MINERALOGICAL EXAMINATION OF SOIL IN SELECTED MORAVIAN VINEYARDS IN TERMS OF THEIR WINE QUALITY

Andrzej Broszkiewicz*, Maciej Pawlikowski**

*/WineQA Sp. z o.o., 10 Zalesie Dolne St., 32-700 Bochnia, Poland
**/Faculty of Geology, Geophysics and Environmental Protection, AGH University of
Science and Technology, 30 A. Mickiewicza Ave., 30-059 Krakow, Poland

Abstract

The goal of this work is to determine the influence of mineral composition of the vineyard soil on the quality and chemical composition of wine. Petrographic examination of sediments from three Moravian vineyards and chemical analysis of elemental composition of wines from respective locations were conducted. Thin sections of the sediment samples were made and hardened with epoxy in order to be used in petrographic examination with a polarizing microscope. The mineral composition analysis was made using point-counting method, counting out 300 grains in each test. For elemental analysis of the wine samples, inductively coupled plasma mass spectrometry (ICP-MS) was used. Preparation of the wine samples for analysis included measuring out 100 ml samples of wine and introducing them to the device. The final result of the analysis was determined using sample data. Acquired results were presented in comparative graphs and related to mineral composition of sediments. Relation between elemental composition of wine and mineral composition of sediments was confirmed and connected with the quality of wine.

Key words: wine quality, vineyard soil, elemental composition, mineral composition, ICP-MS, petrographic examination, Czech Republic

INTRODUCTION

It is commonly known that the vineyard soil is the primary reservoir of nutrients for the vines, and therefore it determines the individual character of wine (Jackson 2000, Amorós et al. 2013, Geana et al. 2013). There are many types of bedrock, with diverse mineral content. Each of them, in the constant process of weathering, enriches the soil solution with new ions, particular for given sediments (Bolewski and Parachoniak 1988, Zawadzki 1999). Grapevine has the ability to selectively absorb mineral compounds from the soil solution and distribute them in varying amounts to all of the plant's organs (Jackson 2000, Kopcewicz and Lewaka 2002, Hellman, 2003, Aceto 2003, Protano and Rossi 2013). Metal ions play important part in the vines' metabolism. Properly nourished plant grows high quality grapes which become a valuable base for wine production (Fernández Pereira 1988).

During fermentation, the content of elements in must is decreased due to the biochemical activity of yeast, which absorbs some of those elements (Aceto 2003, Schut et al. 2010, Geana et al. 2013, Ivanova-Petropulos et al. 2013). Adequate input concentration of elements is important to maintain proper parameters of fermentation – an essential factor in shaping the taste and aroma of wine. Apart from affecting the health of yeast in the fermentation process, the content of metal ions in must translates to the amount of resulting organic compounds which determine the taste and nose of wine (Fernández Pereira 1988, Tariba 2011). Not unimportant for the stability of the end product is using bentonite sorbents, which show the ability to deliver and remove elements from wine through ion exchange, they may change the content of elements taking part in the subsequent stages of aging and maturing, negatively affecting quality (Fernández Pereira 1988, Nicolini et al. 2004).

Proper concentrations of dozens of elements in grapes that undergo vinification significantly affect the quality of wine with additive results in the class of the end product, because in every stage of the process there is different demand for mineral compounds (Fernández Pereira 1988). Hence the result of the geological characteristics and mineral contents of sediments in the vineyard soil, i.e. its productivity and health, is the final quality of wine, which is proven by existence of winemaking regions with longstanding tradition of producing wines of well-deserved reputation (Jackson 2000, Amorós et al. 2013, Geana et al. 2013).

Apart from the taste and stability of the resulting wine, elements concentration affects also its health benefits. Some elements act as nutrients for human body, while excessive concentration of others may be toxic for it (Aceto 2003, Tariba 2011, Czech and Malik 2012). The source of harmful elements is not only environmental pollution, but also natural mineral composition of soils (Prasad et al. 2008).

The goal of the research presented in this article is indicating the correlation between the mineral composition of soil and the elemental composition of wine, as well as assessing the influence of that correlation on the quality of wine – the end product.

MATERIALS AND METHODS

Samples were taken from 3 vineyards owned by different wineries:
1. Mitrberk vineyard in Popice, 48°55'43.541"N, 16°40'7.170"E
2. Pravá Klentnická vineyard in Perná, 48°51'12.636"N, 16°38'10.163"E
3. Staré Vinice vineyard in Havraníky, 48°48'58.274"N, 16°0'35.054"E
The vineyards are situated in the south of Moravia — a historical region in the eastern part of Czech Republic.

Trial pits of 0.45 – 3 m in depth were made, depending on the digging conditions and the level of bedrock. Locations were chosen in immediate vicinity of the grapevine. Obtained profiles were measured, documented, and their outlines were drafted (Figure 1). Soil samples were taken from the walls of each profile, as close to the bottom as possible. Contents of the wine bottles received from each winery relate to small areas of vineyards which are the sole source of material for wine production and correspond to obtained soil samples.

