izvore i (iii) usporediti koncentracije teških metala između različitih načina korištenja zemljišta: maslinika, vinograda i napuštenog poljoprivrednog zemljišta (travnjaka). Analizirano je ukupno 26 uzoraka površinskog sloja tla (0-25 cm) na pH, karbonate, organski ugljik, K_2O, P_2O_5, teksturu i koncentracije teških metala. Elementi su ekstrahirani zlatotopkom i određeni induktivno spregnutom plazmom – optičkom emisijskom spektrometrijom (ICP-OES). Utvrđene su slijedeće srednje vrijednosti koncentracija Cd, Cu, Pb i Zn: 0,39, 46,5, 15,8 i 51,4 mg/kg. Metodom glavnih komponenti (PCA) i korelacijskom matricom (CM) utvrđene su slabe veze teških metala sa svojstvima tla i snažna povezanost između Cd, Pb i Zn koncentracija koja indicira njihovo zajedničko porijeklo kontrolirano različitim antropogenim aktivnostima. Bakar je slabo korelirao s ostalim metalima što upućuje na njegovo različito porijeklo povezano s primjenom zaštitnih sredstava na bazi bakra. Srednje koncentracije Cd, Pb i Zn u vinogradima, maslinicima i travnjacima nisu bile statistički značajno različite. Koncentracije bakra u vinogradima bile su signifikantno više u odnosu na ostale načine korištenja.

Ključne riječi: korištenje zemljišta, onečišćenje, poljoprivreda, teški metali

INTRODUCTION

The knowledge of the heavy metals (HMs) content in soils and the origin of these levels are priority objectives in the European Union according to the European Strategy for Soil Protection (Commission Communication 179/2002). The HMs in soils originated from both geogenic (particularly lithogenic) and anthropogenic sources and they have been discussed in numerous reports and publications (e.g. Alloway, 1995; Adriano, 2001; Facchinelli et al., 2001; Kabata-Pendias and Pendias, 2001). In order to reduce metal inputs and to improve management guidelines according to the legislation it is necessary not only to have knowledge of concentration HMs in soils but also to apportion natural (lithological) and anthropogenic inputs (Facchinelli et al., 2001; Franco-Uría et al., 2009; Li et al 2009; Lu et al., 2012).

The multivariate statistical approach, mostly principal component analysis (PCA), have been widely applied in the identification and classification of the sources controlling the variability of heavy metals content in soils (Facchinelli et al., 2001; Salvagio Manta et al., 2002; Boruvka et al., 2005; Mico et al., 2006; Franco-Uría et al., 2009; Zhang et al., 2009; Sun et al., 2010; Lu et al., 2012). In these studies identification of the pollution sources have been based on the intermetal relationships. Many others studies have examined relationships among HMs and between HMs concentrations and other soil properties (i.e. soil texture, soil organic matter, pH, carbonates) in identifying possible origin of HMs (Navas and Machin, 2002; Vega et al., 2004; Dragović et al., 2008).

Many authors proved the impact of land use types on heavy metals concentration in soils (Luo et al., 2007; Miko et al., 2007; Bai et al., 2010; Kelepertzis et al., 2014). They established higher concentrations of particular heavy metals in the topsoil of intensively used agricultural soils in comparison to natural (uncultivated) soils. One of the most prominent and the most commonly investigated problem related to contamination of agricultural soils is by copper, especially in vineyards. Numerous authors (Rusjan et al., 2007; Wightwick et al., 2008; Komarek et al., 2010; Vitanović et al., 2010; Jurišić et al., 2012; Ruyters et al., 2012) have established elevated levels of Cu in vineyard soils and explained it by long-term use of copper-based fungicides.

The present study was carried out as a preliminary survey on soil contamination of Kaštela Bay coastal area. This area was selected in order to apportion natural vs. anthropogenic sources (urbanization, local industrial facilities and agronomic practice). The aims of this study were: (i) to determine concentrations Cd, Cu, Pb and Zn in terraced soils on flysch deposits of Kaštela Bay coastal area (ii) to examine intermetal relationship and relationship among HMs and other soil properties (pH, carbonates, organic carbon, K_2O, P_2O_5 and texture) in order to define their possible sources by both PCA and Pearson´s correlation and (iii) to compare concentrations of HMs among different agricultural land use types: olive groves, vineyards and abandoned agricultural land (grassland).

