Soil Geochemistry as a Component of Terroir of the Wine-growing Station Jazbina, Zagreb

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Summary

The study of soil geochemistry as a *terroir* component of the University of Zagreb Faculty of Agriculture experimental wine-growing station Jazbina was carried out with the purpose to better understand the role of soil in *terroir* by investigating the basic geochemical factors that may affect grape vines and to contribute to the sustainable management of soils in vineyards. During the field work, soil was drilled with an auger to the parent material, soil samples were collected and analysed in the laboratory. Soil physicochemical characteristics were determined along with the content of elements Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, S and Zn in topsoil and subsoil, and in soil profile horizons as well. Dominant soil type is Rigosol from Pseudogley on slope developed on Pleistocene loam and Pliocene clay deposits. Maps of element spatial distributions were generated applying geostatistics and using GIS, and the grouping feature of elements was studied applying multivariate statistics. The results confirm that the soil type of the studied wine-growing site, originally classified as Pseudogley, differs greatly in geochemistry and fertility from soils belonging to the same class, which may finally explain the contribution of soil to the quality of wine produced.

Key words

GIS, geostatistics, pseudogley, agro- and hydroamelioration, rhizosphere, spatial distribution

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Received: December 20, 2012 | Accepted: March 2, 2013

ACKNOWLEDGEMENTS
This work was supported by the Ministry of Science, Education and Sport of the Republic of Croatia, contract 178-1782221-2039, project "Spatial variability of potentially toxic metals in agricultural soils of Croatia" and it was awarded a Rector's prize for outstanding student research in academic year 2010/2011.

Introduction

Jazbina, a wine-growing and wine-making experimental station, has been in the possession of the Faculty of Agriculture, University of Zagreb, since 1939. Vineyards cover 10 ha of the overall station area of 25 ha on the southern hillsides of Mt. Medvednica. The site is known for exquisite grape and wine quality, and its vineyards and wine cellar are used for teaching and research activities. The National collection of Croatian native grape varieties is located at the Jazbina experimental station, containing more than 120 different cultivars (Voncina et al., 2011), as well as a grapevine rootstock mother block and a small experimental site of interspecies crosses.

A variety of factors, both spatial and temporal, affects the grape quality, many of them being specific exactly to the given wine-growing site. Grape growing conditions and enological potential have been created, among other factors, also by landscape characteristics: soil, climate and topography. These factors are much less changeable than biological (cultivar, stock) or human factors (ampelotechnics, vinification) and for this reason the concept of *viticultural terroir* is based on the simple relationship between soil and wine (White, 2003). *Terroir* actually relates the sensory characteristics of wine to the environmental conditions under which vine is grown and therefore the quality and *style* of wine can be to a large extent explained by this approach (Leeuven and Seguin, 2006). Since *terroir* is defined as an interactive ecosystem (Seguin, 1988), it is very difficult to evaluate scientifically its contribution to plant capacity to accumulate bioactive phytochemicals good for human health (Lila, 2006).

From the commercial aspect, wine-growers are now showing increasing interest in the effects of soil composition, its fertility and texture upon wine quality (de Andres-de Prado et al., 2007). Special importance is laid on the influence of soil geochemical characteristics on grape and wine quality (Mazzariello, 2008). Soil is a factor of the natural environment and its effect on wine quality and grape composition is highly complex, since it affects mineral nutrition of grapevine, water uptake, as well as rooting depth and rhizosphere temperature. The close relation between geology and soil science ensues from the fact that soil is formed by the weathering of parent rock or loose parent material through the interaction of numerous soil formation factors. This is why the concept of *terroir*, i.e., relating soil properties to wine quality, was introduced by geologists, and was later complemented by other professions.

Land use for agriculture causes great changes in the natural properties of soil. Translocation of soil by tillage may be the key reason for redistribution of soil particles within the profile and over the entire site, while erosion due to tillage is especially present in hilly landscapes. Tillage and homogenization of several natural horizons alter both morphological and physicochemical characteristics of soil.

Periodical monitoring of soil quality indicators is an unavoidable wine-growing practice. If systematically collected information is associated to a location, then it can be useful to all participants in the complex process of grape and wine production, wine marketing and consumption. Use of advanced information technologies, such as e.g. the geographic information system, may significantly improve the production and contribute to rational utilization of resources (Romic et al., 2012a; Jones et al., 2004).

From the commercial aspect, producers are very interested in establishing the facts that may be used to identify the origin of wines of a certain region. A number of recent studies have suggested that trace elements could be used in this way (Greenough et al., 2005) regardless of the influence of other cultivation measures such as sanitary treatments (Komarek et al., 2010) or production systems (Mackenzie and Christy, 2005; Smith et al., 2008).

This paper presents geochemical characterization of the soils of the wine-growing station Jazbina, Zagreb, and gives the assessment of their fertility, which may contribute to a better understanding of the relationship between soil and vine as well as the impact of soil upon grape and wine quality. Besides, multivariate statistics was applied to identify the relations between the studied indicators, geostatistical analysis was performed, and maps of element distribution in soil were produced.

Material and methods

Research area

Experimental station Jazbina is situated on the southern slopes of Mt. Medvednica, on the left side of the hillslope Biškupov Čret. Vineyards cover 10 ha of the overall station area of 25 ha (Figure 1). Soils are mainly developed on diluvial loam, and on the narrow NW edge on Upper Pontian loess. Detailed soil survey of Jazbina station was carried out in 1952 by the Department of Soil Science of that-time Faculty of Agriculture and Forestry, University of Zagreb. According to the criteria of that time, Škorić (1957) classified the soils as *anthropogenized podzolized soil* and *podzolized brown soil*. The author, however, pointed out that profile morphology and diagnostic signs were not typical of podzolization processes. According to the current classification system (Škorić et al., 1985), the prevalent soil type is Rigosol from Pseudogley of sloping terrains developed on Pleistocene loam and Pliocene clay substrata, while Eutric Cambisol and Dystric Cambisol are sporadically found in close surroundings.

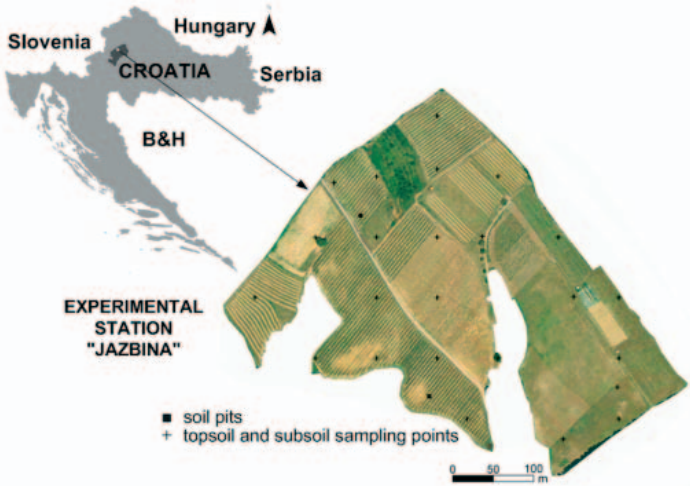


Figure 1. Geographical location of the study area. Soil sampling locations are marked on the orthophotograph

Land use history

Currently utilized plots of the experimental station Jazbina were re-organized in the period from 1994 to 1996. Viticulture and fruit plantations already existed on the site, while leveling of terraces and hydro- and agroamelioration measures were applied for the needs of establishing new plantations. Namely, a part of the area soil was periodically moistened by surplus water, mainly precipitation and surface and interlayer drainage water. Water erosion was enhanced on over 20% inclined terrains. In places where clay cropped out at the surface, springs were formed and they were active during the almost whole year. Springs additionally moisten the soil, and below them surface watercourses are formed that, besides carrying away nutrients, disperse structural aggregates and carry away dispersed soil particles through furrows generated by surface erosion. Land improvement measures were applied according to the projects designed in the Department of Amelioration of the Faculty of Agriculture, University of Zagreb, and comprised terrain systematization, application of detailed pipe drainage and agroamelioration: deep ploughing, liming, fertilization and addition of organic matter.

