Geochemistry of Vrbničko Polje (Croatia) winegrowing site
Géochimie du terroir viticole dans la région de Vrbničko Polje (Croatie)

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Summary

A multi-element pedo-geochemical survey was carried out in Vrbničko polje vineyards on the Krk Island, Croatia. This Mediterranean winegrowing site is famous by Žlahtina wine production. The objectives of this study are (i) to describe characteristics of the site related to climate, topography, geology, soil and geochemistry and (ii) to integrate data on soil quality using GIS which can be applied with management information systems Two soil profiles were excavated and examined, and dominant soil type was determined, as well as physical and chemical characteristics of soil. Topsoil (0-30 cm) and subsoil (30-60 cm) samples were collected from 26 locations inside the site. Total metal contents (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, S, V, Zn) were determined using ICP-OES after aqua regia extraction. A geospatial database was compiled in GIS, and after applying statistics and geostatistisc, the maps of trace metals distribution have been produced. Accumulation of copper in soil, determined in this research, is the most common effect of continuing fertilization and protection against diseases and pests in vineyards. High nickel and chromium concentrations seem to be of the geogenic origin. Associations of heavy metals with the selected soil properties explain the preferential feature of metal retention in soil.

Keywords: anthropogenic vineyard soil, geochemical characterization, GIS, trace metals, parent material, spatial distribution

Introduction

Vrbničko polje is elongated depression near the city of Vrbnik on the Krk Island in the Kvarner Archipelago, the largest island of the Adriatic Sea (Croatia). The term “polje” refers to unique landform feature as large closed karstic depressions of the Adriatic Coast. Most polje floors are arable land, drainage by water flow and thereby regularly flooded. As an extraordinary element in the karst landscape these phenomena are worth of studying from many points of view: hydrogeological, pedological, geochemical. What’s more, many of these karst fields are vinegrowing sites, like Vrbničko polje region famous on growing vine and produce wine Žlahtina, from a unique white grape variety indigenous to this particular site. Nowadays, a spatial concern is dedicated to preserve autochthonous grapevine cultivars, producing wines that reflect the characteristics of the specific site environment. Scientific quantification of the terroir elements that contribute to the quality of autochthonous wines is required to establish legislative framework that would regulate this area as well as and for establishing of a flexible information system that would be used by all participants in the complex system of grape and wine production and consumption. As a part of a national geochemical survey of agricultural soils, the assessing of the soils quality for grapevine cultivation of Vrbničko polje was done. The main goals of the study were (i) to describe characteristics of the site related to climate, topography, geology, soil and geochemistry and (ii) to integrate data on soil quality using GIS which can be applied with management information systems for inventory purposes and for decision making.

Material and methods

Site description

Vrbničko polje is a karst field located on the northeast part of Krk Island in the Kvarner Archipelago (Croatia). It's a typical karstic valley (″polje″) of elongated and asymmetrical shape with the surface of 174.2 hectares of agricultural land which is almost exclusively used for viticulture. The axis of elongation parallels the structural grain from NW to SE. The polje floor is flat on the elevation from 85 to 164 meters above the sea level. The island of Krk has a temperate humid climate with hot summer. Climatic data on air temperature, precipitation, relative air humidity and insolation were obtained from the nearest climatic station Crikvenica and multiannual data set for period from 1965 to 2006 was statistically processed (data not shown). The lowest precipitation occurs in June and July with an annual average of 1238 mm. The mean annual air temperature is 14.3°C, with the highest (23.8°C) in July. Relative air humidity ranged from 64 (July) to 75 (January) per cent through the year. The mean sunshine hours ranged from 301.2 (July) to 98.5 (December) with total annual sunshine hours average of 2201.9.

Soil sampling and laboratory analysis

Two soil profiles were excavated and examined morphologically and dominant soil type was defined. Figure 1 displays soil top- and subsoil sampling scheme and profile locations. For determination of soil physical and chemical characteristics, soil samples were collected separately from soil horizons down to the parent material. To determine geochemical soil characteristics, topsoil (0-30 cm) and subsoil (30-60 cm) composite samples were collected from 26 locations selected randomly within the site. For each sample, a standard soil analysis was carried out to determine pH, using a 1:5 soil weight/water volume ratio, organic carbon (OC, g kg^{-1}) by sulfochromic oxidation, calcium carbonate contents by volumetric calcimeter method after HCl attack, total nitrogen contents by Kjeldahl method available K_2O and P_2O_5 by ammonium lactate method, particle size distribution and effective cation exchange capacity (CEC) using $BaCl_2$ solution. Soil subsamples were digested with aqua regia in accordance with the ISO 11466 procedure. The extraction process was done by the microwave technique on PerkinElmer Multiwave 6MF 100 (1000 W) apparatus in closed TFM vessels and with automatic pressure and temperature regulation. Element concentrations (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, S, V, Zn) in soil extracts were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Vista MPX AX (Varian). All samples were analyzed at the Analytical laboratory 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 program in which the laboratory participates (Houba et al., 1996).