MATERIALS AND METHODS

Study area

Kaštela Bay coastal area is situated on the east coast of the central Adriatic Sea and located in the vicinity of Split (Figure 1). In the past this area has been an important agricultural resource associated with the cultivation of traditional Mediterranean plants, mainly, olive groves and vineyards. After World War II, urbanization, industrialization and the development a more attractive tourism economy caused soil degradation and destruction of agricultural land which is most evident in the abandonment of agricultural production and conversion of the valuable agricultural land into permanent non-agricultural purposes.

According to the Köppen climate classification, the study area has olive climate (Csa) which means that the dry period is in the warm part of the year, and the driest month has even less than 40 mm of precipitation, less than a third of the amount in the rainiest month in the cold part of the year (Zaninović et al., 2008). Geologically, Kaštela Bay coastal area was built of Eocene Flysch marls,

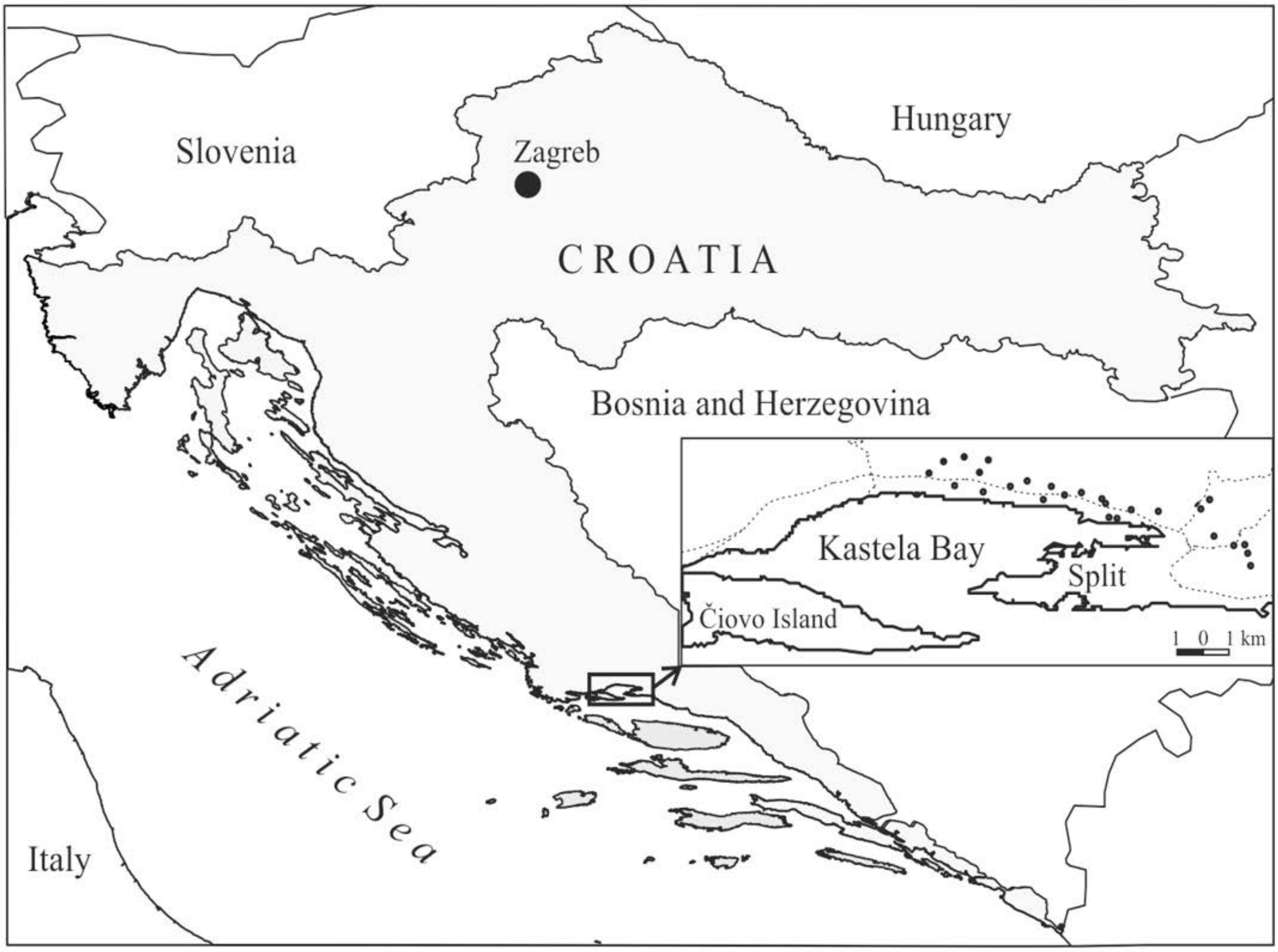

Figure 1. Soil sampling locations in the Kaštela Bay coastal area

sandstones and siltstones with lenses of calcirudites and calcarenites (Marinčić et al., 1971; Marinčić et al., 1977). In a geomorphological sense, the investigated area represents a flysch synclinal valley in which lower parts are defined with the gentle slopes, while higher parts are hilly with steep slopes. The impermeable or poorly permeable flysch deposits are prone to erosion with nearly 25 torrent streams (Barbarić and Pejaković, 1998). For this reason, terracing is a key measure of soil erosion protection and this terrain is terraced, enclosed by dry-stone walls. According to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014) investigated soils were classified as Terric Anthrosols (Calcaric, Siltic/Loamic, Escalic). A total of 26 topsoil samples (0-25 cm) were collected as composite samples on terraced soils, Figure 1. Locations of soil sampling are under the different land use: olive groves (10), vineyards (8), and abandoned land - grassland (8).

Laboratory methods