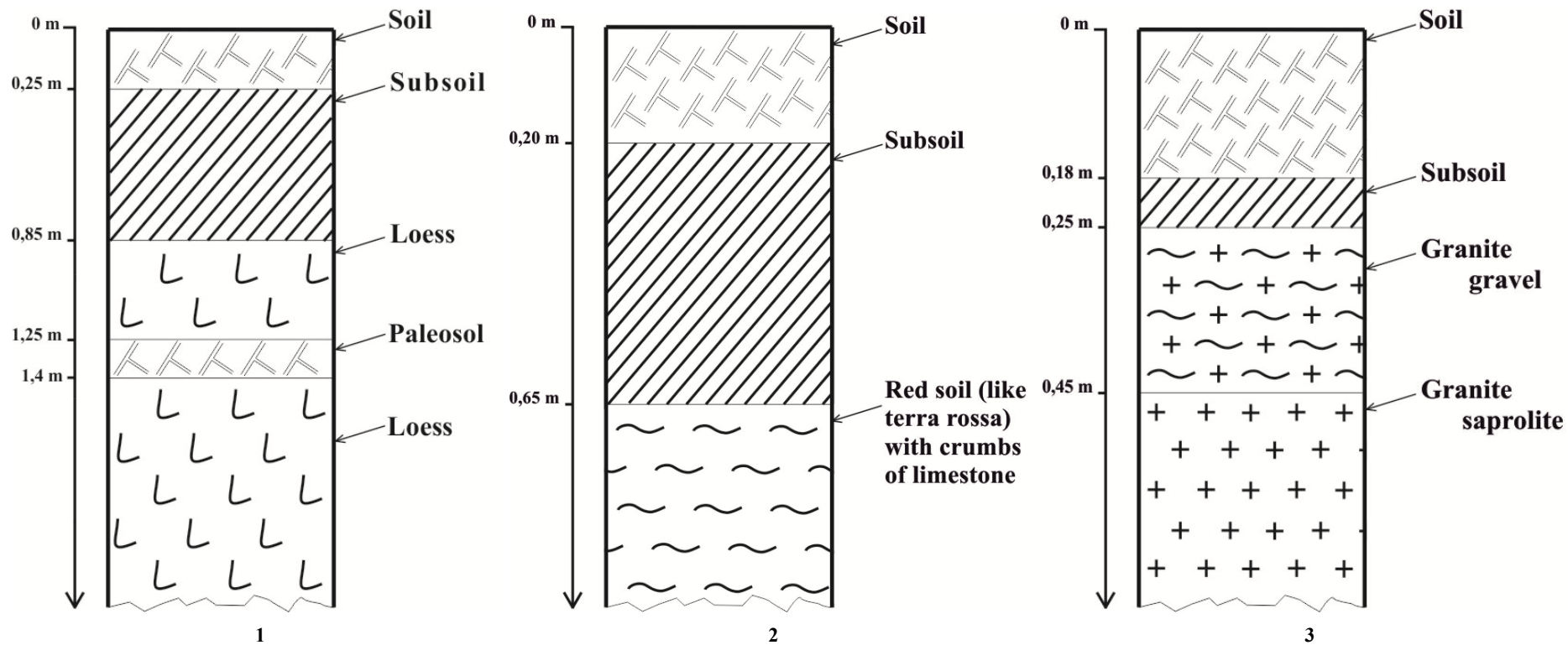Presented tests were conducted at the AGH University of Science and Technology

Figure 1. Schemes of soil profiles made for areas: 1 – Vineyard Mitrberk, 2 – Vineyard Pravá, 3 – Staré Vinice

in Kraków. Preliminary observations of the obtained sediment samples were made using a binocular magnifier L 20 manufactured by PZO – Polskie Zakłady Optyczne (Polish Optical Institute), Poland. After observations material was selected for further testing. Microsections were prepared for testing using polarized light microscopy. Samples were hardened with epoxy resins, then cut with a diamond blade and sanded with sanding powders. In the final stage, the samples were polished to the thickness of 0.02 mm and covered with a cover glass, using saw 500 from the Italian company Masonery to cut the samples. Petrographic analysis was made using M microscope from the Chinese company Motic. Mineral composition of the samples was determined using point-counting method, by counting out 300 grains in each try. A semiautomatic counting device M230062 by the DDR company Elttinor was used in analyses. Obtained results were converted to percents, and presented in tables and diagrams. For elemental analysis of wine samples (ICP-MS) an inductively coupled plasma mass spectrometer ELAN 6100 by the English company Perkin Elmer was used. Preparation of the samples for testing included measuring out 100-ml volume samples and introducing them to the device. Final results of the analysis were determined using model data in Microsoft Office Excel by the Microsoft company, USA.

Because of the cost and the necessity to cover it from our own funds, the research is not statistical in character, offering only preliminary appraisal of the problems we are interested in. Its publication will allow other people to conduct similar research, contributing to improvement of technology and quality of wine. Samples used in the analysis are presented in table 1 and table 2.

RESULTS AND DISCUSSION
Analysis of mineral sediments

Thanks to the petrographic analysis, percentage composition of elements in the loess soil of the Mitrberk vineyard was determined and presented in table 3. Loess is an aeolian sediment with dominating fine fraction that has crucial influence on forming soils (Bolewski and Parachoniak 1988, Zawadzki 1999).

