Heavy Metals Accumulation in Topsoils from the Wine-growing Regions

Part 1. Factors which Control Retention

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SUMMARY

The problem of exposure of agricultural soils to different anthropogenic inputs of heavy metals has been investigated in soils from two wine-producing subregions in northwestern Croatia. The aim of this study was to explore: (i) the main soil properties and topsoil accumulation of heavy metals in vineyards under long-term cultivation, and (ii) the origin and the preferential feature of metal retention in vineyard topsoil using the multivariate statistical method. The investigated area was marked on regular square grid with 1-km spacing. Topsoil samples (0-10 cm) were collected from each sampling point and analyzed for soil chemical properties, particle size distribution and heavy metal concentrations after aqua regia digestion. All soil data were incorporate into the GIS base. Summary statistics of the data set were first calculated to evaluate the distributions, and afterward processed by means of R-mode factor analysis, applying the varimax-raw rotational technique. Anthropogenic input of metals in soils of the studied wine-growing regions mostly originates from agrochemicals, since the direct influence of the urban environment or industry is almost negligible. Accumulation of copper and zinc in topsoil, determined in this research, is the most common effect of continuing fertilization and protection against diseases and pests in vineyards.

KEY WORDS

agrochemicals, aqua regia extraction, viticultural environment, multivariate statistics

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Received: January 23, 2004

INTRODUCTION

It is no coincidence that the steep southern slopes of the mountains surrounding the Croatian capital city of Zagreb are traditionally planted with grapevine. Experience of several centuries has shown that the motivation for planting grapevine on these locations has not waned: in agricultural production there is practically no alternative to grapevine cultivation on steep slopes, while an adequate choice of location ensures a high yield and good quality of wine. Constellation of ecological factors within a wine-growing region (including, among other, the soil type, parent material, mesoclimate, elevation, slope and exposition), makes up the "viticultural potential of a terroir" (Wilson, 1998). It is just because it is so complex that the term "terroir" is rather undefined in literature. It regularly refers to the soil, sometimes to the entire wine-growing location, and often also to the complex effects of ecological factors on the quality of grapes and wine (Tesic et al., 2001). Depending on the ecological environment as well as land use and management, characteristics of cultivated soils get changed in time and space. Their production capacity and influence on the environment change as well. Spatial variability of soils is a natural consequence of pedogenesis, but considerable additional variability appears as a result of long-time tillage and regular application of other growing practices. The problem of exposure of agricultural soils to different anthropogenic inputs of heavy metals, but also of other potentially toxic substances, has acquired global dimensions in the last decades. Besides atmospheric deposition, environmental dispersion of chemicals used in agriculture, such as fertilizers and pesticides, is an important factor directly affecting the natural soil functions, or indirectly endangering the biosphere by bioaccumulation and inclusion into the food chain.

Long-term use of agricultural land and frequent application of certain growing practices have certainly had more or less harmful effects. Therefore, this research was undertaken: (i) to determine the main soil properties and topsoil accumulation of heavy metals in vineyards under long cultivation, and (ii) to establish, using the multivariate statistical method, the origin and the preferential feature of metal retention in vineyard topsoil.

MATERIALS AND METHODS

Study area and soil sampling

Research was carried out on a total area of 242 km^2 in two wine-producing subregions in northwestern Croatia, in the wider Zagreb region (Fig. 1). The region of Medvednica Mt. that surrounds the urban Zagreb area is geologically heterogeneous. The old Paleozoic and Mesozoic mountain core is surrounded by belts of Tertiary hills, with mildly inclined and open slopes prevailing in the piedmont belt. The basic relief is partitioned by river valleys that separate ribbed hills stretching from the mountains towards river valleys.

Anthropogenic vineyard soils, classified as Aric Anthrosols (FAO, 1990), of the Medvednica Mt. foothills, where the wine-growing subregion of Zelina is situated (approximate coordinates: latitude,45° 55' and longitude, 16° 10'), were formed on Tertiary calcareous deposits of marl and limestone.

The second investigated area was located in Zumberak, which is a mountainous territory located to the west of Zagreb, bordered to the north and west by Slovenia, and to the south by Kupa River. The landscape reflects the features of the Dinaric, so numerous formations characteristic of the karst are found on highly dissected limestone terrains. As the Zumberacka Gora piedmont spreads perpendicularly to the mountains, some slopes are firmly interlinked by ridges, forming well protected, amphitheatre-shaped, vineyard areas in the wine-growing subregion of Plesivica. Anthropogenic vineyard soils on this location (approximate coordinates: latitude, 45°42' and longitude, 15°37') developed on Tertiary sediments and Pleistocene loams. Owing to exceptional geomorphological and agro-ecological conditions, these locations have been occupied almost exclusively by vineyards for many decades.