Laboratory analysis was performed by the following methods: pH was determined potentiometrically in a 1:5 suspension of soil and water (HRN ISO 10390:2005), carbonate content by modified volumetric method (HRN ISO 10693:1995), available P_2O_5 and K_2O by the ammonium lactate method (Egner et al., 1960) and particle size distribution by sieving and sedimentation using the 0.1 M Na-metaphosphate solution as a dispersant (HRN ISO 11277:2009). Soil organic carbon (SOC) content was calculated by dividing the content of humus with the Van Bemmelen factor (1.724). Humus content was analysed by acid potassium-dichromate digestion, following the method of Tjurin (Yugoslav Society of Soil Science, 1966). The elements were extracted by aqua regia (HRN ISO 11466:2004) with microwave techniques. Concentrations of cadmium (Cd), lead (Pb), copper (Cu), and zinc (Zn) were determined by the inductively coupled plasma - optical emission spectrometry (ICP OES). Accuracy was controlled by participating in the ISE Wepal (Wageningen University) proficiency testing scheme, as well as using CRMs for internal quality control and it was within range of ±15% of the certified values. Analytical precision was controlled by repeating the analysis of individual samples three times and it was satisfactory (relative standard deviation < 5%).

Statistical analyses

Basic statistical parameters for raw soil data were established and the skewness test was used for asymmetry of distribution data assessment. Principal component analysis (PCA) and correlation matrix (CM) was used to analyze relationships between experimented variables and to elucidate origins of heavy metals. The correlation strength was interpreted according to Evans (1996), meaning less than 0.19 is very weak, 0.2-0.39 weak, 0.4-0.59 moderate, 0.6-0.79 strong and 0.8-1 is very strong. A one-way analysis of variance (ANOVA, *F*-test) was used to test for the significant differences between means of selected metals in different land use types. The Tukey honest significant difference (HSD) post hoc test was performed only for metals for which ANOVA established that significantly contribute to the differences between the agricultural land use types.

RESULTS AND DISCUSSION

Basic soil properties

Investigated soils are alkaline and calcareous with a very wide range of $CaCO_3$ (8.84-55.32%, Table 1). The soil organic carbon (SOC) content is very low to medium, in average low (19.08 g/kg). The soils are medium to rich supplied with physiologically available K_2O and poor to medium in P_2O_5 according to Vukadinović and Vukadinović (2011). The particle size distribution (Table 1) shows that silt dominates with a mean value of 54.75%.