Climate

To characterize climate, data on precipitation, insolation, temperature and humidity provided by the Meteorological and Hydrological Service of Croatia, weather station Maksimir for a 20-year period (1990-2009), were used. Mean annual precipitation of the studied area amounts to 836 mm, with the highest average monthly precipitation of 94 mm in September. Mean annual temperature is 11.5°C, ranging from 1.0°C in January to, at most, 22°C in July. Average relative humidity is 73%, so the area belongs to the category of a moderately humid region. Humidity is generally highest in December (85%) and the lowest in May (66%). Average number of sun hours per year is 2038 hours, the mean monthly values ranging from 295 hours (July) to 46 hours (December). Meteorological data recorded from 1990 to 2009 at the Maksimir weather station were used to assess the regime according to the requirements of Soil Taxonomy (Soil Survey Staff, 2006). The moisture regime of Jazbina soils was assessed by implementing daily rainfall recordings and soil data in the Cropwat model (Smith, 1992) Mesic soil temperature regime.

Soil profile morphology and physicochemical properties

Two soil pits (P-1 and P-2) were excavated within the study area to a 1.6 m depth for full description, detailed by horizon and the dominant soil type was identified (locations shown in Fig. 1). For determination of soil physical and chemical characteristics, soil samples were taken separately from soil horizons down to the parent material.

Soil samples were taken from topsoil (0-30 cm) and subsoil (30-60 cm) at 25 sampling points within the site according the regular square grid with distances of 75 m.

For each sample, a standard soil analysis was carried out to determine pH, using a 1:5 soil weight/water volume ratio (MettlerToledo MPC 227), organic matter (OM, %) was determined by sulfochromic oxidation, calcium carbonate content by the volumetric method after HCl attack, total nitrogen content by the Kjeldahl method, available K_2O and P_2O_5 by the ammonium lactate method (Egner et al., 1960) and effective cation exchange capacity (CEC) using $BaCl_2$ solution. Digestion in aqua regia (HRN ISO 11466:2004) was done using the microwave technique on a MARSXpress system (CEM). Element concentrations in soil digests (Al, Ca, Co, Cr, Fe, Mg, Mn, Ni, P, Pb, S, V and Zn) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Vista MPX AX (Varian). All concentrations were calculated on the basis of sample dry weight (105°C, 24 h).

Quality control procedure consisted of reagent blanks, duplicate samples and several referenced soil and sediment samples of a similar matrix from the inter-laboratory calibration program (Houba et al., 1996). Maximum allowable relative standard deviation between replicates was set to 10%.

Statistical analyses

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. 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.

Multivariate statistics: Factor analysis (FA)

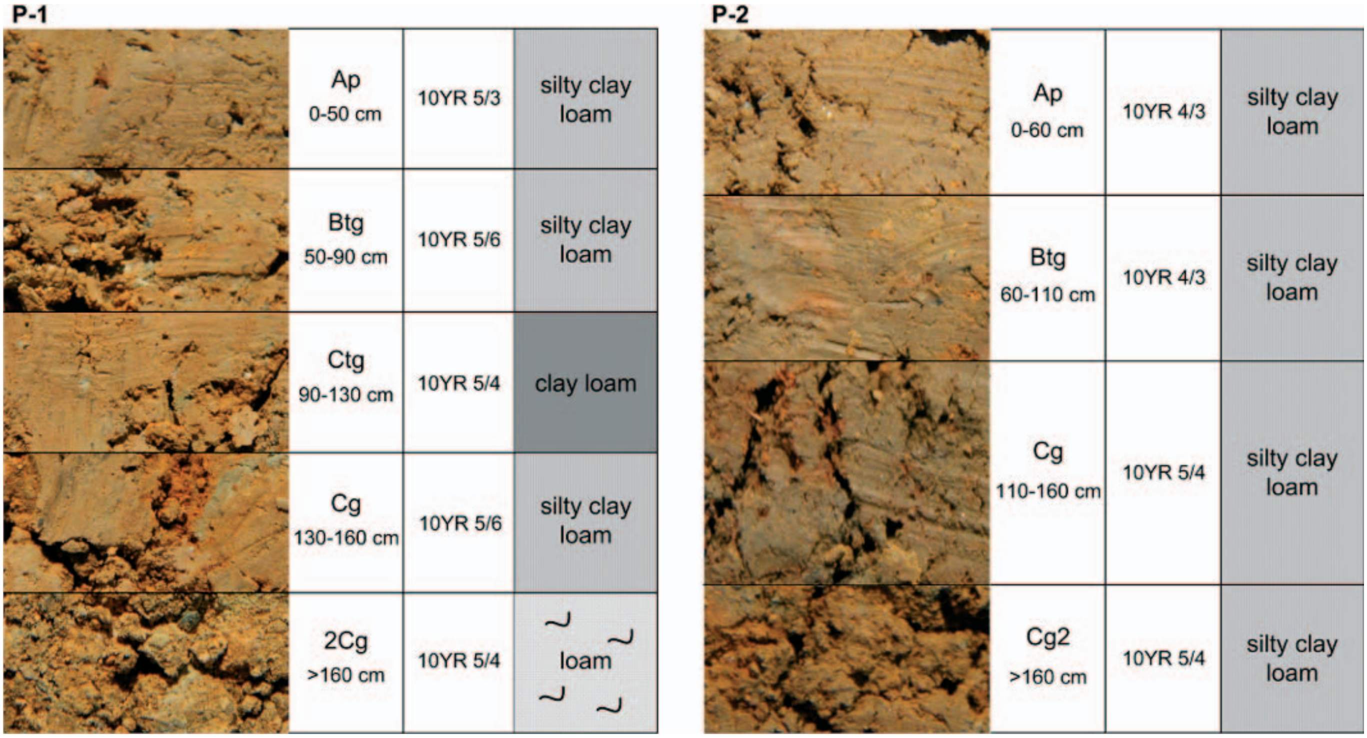
Data were processed by means of R-mode factor analysis, applying the varimax-raw rotational technique. Factor analysis creates a new set of uncorrelated variables, which are linear combinations of the original ones with the same amount of information. FA analyses the variance shared among variables with the general goals of data reduction, description of relationships and testing theories of these relationships. Since FA was conducted if the original variables had significant linear correlations, the first few factors included the largest part of total variance. Total variance of the data was divided into three parts: common feature variance, specific feature variance and residuals or errors. Factors represent the common variance of features. In FA, the data matrix X was decomposed as:

$$X = FL^T + E$$

where F is the score matrix, LT is the transpose of the loading matrix L and E expresses the specific feature variance and residuals (Abollino et al., 2011). Interpretation of dominant factors was made by taking into account the highest factor loadings on chemical elements. The theoretical details of FA were given by Johnson (1998). Statistical analysis was done using SAS (SAS Institute, 2002/2003).

Geostatistical interpolations

Inverse Distance Weighting (IDW) was used to estimate the values for points in an area not actually sampled and to present the concentration of a particular element as accurately as possible. This technique is an exact deterministic interpolator that requires very few decisions regarding model parameters because it accounts for distance relationships only. This method assigns weights in an averaging function based on the inverse of the distance (raised to some power) to all data points located within a given search radius centered on the point of estimate.



