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Differentiation of Czech wines using multielement composition – A comparison with vineyard soil

Petr Kment [a], Martin Mihaljevič [a,*], Vojtěch Ettler [a], Ondřej Šebek [b], Ladislav Strnad [b], Ladislava Rohlová [a]

[a] *Faculty of Science, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic*
[b] *Laboratories of Geological Institutes, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic*

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Abstract

Chemical compositions of wines and soil extracts from six viticulture areas of the Czech Republic were examined using statistical multivariate analyses – principal component analysis, factor and cluster analysis. In the group of the 27 studied elements determined by ICP-MS and AAS, only Mg exhibits a statistically significant dependence between its concentration in Mehlich's soil extract and in wine. Contents of lithophile elements, such as Mg, Mn, Cs, Ba and Sr, in wines are mutually dependent. Some of these lithophile elements exhibit a positive correlation with the elements with the lowest concentration (e.g., Ag and Tl). The most probable source of these lithophile elements was determined to be the vineyard soil and dust. Some of the lithophile biogenic elements show negative correlations with elements from anthropogenic contamination: K is correlated with Pb; Mg and Mn are correlated with V. It is likely that these elements exhibit antagonistic competition with each other in the vine. A strong positive correlation between Cu and As in wines indicates the origin of both elements in inorganic pesticides employed in viticulture. Both wine and soil samples are very well clustered according to their locality. However, the clustering of wines did not follow clustering of soils and it is possible that major and trace element fingerprints of wines reflect soil chemistry, pollution and wine manufacturing practices by individual producers.
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1. Introduction

The total element content in wine has two major sources. The first, natural source, is supposed to include the soils, resulting from the weathering of their parent rocks. The second, anthropogenic source, may be divided into 3 subgroups:

(1) Application of organic and mineral fertilizers, inorganic pesticides and other substances employed in growing practices. For example, phosphatic fertilizers are known to have higher concentrations of Cd (Ramachandran & D'Souza, 1998). Pesticides may increase the contents of Cu, As and Zn.
(2) Pollution of the surrounding environment, which is not directly associated with viticulture practice. This source is mainly related to suspended particular matter, of either geogenic (natural) origin, leading to an increase of lithophile elements (Sr, Mn, Al, Ti) or of anthropogenic origin, leading to higher flux of volatile elements (Pb, V, Zn, Ni, Cd).
(3) Application of food additives, machinery and other operations employed in the production of wine from grapes (Frías, Trujillo, Peña, & Conde, 2001; Jakubowski, Brandt, Stuewer, Eschnauer, & Görtges, 1999). Particularly Fe, Al and Cr can be

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[*] Corresponding author. Tel.: +420-221951494; fax: +420-221951496.
E-mail address: mihal@natur.cuni.cz (M. Mihaljevič).

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released from machinery, piping and storage tanks. Bentonite and other additives, employed for the purification of wines from tarnishing components, can constitute an important source of Al (McKinnon, Cattrall, & Scollary, 1992) and source or sink of base cations and/or rare-earth elements (REEs) (González & Peña-Méndez, 2000; Jakubowski et al., 1999).

The concentrations of some major and trace elements in wines are further monitored for various reasons. For example, maximum permissible concentrations of As, Sn, Cr, Cd, Cu, Ni, Pb, Hg, Zn and Fe in wine are stipulated in the legislation of the Czech Republic (Czech regulation No. 298/1997). Al, Zn, Fe an Cu contents in wine are monitored due to their effects on the organoleptic properties of the wines (Gennaro, Mentasti, Sarzanini, & Pesticcio, 1986).