According to soil textural triangle (Soil Survey Division Staff, 1993) analysed soil samples are assigned in the three texture classes: silty loamy (19 samples), loamy (5 samples) and clayey loamy (2 samples). A wide range of variations of the basic soil properties is the result of a great diversity and the lithological complexity of the Kaštela flysch deposits. These results are in a line with the results of previous soil research of the Kaštela Bay coastal area (Miloš and Maleš, 1998). The skewness (Skew) values (Table 1) show that the distribution of $CaCO_3$ and P_2O_5 are highly skewed. The distribution of pH in H_2O, SOC, K_2O, sand and silt are moderately skewed, while the pH in KCl and clay data sets have approximately symmetric distribution.

Heavy metal concentrations in soil

The descriptive statistics for analysed elements is shown in Table 2. The mean values of Cd, Cu, Pb and Zn concentrations were 0.39, 46.5, 15.8 and 51.4 mg/kg respectively. The mean values of all analysed metals are lower than the maximum admissible concentration (MAC) values given in the Croatian Regulation on the Protection of Agricultural Land (Ministry of agriculture and forestry, 2014). Taking into account mentioned Croatian guidelines the Cd and Pb concentrations were below MACv in all analysed samples. The Cu concentrations exceeded MAC values in 4 of 26 samples (15% of analysed samples). The Zn concentration exceeded MAC in only 1 sample (4% of analysed samples).

The Cu concentration has a very wide range (16.3 – 149.8 mg/kg) and frequency distributions are not tightly clustered around the mean value. The concentrations of Cd, Pb and Zn have a narrower range of variations and scattered closer to the mean. The skewness coefficients (Skew; Table 2) for all analysed heavy metals concentrations are higher than 1 indicating highly skewed distributions with a right tail. A highly skewed distributions of HMs could indicate geochemical anomalies caused by anthropogenic activities, that has been shown in many other researches (Martinez Garcia et al., 2000; Loska et al., 2004; Biasioli et al., 2006; Xia et al., 2011; Wang et al., 2012).

Table 1. Descriptive statistics for soil properties

	pH		$CaCO_3$	SOC	P_2O_5	K_2O	Particle size distribution (%)		
	H_2O	KCl	(%)	(g/kg)	(mg/100 g)		Sand[a]	Silt[a]	Clay[a]
Mean	8.4	7.65	39.2	19.08	3.97	41.07	25.2	54.75	20.05
Median	8.37	7.63	38.6	18.55	2.39	34.67	21.5	57.5	19
Min	8.03	7.32	8.84	9.01	0.92	13.95	14	38	8
Max	8.83	8.03	55.32	37.56	16.29	83.3	41	68	32
Range	0.8	0.71	46.48	28.55	15.37	69.35	27	30	24
SD	0.22	0.18	10.42	8.12	4.22	22.28	8.44	8.3	5.36
Skew	0.52	0.42	-1.06	0.94	2.07	0.87	0.63	-0.63	0.15

[a] Sand 2 - 0.063 mm, silt 0.063 - 0.002 mm, clay < 0.002 mm; SD - standard deviation; skew -skewness coefficient.

Table 2. Descriptive statistics for Cd, Cu, Pb and Zn concentrations in 26 topsoil samples

	Mean	Minimum	Median	Maximum	Range	SD	Skew
Cd	0.39	0.21	0.35	0.82	0.61	0.16	1.29
Cu	46.5	16.3	39.6	149.8	133.5	29.77	2.37
Pb	15.8	8.3	13.3	34.3	26	6.88	1.31
Zn	51.4	24.1	44.8	105.9	81.9	19.45	1.46

SD – standard deviation; skew - skewness coefficient.

The median of Cd and Cu concentration in current study (0.35 and 39.57 mg/kg, respectively; Table 2) are much higher than established in the geochemical soil surveys at continental scale (0.18 and 14.5 mg/kg, respectively) in GEMAS project (Reimann et al., 2018) and 0.145 and 12 mg/kg FOREGS project (Salminen et al., 2005; Table 3). The median value of Pb and Zn concentration (Table 2) are in line with values for the Pb and Zn concentration in the agricultural soil established in GEMAS and FOREGS projects (Table 3). The maximum value for Cd, Cu, Pb and Zn concentration in this study (Table 2) are several times lower than maximum values established in above-mentioned Projects (Table 3).