Table 1. Statement of samples for studies

Sampling location	Sample Name	Sampling depth [m]	Date of sampling
Vineyard Mitrberk	Ms.1	3	07.07.2014
Vineyard Pravá	Ms.2	0.85	07.07.2014
Staré Vinice	Ms.3	0.45	08.07.2014

Table 2. Statement of wine samples for ICP-MS

Sampling	Sample Name	Variety and
Vineyard	Mw.1 (białe)	Rulandské Šedé.
Vineyard Pravá	Mw.2 (białe)	Ryzlink rýnský,
Staré Vinice	Mw.3 (białe)	Viognier, 2010

High content of clay minerals in sample Ms.1, 65.5%, indicates it is loess loam (Bolewski and Parachoniak 1988). Quartz and clay minerals are particularly resistant to erosion. Clay minerals, due to their high sorption capacity, intercept cations from the soil solution, contributing to condensation of mineral matter (Stoch 1974). Another significant phase is calcite, 12.8%, which in the profile had partially taken form of calcite concretions. They form as a result of calcite being leached from the topmost parts of sediments by rain water, which indicates that the soil solution is rich in Ca^{2+} ions. Loess sediments are often separated by layers of paleosols (Bolewski and Parachoniak 1988) – which is a feature shared by the presented profile. Rust-colored stains were present in the profile, which indicates presence of Fe^{3+} ions. K-feldspars, 0.8%, plagioclases, 0.6% and biotite, 0.1%, are rocks of relatively good solubility, they may increase the distribution of K^+, Na^+, Ca^{2+}, Mg^{2+}, and Mn^{2+} ions. Muscovite, 0.5%, is very poorly soluble. Loam has rich mineralogical composition because its fine fraction is highly volatile, which may be connected to the presence of small amounts of widely varying groups of minerals, e.g. heavy minerals (Bolewski and Żabiński 1987, Bolewski and Parachoniak 1988, Zawadzki 1999).

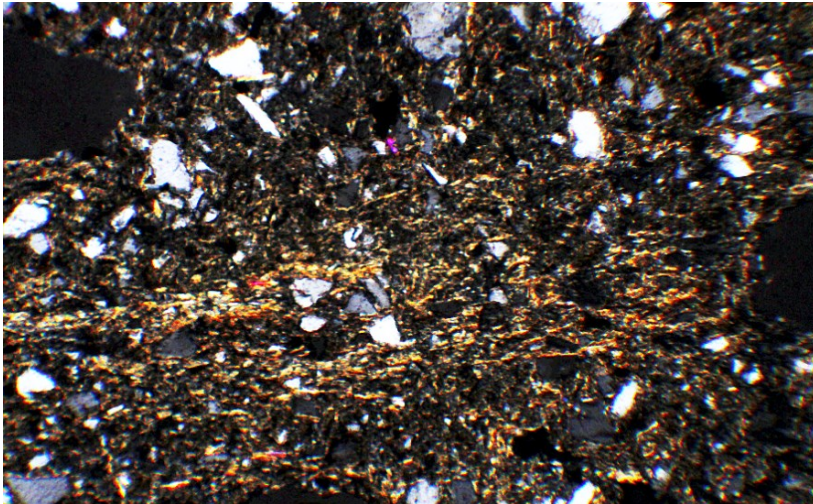**Figure 2.** The microscopic photography of thin section of Ms.1 sample – loess soil (mag. 120x)

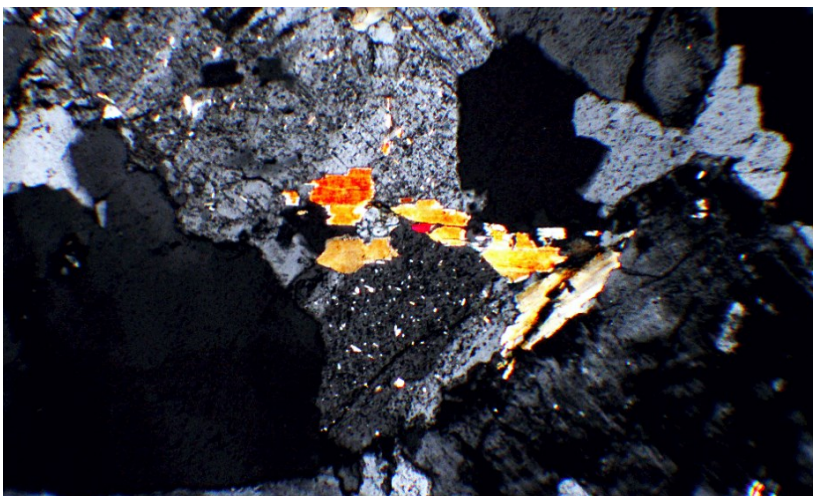**Figure 3.** The microscopic photography of thin section of Ms.2 sample – terra rossa soil (mag. 120x)

Figure 4. The microscopic photography of thin section of Ms.3 sample – granite saprolites (mag. 120x)

Table 3. Mineralogical composition of sediment – samples Ms.1, Ms.2, Ms.3

Mineral component	Content [%]		
	Ms.1	Ms.2	Ms.3
Clay minerals	65.5	85.3	-
Quartz	19.5	14.4	45.4
Calcite	12.8	-	-
K-feldspar	0.8	0.1	44.8
Plagioclase	0.6	-	9.4
Muscovite	0.5	0.1	0.3
Biotite	0.1	-	-
Heavy minerals	0.1	-	-
Other	0.1	0.1	-

Next, petrographic analysis was performed on the thin section Ms.2, which corresponds to soil from the Pravá vineyard. Results are show in table 3. Terra rossa, a sedimentary sandy loam, is formed as a result of physical and chemical erosion of limestone due to dissolving of its carbonate parts and leaving behind non-carbonate residue. The resulting residue, which has characteristics of both loam and sand, is moved due to erosion and settles according to particular landforms. Digging spot and very high thickness of the analyzed profile suggest such genesis (Konecka-Betley 1976).