P-1

Horizon	Colour	Texture
Ap 0-50 cm	10YR 5/3	silty clay loam
Btg 50-90 cm	10YR 5/6	silty clay loam
Ctg 90-130 cm	10YR 5/4	clay loam
Cg 130-160 cm	10YR 5/6	silty clay loam
2Cg >160 cm	10YR 5/4	loam

P-2

Horizon	Colour	Texture
Ap 0-60 cm	10YR 4/3	silty clay loam
Btg 60-110 cm	10YR 4/3	silty clay loam
Cg 110-160 cm	10YR 5/4	silty clay loam
Cg2 >160 cm	10YR 5/4	silty clay loam

Figure 2. Photographs of soil micromonolites, showing diagnostic horizons, soil colour and texture

The interpolating function is:

$$Z(X) = \frac{\sum_{i=1}^{n} w_i z_i}{\sum_{i=1}^{n} w_i}$$

$$w_i = d_i^{-u}$$

where Z(X) is the predicted value at an interpolated point, Z_i is at a known point, n is the total number of known points used in interpolation, d_i is the distance between point i and the prediction point, and w_i is the weight assigned to point i. As the distance increases, the weight decreases (Shepard, 1968) and u is the weighting power that decides how the weight decreases as the distance increases. An interpolated map for each element was generated using the ArcGIS Geostatistical Analyst extension (ArcGIS, ESRI).

Results and discussion

Soil profiles

Table 1 reports the selected physical and chemical analytical features of soil profiles. Profile P-1 shows a sequence of horizons Ap-Btg-Ctg-Cg-2Cg (Figure 2). It's evident that eluvial (E) horizon, being a characteristic diagnostic feature of pseudogley soils, had disappeared due to the mixing of anthropogenic (A) and eluvial (E) horizons through deep cultivation (>40 cm). Deep ploughing to improve the moisture storage capacity of the soil and/or to eliminate a dense illuviation horizon, liming and fertilization are the main measures regularly undertaken to improve productivity of pseudogleyed soils. Argiluvic (Btg) horizons contain more clay, leached from upper layer, 35% in P-1, and 41% in P-2. This horizon was formed by stagnation of surface water with intermittent exchange of wet and dry phases; it is characterized by marbling, but the degree of hydromorphism often can be correlated to dominant colour patterns among geographically associated soils (Moore, 1974). Many soils that are periodically water saturated have strong textural differentiation between surface and subsurface horizons. This clay translocation into lower subsoils may cause macropores plugging, decreasing of permeability and seasonal perching of water. In P-1, horizon Ctg contains even more clay than the overlaying soil Btg layer, as much as 40% (Table 1). Cation exchange capacity corresponds to the clay content, which is the highest in this horizon and amounts 35.8 $\mathrm{cmol}_{(+)}\ \mathrm{kg}^{-1}$. Horizon Cg represents the pseudo-gleyed parent material. Horizons 2Cg contain more organic matter than the plough-layer to 60 cm and are characterized by lighter texture with 19% coarse sand in P-1 and 6% in P-2, which have higher humus contents than those of all the horizons above them. Occurrence of such horizons may indicate lithological discontinuity caused by covering up of fossil soil or anthropogenic influence. Profile P-2 shows a sequence of horizons Ap-Btg-Cg-Cg2 (Figure 2). The horizons of this profile show increasing thickness compared to the profile 1, with no evidence of Ctg horizon. Organic matter content is rather high along the whole profile depth (Table 1). Organic matter in subsoil seems to be strongly bonded to clay mineral surfaces. Organic solutes may also serve as Al and Fe chelators, enhancing thus the translocation of these elements. According the World reference base for soil resources, the soil can be classified as Luvic Stagnosol (Hypereutric, Siltic) (IUSS, 2006).

Increased organic matter content at the profile 2 depth of ca. 160 cm can be also attributed to the levelling of terraces where

Table 1. Selected physical and chemical analytical features of soil profiles

Horizon		Depth	pH_{H2O}	OM	Al-extractable (mg kg^{-1})		Exchangeable cations (cmol$_{(+)}$kg^{-1})					CEC	(%) Sand		(%) Silt		(%) Clay
		cm		%	P_2O_5	K_2O	Ca_{ex}	K_{ex}	Mg_{ex}	K_{ex}/Mg_{ex}	Na_{ex}	cmol$_+$kg^{-1}	Coarse	Fine	Coarse	Fine	
Profile 1	Ap	0-50	6.28	1.81	28.6	154	10.7	0.43	4.66	0.09	0.06	17.2	7	5	26	36	26
	Btg	50-90	5.93	0.79	23.5	120	12.0	0.27	7.95	0.03	0.15	21.7	6	6	22	31	35
	Ctg	90-130	6.02	0.33	30.7	144	18.1	0.37	15.9	0.02	0.29	35.8	3	4	22	31	40
	Cg	130-160	6.40	0.38	19.6	121	18.1	0.33	15.2	0.02	0.37	33.7	3	8	22	35	32
	2Cg	>160	6.89	5.14	34.9	91	16.9	0.24	12.4	0.02	0.28	30.4	19	10	17	32	22
Profile 2	Ap	0-60	6.67	5.34	36.8	180	12.1	0.44	4.86	0.09	0.09	18.3	4	2	27	35	32
	Btg	60-110	5.88	2.36	19.7	174	11.9	0.46	8.12	0.06	0.16	21.2	3	2	27	27	41
	Cg	110-160	6.23	4.10	15.7	112	10.1	0.31	10.4	0.03	0.35	21.6	2	3	29	30	36
	Cg2	>160	7.20	3.15	21.7	79.1	8.12	0.20	6.35	0.03	0.43	16.0	6	5	27	33	29

Table 2. Total trace metal concentrations of soil profiles

Horizon		Depth	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	S	V	Zn
		cm	g kg^{-1}		mg kg^{-1}			g kg^{-1}		mg kg^{-1}						
Profile 1	Ap	0-50	45.9	4.21	21.9	59.3	39.2	42.4	5.65	628	29.6	412	20.7	141	104	71.2
	Btg	50-90	54.5	5.17	45.0	68.4	43.2	49.4	6.22	608	34.5	252	24.8	111	126	75.0
	Ctg	90-130	68.0	8.60	50.4	97.8	62.9	66.0	9.47	783	57.1	125	23.0	87.2	155	99.2
	Cg	130-160	53.5	9.27	41.3	84.8	64.4	72.3	8.43	1334	82.0	163	27.6	67.9	150	106
	2Cg	>160	45.4	12.1	31.0	103	54.6	53.3	8.77	1261	72.9	136	19.2	38.0	135	93.4
Profile 2	Ap	0-60	52.1	3.15	17.6	56.7	70.6	39.8	5.59	409	25.4	389	21.7	134	98.7	67.0
	Btg	60-110	58.7	2.70	14.8	60.6	55.1	42.8	6.04	281	26.3	297	23.0	126	99.2	62.4
	Cg	110-160	46.6	2.13	11.4	51.4	29.0	40.1	6.62	201	27.3	208	20.8	72.0	79.3	60.0
	Cg2	>160	40.7	2.20	35.9	39.1	18.4	32.5	4.17	544	30.3	196	20.9	45.4	85.0	47.4

the surface soil layer sank to that depth. However, this phenomenon should be further pedologically investigated, since one of the reasons for its occurrence may be lithological discontinuity that caused covering up of fossil soil, as indicated by the proportion of rough sand higher than in upper horizons. Table 1 shows that the content of plant available nutrients, like e.g. phosphorus and potassium, is relatively uniform along the whole profile depth. Cation exchange capacity is related to clay content, being expectedly higher in horizons with higher clay contents. The highest clay content was recorded in the Btg horizon, in which clay leached from the overlying Ap horizon is accumulated.