In comparison to data given in Geochemical atlas of Croatia (Halamić and Miko, 2009; Table 3) the median value of Pb concentration in the current study (15.8 mg/kg; Table 2) is more than twice lower, whereas the medians of Cd concentration are almost equal. The median of Cu concentration in this study is higher, whereas the median of Zn concentrations is lower compared to data given in national scale (Halamić and Miko, 2009; Table 3). In flysch-derived soils of the Istrian Peninsula, Croatia, Peh et al. (2003) established a higher median value for Pb and Zn concentration (18.5 and 70 mg/kg) and a lover median Cu concentration (30.5 mg/kg) compared to this study. In the study of distributions of the anthropogenic elements in topsoil (5-15 cm) on flysch deposits of Kaštela Bay,

Table 3. The maximum (Max) and median (Med) values measured in an aqua regia extract Cd, Cu, Pb and Zn concentration (mg/kg) in topsoil samples of geochemical soil surveys at a continental, national, regional and local scale

	GEMAS (Reimann et al., 2018)		FOREGS (Salminen et al., 2005)		Geochemical atlas, Croatia (Halamić and Miko, 2009)		Flysch derived soil survey			
							Istria, Croatia (Peh et al., 2003)		Kaštela Bay (Buljac, 2012)	
N	2,211		840		2,521		26		8	
	Max	Med	Max	Med	Max	Med	Max	Med	Max	Med
Cd	7.5	0.18	14.1	0.145	15.5	0.4	-	-	0.72	0.45
Cu	395	14.5	239	12	429	25.4	68	30.5	84	40.7
Pb	1,309	16	886	15	699	33	53	18.5	45.8	29.4
Zn	1,396	45	2,270	48	1,432	88	130	70	215.2	107.6

N - the number of samples.

Buljac (2012) established slightly a higher median value for Cd, almost equal for Cu and about a twice higher for Pb and Zn (Table 3) compared to results in the current study. In the soils derived on Flysch in central Dalmatia (Miko et al., 2007) have established a higher mean concentration of Cd, Cu, Pb and Zn (0.49, 242, 23.3 and 94.6 mg/kg respectively) compared to current study (Table 2). In the study of distribution and origin of major, minor, and trace elements in flysch stream sediments of the Kaštela Bay (Croatia) coastal area (Lovrenčić Mikelić et al., 2013) the median of the Cu, Pb and Zn values of 36, 14 and 92 mg/kg, respectively have been determined. The median value of Cu and Pb were in line with results in this study, whereas Zn was about twice a higher (Table 2). They established wider ranges with higher maximum values for Cu, Pb and Zn in stream sediments (277, 147 and 223 mg/kg, respectively) compared to marls where maximum values for Cu, Zn and Pb were 27, 101 and 41 mg/kg, respectively. This indicates the effect of different anthropogenic sources.

Comparing the data of this study to the literature findings could be indicative due to differences in soil sampling (depth and horizon), methods of sample preparation (size of analysed soil fraction) and analysis (methods of extraction and determination). Also, data for heavy metals concentrations selected according to soil type, parent material and land use are missing in mentioned projects.

Correlations between heavy metals and soil properties

The relationships heavy metals - soil properties were analysed by Pearson s correlations and summarized in the correlation matrix (CM), Table 4. The Pb and Zn strongly positively correlated with K_2O at the P≥0.01. The Cu and Cd moderately positively correlated with K_2O at the 0.01 and 0.05 level, respectively. The Cu strongly positively correlated with P_2O_5 at the P≥0.01. The Cd and Zn moderately positively correlated with P_2O_5 at 0.05 level. The Cd, Cu, Pb and Zn are not significantly correlated with other soil properties. These weaker correlations between metals and soil properties indicate their origin from external sources.