Many research papers have recently focussed on the development of analytical methods to determine the contents of trace elements (Fournier, Hirsch, & Martin, 1998) or isotopic compositions of lead (Almeida & Vasconcelos, 1999) and strontium (Almeida & Vasconcelos, 2001) in wine, employing multi-elemental techniques, such as ICP-MS. Other extensively employed techniques include AAS, ICP-OES and electrochemical methods (e.g., Cvetković, Stafilov, & Mihajlović, 2001; Ražić, Todorović, Holclajtner-Antunović, & Stoiljković, 1999) and total reflection X-ray spectrometry (Castiñeira, Brandt, von Bohlen, & Jakubowski, 2001)

Statistical multivariate analyses were also employed to determine the correlation between the contents of elements in wines and to investigate the possibility of differentiating production areas on the basis of the trace or major element association of wines (Frías et al., 2001; González & Peña-Méndez, 2000; Marengo & Aceto, 2003; Moret, Scarponi, & Gescon, 1994). A recent study of Jakubowski et al. (1999) focussed on the possibility of determining the provenance of wine on the basis of the REE contents, in order to reveal falsification.

The Czech viticulture region (Fig. 1) is one of the most northerly viticulture territories in Europe. In most areas, the viticulture tradition extends back to the Middle Ages. On the other hand, in the Most area (NW Bohemia), grape vines were planted as a reclaiming crop on the recultivated dumps of former brown-coal mines. The pollution of the surrounding environment in the studied areas varies and is highest in the industrial areas (Most) and in areas with high population densities (Prague).

The aim of this study was to provide statistical comparison of wine major and trace element composition with the composition of vineyard soils. The main objective consists in the distinction and determination of the origin of studied elements in wines.

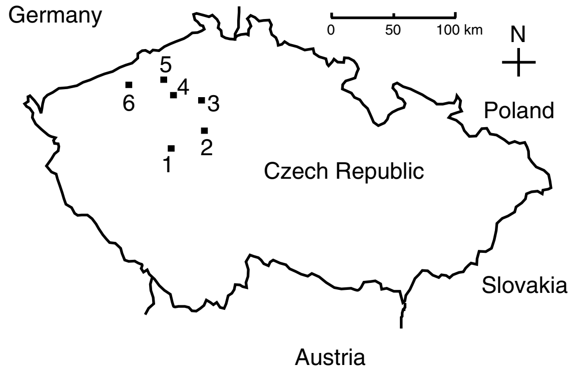

Fig. 1. Viticulture areas of the Czech Republic. 1. Karlštejn; 2. Praha; 3. Mělník; 4. Roudnice; 5. Žernoseky; 6. Most.

2. Materials and methods

2.1. Sampling

Thirty one wine samples and 31 soil samples were taken in 6 viticulture areas in the Czech viticulture region (Prague, Karlštejn, Mělník, Roudnice, Žernoseky and Most) (Fig. 1). Table 1 gives a summary of the wine samples and corresponding geological background. Some of the wines were bottled and, for others, 250-ml samples were taken from barrels.

2.2. Analyses of wines

The pH values of the wines were determined using a digital pH meter (Radelkis, Hungary) and the titrable acidity was determined by titration with 0.1 M NaOH to a pH value of 7 (Darias-Martín, Socas-Hernández, Díaz-Romero, & Díaz-Díaz, 2003; OIV, 1969). The wine samples were prepared for elemental analysis in several steps: (a) 50 ml of sample was stabilised by addition of 1 ml of concentrated HNO_3 (for ICP-MS analysis); (b) 50 ml of wine was stabilised by 1 ml of concentrated HCl (for AAS analysis). Mineralization of samples for ICP-MS was carried out in Savillex teflon vessels (Savillex® Minnetonka, USA), using the following procedure: 5 ml wine + 2 ml HNO_3 + 1 ml H_2O_2 were heated for 3 h at 150 °C. This procedure helped to eliminate the organic matrix of the wine samples. Both mineralised and HCl stabilised wine samples were diluted for spectral analyses.