Topsoil and subsoil layers

Average pH value in topsoil is 6.08, ranging from 5.57 to 7.55. In subsoil, pH values are similar to those in topsoil. Mean value is 5.87 and all results are within the range from 5.33 to 7.53.

Average organic matter content in topsoil is 2.21%, ranging from 0.52 to 6.43%. There is slightly less OM in subsoil, its values ranging from 0.57 to 4.83%, with an average of 1.62%.

Average electrolytic conductivity in topsoil is 61.5 µS cm^{-1}, with the lowest value of 26.5 and the highest of 215 µS cm^{-1}. In subsoil, the mean electrical conductivity amounts to 54.7 µS cm^{-1}, its values ranging from 33.6 to 181 µS cm^{-1}.

Average content of plant available phosphorus in topsoil is 60.4 mg kg^{-1}, the lowest 11.0 mg kg^{-1} and the highest 463 mg kg^{-1}. Average content of plant available potassium (K_2O) is 224 mg kg^{-1} soil, ranging from 114 to 870 mg kg^{-1} soil. As expected, the values for nutrients are lower in subsoil. Thus, the average content of plant available phosphorus is 49 mg kg^{-1}, and that of potassium 149 mg kg^{-1} soil.

Interpolations

Average chromium content in topsoil is 51.9 mg kg^{-1}, with the highest value of 77.0 mg kg^{-1}, and the lowest of 43.1 mg kg^{-1}. In subsoil, the average chromium content is 52.6 mg kg^{-1} ranging from 41.7 mg kg^{-1} to 79.2 mg kg^{-1}. No chromium concentrations exceeded the threshold value according to the legal regulations of the Republic of Croatia (Narodne Novine 32/10). These values do not exceed the median for central Croatia, but are slightly higher than the median values for Zagreb County (Table 3). Cr content in soils worldwide differs greatly, ranging from 7 to 2221 mg kg^{-1} (McBride, 1994) that depends mostly on the parent material and soil mineralogy. Reinman et al. (2003) reported Cr baseline of 12 mg kg^{-1} in agricultural soils in Northern Europe, and Fay and Zhang (2007) reported 42.6 mg kg^{-1} of Cr as a median for Irish soils, but Cr levels below 35 mg kg^{-1} being mostly associated with areas with underlying limestone geology. Levels of Cr higher of 50 mg kg^{-1} are mainly attributed to soils developed on igneous rocks. Most sedimentary rocks show substantially lower Cr-concentrations than mafic and ultramafic rocks (Wedepohl, 1995). The distribution pattern of soil Cr in the study area shown in the Figure 3 coincides with the spatial distribution of soil Fe and to a certain degree with Ni.

Average copper content in topsoil amounts to 51,1 mg kg^{-1}, and to 47.4 mg kg^{-1} in subsoil. There is a very wide range of copper concentrations, from 19.1 to 133 mg kg^{-1} for subsoil, and from 21.1 to 95.5 mg kg^{-1} Cu for topsoil. Topsoil samples have a somewhat higher median value compared to the median value for subsoil copper, but they do not exceed the threshold value of 120 mg kg^{-1} according to the Rulebook (Narodne Novine 32/10). Copper concentration higher than allowable was found in only one sample. The median value for copper in comparison with the median for central Croatia and the soils of Zagreb County is almost three times higher for topsoil samples and twice higher than the median value for subsoil. Such high copper concentrations in topsoil result from the yearlong grapevine protection with copper based agents, high copper reactivity and hence its aggravated leaching into deeper soil layers (Romić et al., 2004a). Application of copper salts as fungicides against mildew of grape vine over decades has resulted in considerable build-up of total Cu concentrations in the topsoils worldwide (Komárek et al., 2010). The distribution pattern of soil Cu in the study area shown in the Figure 3 is likely to be the after effect of the levelling of teraces.

Average lead content in topsoil amounts to 22.0 mg kg^{-1}, and to 22.3 mg kg^{-1} in subsoil. The highest lead content in topsoil was 40.7 mg kg^{-1}, the lowest 15.7 mg kg^{-1}. A similar range from the highest concentration of 44.8 mg kg^{-1} to the lowest of 15.5 mg kg^{-1} lead was recorded also in subsoil. No pollution was detected in the studied area, namely, all samples comply with the postulations of the Rulebook (Narodne Novine 32/10). Median values for lead concentrations are slightly higher compared to the median for Zagreb County, but are lower than the median for central Croatia.

Average zinc content in topsoil is 70.5 mg kg^{-1}, and that in subsoil is 68.3 mg kg^{-1}. The lowest zinc content determined in topsoil was 54.5 mg kg^{-1}, while the highest was 113 mg kg^{-1}. In topsoil, the lowest zinc content was 54.0 mg kg^{-1} and the highest 98.1 mg kg^{-1}. Not a single site in the studied area is loaded with zinc in concentrations higher than those allowed by the Rulebook.

Average nickel content in topsoil of the experimental station Jazbina is 26.2 mg kg^{-1}, and that in subsoil is 26.6 mg kg^{-1}. Nickel concentration in topsoil ranges from 21.7 mg kg^{-1} to 36.7 mg kg^{-1}, and from 21.5 mg kg^{-1} to 34.6 mg kg^{-1} in subsoil. According to the current Croatian regulation the allowable limit for nickel in the soil depends on many factors, and for agricultural soils is set as 50 mg kg^{-1} d.w. This metal apparently does not seem to be a major concern outside urban areas (Romic and Romic, 2003). Nickel may present a problem in agricultural land receiving wastes such as sewage sludge. It can be deposited in the sediment by such processes as precipitation, complexation and adsorption on clay particles and via uptake by biota. No sample from either topsoil or subsoil contained more nickel than allowed by the Rulebook. Median nickel values for topsoil and subsoil are lower than the median for the Zagreb County soils and the median for central Croatia (Table 3).

Average cobalt content at the experimental station Jazbina is 18.1 mg kg^{-1} for both topsoil and subsoil. Soil cobalt concentrations range from 14.2 mg kg^{-1} to 26.0 mg kg^{-1} for topsoil and from 14.3 to 25.4 mg kg^{-1} for subsoil. These median values for cobalt are higher than the medians for the soils of central Croatia (11 mg kg^{-1}) and agricultural soils of Zagreb County.

Mn concentrations vary widely in soils in the study area and the Mn-map are rather noisy and locally enhanced levels of Mn are evident (Figure 3). The Mn concentrations range from 278 mg kg^{-1} to 1099 mg kg^{-1}, with the median value of 628 mg kg^{-1}. The last value is higher than the median for the Central Croatia of 550 mg kg^{-1} (Table 3). The biogeochemistry of Mn in soils is very complex and oxidation-reduction reactions involving Mn are influenced by a variety of physical, chemical, and microbiological processes (Bradl, 2004). The study of the distribution pattern of Fe-Mn oxides in the nodules may provide interesting information about the redox history of the pedoenvironment and the fate of some heavy metals in soil (Liu et al., 2002).