The climate of the wider area is humid and the average annual rainfall is 836 mm. The mean annual temperature is 10.3°C, ranging from –0.6°C (January) to 20.4°C (July).

To investigate the spatial variability of vineyard soils, 67 soil samples were taken at the nodes of a square grid at intervals of 1 km. The samples were defined as composite samples made up of 10 increments collected from the soil upper 10 cm in a cross pattern, with a 5 m distance between increments (Eijkelkamp soil sampling kit used). Site descriptions were registered at the time of sampling to record the sample location in relation to vineyard characteristics and major environmental features.

Soil properties and total metal contents

Soil samples (average weight 2 kg) were air-dried and after homogenisation, half of each sample was passed through a 2-mm mesh screen. On each sample, the following soil analysis were made: (1) the soil texture, expressed as proportions of sand, silt and clay (%); (2) pH potentiometrically in 1:2.5 (*v*/*v*) soil suspension in water i 1 *M* potassium chloride (using Mettler Toledo MPC 227 pH-metter); (3) organic carbon (OC, g kg^{-1}) by sulfochromic oxidation; (4) calcium carbonate contents by volumetric calcimeter method after HCl attack, (5) total phosphorus by sodium

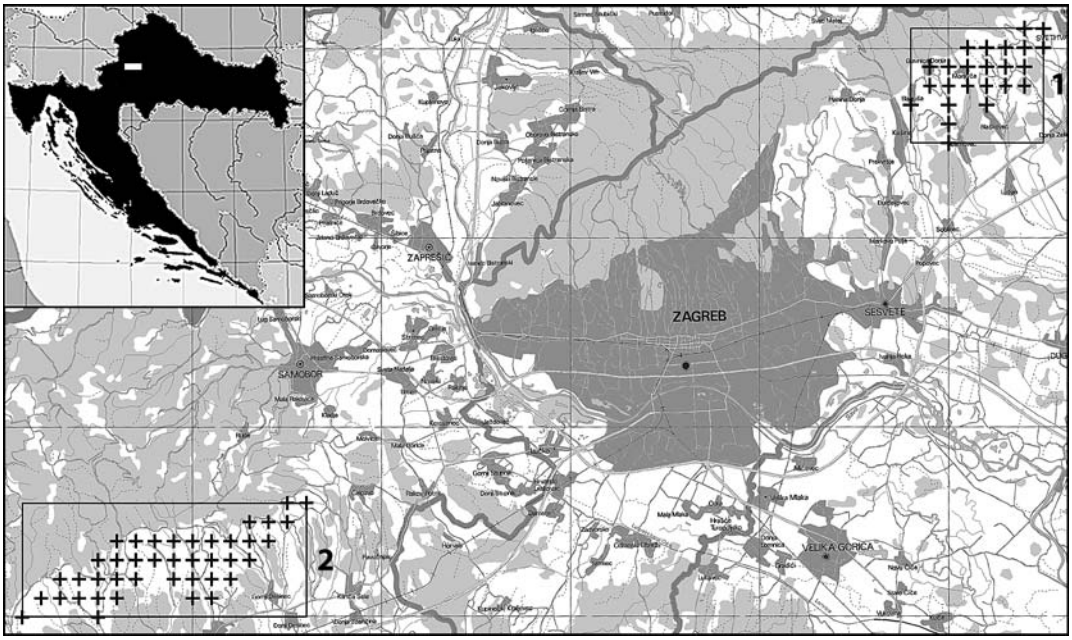

Figure 1.
Study area showing vineyard sites and sampling design:
1. Zelina wine-growing subregion,
2. Plesivica wine-growing subregion

carbonate fusion and (6) actual cation exchange capacity (CEC) with 0.01 *M* $BaCl_2$ according ISO 11260 procedure (ISO, 1994). The other half was sieved through a 500 μm mesh (Fritsch laboratory sieving set used) and used for determining soil "total" Cd, Cr, Cu, Ni, Pb, Zn, Fe, and Mn. Soil subsamples were digested with *aqua regia* in accordance with the ISO 11466 procedure (ISO, 1995). The choice of this method was dictated by Croatian Government regulations, which set norm values according to this procedure (OFFICIAL GAZETTE, 1992). The extraction process was done by the microwave technique on a Perkin Elmer Multiwave 6MF 100 (1000 W) apparatus in closed TFM vessels and with automatic pressure and temperature regulation. Heavy metal content in soil extracts were determined by flame atomic absorption spectrometry (AAS Perkin Elmer 3110).