2.3. Soil analysis

About 0.5-kg samples of soils were obtained from the mineral (B) horizon. This level was selected because the element contents here are not affected to such a high degree as the organic (upper) horizon by anthropogenic activities. The samples were first dried to a constant weight and sieved through a 2-

Table 1
Summary of studied wine samples

Area	Grape variety	Vintage	Storage	Geological setting
Roudnice	SV	2000	Metal barrel	Cretaceous marlstones
	SZ	2000	Metal barrel	
	RM	2000	Metal barrel	
Prague	RB	2001	Metal barrel	Ordovician shales and quartzites
	MT	2001	Metal barrel	
	SV	2001	Metal barrel	
	RM	2000	Bottled	
	MT	2000	Bottled	
Most	RR	2000	Metal barrel	Tertiary volcanites, tertiary claystones, anthropogenic dumps
	ZW	2000	Wooden barrel	
	RŠ	2000	Metal barrel	
	IO	2000	Wooden barrel	
	ZW	2000	Metal barrel	
	SV	2000	Metal barrel	
	SV	2000	Metal barrel	
	RM	2000	Metal barrel	
	MT	2000	Metal barrel	
	SV	2000	Metal barrel	
Mělínk	SV	2000	Metal barrel	Cretaceous marlstones and sandstones
	RR	2001	Metal barrel	
	MT	2001	Metal barrel	
	Mopr	2000	Wooden barrel	
Karlštejn	TR	2000	Metal barrel	Devonian limestones
	RB	2000	Metal barrel	
	ZW	2000	Metal barrel	
	André	2000	Metal barrel	
Žernoseky	MT	2000	Wooden barrel	Tertiary volcanites
	RR	2000	Wooden barrel	
	TR	2000	Wooden barrel	
	RR	2000	Metal barrel	
	SV	2000	Wooden barrel	

IO, Irsay Oliver; MT, Müller-Thurgau (Rivaner); TR, Red Tramin; RB, Pinot blanc; RM, Pinot noir; SV, Saint Laurent; SZ, Sylvan green; RŠ, Pinot gris; RR, Rhine riesling; Mopr, Moravian Muscat.

Table 2
Measured isotopes, detection limits (DL) and operating conditions used for ICP-MS

Element	Measured isotope	DL wines (μg/l)	DL soils (mg/kg)
Li	7	5	0.1
Be	9	0.1	0.1
Al	27	2	5
V	51	0.02	3
Cr	53	0.2	5
Co	59	0.02	0.03
Ni	60	0.3	0.3
Cu	65	0.5	0.6
Zn	66	0.5	0.2
As	75	0.05	0.8
Rb	85	0.05	0.1
Sr	88	0.01	0.05
Ag	109	0.01	n.a.
Cd	111	0.05	0.07
Sb	121	0.07	n.a.
Cs	133	0.03	0.01
Ba	138	0.02	0.1
Tl	208	0.02	n.a.
Pb	208	0.1	0.05
U	238	0.07	n.a.

Parameter	Value
ICP-MS operating parameters	
Rf power (W)	1420
Gas flows (l/min Ar 5.0)	13.5, 1.3, 0.72
Acqusition time	3 × 50 s
Nebuliser	Meinhard type
Acqusition mode	Peak jump
Points per peak	3
Dwell time	10.24
Replicates	3
Detector mode	Pulse
Internal standards	45Sc, 115In, 185Re

n.a., not analysed.

mm nylon sieve. Extraction was then carried out in a Mehlich 3 solution (Mehlich, 1984). This solution simulates the ability of plant roots to uptake nutrients from the soil into the organism. About 5 g of soil were extracted into 50 ml of Mehlich solution and diluted 1:500 in 2% (v/v) HNO_3 for ICP-MS analysis and 1:100 in 2% (v/v) HCl for AAS analysis. All chemicals used in the mineralisation and leaching procedure were of analytical grade (Suprapur quality, Merck, Germany). MilliQ+ deionised water from a Millipore system was used for all dilutions.