Correlation analysis

Correlation analysis is a bivariate technique for the measurement of the degree of association between two variables. The values of correlation coefficients are useful for making hypotheses on the sources or on the chemical and environmental behaviour of elements. Soil properties are often inter-correlated, especially soil matrix characteristics. Table 5 is the correlation matrix, listing Pearson's product moment correlation coefficients of studied soil properties and trace metal contents in topsoil, and Table 6 shows the same parameters for subsoil. Soil pH and organic matter content were significantly correlated in both topsoil and subsoil. In general, the environmental geochemical phenomena, including trace metal content, are correlated due to physicochemical features of elements and geochemical processes (Zang and Selinus, 1998). In topsoil, a strong correlation was observed between the pairs of soil constitutive elements Ni-Co, Ni-Cr, Ni-V, V-Co, V-Cr, Al-Co, Al-Cr, Al-Ni, Al-Fe, Fe-Co, Fe-Cr, Fe-Ni and Fe-V. In topsoil, Pb does not show any significant correlation with other elements, with the exception of a weak correlation with Mo (Table 5). Manganese also shows a weak correlation with Zn, and a weak negative correlation with Al and Fe. No significant correlation at all was observed between copper and other elements, neither between Mg and other elements in topsoil, and only a weak correlation with lead in subsoil (Table 6). There are high correlation coefficients for the contents of P-S, P-Zn, P-Ca, S-Zn and S-Ca in topsoil.

Factor analysis (FA)

Factor analysis (FA) is a multivariate technique aimed at finding common factors explaining experimental results. It has been widely used in soil contamination assessment to identify sources, in characterization of chemical behaviour of available elements and to evaluate an experimental procedure (Romic and Romic, 2003; Abollino et al., 2011). Considering the influence they exerted on the distribution of trace metals at the investigated vine-growing station, the multi-element factors were divided into two groups: (1) factors caused mainly by geogenic processes, and (2) factors caused by specific, yearlong agricultural practice. In topsoil, the matrix of components for a series of data on soil properties and element contents displays grouping of pH, EC, OM, available P_2O_5, available K_2O, Zn, Ca, P, S in factor 1. Factor 2 groups elements Co, Cr, Ni, V, Al, Fe and clay content (Table 8). In subsoil, elements Cr, Ni, V, Al, Fe and clay content are grouped in F1, while F2 comprises pH, EC, OM, P_2O_5, Zn, Ca, P and S (Table 10). However, as expected, the dominant influence of these factors differs in topsoil and subsoil. In topsoil, factor 1 groups the soil properties that were greatly determined by yearlong cultivation, whereas factor 2 includes elements of predominantly geogenic origin. In subsoil, factor 1 groups elements of predominantly geogenic origin, while factor 2 indicates

Table 3. Descriptive statistics of soil properties and total trace metal concentrations (topsoil samples, n = 25)

Variable	Symbol	Unit	Mean	Median	SD[a]	Min.[b]	Max.[c]	Skewness	Kurtosis	Threshold value[d]	Central Croatia[e]	Zagreb region
pH	pH		6.08	5.90	0.522	5.57	7.55	1.55	1.97			
Electrical conductivity	EC_e	μS cm^{-1}	61.5	47.7	39.3	26.5	215	2.90	9.66			
Organic matter	OM	%	2.21	2.03	1.11	0.52	6.43	2.33	8.53			
Available phosphorus	P_2O_5	mg kg^{-1}	60.4	28.3	94.5	11.0	463	358	144			
Available potassium	K_2O	mg kg^{-1}	224	170	150	114	870	36.5	153			
Aluminium	Al	g kg^{-1}	45.3	43.5	5.22	37.4	56.7	0.956	-0.015		66	
Calcium	Ca	g kg^{-1}	3.16	2.58	1.69	1.77	8.70	2.31	5.06		5.2	5.20
Cobalt	Co	mg kg^{-1}	18.1	17.5	3.02	14.2	26.0	1.10	1.01		11	10.8
Chromium	Cr	mg kg^{-1}	51.9	50.1	7.60	43.1	77.0	2.12	4.80	120	74	51.2
Copper	Cu	mg kg^{-1}	51.1	51.7	19.9	21.1	95.5	0.255	-0.840	120	19	23.5
Iron	Fe	g kg^{-1}	36.5	34.9	5.96	28.5	55.2	1.78	3.57		30	28.9
Magnesium	Mg	g kg^{-1}	5.78	5.79	0.664	4.75	7.02	0.169	-1.05		6.7	6.51
Manganese	Mn	mg kg^{-1}	669	628	224	278	1099	0.405	-0.274		550	556
Molybdenum	Mo	mg kg^{-1}	0.290	0.200	0.191	0.200	0.870	2.08	3.63			
Nickel	Ni	mg kg^{-1}	26.2	25.0	3.61	21.7	36.7	2.02	3.95	75	33	29.7
Phosphorus	P	mg kg^{-1}	502	407	385	187	2212	3.90	17.4			
Lead	Pb	mg kg^{-1}	22.0	21.12	5.65	15.7	40.7	2.14	5.36	150	27	19.6
Sulfur	S	mg kg^{-1}	167	149	103	72.3	621	3.94	17.4			
Vanadium	V	mg kg^{-1}	90.7	86.3	12.8	77.1	127	1.94	3.34		96	
Zinc	Zn	mg kg^{-1}	70.5	69.3	11.2	54.5	113	2.29	8.15	200	73	70.7

SD standard deviation; Min minimum value; Max maximum value; [a] Maximal permitted concentrations as defined by Narodne Novine 32/10 (mg kg^{-1}); [b] Median after Halamic and Miko (2009); [c] Median, after Sollitto et al. (2010)

Table 4. Descriptive statistics of soil properties and total trace metal concentrations (subsoil samples, n = 25)

Variable	Symbol	Unit	Mean	Median	SD[a]	Min.[b]	Max.[c]	Skewness	Kurtosis
pH	pH		5.87	5.69	0.483	5.33	7.53	1.96	4.82
Electrical conductivity	EC_e	μS cm^{-1}	54.7	45.7	28.7	33.6	181	3.83	16.7
Organic matter	OM	%	1.62	1.38	1.03	0.57	4.83	2.16	4.88
Available phosphorus	P_2O_5	mg kg^{-1}	49.0	20.8	88.7	9.5	439	39.4	168
Available potassium	K_2O	mg kg^{-1}	149	116	107	36.7	628	39.6	180
Aluminium	Al	g kg^{-1}	46.6	45.6	6.65	36.0	59.4	0.250	-0.802
Calcium	Ca	g kg^{-1}	2.84	2.31	1.21	1.92	6.63	1.93	3.37
Cobalt	Co	mg kg^{-1}	18.1	17.0	3.02	14.3	25.4	0.930	0.213
Chromium	Cr	mg kg^{-1}	52.6	51.2	7.96	41.7	79.2	1.74	4.30
Copper	Cu	mg kg^{-1}	47.4	38.6	26.1	19.1	133	1.72	3.63
Iron	Fe	g kg^{-1}	37.4	37.1	5.27	28.0	51.5	0.805	1.13
Magnesium	Mg	g kg^{-1}	5.91	5.72	0.880	4.60	7.89	0.686	-0.120
Manganese	Mn	mg kg^{-1}	660	614	252	219	1125	0.233	-0.816
Molybdenum	Mo	mg kg^{-1}	0.260	0.200	0.155	0.200	0.820	2.66	6.92
Nickel	Ni	mg kg^{-1}	26.6	25.7	3.21	21.5	34.6	1.07	0.978
Phosphorus	P	mg kg^{-1}	426	374	293	175	1654	3.32	13.4
Lead	Pb	mg kg^{-1}	22.3	20.2	6.84	15.5	44.8	2.04	4.32
Sulfur	S	mg kg^{-1}	138	129	68.5	75.6	445	3.99	18.3
Vanadium	V	mg kg^{-1}	91.1	88.7	12.2	74.4	128	1.38	2.63
Zinc	Zn	mg kg^{-1}	68.3	67.6	8.95	54.0	98.1	1.44	4.01