All chemicals were declared *pro analysi*, and all solutions were prepared with double-distilled water. Standard working solutions were prepared from original certified stock solutions (MERCK), concentration 1000 mg l^{-1} in 1% (*v/v*) HNO_3. All samples were analysed at the Analitical laboratory of the Dept. of Amelioration of the Faculty of Agriculture, University of Zagreb. The quality control procedure consisted of reagent blanks, duplicate samples and several referenced soil and sediment samples of a similar matrix from the interlaboratory calibration programme in which the laboratory participates (HOUBA ET AL., 1996).

Processing of analytical data

Univariate statistics and data transformation

Summary statistics of the data set were first calculated to evaluate the distributions. Frequency distribution for each of the elements analysed was examined based on histograms, background normality tests and calculation of skewness. Skewness measures the asymmetry of the observations. Geochemical variables, especially trace elements, have low concentrations in the environment, while the anomalies resulting from both natural processes and anthropogenic activities cause the occurrence of high concentrations in data sets. This makes the probability distribution positively skewed. The problem of processing geochemical and environmental data sets is elaborated in detail elsewhere (ZHANG & SELINUS, 1998; REIMANN & FILZMOSER, 2000; WEBSTER & OLIVER, 2001). The data were log-transformed before further statistical analysis to improve normal distribution and to reduce the influence of high values. The correlation between the studied elements was estimated by Pearson's product-moment correlation coefficient.

Factor analysis

Data were processed by means of R-mode factor analysis, applying the varimax-raw rotational technique. As a multivariate method, it facilitates the reduction, transformation and organization of the original data by the use of intricate mathematical techniques, which eventually results in a sample form of factor model. Factor analysis creates a new set of uncorrelated variables, which are the linear combinations of the original ones with the same amount of information. Since the FA is conducted if the original variables have significant linear intercorrelations, the first few factors will include the largest part of the total variance. The interpretation of dominant factors was made by taking into account the highest factor loadings on chemical elements. The theoretical details of the FA are given by JOHNSON (1998). The statistical analysis was done by using the SAS/STAT program (SAS INSTITUTE, 1999).

Data management

All soil data were incorporated into the GIS database. Spatial visualization of the sampling locations was carried out using the grid-based graphics program Surfer for Windows version 7.0 (Golden Software, 1999) on a digitalized topographic map, scale 1:25000.

RESULTS

Soil properties and total metal concentrations

The important feature of all soil samples examined was their alkalinity, with pH value in water ranging from 5.8 to 8.3, with relatively low variability (CV_{pH} =6.2%). Organic matter contents in soils are generally low, in the range of 9.5 - 57 g kg^{-1} of organic C ($CV_{org\ -C}$=3%). Texture varied considerably from sandy to clayey, with the content of clay fraction (<2 μm) showing high variability (CV_{clay}=38%), since the range of the clay content was extremely high as well (8% to 56%). Total phosphorus amounted on average to 0.06%, ranging from 0.02-0.24%.

To determine the variability of the content of heavy metals in vineyard topsoils, comparative analysis of the elements was first performed. Table 1 summarises the statistics of the data. Maximal permitted soil concentrations of potentially toxic metals prescribed by the Government regulation (Official Gazette, 1992) are also given.

Distributions of Cr, Mn, Ni and Zn are strongly skewed (the skewness coefficient exceeded 1.0). In order to stabilise variances in all subsequent statistical analyses, the values of data sets were transformed to their common logarithms (Table 2). Regardless of skewed distributions, the mean value and the median were similar for most metals except zinc, considering that the median value was lower. The highest skewness was found in nickel and zinc, with the value of 2.97 and 2.79, respectively. However, after the logarithm transformation the mean value and the median equalized, indicating that these values could be further tested by applying more complex statistical methods. After the logarithm transformation only Zn still showed low skewness.

Typical geogenic elements, iron, manganese, chromium and nickel, showed a highly significant mutual correlation, whereas their correlation with copper, lead and zinc was generally not significant (Table 3). Only cadmium showed a significant correlation with lead and copper, and a significant negative correlation with iron.