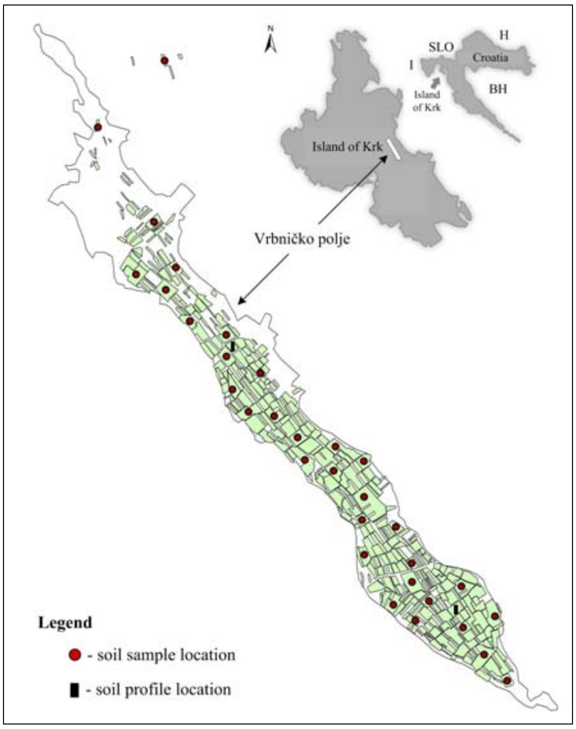

Figure 1 Study area showing vineyard cadastre, top- and subsoil sampling scheme, soil sample and profile locations

Data analysis, statistics and geostatistics

All soil data were incorporated into the GIS database. For the sampling locations the coordinates were taken by GPS and recalculated afterwards to the zone 16,30. The visualization of the spatial variables was done in GIS using software packages ArcView 9.0 (ESRI) i Erdas Imagine (LEICA). Basic statistic analysis was done using Statistica V 5.1 (StatSoft, 1996) software, consisting of number of samples, minimum and maximum, arithmetic mean, median, variance, standard deviation, skewness and kurtosis.For the variables which have shown the no-normal distribution, the logarithmic transformation of data was done prior the interpolation. The interpolation of elements was done in GS+ version 7.0 (Gamma Design Software) applying inverse distance weight (IDW) method.

Results and Discussion

Geology and soil

The area of Vrbničko polje is covered by deluvial deposits derived mostly from geological materials of a calcareous nature with marls, limestones, limestone breccias and Middle Eocene conglomerates on the upper edge (Fig.2). On the Eastern side, field is bordered by Upper Cretaceous deposits which consist of Touronian reef limestone. Lower and Middle Eocene foraminiferal limestones, which are transgressive on Cretaceous sediments are exposed on West-southern part. On some places on the Western side, the field is adjacent to Touronian reef limestones. Foraminiferal limestone locally contains the limestone - bauxite breccia and bituminous limestone, with brackish and marine fossils and plant fragments (Grimani et al. 1973).

For the whole area of the Island od Krk, the soil map in the scale 1:50000 was produced, with the totals of 18 cartographic units delineated. The mapping units are actually consociations of soil series including Leptosols, Regosols, Cambisols, Chromic cambisols, Chromic luvisols, Anthrosols and Gleyisols. The dominant soil type determined in Vrbničko polje area is Aric Anthrosols (FAO, 1990) on colluvial deposits. This soil was formed by the deposition and translocation of the flish deposits in the synclinal area. Used for agriculture, soil has been greatly affected by anthropogenic actions, being strongly altered both chemically and morphologically. The area used to be periodically fooded, and in the mid 20^th century the tunnel which drainage the excess water was bored through. But even today during the season of high precipitation the groundwater level rises, resulting in water stagnating in the rizosphere. The gleyization in soil is visible on the depth >60 cm. The plowing depth varies from 20 to 39 cm.