85.3% content of clay minerals, which have high sorption capacity, is favorable for accumulation of cations that is beneficial for the plant's growth (Stoch 1974). Formation of red saprolites, dependant on the presence of iron compounds, appears in strongly contrasting climatic conditions (wet periods, dry periods), due to the processes of dehydration and oxidation. Outline of the presented profile was brown in color, which can be explained by the presence of hydrated iron compounds and dominance of leaching over evaporating, which, in favorable conditions, is the cause of ions from soil solution moving upwards, in a capillary effect (Konecka-Betley 1976, Bolewski and Parachoniak 1988). In sample Ms.2, crumbs of limestone were found in the loam matrix, which is a typical characteristic of saprolites like terra rossa. The effect of chemical erosion of the remaining limestone crumbs is supplying the soil solution with Ca^{2+} ions (Bolewski and Parachoniak 1988). Clay minerals, quartz, 14.4%, and muscovite, 0.1% of the analyzed sample, don't directly increase the concentration of free ions in saprolites due to their poor solubility (Stoch 1974, Bolewski and Żabiński 1987). Scant presence of K-feldspars – 0.1% – may slightly increase the content of K^+ ions and silica (Zawadzki 1999).

Results from the last of the analyzed sediment thin sections, corresponding to the soil from Staré Vinice, is presented in table 3. Granitoids are the most common plutonic rocks in the earth's crust (Bolewski and Parachoniak 1988). In the analyzed profile, the saprolites have a form of granite gravel, and above, fine granite gravel, which is typical for dominationof the mechanical weathering processes over chemical, in moderate or cool climate (Bolewski and Parachoniak 1988, Zawadzki 1999).

In contrast to the previously described profiles, no clay fraction was found in analyzed sample Ms.3. In its mineral composition the dominating components are definitely quartz, at 45.4%, and K-feldspars at 44.8%. In case of quartz, as already mentioned, there is virtually no ion release present, while feldspars undergo chemical weathering, increasing the availability of K^+ ions and silica (Bolewski and Żabiński 1987). Chemical weathering of plagioclases, 9.4%, may be connected with supplying cations of elements such as Na, K, Ca and silica. Muscovite, 0.3%, is very poorly soluble (Zawadzki, 1999). In granites, inclusions of other minerals, e.g. zirconium and apatite, are often present, which increases the spectrum of supplied ions (Bolewski and Parachoniak 1988). Red-colored granite was found in the area of the trial pit. According to (Bolewski and Parachoniak 1988), it may be related to the presence of iron that had been oxidized due to the influence of radioactive minerals.

Chemical analysis of wine

Test results of the ICP-MS analysis concerning concentration values of elements above 0.1 mg·l^{-1} were presented in figure 5. Concentrations of elements in sample Pw.3

Table 4. Values of the elements contained in the samples: Mw.1, Mw.2, Mw.3; ICP-MS