The average concentrations of cadmium, copper and zinc in vineyard soils are higher than their background concentrations in agricultural soils of the wider Zagreb

Table 1. Statistical summary of the studied topsoil properties (n = 67)

Parameter	pH_{H2O}	pH_{KCl}	Org. C	Total P	$CaCO_3$	CEC^a	Sand	Silt	Clay
			g/kg	%		$cmol_{(+)}$/kg	%		
Mean	7.74	7.06	32.0	0.06	25.4	32.0	13.6	58.1	28.9
Median	7.90	7.26	31.3	0.05	28.9	31.4	12.0	59.1	28.0
Minimum	5.82	4.43	9.50	0.02	0.0	9.1	4.00	29.0	8.00
Maximum	8.26	7.46	57.0	0.24	57.3	55.1	43.0	78.0	56.0
Standard deviation	0.48	0.34	0.94	0.03	16.6	8.3	6.04	9.32	10.9
Coef. of variation %	6.2	4.8	2.9	50	65	26	44	16	38

[a] CEC, cation exchange capacity

Table 2. Statistical summary of metal concentrations of vineyard topsoils (in mg kg^{-1}; n=67)

Parameter	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Mean	2.20	67.6	368	29.4	573	52.7	36.6	114.3
Median	2.18	65.7	381	27.3	526	50.0	35.5	93.7
Standard deviation	0.71	18.0	191.5	7.86	210	19.5	7.55	60.4
Minimum	0.62	42.6	29.8	16.5	228	20.1	19.8	56.0
Maximum	4.57	134	700	50.0	1253	158	53.9	420
Skewness	0.28	1.51	-0.14	0.69	1.28	2.97	0.30	2.79
Kurtosis	0.94	3.20	-1.04	-0.10	2.29	13.72	-0.37	10.02
Threshold value^a	1-2	60-100	60-100	-	-	50-60	100-150	200-300
Mean (log_{10})		1.82			2.73	1.70		2.02
Median (log_{10})		1.82			2.73	1.70		1.97
Standard dev. (log_{10})		0.11			0.15	0.13		0.17
Skewness (log_{10})		0.66			0.08	0.43		1.33

[a] Maximal permissible concentrations as defined by Croatian government regulations

Table 3. Pearson correlation between heavy metal concentrations (in mg kg^{-1}) in vineyard topsoils (lower triangle)

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cadmium	1							
Chromuim	-0.19 ns	1						
Copper	0.39^{**}	-0.14 ns	1					
Iron	-0.47^{***}	0.83^{***}	-0.14 ns	1				
Manganese	-0.19 ns	0.50^{***}	-0.02 ns	0.60^{***}	1			
Nickel	0.17 ns	0.80^{***}	-0.06 ns	0.50^{***}	0.44^{***}	1		
Lead	0.41^{***}	0.10 ns	0.16 ns	-0.17 ns	0.00 ns	0.22 ns	1	
Zinc	-0.04 ns	0.08 ns	-0.02 ns	0.06 ns	0.00 ns	0.05 ns	-0.10 ns	1

*Correlation significant at $p \leq 0.05$; **correlation significant at $p \leq 0.01$; ***correlation significant at $p \leq 0.001$; *ns* Not significant

Table 4. Pearson correlations between selected soil properties and heavy metal concentrations (in mg kg^{-1})

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Organic C (%)	0.51^{***}	-0.03 ns	0.55^{***}	-0.06 ns	0.15 ns	0.09 ns	0.27^{*}	-0.16 ns
pH$_{H2O}$	0.46^{***}	-0.23 ns	0.40^{**}	-0.25^{*}	-0.24 ns	0.01 ns	-0.1 ns	0.09 ns
CEC (cmol$_c$kg^{-1})	0.33^{**}	0.40^{**}	0.21 ns	0.21 ns	0.13 ns	0.53^{***}	0.22 ns	0.04 ns
Clay (%)	0.15 ns	0.72^{***}	-0.08 ns	0.42^{***}	0.24 ns	0.96^{***}	0.43^{***}	0.14 ns
CaCO$_3$ (%)	0.70_{***}	-0.47^{***}	0.37^{**}	-0.66^{***}	-0.39^{**}	-0.13 ns	0.14 ns	-0.37 ns
Total P (%)	0.16 ns	-0.02 ns	0.13 ns	-0.06 ns	-0.09 ns	-0.01 ns	-0.04 ns	0.02 ns

*Correlation significant at $p \leq 0.05$; **correlation significant at $p \leq 0.01$; ***correlation significant at $p \leq 0.001$; *ns* Not significant

region (Romic & Romic, 2003), which may be associated with the more intensive fertilization and protection of grapevine against pests compared to field crops in the studied area, though the pedo-geogenic origin cannot be excluded either. This could be one of the reasons for the low correlation between elements in vineyard topsoil. Some characteristic features of the behaviour of metal ions can also contribute to the low correlation between concentrations of the particular elements n vineyard soils (Table 3). For example, the ion radius Zn^{2+} is very similar to those of Fe^{2+} i Mn^{2+}. Consequently, Zn^{2+} could, to a certain extent, be liable to isomorphic exchange with the said ions in the structure of minerals (Mengel & Kirkby, 1979). Correlations between the concentrations of the studied elements and some soil properties, primarily organic matter and clay contents, may indicate the prevailing way of retention of these elements in soil (Table 4).