Inter-metal relationships (Table 5) show a very strong positive correlation between Pb and Zn at the P≥0.001 level. The Cd strongly positively correlated with Pb and Zn at the P≥0.01 level. These correlations could indicate common influential factors (origin) for these three HMs. The Cu is not significantly correlated with Cd, Pb and Zn. This indicates that Cu has a source different from the other analysed metals. Sun et al. (2010) found significant correlations between Cd, Cu, Pb and Zn in urban soils in China and attributed it to a similar source of pollution for

Table 4. The Pearson correlation matrix of HMs (Cd, Cu, Pb and Zn) and soil properties (pH H_2O, $CaCO_3$, SOC, P_2O_5, K_2O, sand, silt and clay)

	pH H_2O	$CaCO_3$	SOC	P_2O_5	K_2O	Sand	Silt	Clay
Cd	0.13	-0.01	0.32	0.54*	0.47*	0.32	-0.15	-0.27
Cu	-0.28	-0.04	-0.21	0.7**	0.58**	0.16	-0.26	0.15
Pb	0.25	0.29	0.42	0.39	0.62**	0.2	0.02	-0.35
Zn	0.32	0.35	0.3	0.47*	0.63**	0.07	0.24	-0.38

* Correlation is significant at the 0.05 level; ** correlation is significant at the 0.01 level.

Table 5. The Pearson correlation matrix of HMs (Cd, Cu, Pb and Zn)

	Cd	Cu	Pb	Zn
Cd	1			
Cu	0.13	1		
Pb	0.77**	0.06	1	
Zn	0.64**	0.04	0.85**	1

** Correlation is significant at the 0.01 level.

these heavy metals. In arable land in China Li et al. (2009) found significant correlations between these HMs and related it to anthropogenic activities.

Multivariate analysis

The Principal Component Analysis (PCA) was conducted to analyse the relationships between the 11 experimented variables (4 HMs and 7 soil properties) and the results are shown in Table 6 and Figure 2. The number of significant principal components were three and it is selected using the Kaiser criterion (Kaiser, 1960) with an eigenvalue higher than 1.

The first two principal components explained more than 60%, the first three together account for 76.88% of the total variance (Table 6). The largest contribution to the first principal component (PC1) is given by the Zn, Pb, P_2O_5, and Cd. The principal component 2 (PC2) had the greatest contribution from silt, pH (H_2O), $CaCO_3$ and sand. The largest contribution to the PC3 was by Cu. These results show that PC1 could significantly reflect anthropogenic influence whereas PC2 explain natural (lithogenic) factor. The third component (PC3) alone explains 16.74% of the variance. The largest contribution to the PC3 by Cu may be associated with anthropogenic activities, first of all, application of copper-based fungicide. These results point to the different origin of Cu in soils compared to Cd, Pb and Zn or that they accumulated by different processes and different type of anthropogenic activity. The obtained results demonstrate that used multivariate statistical procedures are a useful tool to identify probable origin of heavy metals in soil in terms of heavy metal-soil properties and metal-metal relationships.

Many studies have applied multivariate statistical approach, mostly PCA, for the identification of the sources controlling the variability of heavy metals content in soils. Most of them showed that Cd, Cu, Pb and Zn are mainly of anthropogenic origin.

Facchinelli et al. (2001) established that Cu and Zn are controlled by long-term anthropic activity connected to grape growing, while Pb is related to road transport and industrial and urban areas. Mico et al. (2006) drew similar conclusions that Cd, Cu and Pb constitute an anthropogenic component related to specific human activities (production of vegetable crops), while Zn has both natural and anthropic origin. As possible sources for particular metals, they listed Cu-based agrochemicals for Cu, vehicle and industrial fumes for Pb and inorganic fertilizers, atmospheric deposition or anthropic wastes such as sewage sludge or wastewater for Cd. Li et al. (2009) also identified that Cd, Cu and Pb had

Table 6. Principal component loadings for experimented variables (4 elements and 7 soil properties), eigenvalues, total and cumulative variance