2.4. Analytical techniques

Determination of Na, K, Ca, Mg, Mn and Fe in both wines and soil leachates was performed by AAS (Varian SpectrAA200 HT, Australia) in an air-acetylene flame under the conditions recommended by the manufacturer. CsCl (99%) was used as ionic supressor for determination of Na and K, $LaCl_3$ (99%) was used as molecular supressor for determination of Mg and Ca. A quadrupole-based ICP-MS (VG Elemental PQ3, UK) was used for determination of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Li, Ni, Pb, Rb, Sr, Sb, Tl, U, V and Zn. Detailed analytical conditions, for measuring isotopes and internal standards are given in Table 2. The P content was determined spectrophotometrically as phosphomolybdenum blue at a wavelength of 820 nm on a CARY 50 instrument (Varian, Australia). Procedural blanks were determined, together with the samples. Certified reference materials NIST 2711 (Montana Soil), NIST 2709 (San Joaquin Soil, Gaithersburg, USA) and Seronorm FE 1114 (Trace Elements Urine) were analysed for quality control of analytical data.

2.5. Statistical data treatment

The data were treated statistically using the programme NCSS 2001 (Hintze, 2001). The correlations between the contents of the elements in the soils and wines were expressed by Pearson correlation coefficients (c.c.). Statistically outlying values of contents in soils and wines were excluded.

For the purposes of multivariate analyses, each of the 31 wine samples was considered to be a vector with 29 variables (element concentration, pH and titrable acidity). Thus, a data matrix with dimensions of 31×29 formed the basis for the correlation matrix, principal components analysis, factor analysis and cluster analysis. Data were prepared for the purpose of transformation of the variables so that their values exhibited normal distribution. The following operations were involved: (a) removal of values lower than the limit of detection (LOD), (b) removal of statistically remote values. Less than ten of the analytical values (two orders higher than the mean value) was removed from a set of approximately 900 values of original data.

Cluster analysis was carried out to discover the similarity of the samples from studied localities. The initial assumption of this analysis is that the nearness of the objects, defined by their variables, reflects the similarity of their properties (Massart & Kaufmann, 1983). The cluster analysis was performed using the following settings: the used linkage type was Ward's Minimum Variance; distance method was Euclidean and scaling method was standard deviation.

The correlation matrix was created from the values of the variables of all 31 wine samples. The *Pair-Wise* method was employed for the missing values.

Principal component analysis (PCA) was carried out to reduce the number of original variables through their linear combinations (principal components) and to discover further dependencies among the original variables (Mardia, Kent, & Bibby, 1979). PCA was performed under the following conditions: the analysis was based on the correlation matrix, with no factor rotation (this is the suggested option for PCA) and the average-value imputation method was used for missing remote values (each missing value is replaced by the average value of that variable).

Factor analysis (FA) was carried out to determine the basic latent data structures (González & Peña-Méndez, 2000). FA was performed using the following settings: the analysis was based on the correlation matrix; the varimax rotation technique was used; the average-value imputation method was applied for missing outlying values (as for PCA) and number of factors was set at four.

3. Results and discussion

Table 3 gives the contents of the elements in wines and soils. The contents of the elements in wines exhibited greater scatter than those in soils, even though the studied soils were formed on various geological basements. A high scatter of the contents of the elements in wines was also described in the literature (Castiñeira et al., 2001; Fournier et al., 1998; González & Peña-Méndez, 2000).

The average contents of the major elements (content >1 mg/l) in the studied wines decreased in the order K > Ca > Mg > P Na > Fe > Mn. The average contents of trace elements (content <1 mg/l) in the studied wines decreased in the order Rb and Al > Cu and Sr Zn > Ba > Pb > Cr > Li > Ni > V > As > Cs > Sb and Co > Cd, U, Be and Ag > Tl. The order of the contents of elements in wines approximately corresponds to the general order of the contents of elements in plants (Kabata-Pendias & Pendias, 1984).

The lower content of Na in Czech wines in comparison with literature data can be attributed to the considerably lower influence of sea salts in Central Europe (Fournier et al., 1998; Frías et al., 2001). For this reason, we suppose Na not to be suitable for geographic origin discrimination. The mean contents of K, Ca, Mg and other studied elements are consistent with the contents given in the literature (e.g., González & Peña-Méndez, 2000; Martin et al., 1999; Šebečić, Pavišić-Strache, & Vedrina-Dragojević, 1998).