Thus, copper and cadmium showed a highly significant correlation with the content of organic matter, while lead showed a lower, but still significant, correlation. Concentrations of nickel, chromium, lead and iron highly significantly correlated with the soil clay content. A significant positive correlation between total cadmium and lead content and $CaCO_3$ was also determined, as well as a significant but negative correlation between total $CaCO_3$ and iron, chromium and manganese. From the agronomic point of view, the highly significant negative correlation between total iron and $CaCO_3$ ($r = -0.66$) is particularly interesting because of the occurrence of plant chlorosis due to iron deficiency in carbonate soils. Since solubility of Fe oxides in soil is pH dependent, alkaline and carbonate soils have insufficient available iron, which cannot meet the plant requirements (Bergmann, 1992). No significant correlation was determined between soil total phosphorus and content of any of the studied elements.

Factor analysis

Associations of heavy metals in soil and their correlation with the selected soil properties (organic matter content, $CaCO_3$, clay content) were determined applying factor analysis to topsoils in wine-growing regions, assuming that it would to help identify the predominant features of metal retention. Meeting the Kaiser criterion of the typical eigenvalue ≥1, that is, including the factors that explain >75% of variance, four factors were extracted. It was further assumed that the thus defined model of factor analysis would be more useful in explaining the mechanism of metal retention in soil than in identifying their origin. The model is presented in the form of the matrix of varimax-raw rotated factors (Table 5) where four factors explained as much as 79% of total variability. Table 6 shows factor loadings for discrete variables in the four extracted factors.

The first factor (F1) of unipolar character explained 31.4% of total variance, and grouped the elements of pedogenic and lithogenous origin, nickel and chromium. These elements highly positively correlated with the clay content. The significant individual correlation with iron and manganese and grouping

Table 5. Eigenvalues of factors for vineyard topsoils

Factor	Initial eigenvalues		
	Total	Percent of variance	Cumulative %
1	3.75	34.1	34.1
2	2.59	23.5	57.6
3	1.34	12.1	69.7
4	1.01	9.22	79.0
5	0.71	6.49	85.4
6	0.57	5.16	90.6
7	0.44	4.02	94.6
8	0.24	2.22	96.8
9	0.16	1.43	98.3
10	0.14	1.26	99.5
11	0.05	0.46	100

Table 6. Loadings of the first four factors for the variables included in model

Variable	Rotated component matrix			
	Factor 1	Factor 2	Factor 3	Factor 4
Organic carbon	0.059	0.068	0.863	-0.202
Clay	0.917	0.034	-0.069	0.080
$CaCO_3$	-0.108	0.801	0.277	0.091
Cd	0.233	0.726	0.504	-0.026
Cr	0.806	-0.508	-0.026	0.057
Cu	-0.105	0.157	0.830	0.101
Ni	0.864	-0.170	0.104	0.032
Pb	0.524	0.462	0.139	-0.327
Zn	0.097	0.016	-0.060	0.942
Fe	0.470	-0.816	-0.007	0.064
Mn	0.356	-0.644	0.286	-0.059
Explained variance	2.948	2.780	1.885	1.072
Proportion of total variance	0.268	0.253	0.171	0.097

with clay in the factor analysis may result from the Fe and Mn hydroxide coatings on the surface of clay minerals. Among the many oxidation states in which it may appear, the most stable and most frequent chromium forms are Cr(III) and Cr(VI). Relatively insoluble and slightly mobile Cr(III) prevails in most soils, generally appearing in the form of insoluble hydroxides and oxides (Koons, 1980). Nickel chemism in soil is simpler and is based on the bivalent Ni^{2+} ion.

The second factor (F2) explained 23.5% of total variance, pointing out the strong positive correlation between cadmium and total carbonates. Bipolarity of the second factor with a high negative factor loading for iron, and somewhat lower loadings for manganese and chromium, was observed as well (Table 6). Cadmium is a chalcophile but in the conditions of pH>7, Cd^{2+} can co-precipitate with $CaCO_3$ or precipitate as $CdCO_3$. For this reason, cadmium mobility and bioavailability are low in neutral and alkaline soils. Since the average value of pH_{H2O} = 7.74 and the carbonate content is 25.4%, grouping in the second factor is accountable. The fact that cadmium is less liable to chemisorption on Fe, Al and Mn oxides may explain the higher factor loadings in the second factor.