Property	Principal component		
	PC1	PC2	PC3
pH H_2O	-0.18	-0.82	-0.12
$CaCO_3$ (%)	-0.42	-0.75	0.26
SOC (g/kg)	-0.45	0.22	-0.62
P_2O_5 (mg/100 g)	-0.79	0.17	0.46
K_2O (mg/100 g)	-0.62	0.4	0.57
Sand (%)	-0.25	0.7	-0.44
Silt (%)	-0.1	-0.91	0.18
Clay (%)	0.54	0.31	0.42
Zn (mg/kg)	-0.9	-0.2	-0.04
Pb (mg/kg)	-0.89	-0.03	-0.16
Cu (mg/kg)	-0.28	0.46	0.7
Cd (mg/kg)	-0.77	0.19	-0.29
Eigenvalues	4.04	3.12	2.01
Total variance (%)	33.66	26.48	16.74
Cumulative (%)	33.66	60.15	76.88

anthropogenic sources (e.g. overuse of chemical fertilizers and pesticides, industrial and municipal discharges, animal wastes, sewage irrigation, etc.), while Zn was associated with parent materials and therefore had natural sources (e.g., the weathering process of parent materials and subsequent pedogenesis). Unlike them, Franco-Uría et al. (2009) related Cd, Pb and Zn with anthropogenic sources, while Cu mainly associated with parent material of an alluvial area, in an arable layer of pastureland. Lu et al (2012) studied HMs in 2 soil types under 4 land use types and concluded that Pb concentrations appeared to be associated with parent material, whereas Cd, Cu and Zn were controlled by anthropogenic input from agricultural production.

The above-mentioned studies were conducted on different soil types, parent material and under different land use, including the application of different agricultural practices, so the differences among them in comparison to results in this study are expected.

HMs concentrations and land use

The mean concentrations of Cd, Cu, Pb and Zn (mg/kg) in 3 land use types are listed in Table 7.

For testing the significance of differences between means of selected metals in different agricultural land use types analysis of variance (one-way ANOVA, F-test) is used. The results listed in Table 8 show significant differences ($P<0.05$) only for means of Cu concentrations

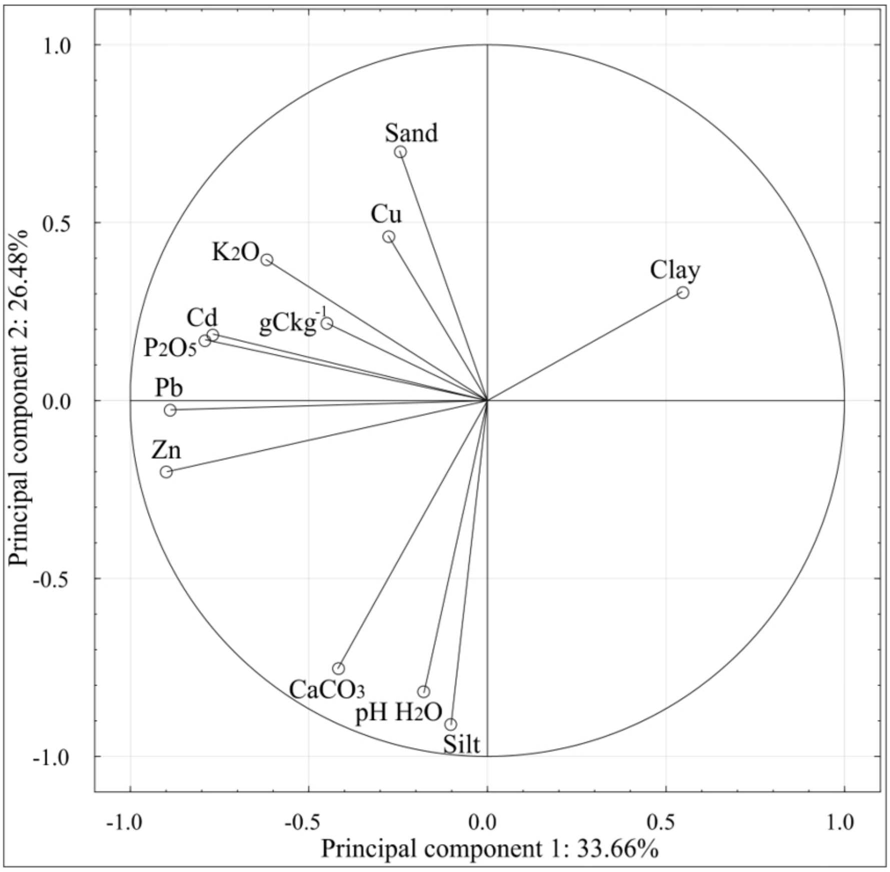

Figure 2. Projection of the variables on the plane of the first two principal components