SD standard deviation; Min minimum value; Max maximum value

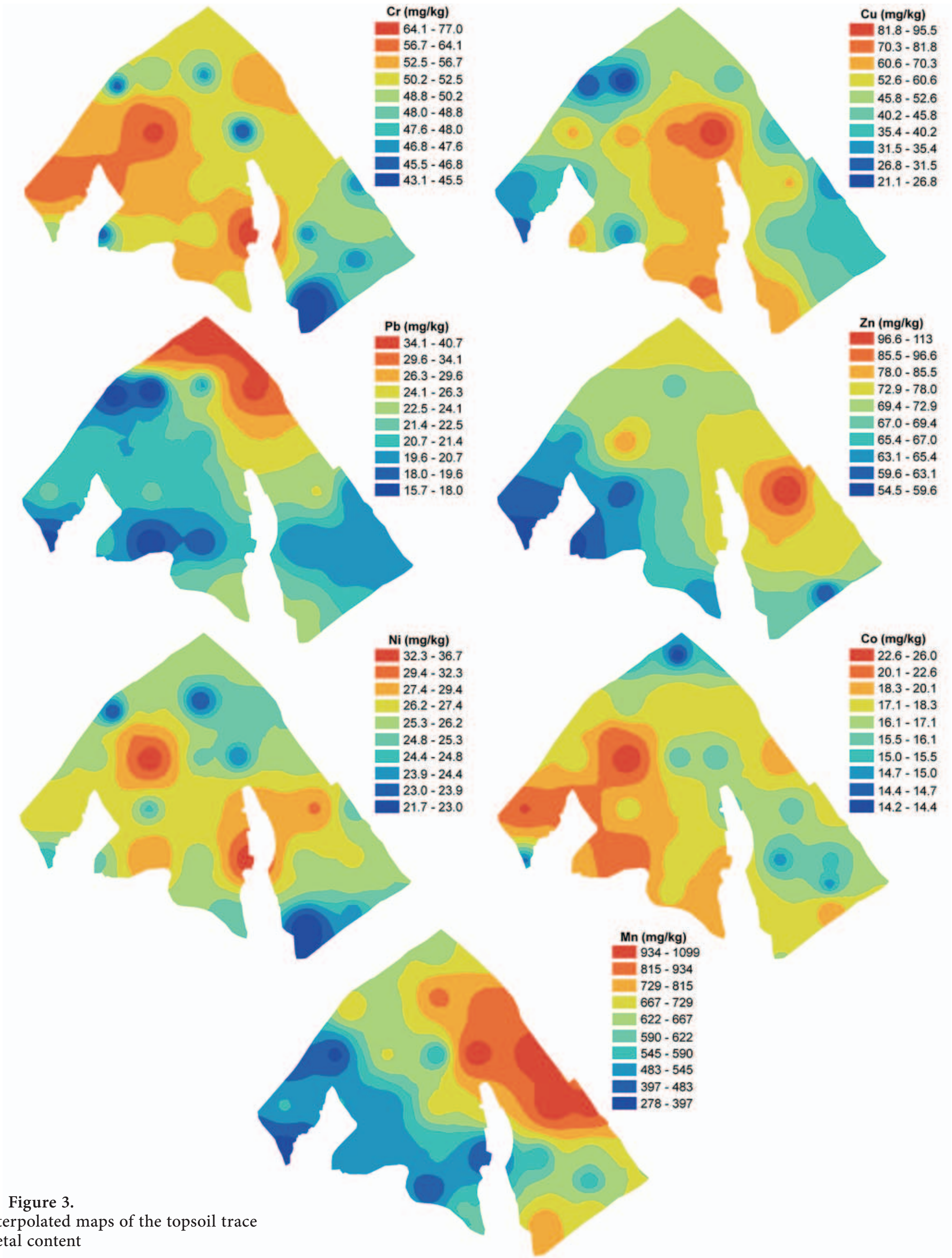


Figure 3.
Interpolated maps of the topsoil trace metal content

Table 5. Correlation matrix between trace metal total concentrations and soil properties (topsoil samples, n = 25)

	pH	OM	Co	Cr	Cu	Mo	Ni	Pb	V	Zn	Al	Ca	Fe	Mg	Mn	P	S	Sand	Silt	Clay
pH	1																			
OM	0.67**	1																		
Co	0.16$^{n.s}$	-0.20$^{n.s}$	1																	
Cr	0.23$^{n.s}$	-0.04$^{n.s}$	0.50*	1																
Cu	0.45*	0.47*	-0.01$^{n.s}$	0.10$^{n.s}$	1															
Mo	0.08$^{n.s}$	-0.12$^{n.s}$	0.00$^{n.s}$	0.38$^{n.s}$	0.06$^{n.s}$	1														
Ni	0.33$^{n.s}$	0.10$^{n.s}$	0.52**	0.83**	0.08$^{n.s}$	0.06$^{n.s}$	1													
Pb	0.16$^{n.s}$	0.29$^{n.s}$	-0.15	0.09$^{n.s}$	0.25$^{n.s}$	0.48*	-0.08$^{n.s}$	1												
V	0.22$^{n.s}$	-0.10$^{n.s}$	0.63**	0.98**	0.10$^{n.s}$	0.37$^{n.s}$	0.80**	0.08$^{n.s}$	1											
Zn	0.55**	0.74*	-0.14	0.17$^{n.s}$	0.18$^{n.s}$	-0.09$^{n.s}$	0.44*	0.23$^{n.s}$	0.10$^{n.s}$	1										
Al	0.02$^{n.s}$	0.23$^{n.s}$	0.50**	0.81**	-0.10$^{n.s}$	0.57**	0.60**	0.14$^{n.s}$	0.80**	-0.6$^{n.s}$	1									
Ca	0.76**	0.70**	0.26$^{n.s}$	0.55**	0.30$^{n.s}$	0.04$^{n.s}$	0.71**	0.11$^{n.s}$	0.50*	0.76**	0.27$^{n.s}$	1								
Fe	0.14$^{n.s}$	-0.23$^{n.s}$	0.62**	0.96**	0.50$^{n.s}$	0.40$^{n.s}$	0.79**	-0.02$^{n.s}$	0.97**	-0.2$^{n.s}$	0.84**	0.41*	1							
Mg	0.09$^{n.s}$	-0.04$^{n.s}$	-0.08$^{n.s}$	0.03$^{n.s}$	-0.22$^{n.s}$	-0.20$^{n.s}$	0.34$^{n.s}$	-0.20$^{n.s}$	-0.3$^{n.s}$	0.33$^{n.s}$	-0.06$^{n.s}$	0.09$^{n.s}$	0.00$^{n.s}$	1						
Mn	0.29$^{n.s}$	0.41*	-0.05$^{n.s}$	-0.33$^{n.s}$	0.10$^{n.s}$	-0.17$^{n.s}$	-0.24$^{n.s}$	0.30$^{n.s}$	-0.28$^{n.s}$	0.47*	-0.42*	0.17$^{n.s}$	-0.45*	-0.07$^{n.s}$	1					
P	0.57**	0.85**	-0.19$^{n.s}$	-0.03$^{n.s}$	0.19$^{n.s}$	-0.13$^{n.s}$	0.23$^{n.s}$	0.26$^{n.s}$	-0.09$^{n.s}$	0.90**	-0.18$^{n.s}$	0.72**	-0.22$^{n.s}$	0.09$^{n.s}$	0.54**	1				
S	0.67**	0.9**	-0.08$^{n.s}$	0.03$^{n.s}$	0.29$^{n.s}$	-0.12$^{n.s}$	0.27$^{n.s}$	0.22$^{n.s}$	0.00$^{n.s}$	0.85**	-0.12$^{n.s}$	0.80**	-0.14$^{n.s}$	-0.00$^{n.s}$	0.47*	0.96**	1			
Sand	0.52**	0.30$^{n.s}$	0.34$^{n.s}$	0.58**	0.33$^{n.s}$	0.00$^{n.s}$	0.65**	-0.04$^{n.s}$	0.57**	0.30$^{n.s}$	0.22$^{n.s}$	0.74**	0.55**	-0.22$^{n.s}$	-0.11$^{n.s}$	0.29$^{n.s}$	0.38$^{n.s}$	1		
Silt	-0.25$^{n.s}$	0.12$^{n.s}$	-0.52**	-0.81**	-0.13$^{n.s}$	-0.40$^{n.s}$	-0.63**	0.03$^{n.s}$	-0.81**	0.17$^{n.s}$	-0.76**	-0.42*	-0.87**	0.24$^{n.s}$	0.52**	0.20$^{n.s}$	0.08$^{n.s}$	-0.67**	1	
Clay	-0.19$^{n.s}$	-0.47*	0.35$^{n.s}$	0.49*	-0.16	0.52**	0.18ns	-0.00ns	0.50*	-0.52**	0.79**	-0.19ns	0.60**	-0.10ns	-0.59**	-0.55**	-0.49*	-0.13ns	-0.65**	1