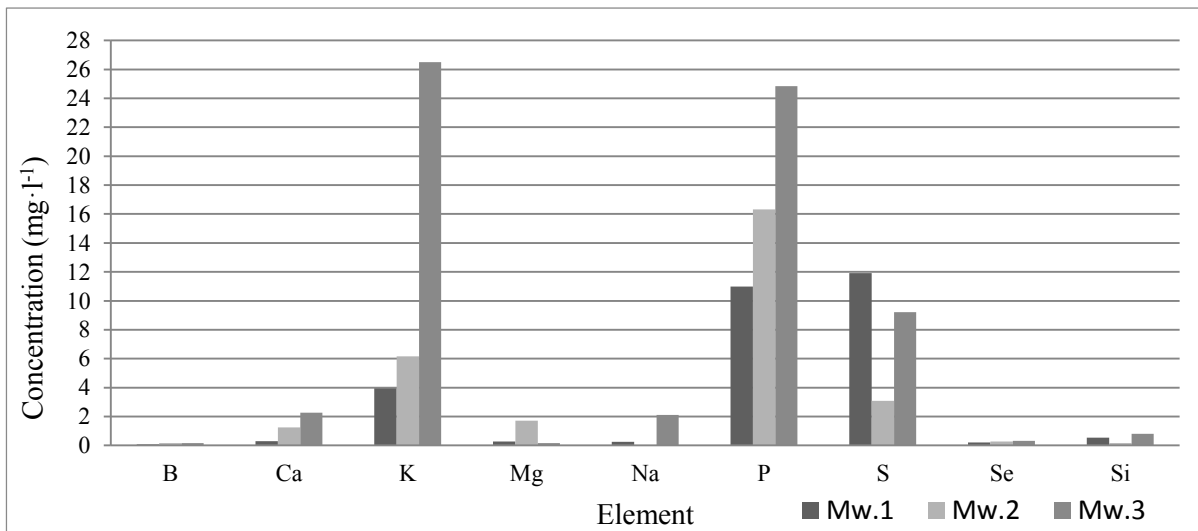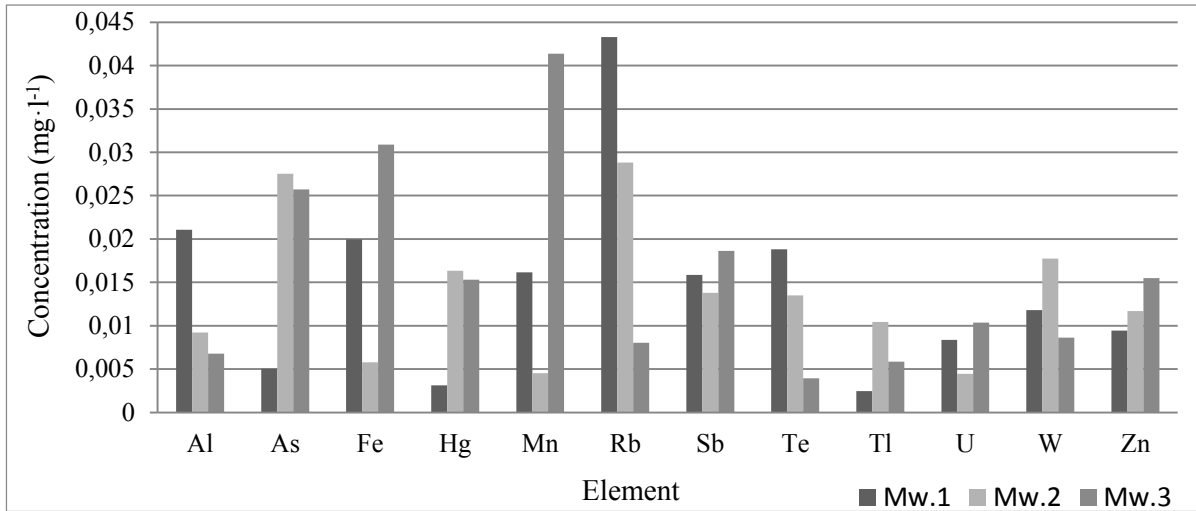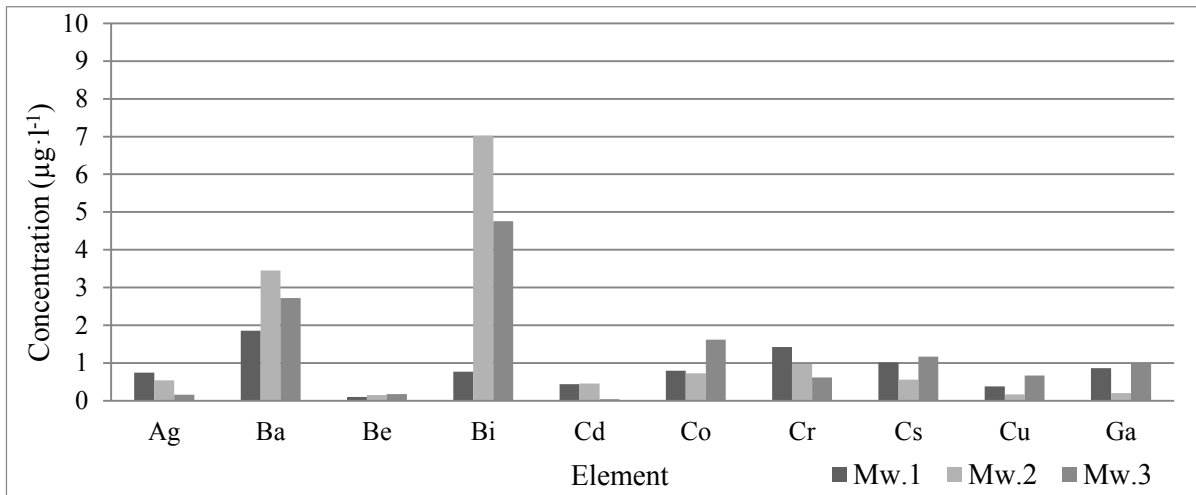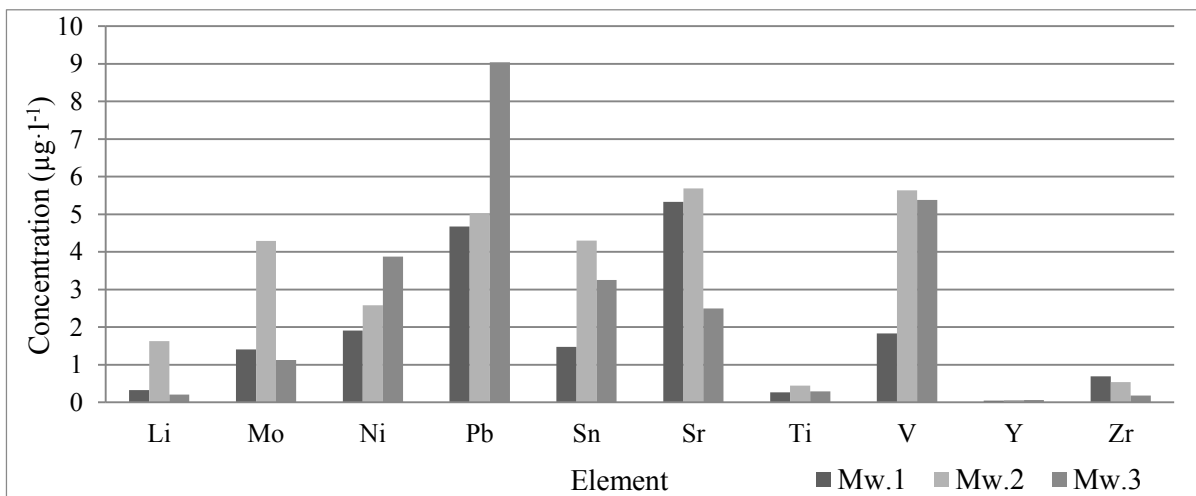| Element	Concentration			Element	Concentration			Element	Concentration		
	Mw.1	Mw.2	Mw.3		Mw.1	Mw.2	Mw.3		Mw.1	Mw.2	Mw.3
B (mg·l⁻¹)	0.078	0.153	0.157	Rb (mg·l⁻¹)	0.043	0.029	0.008	Cs (µg·l⁻¹)	1.012	0.560	1.169
Ca (mg·l⁻¹)	0.305	1.258	2.257	Sb (mg·l⁻¹)	0.016	0.014	0.019	Cu (µg·l⁻¹)	0.376	0.169	0.668
K (mg·l⁻¹)	3.946	6.159	26.500	Te (mg·l⁻¹)	0.019	0.013	0.004	Ga (µg·l⁻¹)	0.861	0.198	1.001
Mg (mg·l⁻¹)	0.268	1.715	0.158	Tl (mg·l⁻¹)	0.002	0.010	0.006	Li (µg·l⁻¹)	0.326	1.627	0.205
Na (mg·l⁻¹)	0.248	0.042	2.109	U (mg·l⁻¹)	0.008	0.004	0.010	Mo (µg·l⁻¹)	1.403	4.290	1.126
P (mg·l⁻¹)	10.987	16.313	24.837	W (mg·l⁻¹)	0.012	0.018	0.009	Ni (µg·l⁻¹)	1.909	2.584	3.871
S (mg·l⁻¹)	11.916	3.077	9.210	Zn (mg·l⁻¹)	0.009	0.012	0.015	Pb (µg·l⁻¹)	4.675	5.002	9.045
Se (mg·l⁻¹)	0.215	0.275	0.322	Ag (µg·l⁻¹)	0.744	0.537	0.160	Sn (µg·l⁻¹)	1.472	4.297	3.252
Si (mg·l⁻¹)	0.530	0.160	0.810	Ba (µg·l⁻¹)	1.851	3.451	2.719	Sr (µg·l⁻¹)	5.331	5.685	2.497
Al (mg·l⁻¹)	0.021	0.009	0.007	Be (µg·l⁻¹)	0.102	0.153	0.173	Ti (µg·l⁻¹)	0.269	0.447	0.289
As (mg·l⁻¹)	0.005	0.028	0.026	Bi (µg·l⁻¹)	0.772	7.023	4.761	V (µg·l⁻¹)	1.830	5.641	5.379
Fe (mg·l⁻¹)	0.020	0.006	0.031	Cd (µg·l⁻¹)	0.439	0.460	0.041	Y (µg·l⁻¹)	0.046	0.061	0.058
Hg (mg·l⁻¹)	0.003	0.016	0.015	Co (µg·l⁻¹)	0.796	0.728	1.616	Zr (µg·l⁻¹)	0.694	0.533	0.182
Mn (mg·l⁻¹)	0.016	0.005	0.041	Cr (µg·l⁻¹)	1.426	0.974	0.621	–	–	–	–