The third factor (F3) explains 12.2% of total variance and pointed out a high positive correlation between copper and the soil organic matter content. In the third factor also cadmium had a somewhat higher factor loading (0.50), which might be explained by the chalcophilic character of both copper and cadmium (they form with sulphides poorly soluble minerals, Cu_2S and CuS, and CdS). Nevertheless, in contrast to cadmium, most of the colloidal particles in soil strongly adsorbs copper. Copper forms stronger organic complexes than other bivalent transition metals and therefore soils rich in organic matter can retain more copper, without causing plant toxicity.

The fourth factor (F4) explained 9.2% of variance, but zinc, which was represented in this factor with a high factor loading, showed no correlation with any of the soil properties included in the model, and neither with any of the studied elements (Table 6). This means that the model of factor analysis did not indicate the predominant mechanism of zinc retention in soil, but was more likely to point out its anthropogenic origin.

DISCUSSION

Variability of the major chemical and physical properties in vineyard topsoil is characteristic of cultivated soils. The study areas were entirely reclaimed for viticulture during the 19th century. Some of the plots were abandoned recently, but many plantations were renewed, or new grapevine plantations were formed by forest clearing. Research has shown that long-term cultivation homogenizes topsoil, which is most evident in properties such as uniform pH, uniform and low organic matter content and a smaller variability of the cation exchange capacity compared to the clay content in soils (Paz-Gonzales et al., 2000). In general, the cation exchange capacity mostly depends on the content of organic and mineral colloids in soil. Reduction of the organic component in vineyard soils would probably be reflected also in reduced cation exchange capacity if soils were poorer in the clay fraction. This might be the reason for the smaller variability of the cation exchange capacity compared to the variability of clay content.

Anthropogenic input of metals in soils of the studied wine-producing regions mostly comes from agrochemicals, since the direct influence of the urban environment or industry is almost negligible. Production technology of perennial crops like grapevine generally requires regular application and frequent repetition of agricultural management

Table 7. Comparison of heavy metal concentrations in upper continental crust and soils (mg kg^{-1})

Element	Upper continental crust (Wedepohl, 1995)	Soils worldwide (median, after Reinmann & de Caritat, 1998)	Agricultural topsoil of Zagreb region (median, n=331)	Topsoil NW Croatia (median, n=293; 7,350 km^2 covered, after Miko et al., 2001)
Cd	0.1	0.3	0.66	-
Cr	35	80	67.6	80
Cu	14	25	20.8	23
Mn	530	545	613	562
Ni	19	20	49.5	36
Pb	17	17	25.9	30
Zn	52	70	77.9	80

practices for a number of years. In terms of heavy metals, accumulation of copper, zinc and cadmium is the most common effect of fertilization and diseases and pests control in vineyards. Quantification of input through growing practices is possible, however only at an estimation level. Contribution of aerial deposition to metal accumulation in soils is much more difficult to estimate for this region, but it not likely or almost impossible that it could results in anomalous concentrations.

A comparison of element concentrations in the vineyard topsoil of the Zagreb region with average element concentrations of the upper continental crust (Wedepohl, 1995) and the median value of element concentrations of soils worldwide (Reinmann & de Caritat, 1998; Romic & Romic, 2003) showed that, besides copper, higher concentrations of cadmium and zinc were also obvious (Table 7).

Cadmium. Long-term investigations worldwide have shown that application of phosphate fertilizers has resulted in soil enrichment with cadmium (0.3-4.4 g ha^{-1} year^{-1}), depending on the rates and kinds of fertilizers applied (Singh, 1994). Andrews et al. (1996) and Gray et al. (1999) also determined a highly significant correlation between total concentrations of cadmium and phosphorus in agricultural soils of New Zealand, which they attributed to long-term application of phosphate fertilizers. However, no significant correlation between total cadmium and phosphorus content in vineyard soils was recorded in this research (Table 4), which may indicate that relatively high cadmium concentrations in topsoil are not due to the application of phosphate fertilizers. Factor analysis pointed to the importance of $CaCO_3$ for cadmium retention in soil. In acid and neutral soils Cd^{2+} is adsorbed through cation exchange, while in carbonate and alkaline soils it can precipitate in the carbonate or phosphate forms. A significant correlation between total cadmium and $CaCO_3$ in natural carbonate soils of the Valladolid province in Spain was recorded by Sanchez-Camazano et al. (1998). Precipitation processes in Cd^{2+} contaminated carbonate soils prevent oversaturation of the solution and thereby reduce cadmium mobility. Numerous studies of cadmium origins in carbonate soils cite cadmium adsorption on $CaCO_3$ or its precipitation as $CdCO_3$ to be the predominant mechanisms of cadmium retention in soils (McBride, 1994; Papadopoulos & Rowell, 1988). Baize & Steckerman (2001) found that soils developed on Jurassic limestones in different parts of Switzerland naturally contained very high cadmium content, mostly between 1 and 4 mg kg^{-1}, in places as high as 16 mg kg^{-1}. Soils from the the studied regions of northwestern Croatia are anthropogenic vineyard soils on marl, with the geological substratum of clastic or clastic and carbonate rocks. Cadmium concentrations of 1.1 mg kg^{-1} (50th percentile) and 2.4 mg kg^{-1} (90th percentile) were determined in the surface layers of soils developed on carbonate parent material in Austria (Arge Alp, 2000).