Table 7. The mean concentration of Cd, Cu, Pb and Zn (mg/kg) in 3 land use types

No. of samples	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Land use
8	0.36	29.5	14.8	54.7	Grassland
10	0.39	38.1	15.7	50.1	Olive groves
8	0.42	74.9	17	49.7	Vineyards

Table 8. Summary table of the analysis of variance for Cd, Cu, Pb and Cd in three different land use types

	SSb	df (k-1)	MSb	SSw	df (N-1)	MSw	F	P
Cd	0.01	2	0.01	0.47	17	0.03	0.18	0.83
Cu	7,128.8*	2	3,564.4*	9,710.1*	17	571.2*	6.24	0.01
Pb	15.32	2	7.66	884.05	17	52	0.15	0.86
Zn	95.54	2	47.77	7,093.89	17	417.29	0.11	0.89

SSb and SSw are sums of squares between (b) and within (w) groups; MSb and MSw are mean squares between (b) and within (w) groups; F is test statistic, df is the degrees of freedom between-group (k-1) and the degrees of freedom within-group (N-1); P-values for the F test; * differences are significant at $P<0.05$.

in the different land use types. The P-values for Cd, Pb and Zn (>0.05; Table 8) show that differences between the means of these metals are not statistically significant indicating that land uses had no significant effects on the distribution of this metals in the studied soils.

The mean values of Cu concentration in 3 land use types (Table 7) followed the sequence: vineyards (74.9 mg/kg) > olive groves (38.1 mg/kg) > grassland (29.5 mg/kg). In order to compare the mean values in the Cu concentration among land use types, the Tukey's honestly significant difference test was applied. The results of the Tukey test (Table 9) show the significant differences (P<0.05) between mean Cu concentration in vineyards and olive groves (P=0.03) and vineyards and grassland (P=0.01). The difference between the means of the Cu concentrations in olive groves and grassland was not significant (P=0.79). These results show the significant effect of land use on the Cu concentration in the topsoil indicating an obvious increment from agricultural practices, particularly with the application of copper-based protective agents.

Table 9. Tukey HSD test for the significant differences between 3 land use types: olive groves (1), grassland (2) and vineyards (3) in the Cu mean concentration

	(1)	(2)	(3)
Olive groves (1)		0.79	0.03*
Grassland (2)	0.79		0.01*
Vineyards (3)	0.03*	0.01*	

* Differences are significant at P<0.05.

Increased copper concentrations in vineyard soils due to long-term and intensively application of copper-based fungicides are well-known problem observed in many other studies (Wightwick et al., 2008; Komarek et al., 2010; Ruyters et al., 2012). In previous research of anthropogenic soils on flysch in Kaštela Bay coastal area under the old vineyards, Vitanović et al. (2010) established a wider range of Cu (163.7-302.1 mg/kg) and about 3 times higher mean value (213.1 mg/kg) compared to Cu concentration in the vineyards of the current study. In terraced soil on the Eocene flysch in the Sub-Mediterranean winegrowing region of Slovenia Rusjan et al. (2007) in topsoil (0-20 cm) established a narrower range of Cu concentration (71-120 mg/kg) compared with a range of 40.1-149.8 mg/kg) in this study (Table 2).

CONCLUSIONS

Based on the obtained results the following conclusions can be drawn:

1. The mean values of the Cd, Cu, Pb and Zn concentration in soils of the study area were 0.39, 46.5, 15.8 and 51.4 mg/kg, respectively, all characterized with a highly skewed distribution.
2. The Cd, Pb and Zn have common, mainly anthropogenic origin controlled by different anthropogenic activity, whereas the concentration of Cu in soils related to the agronomic activities - application of copper-based fungicide
3. Land use significantly influenced only on the Cu concentration in terms of higher concentrations in vineyard (74.9 mg/kg) compared to olive groves (38.1 mg/kg) and grassland (29.5 mg/kg).
4. The obtained results demonstrate that used multivariate statistical procedures are a useful tool for identifying possible origin of heavy metals in soil in terms of the heavy metal-soil properties and metal-metal relationships.

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