Figure 5. Comparison of the results of the ICP-MS for the specified range of concentrations, shown in the sequence of samples Mw.1, Mw.2, Mw.3, wherein the at least one sample element concentration matches the C > 0.1 mg·l⁻¹.

Figure 6. Comparison of the results of the ICP-MS for the specified range of concentrations shown in the sequence of samples Pw.1, Pw.2, Pw.3, wherein the at least one sample element concentration matches the 0,1 mg·l^{-1} ≥ C > 0,01 mg·l^{-1}

A

B

Figure 7. Comparison of the results of the ICP-MS (A and B) for the specified range of concentrations, shown in the sequence of samples Pw.1, Pw.2, Pw.3, wherein the at least one sample element concentration matches the C ≤ 0,01 mg·l^{-1}.

are higher than in the other ones, except for Mg. Particularly high contents of K, P, Ca, Na, and Si were detected, which indicates that the granite soil is rich in nutrients. That confirmed the assumptions related to the process of weathering of feldspars and plagioclases, as well as the increased availability of those elements for the grapevines. Additionally, high concentration of calcium and phosphorus in sample Mw.3 may indicate apatite inclusions within analyzed soil. Profiling the sediments from the Staré Vinice vineyard supplied information about small depth of the soil, because there was a homogenous layer of granite waste found on the depth of 0.45 m. In such situation, grapevine roots surpass the rock material and absorb nourishing ions from the soil solution without significant contribution of the silt minerals (Hellman 2003, Callejas at al. 2009). Despite noticeable presence of calcite in sample Mw.1, calcium content is lower than that of samples Mw.2 and Mw.3. The only dominating concentration in sample Mw.1, corresponding with the loess soil, is S. Limestone crumbs found in sample Ms.2 could indicate high content of Ca^{2+} ions in wine, and yet only moderate amounts of that element are actually present. The change of Ca content in wine is related to the yeast's demand for nutrients and the process of wine stabilization, i.e. clarification, sludge precipitation (Nabais et al. 1988, Fernández Pereira 1988). Moreover, in sample Mw.2 high content of Mg was identified. Correlation between the contents of K and P in each sample was found.