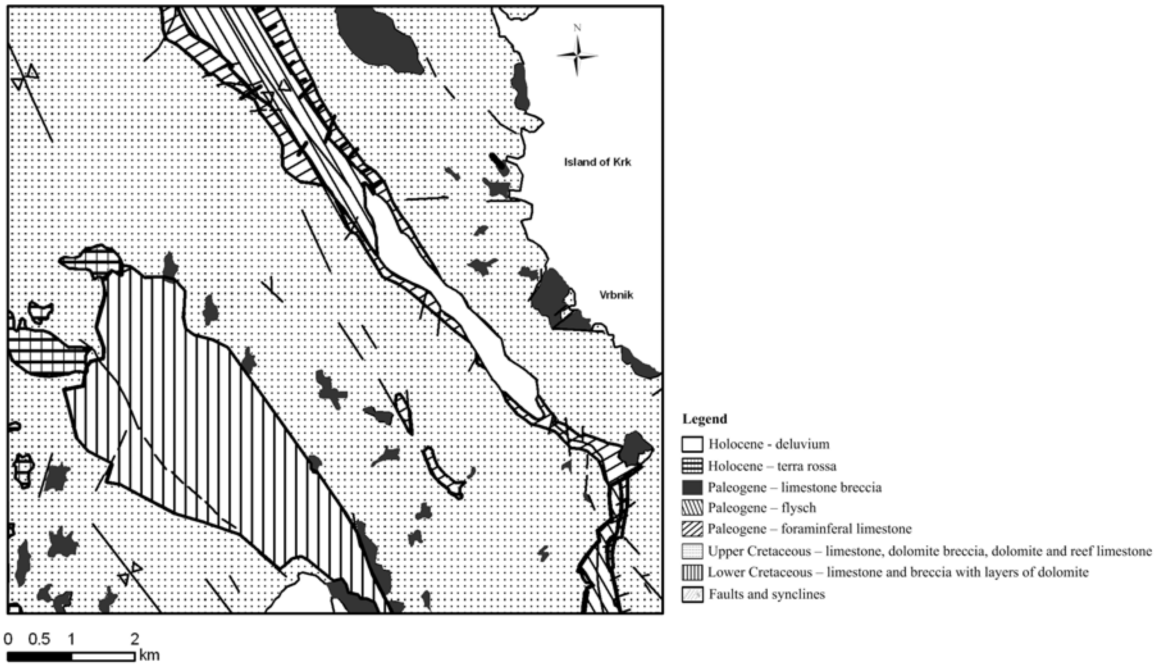

Figure 2 Simplified Geological map of the Vrbničko polje (adapted from Susnjar et al., 1970)

The important feature of all soil samples examined (Table 1) was their alkalinity, with pH value ranging from 7.18 to 7.57, organic matter contents in soils are generally low, in the range of 1.15 -2.79 % of organic C. Soils are well supplied by available nutrients, with exception of available phosphorus, which is result of the very low P content in the parent material. Two profiles differ considerably in the soil texture, what is also result of the both local geology and redistribution of soil particles within the field.

Profile	Depth cm	pH_{CaCl2}	EC ds m^{-1}	OM (%)	N (%)	P_2O_5 mg kg $^{-1}$	K_2O	CEC[a] $cmol_{(+)}$ kg^{-1}	Particle size distribution (%) Sand	Silt	Clay
P-1	0 - 35	7.47	0.11	2.79	0.15	0.694	3.06	31.4	7	67	26
	35 - 65	7.56	0.11	1.69	0.10	0.161	1.25	34.9	5	63	32
	65 - 150	7.57	0.12	1.26	0.09	/	/	34.1	5	66	29
	150 - 180	7.36	0.07	1.43	0.07	/	/	33.2	11	55	34
P-2	0 - 18	7.44	0.20	1.95	0.13	0.769	2.49	22.3	21	62	17
	18 - 56	7.49	0.15	1.15	0.01	0.534	1.46	23.8	18	62	20
	56 - 92	7.35	0.12	0.12	1.57	0.06	/	/	26	49	25
	92 - 140	7.26	0.13	0.13	1.21	0.04	/	/	44	40	16
	140 - 200	7.18	0.17	0.17	1.33	0.04	/	/	45	37	18

Table 1Studied characteristics of two soil profiles (P-1 and P-2) properties at the Vrbničko polje
[a]CEC, catione xchange capacity

Variability of the major chemical and physical properties in vineyard soils is common characteristic of cultivated soils.To determine the variability of the content of heavy metals in vineyard top- and subsoils, comparative analysis of the elements was first performed. Table 2 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.
The average concentrations of cadmium, copper and zinc in vineyard soils are higher than their background concentrations in agricultural soils of Croatia (Romic and 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.

	Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	S	V	Zn
	g kg^{-1}			mg kg^{-1}			g kg^{-1}					mg kg^{-1}			
Mean	44,6	15,8	0,38	14,7	89,4	161	33,2	8,69	927	86,9	1095	14,9	270	76,9	72,8
St.dev.	12,8	9,67	0,18	2,45	24,4	55,7	7,90	2,71	171	24,5	557	3,84	66,5	19,6	19,8
Min	26,7	1,88	0,22	8,90	42,9	46,7	17,6	2,28	571	22,1	455	11,1	162	51,3	45,2
Max	72,1	33,5	1,03	20,2	147	285	49,0	12,5	1408	131	2587	26,8	445	125	135
Skw.	0,52	0,12	2,32	-0,47	0,53	0,04	-0,08	-0,93	0,36	-1,01	0,94	1,66	0,76	0,89	1,22
Kurtosis	-0,64	-1,07	6,59	1,26	0,52	-0,10	-0,35	0,37	1,84	1,74	0,30	2,78	0,82	0,22	2,31
MPC*	-	-	2	50	100	100	-	-	-	60	-	150	-	-	300

Table 2 Statistical summary for topsoil (0 - 30 cm) element contents (n=26
*maximal permissible concentrations as defined by Croatian government regulations

	Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	S	V	Zn
	g kg^{-1}			mg kg^{-1}			g kg^{-1}					mg kg^{-1}			
Mean	47,1	18,0	0,28	15,1	92,8	96,4	35,0	9,06	965	90,9	475	14,0	216	78,4	66,1
St.dev.	13,6	10,3	0,13	2,34	26,7	45,0	8,03	2,79	179	24,9	140	2,85	45,6	18,4	15,8
Min	29,1	2,03	0,18	9,50	46,6	22,0	20,5	2,55	584	26,7	269	10,8	133	56,5	40,8
Max	74,5	34,0	0,85	19,5	149	217	50,7	12,9	1308	134	879	21,9	296	121	101
Skw.	0,58	-0,17	3,31	-0,86	0,51	0,80	0,01	-0,89	-0,25	-1,09	1,13	1,32	-0,03	0,77	0,44
Kurtosis	-0,63	-1,17	13,5	1,03	-0,02	0,77	-0,37	0,48	0,15	1,82	1,45	1,51	-0,53	-0,18	-0,31

Table 3 Statistical summary for subsoil (30 - 60 cm) element contents (n=26)

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. Some of the plots were abandoned, but many plantations were renewed, or new grapevine plantations were formed.

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 practices for a number of years. In terms of heavy metals, accumulation of copper, zinc and cadmium is the most common effect of continuing fertilization and protection against diseases and pests in vineyards.

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. In this particular study, the significant correlation between total cadmium and phosphorus concentrations in vineyard topsoil was recorded (data on correlations not shown), which may indicate that higher cadmium concentrations in topsoil in the lower part of the field might be due to the application of phosphate fertilizers. What's more, no significant correlation between total Cd and P content was recorded in the bottom soil layer (30-60 cm of depth).

High copper concentrations are not unusual for vineyard soils. 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.

The average manganese concentration in the topsoil of the Vrbničko polje equals 927 mg kg^{-1} and 965 in subsoil as well, ranging from 571 to 1408 mg kg^{-1}. Manganese is one of the main soil constituents and its variations is affected mostly by the composition of different regolithic substrates of colluvial origins in the recent pedogenesis but cyclical reduction-oxidation processes can influence manganese behaviour and redistribution in the soil as well.

High nickel and chromium concentrations seem to be of the geogenic origin (foraminiferal limestones, boxite breccas).

Conclusion

The geochemistry of the vineyard soils in Vrbničko polje is related to geology, geomorphology and pedogenesis. Heavier texture and higher concentration of the constitutive elements in soil (mainly Fe, Co, Cr, Ni, Mn, V) are result of the particle translocation and redistribution within the field.
Accumulation of copper in soil, determined in this research, is the most common effect of continuing protection against diseases and pests in vineyards. Associations of heavy metals with the selected soil properties explain the preferential feature of metal retention in soil.

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