All wines had Fe contents below 7 mg/l (mean value was 2.64 mg/l), considered to be the minimum concentration necessary to form ferric cases. Most samples have Cu contents below the 1 mg/l recommended by OIV to prevent formation of cupric cases (Frías et al., 2001). The mean Al content of studied wine samples (0.56 mg/l) is lower than Al concentrations in wines summarised by Šeruga, Grgić, Grgić, and Šeruga (1998).

In contrast to wines, not all of elements could be determined in soil extracts because of the high salt content. The average contents of elements in soils (Mehlich's extract) decrease in the order: Ca > K > Mg > Al > Fe > Mn > Na > P and Sr > Ba > Cu > Zn > Pb > Ni > Co and Rb > Be and Li > Cd > Cs. A similar trend was observed in the pool of exchangeable cations in most non-acidified soils of the Czech Republic (Hofmeister, Mihaljevič, Hošek, & Sádlo, 2002).

The contents of major elements Mg and Ca in soils are strongly influenced by the composition of the parent rocks. It was found that soils from Žernoseky and Most (located on Tertiary basic volcanic rocks) have higher Mg contents in Mehlich's extract, whereas soils of the Roudnice vineyards (located on Cretaceous marlstones) and Karlštejn vineyards (located on Silurian and Devonian limestones) have high Ca contents. This is in agreement with findings of Frías et al. (2001) who described

Table 3
Concentrations of selected elements in wines and soils, pH and total acidity of wines

Wines					Soils				
Element	Unit	Range	Mean	SD	Element	Unit	Range	Mean	SD
Na	mg/l	2–62	14.7	12.7	Na	mg/kg	3.81–478	95.7	139
Mg	mg/l	48.9–108	75.4	16.8	Mg	mg/kg	22.6–916	366	188
K	mg/l	493–3056	1126	601	K	mg/kg	76.6–2143	510	487
Ca	mg/l	47.7–210	108	45	Ca	%	0.045–4.15	0.844	0.882
Mn	mg/l	0.282–3.26	0.925	0.712	Mn	mg/kg	7.69–352	104	73
Fe	mg/l	0.929–5.2	2.64	1.06	Fe	mg/kg	35.2–432	165	112
P	mg/l	0.26–47.3	15.3	13	P	mg/kg	0.116–194	31.7	61.2
Cu	μg/l	12.8–6827	448	1237	Cu	mg/kg	0.48–86	11.7	17.6
Zn	μg/l	33.9–1172	401	252	Zn	mg/kg	0.78–51	9.22	12.4
Be	μg/l	0.05–3.02	0.695	0.813	Be	mg/kg	0.039–0.608	0.284	0.177
Al	μg/l	132–1665	560	387	Al	mg/kg	96.4–626	317	136
V	μg/l	0.015–70.2	12.9	18.8	–	–	–	–	–
Cr	μg/l	27–88.3	58.9	15.9	–	–	–	–	–
Co	μg/l	0.359–5.24	2.07	1.02	Co	mg/kg	0.375–5.24	1.72	1.11
Ni	μg/l	19.8–34.5	26.2	4.12	Ni	mg/kg	0.26–5.56	2.52	1.32
As	μg/l	1.66–15.2	7.08	3.4	–	–	–	–	–
Sr	μg/l	148–895	434	153	Sr	mg/kg	3.62–161	35.9	32.8
Ag	μg/l	0.008–2.77	0.614	0.741	–	–	–	–	–
Cd	μg/l	0.055–3.37	0.78	0.848	Cd	mg / kg	0.006–0.47	0.093	0.086
Sb	μg/l	0.18–29.7	2.26	5.54	–	–	–	–	–
Ba	μg/l	41.6–193	86.1	35.9	Ba	mg/kg	6.01–94.3	26.2	17
Tl	μg/l	0.01–0.515	0.221	0.154	–	–	–	–	–
Pb	μg/l	10.9–1253	67.1	217	Pb	mg/kg	1.1–31.7	8.67	7.16
U	μg/l	0.035–4.9	0.712	1.05	–	–	–	–	–
Li	μg/l	1.16–299	38.2	74.9	Li	mg/kg	0.027–0.938	0.239	0.237
Rb	μg/l	96–2470	702	558	Rb	mg/kg	0.055–4.34	1.23	1.18
Cs	μg/l	0.02–59.3	6.3	12.2	Cs	mg/kg	0.007–0.405	0.069	0.092
pH	Std. units	2.94–3.81	3.44	0.219					
Total acidity	g/l	3.01–8.8	4.65	1.43					