Analysis of the concentration values between 0.1 and 0.01 mg·l⁻¹ presented in figure 6 shows elevated amounts of Al, Rb and Te in sample Mw.1. It was proven that high content of Al in wine may be the reason for its cloudiness (Fernández Pereira 1988). Concentration of Al may be increased as a result of using sorbents, i.e. bentonite, in the clarification process (Nicolini et al. 2004). The source of Mn in wine are probably anhydrous carbonates from the loess soil. Low concen-tration of Mn in sample Mw.2, corresponding to the terra rossa soil which is rich in carbonates, results from the wealth of Ca in the soil solution, which blocks bioavailability of Mn ions.

Additionally, small air capacity of heavy soil causes decrease in availability of properly oxidized forms of Mn, which are easily absorbed by plants (Maas et al. 1969). ICP-MS analysis confirmed high content of Fe in samples Mw.1 and Mw.3, which unambiguously confirms the assumptions regarding presence of Fe ions in loess and granite soils. Low content of Fe in sample Mw.2 doesn't undermine the concept of high Fe concentration in terra rossa soil, but results from low bioavailability of that element for grapevines. It is caused by Fe occurring in insoluble compounds or unsuitable oxidation number, low oxygenation of high-compact soil and high pH (Konecka-Betley 1968). Analyses showed that wines contain elements that are toxic for human body, i.e. As, Hg, Te, Tl, U. Their concentrations differ in each sample. The highest concentration of U was found in sample Mw.3, which is directly related to the granite soil which, depending on its composition, may be rich in that element. Sample Mw.3 contains increased amounts of Fe, Mn and Zn, which qualify as nutrients, as well as As, Hg and U, which are toxic to human body. Increased amounts of toxic metals indicate that, aside from being a good source of beneficial microelements, granitic soil is also the source of elements that are harmful to human health.

Figure 7 shows concentration values from the range of below 0.01 mg·l⁻¹. Concentrations of Pb, Bi, Sr and V have particularly high values in relation to other elements in this range. Analyzed wine samplesshowed very low concentration of elements: Ag, Be, Cd, Cs, Cu, Ga, Ti, Y, Zr. In sample Pw.3 the content of Pb was almost twice as high as in the other samples. High content of Mo in sample Pw.2 is beneficial in terms of this element's wealth in the soil. Mo stimulates the growth of grapevines, increases the size and quality of grapes, and in wine, it strengthens oxidation process (Fernández Pereira 1988).

During the clarification of wine using sorbents, some of the elements' concentrations change. According to (Nicolini et al. 2004), significant changes may be observed in Y and U, i.e.: from 0.52 µg·l⁻¹ and 0.45 µg·l⁻¹ to, respectively, 2.25 µg·l⁻¹ and 4.18 µg·l⁻¹. In all analyzed by us wine samples

the content of Y oscillates around 0.5 $\mu g \cdot l^{-1}$ and used sorbents don't release Y in the amount similar to the results of (Nicolini et al. 2004), or that element is removed in a different way, e.g. by filtration. Levels of concentrations of some elements in the analyzed samples are significantly lower (Cr, V, Ni, Cu) or significantly higher (Tl, U) that those analyzed by (Nicolini et al. 2004). That fact shows a great diversity in the mineral composition of wine, and in result, in its quality and health benefits. In this case, wines show good health qualities in relation to heavy metal contents. Overall concentrations of the mineral substance in wine samples for elements from the range below 0.01 mg·l^{-1} are: Mw.1 – 0.026 mg·l^{-1}, Mw.2 – 0.044 mg·l^{-1}, Mw.3 – 0.039 mg·l^{-1}. Those values show that loess soil has the lowest bioavailability of heavy metals, in comparison with terra rossa and granite soil.

CONCLUSIONS

1. In most cases we were able to correctly foresee the richness of soil in elements that are nutritious for the vines, coming from weathering minerals. That confirms the existence of correlation between the elemental composition of soil and elemental composition of wine.
2. Nutrients, which are absorbed by the vines from soil, play a very important role in all the stages of the cultivation and wine production, influencing the dynamics of metabolic processes in maturing fruit, metabolic processes of yeast and bacteria – during fermentation and aging, as well as stabilizing the wine. The sum of all the most important qualities of wine recorded as proportions of organic compounds corresponds to the same proportions in elemental composition of wine.
3. Type of soil determines type of mineral compounds absorbed in the wine. Based on comparison of 3 samples, and disregarding the influence of different production processes, it was recognized that ICP-MS analysis of sample Mw.2, connected to terra rossa soil, showed increased contents of elements from the range below 0.01 mg·l^{-1}. Moreover, wine correlating with the granite soil shows

increased concentration of elements from the range above 0.01 mg·l^{-1}.
4. Analyses of sediments profiles from vineyards are essential source of information about soil characteristics, and may serve as preliminary assessment of the quality of produced wine, as well as for perfecting technologies of cultivation and production.
5. Increased contents of heavy metals in analyzed wines in connection with other test results proves the grapevines' ability to bioaccumulate harmful mineral substances from the soil. Mineralogical analysis of soil and layers beneath it may help identify potential risks and factors decreasing the quality of wine.