Chromium and nickel. Factor analysis revealed a strong correlation between the clay content and chromium concentration in soil. Namely, soil conditions generally favour the Cr^{3+} form. This expressly immobile cation forms strong complexes with organic matter also through adsorption on oxides and clay, and chemisorption obviously prevails in the soils studied. At higher pH, a small part of soil Cr^{3+} can get oxidized to CrO_4^{2-}, a very toxic form of chromium. Such oxidation is especially enhanced by Mn oxides, while the adsorption of the chromate form is less strong, which implies its higher mobility and bioavailability. Even when the soil takes up pollutants that include CrO_4^{2-}, most of it is spontaneously reduced into Cr^{3+}, whereby organic matter plays a very important part. It was established that chromium in the studied soils is of lithogenous origin, while no anthropogenic sources of contamination were identified. Miko et al. (2001) determined an average chromium concentration of 80 mg kg^{-1} in topsoils of northwestern Croatia, and high anomalous concentration up to as much as 500 mg kg^{-1} on the southern slopes of Medvednica Mt., where also this research was conducted. The authors maintain that this is most probably a consequence of magmatic rocks and clastic rocks formed from older chromite-containing magmatic rocks. Higher nickel concentrations, ranged from 20.1-158 mg kg^{-1}, also seem to be of geogenic origin, formed by weathering of basic and ultrabasic magmatic rocks. Correlation of this element with the clay content, as determined by simple correlation (Table 4) and factor analysis (Table 6), may be explained by the fact that Ni^{2+}, as the smallest bivalent cation of transition metals, easily fits into the octahedral structure, readily co-precipitating with Mn and Fe in soil. At this research level, however, it si not possible to identify the differences between the potential influence of metal oxides and organic matter on the prevailing adsorption processes of either nickel or other heavy metals in a heterogeneous medium such as soil. It can be concluded that the presence of lithogenous chromium and nickel in vineyard soils of NW Croatia is a result of the process of redistribution, both vertical (weathering of rocks and pedogenesis) and lateral (homogenization through cultivation and erosion). Mobility of these elements can naturally increase under the new conditions. Quantin et al. (2002) reported that in the reducing conditions, similar to those in soils with stagnating water, cobalt and nickel might get released from manganese oxides, which could increase their bioavailability. Cooper (2002) confirmed also the potential toxicity and Cr(VI) in such soils.