OM - organic matter; *$p \le 0.05$; **$p < 0.01$

Table 6. Correlation matrix between trace metal total concentrations and soil properties (subsoil samples, n = 25)

	pH	OM	Co	Cr	Cu	Mo	Ni	Pb	V	Zn	Al	Ca	Fe	Mg	Mn	P	S	Sand	Silt	Clay
pH	1																			
OM	0.65**	1																		
Co	0.14$^{n.s}$	0.11$^{n.s}$	1																	
Cr	0.01$^{n.s}$	-0.06$^{n.s}$	0.08$^{n.s}$	1																
Cu	0.25$^{n.s}$	0.40*	0.03$^{n.s}$	0.10$^{n.s}$	1															
Mo	-0.23$^{n.s}$	-0.30$^{n.s}$	0.26$^{n.s}$	0.22$^{n.s}$	-0.26$^{n.s}$	1														
Ni	0.06$^{n.s}$	0.17$^{n.s}$	0.19n.s	0.69**	-0.04$^{n.s}$	0.05$^{n.s}$	1													
Pb	0.25$^{n.s}$	0.25$^{n.s}$	0.02n$^{n.s}$	-0.15$^{n.s}$	0.41*	-0.14$^{n.s}$	-0.24$^{n.s}$	1												
V	0.00$^{n.s}$	-0.07$^{n.s}$	0.17$^{n.s}$	0.98**	0.13n.s	0.23$^{n.s}$	0.63**	-0.17$^{n.s}$	1											
Zn	0.47*	0.64**	-0.22$^{n.s}$	-0.10$^{n.s}$	0.17$^{n.s}$	-0.35$^{n.s}$	0.35$^{n.s}$	0.29$^{n.s}$	-0.20$^{n.s}$	1										
Al	-0.14$^{n.s}$	-0.33$^{n.s}$	0.11$^{n.s}$	0.87**	-0.04$^{n.s}$	0.42*	0.52**	-0.23$^{n.s}$	0.88**	-0.37$^{n.s}$	1									
Ca	0.72**	072**	0.11$^{n.s}$	0.40*	0.32$^{n.s}$	0.00$^{n.s}$	0.42*	0.17$^{n.s}$	0.35$^{n.s}$	0.57**	0.10$^{n.s}$	1								
Fe	-0.11$^{n.s}$	-0.20$^{n.s}$	0.16$^{n.s}$	0.95**	-0.04$^{n.s}$	0.33$^{n.s}$	0.64**	-0.16$^{n.s}$	0.94**	-0.21$^{n.s}$	0.90**	0.25$^{n.s}$	1							
Mg	-0.13$^{n.s}$	-0.02$^{n.s}$	-0.15$^{n.s}$	0.02$^{n.s}$	-0.28$^{n.s}$	-0.16$^{n.s}$	0.51**	-0.22$^{n.s}$	-0.08$^{n.s}$	0.46*	0.04$^{n.s}$	-0.13$^{n.s}$	0.01$^{n.s}$	1						
Mn	0.34$^{n.s}$	0.35$^{n.s}$	0.22$^{n.s}$	-0.58**	0.16$^{n.s}$	-0.18$^{n.s}$	-0.42*	0.46*	-0.55**	0.34$^{n.s}$	-0.70**	0.12ns	-0.63**	-0.15$^{n.s}$	1					
P	0.59**	0.72**	-0.21$^{n.s}$	-0.31$^{n.s}$	0.25$^{n.s}$	-0.30$^{n.s}$	-0.3$^{n.s}$	0.42*	-0.38$^{n.s}$	0.83**	-0.53**	0.62**	-0.42*	0.02$^{n.s}$	0.51**	1				
S	0.60**	0.80**	-0.14$^{n.s}$	-0.30$^{n.s}$	0.25$^{n.s}$	-0.26$^{n.s}$	-0.06$^{n.s}$	0.27$^{n.s}$	-0.35$^{n.s}$	0.74**	-0.47*	0.65**	-0.40*	-0.06$^{n.s}$	0.43*	0.93**	1			
Sand	0.27$^{n.s}$	0.27$^{n.s}$	0.00$^{n.s}$	0.62**	0.29$^{n.s}$	-0.10$^{n.s}$	0.38$^{n.s}$	-0.07$^{n.s}$	0.62**	-0.07$^{n.s}$	0.37ns	0.55**	0.46*	-0.38$^{n.s}$	-0.28$^{n.s}$	0.00$^{n.s}$	0.04$^{n.s}$	1		
Silt	-0.01$^{n.s}$	0.02$^{n.s}$	-0.13$^{n.s}$	-0.86**	-0.12$^{n.s}$	-0.29$^{n.s}$	-0.54**	0.24$^{n.s}$	-0.87**	0.32$^{n.s}$	-0.84**	-0.35$^{n.s}$	-0.85**	0.30$^{n.s}$	0.64**	0.35$^{n.s}$	0.26$^{n.s}$	-0.73**	1	
Clay	-0.21$^{n.s}$	-0.27$^{n.s}$	0.18$^{n.s}$	0.70**	-0.08$^{n.s}$	0.50*	0.44*	-0.28$^{n.s}$	0.71**	-0.40*	0.88**	0.03$^{n.s}$	0.81**	-0.10$^{n.s}$	-0.67**	-0.51*	-0.40*	0.18$^{n.s}$	0.80**	1

OM - organic matter; *$p \le 0.05$; **$p < 0.01$

Table 7. Eigenvalues of factors for soil properties and trace metal concentrations in soils (topsoil samples, n = 25)

Factor	Eigenvalue	% total variance	Cumulative Eigenvalue	Cumulative (%)
Total variance explained				
1	7.99	34.75	7.99	34.75
2	6.96	30.25	14.95	65.00
3	2.14	9.29	17.09	74.29
4	1.59	6.90	18.67	81.19
5	1.09	4.74	19.76	85.93