SD, standard deviation.

Mg to be one of the elements useful for discriminating the denomination of wine origin.

Cluster analysis was used to find the similarity of the samples of wines and soils using all of their determined variables as the input data. As shown in Fig. 2, wine samples from Roudnice, Most and Žernoseky are each clustered together, indicating that they are well distinguishable from the others. The wines from Most are further subdivided into groups of white and red wines (Fig. 2(a)). The wines from Karlštejn are also clustered together but also with 3 samples from Mělník as well as the wines from Prague, which are clustered together with 1 sample from Mělník. The cluster analysis of soils from studied localities (Fig. 2(b)) shows that the soil samples are clustered better than the samples of wines: all the localities are well separated from the others with exception of one sample from Roudnice, which is clustered together with the soils from Most.

It was found that only Mg exhibits a statistically significant dependence between its content in soils and in wines (c.c. = 0.616). This means that the Mg content in wine is dependent on its concentration in the vineyard soil and that the source of this element in wine is most probably the vineyard soil. The contents of the other elements in the soils and wines are mutually independent, for two reasons: (i) selectivity of uptake of the individual ions in the soil substrate and the different distributions among the individual parts of the plant: transport of inorganic ions by the plant occurs mainly between the roots and leaves, where metabolic conversion occurs. Transport from roots to fruit is less important (Kabata-Pendias & Pendias, 1984); (ii) elements in wines are derived from sources other than the vineyard soils.

Calcium is present in the largest amounts in the sorption complex of studied soils. The dependence between its contents in the soil and in wine has, however, not been demonstrated, although Ca and Mg are chemically similar elements. For example, their role in photosynthesis in plants has been demonstrated, and both elements catalyse some enzymatic reactions and enter into the cell wall structure (Fournier et al., 1998).

Correlations between the contents of elements in Mehlich's soil complex were also investigated and several statistically significant dependencies ($p < 0.01$ or