LITERATURE

Aceto, M. (2003) Metals in wine. Watson R. and Preedy V., eds. Reviews in food and nutrition toxicity. Volume 1. (Taylor & Francis Inc, London, UK) pp. 169-197.

Amorós, J.A. Pérez-de-los Reyes, C. García Navarro, F.J. Martínez, J. and Jiménez Ballesta, R. (2013) Bioaccumulation of mineral elements in grapevine varieties cultivated in "La Mancha". Journal of Plant Nutrition and Soil Science, **176**, 843–850.

Bolewski, A. and Parachoniak, W., eds. (1988) Petrografia. (Wydawnictwa Geologiczne, Warszawa, Poland).

Bolewski, A. and Żabiński, W. (1987) Zarys mineralogii. (Wydawnictwa AGH, Kraków, Poland).

Callejas, R.R. Canales P. and García de Cortázar, V.G. (2009) Relationship between root growth of 'thompson seedless' grapevines and soil temperature. Chilean Journal of Agricultural Research, **69**, 4, 496-502.

Coetzee, P.P. van Jaarsveld, F.P. and Vanhaecke, F. (2014) Intraregional classification of wine via ICP-MS elemental fingerprinting. Food Chemistry, **164**, 485-492.

Czech, A. and Malik, A. (2012) Content of bioactive compounds in semi-dry red wine. Journal of Elementology, **2**, 191–200.

Fernández Pereira, C. (1988) The importance of metallic elements in wine. A literature survey. Zeitschrift für Lebensmittel-Untersuchung und Forschung, **186**, 4, 295-300.

Geana, I. Iordache, A. Ionete, R. Marinescu, A. Ranca, A. and Culea, M. (2013) Geographical origin

identification of Romanian wines by ICP-MS elemental analysis. Food Chemistry, **138** (2-3), 1125-1134.

Hellman, E.W. (2003) Grapevine Structure and Function. Hellman E.W., ed. Oregon Viticulture. (Oregon State University Press, Corvallis, Oregon, USA)

Hopfer, H. Nelson, J. Collins, T.S. Heymann, H. and Ebeler, S.E. (2014) The combined impact of vineyard origin and processing winery on the elemental profile of red wines. Food Chemistry, **172**, 486-496.

Ivanova-Petropulos, V. Wiltsche, H. Stafilov, T. Stefova, M. Motter, H. and Lankmayr, E. (2013) Multi-element analysis of Macedonian wines by inductively coupled plasma–mass spectrometry (ICP–MS) and inductively coupled plasma–optical emission spectrometry (IP–OES) for their classification. Macedonian Journal of Chemistry and Chemical Engineering, **32**, 2, 265–281.

Jackson, R. S. (2000) Wine Science: Principles and Applications. 2nd ed. (Academic Press, San Diego, USA)

Konecka-Betley, K. (1968) Zagadnienie żelaza w procesie glebotwórczym. Roczniki Gleboznawcze, **XIX**, 1, 51-97.

Konecka-Betley, K. (1976) Gleby reliktowe wytworzone ze skał węglanowych na obszarze Gór Świętokrzyskich i ich obrzeżenia. Roczniki gleboznawcze, Warszawa, **XXVII**, Nr 2, 49-71.

Kopcewicz, J. and Lewaka, S., eds. (2002) Fizjologia Roślin. (Wydawnictwo Naukowe PWN SA, Warszawa, Poland) pp. 228-271.

Nabais, R.C. Sa Correia, I. Viegas, C.A. and Novais, J.M. (1988) Influence of Calcium Ion on Ethanol Tolerance of Saccharomyces bayanus and Alcoholic Fermentation by Yeasts. Applied and Environmental Microbiology, **54**, 10, 2439-2446.

Maas, E.V. Moore, D.P. and Mason, B.J. (1969) Influence of Calcium and Magnesium on Manganese Absorption. Plant Physiology, **44**, 6, 796–800.

Nicolini, G. Larcher, R. Pangrazzi, P. and Bontempo, L. (2004) Changes in the contents of micro- and trace-elements in wine due to winemaking treatments. Vitis, **43**, 1, 41–45.

Protano, G. and Rossi, S. (2013). Relationship between soil geochemistry and grape composition in Tuscany (Italy). Journal of Plant Nutrition and Soil Science, **177**, 500–508.

Prasad, M.N.V., eds. (2008) Trace elements as contaminants and nutrients - Consequences in Ecosystems and Human Health. (John Wiley & Sons, Inc., New Jersey, USA) .

Schut, S. Zauner, S. Hampel, G. König, H. and Claus H. (2010) Biosorption of copper by wine-relevant lactobacilli. International Journal of Food Microbiology, **145**, 1, 126-131.

Stoch, L. (1974) Minerały ilaste. (Wydawnictwa Górnicze, Warszawa, Poland)

Tariba, B. (2011) Metals in Wine—Impact on Wine Quality and Health Outcomes. Biological Trace Element Research, **144**, 143–156.

Zawadzki, S., eds. (1999) Gleboznawstwo: podręcznik dla studentów. (Państwowe Wydawnictwo Rolnicze i Leśne, Warszawa, Poland)