Table 8. Total variance explained and component matrix of applied FA for soil properties and trace metal concentrations in soils (subsoil samples, n = 25)

Parameter	Component matrix	
	PC1	PC2
Component matrix		
pH	0.78	0.28
EC$_e$	0.85	0.19
OM	0.83	-0.11
P$_2$O$_5$	0.84	-0.14
K$_2$O	0.81	-0.32
Co	-0.09	0.61
Cr	0.08	0.95
Cu	0.51	0.15
Mo	-0.06	0.49
Ni	0.26	0.78
Pb	0.44	0.06
V	0.04	0.95
Zn	0.83	0.02
Al	-0.21	0.87
Ca	0.74	0.57
Fe	-0.14	0.97
Mg	0.04	-0.04
Mn	0.54	-0.45
P	0.93	-0.19
S	0.95	-0.05
sand	0.48	0.48
silt	0.08	-0.93
clay	-0.62	0.61
Explained variance	7.90	7.06
Proportion of total variance	0.34	0.31

Table 9. Eigenvalues of factors for soil properties and trace metal concentrations in soils (subsoil samples, n = 25)

Factor	Eigenvalue	% total variance	Cumulative Eigenvalue	Cumulative (%)
Total variance explained				
1	9.04	39.31	9.04	39.31
2	4.99	21.70	14.00	61.00
3	2.39	10.39	16.42	71.40
4	1.54	6.71	17.96	78.11
5	1.14	4.95	19.10	83.05

Table 10. Factor loadings for soil properties and trace metal concentrations in soils (subsoil samples, n = 25)

Parameter	Rotated component matrix	
	PC1	PC2
Component matrix		
pH	0.07	0.79
EC$_e$	0.03	0.70
OM	-0.15	0.86
P$_2$O$_5$	-0.36	0.76
K$_2$O	-0.63	0.54
Co	0.13	0.04
Cr	0.97	0.00
Cu	0.15	0.54
Mo	0.23	-0.39
Ni	0.66	0.18
Pb	-0.19	0.51
V	0.96	-0.05
Zn	-0.20	0.72
Al	0.90	-0.28
Ca	0.42	0.81
Fe	0.93	-0.15
Mg	-0.09	-0.04
Mn	-0.67	0.42
P	-0.45	0.83
S	-0.40	0.83
sand	0.52	0.37
silt	-0.95	0.02
clay	0.80	-0.32
Explained variance	7.49	6.54
Proportion of total variance	0.33	0.28

the existing, but less expressed influence of anthropogenization upon the grouping of soil properties and elements.

In topsoil, the two separated factors explain 65% of total variance (Table 7) while in subsoil, the two main factors amount to 61% of total variance (Table 9) for factors >0.6.

Discussion

Spatial variability and distribution of heavy metals, as well as their mobility and availability in soils is to a large extent determined by topography. Rather weak inter-correlations of trace metals in soils are certainly caused by soil movement within the site, changes in soil profile characteristics induced by intensive cultivation and improvement measures applied in the recent history of the vine-growing site. Liming is known as an agricultural measure that greatly affects soil chemistry, improves microbial activity and soil physical condition. Many of soil properties are highly dependent on pH and calcium carbonate levels, including bioavailability of toxic elements.

When the natural process of sedimentation and pedogenesis are changed under anthropogenic influence, the proportions of elements are likely to change due to altered environmental conditions. The presence of certain elements, e.g. Cr or Mn, may be partially ascribed to sediment deposition by torrents.

Active clay surface and Fe and Al hydroxides as well as negatively charged surfaces of organic matter greatly increase retention of metals in soil. Under oxidized conditions of fluvial sediments, Fe/Mn hydroxides are the main carriers of Zn and Ni. The presence of Ni, Co, Cr, Zn cannot be directly associated with any of the existing lithological units. The presence of these elements results from intensive mixing of the different lithological units in sediment material brought with watercourses.

The soil property with the strongest influence on metal sorption particularly that of copper, is the organic matter content. Copper adsorption to organic matter restricts its bioavailability and also greatly reduces the risk of phytotoxicity and vertical migration. Accumulation of copper in soil is a consequence of permanent plant protection against fungal diseases with copper based agents. High copper concentrations are frequent in the vineyard soils. The Bordeaux mixture is an efficient fungicide for prevention of grapevine fungal diseases and has been routinely used in Croatia since the end of the 19th century. Its concentrations and the number of treatments depend on weather conditions, severity of infection and vineyard location. Increased concentrations of Cu and Zn in soils under long-term production of grapevine, citrus or other fruit crops have been recorded in numerous studies (Romić et al., 2004a). Romić et al. (2004b) applied multiple linear regression analysis to establish the relation between copper fractions after particular single extractions (aqua regia, DTPA and $CaCl_2$) and soil properties that may affect their behaviour in soil and availability to plants. Most of the colloidal particles in soil strongly adsorb 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 (Romic, 2012b).

Phosphate and micronutrient fertilizers contain potentially harmful trace elements, such as arsenic (As), cadmium (Cd), and lead (Pb). Chen et al. (2008) observed significant correlations between Cd and Pb and soil phosphorus in Californian vegetable croplands, indicating that the application of P-fertilizers contributes significantly to the accumulation of Cd and Pb in soils. Romic et al. (2012b) pointed out that the application of P-fertilizers contributes significantly to the accumulation of Cd in horticultural soils of fluvial terraces in the Croatian coastal region and by diffuse sources such as atmospheric deposition and irrigation in the urban areas (Romic and Romic, 2003).

Obviously, soil Zn concentrations observed in the study area didn't reveal the potential role of agricultural practices and application of agrochemicals in Zn build-up in the soils. Studying trace metals distribution in cropland of alluvial plain of the Sava River (NW Croatia), Sollitto et al. (2010), by applying multivariate geostatistics, explained that large-scale variability of Zn concentrations exists not only by the lithological composition of the subsoil, but also due to geomorphological processes acting at a catchment scale, such as soil degradation and erosion, transportation and accumulation of the residual products.

Thus, the impact of trace metals on soil and the surrounding environment in most cases cannot be predicted simply by measuring their total concentration. This is because only soluble and mobile fractions have the potential to leach or to be taken up by plants, and enter the food chain. Metal speciation is one of the most important properties that determine the behaviour and toxicity of metals in the environment.

Conclusions

Grapevine can be successfully grown under different *terroir* conditions. Naturally, the vineyard maintenance technologies differ in dependence on the environmental conditions, with the aim to produce good quality grapes for wine production. Therefore the main principle of nutrient management is their precisely calculated and time synchronized application that can be achieved by regular analyses of the nutrient status in soils at adequately equipped laboratories. An understanding of soil status is essential for the selection of growing practices and improving the quality of grapes, in which the spatial information system is of great help. GIS application can be targeted at specific features of a vineyard site. The purpose of using GIS technology is to provide an information model that can be used by wine-growers and scientists to study the inter-relations between the site characteristics, soil, climate, cultivars grown and viticultural practice determining grape and wine quality. Modern GIS technology facilitates manipulation and analysis of a large number of data associated with a site, and can be also used to produce spatial distribution maps.

When such a data survey is at our disposal, we can adopt zonal vineyard management, in which instead of uniform management over the whole site, a specific method of vineyard maintenance can be applied in each particular zone of characteristic features. For this reason, these investigations should be continued by including plant material testing, grape and must analyses, which would contribute to the characterization of wines produced at the given site.

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