Copper. High copper concentrations are not unusual for vineyard soils. Over 65% of vineyards under study are more than 40 years old, and some have been continuously cultivated for more than 100 years. The Bordeaux mixture, an efficient agent for prevention of vine downy mildew, has been routinely used in Croatia since the end of the 19th century, its concentrations and the number of treatments depending on the weather conditions, infection intensity and vineyard location. In France, for example, the Bordeaux mixture has been used since 1855, and it was found that after several decades of its continuous application the soil total copper reached a concentration of as much as 1.0 g kg^{-1} (Delas & Dartigues, 1970). Research done by Deluisa et al. (1996) on 43 plots in a humid region of northern Italy revealed an average copper accumulation in topsoil of 297 mg kg^{-1}. Moolenar & Beltrami (1998) have calculated that organic protection of grapevine, which implies exclusive use of the Bordeaux mixture, can result in an increase of soil copper concentration up to 600 mg kg^{-1} after 100 years. Determination of the total metal content in soils is an important step in assessing the hazards to the vital roles of soils in the ecosystem, but also in comparing them with quality standards with respect to the effects of contamination and system sustainability. However, the mobility and availability of soil copper are governed by the processes of dynamic equilibrium, and not only by its total concentration (Kuo et al., 1983). As Cu is very reactive in soil, it is found in all matrix components, and its complexation with organic matter is one of the most efficient mechanisms of Cu^{2+} retention in soil (McBride, 1981). This restricts its bioavailability, but also considerably reduces the risks of phytotoxicity of the accumulated anthropogenic input and its vertical migration. Romic (2002) established that the mobile ($CaCl_2$-extractable) fraction of copper in vineyard soils amounted only to 0.2 – 3.1% of its total content. As Cu accumulation in the studied soils is restricted to topsoil the risk of Cu phytotoxicity for grapevine is small, since grapevine develops most of its roots at a depth >30 cm, depending on the soil type and the profile depth. Material suspended by erosion, however, carries away also part of the applied copper, and redistribution of this material depends on a number of factors (relief, size and shape of the drainage basin, etc.). Halamic et al. (2001) applied factor analysis in geochemical investigations of stream sediments in drainage basins in the Mt. Medvednica region, which also includes part of the area studied in this paper, without determining correlation of copper concentrations with any lithological unit, so they assumed anthropogenic influence (vineyards). Ribolzi et al. (2002) did research in the Mediterranean drainage basins of wine-growing regions in France with the aim to characterize copper forms in suspended material and recorded an average total concentration as high as 245 mg Cu kg^{-1}, but Brun et al. (1998) reported the maximum of 250 mg kg^{-1} of copper in vineyard soils of the Mediterranean part of France.

Lead. Factor analysis showed that lead was the only of the elements analyzed in vineyard soils that did not manifest expressive grouping in any factor. Higher factor loadings in the first and second factors (Table 6) may only partially indicate the prevailing feature of its retention in soil. Namely, these two factors are related to the content of mineral colloid fraction and total carbonates. As already mentioned, arable agricultural soils are almost regularly poorer in organic matter content than uncultivated soils, so neither in this research humus content was found to be the primary mechanism of lead retention in vineyard soils. It is also noteworthy that no anthropogenic contamination of these soils with lead was recorded.

Zinc. Single correlations did not reveal a significant correlation between soil properties and the total zinc concentration (Table 4). Also factor analysis confirmed the low correlation between zinc concentrations and other metals, but also between most vineyard soil properties (Table 6). Zinc is a frequent component of different agrochemicals for protecting grapevine against diseases and pests. Some pesticides contain as much as 25% of zinc and can thereby contribute to its accumulation in soils (Müller, 2000). All fertilizers, both mineral and organic, as well as different additives to soil, contain zinc, mostly as contamination; zinc content in inorganic phosphate fertilizers ranges from 35-6040 mg kg^{-1} and in stable manure from

15-250 mg kg^{-1}(LAEGREID ET AL., 1999). All these data point to the conclusion that the spatial variability and occasional accumulation of zinc in topsoil of vineyard soils primarily depend on the manner of their use. Still, with regard to the variability of soil properties even at a relatively small distance, a correct pedological interpretation, including pedogenesis, morphology and the actual processes, is of the utmost importance for estimating the anthropogenic contribution to metal accumulation and soil quality in rural environments. Namely, carbonate and alkaline soils are characterized by very low solubility and thereby also mobility of zinc. Predominant mechanisms of zinc retention in soil are chemisorption on oxides and alumosilicates, and its complexing with organic matter. Nonetheless, despite the very low activity of free Zn^{2+} ions in poorly alkaline soils, organic complexes with zinc can increase its solubility and mobility.

CONCLUSIONS

Investigation of physical and chemical properties of topsoil in two vine-growing region in NW Croatia, followed by descriptive and multivariate statistical analysis aimed at finding relationships between soil properties and total metal content, yielded the following conclusions. Determined spatial variability of the major chemical and physical properties in vineyard soils is characteristic for cultivated soils. Typical geogenic elements, iron, manganese, chromium and nickel, showed a highly significant mutual correlation, whereas their correlation with copper, lead and zinc was generally not significant. Total concentrations of cadmium, copper and zinc in vineyard soils are higher than their background concentrations, which may be associated with long-time intensive fertilization and protection of grapevine. Associations of heavy metals with the selected soil properties, determined applying factor analysis, might explain the preferential feature of metal retention in soil. The first factor (F1) grouped the elements of pedogenic and lithogenous origin, nickel and chromium, which highly positively correlated with the clay content. The second factor (F2) pointed out the strong positive correlation between cadmium and total carbonates, and the third (F3) a high positive correlation between copper and the soil organic matter content. Zinc is represented in fourth factor (F4) with a high factor loading, but this element showed no correlation with any of the soil properties included in the model, and neither with any of the studied elements.

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