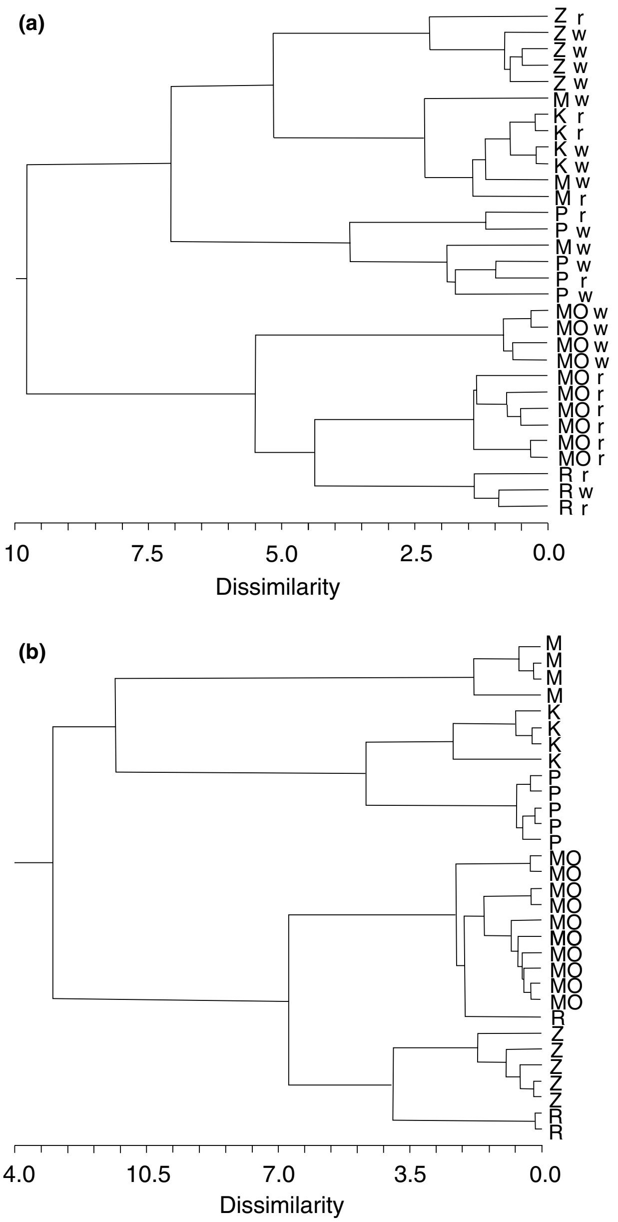

Fig. 2. (a) Dendrograms of the cluster analysis of wine samples; (b) Dendrograms of the cluster analysis of soil samples: r, red wine; w, white wine; P, Prague; K, Karlštejn; R, Roudnice; M, Mělník; Z, Žernoseky; MO, Most.

better) were found. Lithophile elements, such as Ca and Sr, show a very strong correlation (c.c. = 0.819). A similarly close relationship was found between the contents of Li and Be (c.c. = 0.668) and between the contents of Ni and Co (c.c. = 0.718). These facts can be explained by the similar geochemical behaviour of these elements in soils (Kabata-Pendias & Pendias, 1984). In addition, dependencies were found also between the soil content of Zn and P, K and Cu (c.c. between 0.649 and 0.797). It is possible that these dependencies may be caused by the presence of Zn as an admixture in fertilizers or pesticides, whose main components are P, K and Cu.

The correlation coefficients (c.c.) between the contents of elements in wines are given in Table 4. Only correlations with $p < 0.01$ or better, that simultaneously have c.c. > 0.5 and that are not affected by statistically outlying values are discussed. The elements can be divided into several groups on the basis of statistically significant correlations.

(1) The largest group consists of lithophile elements Mg, Mn and Cs, whose contents are mutually positively correlated, and also Sr (correlated with Mg) and Ba (correlated with Mn). Elements in this group are also positively correlated with the contents of some trace elements with very low concentration. Tl and Ag. Mg, Mn and Cs in this group are also positively correlated with Cr and negatively with V.
(2) Cu and As, are positively correlated (c.c. = 0.574).
(3) Be and Al, are positively correlated (c.c. = 0.670).
(4) Pb and K, are negatively correlated (c.c. = –0.557).

The fact that some pairs or groups of elements are significantly correlated indicates either similar ability to enter into the grape, or the existence of the same source. Since the lithophile elements form main components of rocks and corresponding soils, it can be assumed that their origin in wines is entirely or mostly derived from the vineyard soils. Copper and As probably have the same source, e.g., inorganic pesticides applied to the grape vines. The dependence between Be and Al may be explained by similar chemical properties, in particular easy mobilization in acidic media of wines. The reason for a negative correlation between K and Pb contents most probably consists in their antagonistic competition.

Besides the dependencies among elements, a positive correlation between Mg and pH of wine and between the K and pH were also found (Table 4). This is in agreement with the results of González and Peña-Méndez (2000). We assume that this dependence may be associated with the ion-exchange of H^+ from wine organic acids and bentonites. There is also an apparent and comprehensible negative correlation between the pH and the total acidity of wines (c.c. = –0.566).

Because the number of the original variables was very high, PCA was performed to reduce the number of variables and to detect the relationships among the contents of elements in wines. The first six principal components explained 76% of the total variability among the 29 variables, where the first component (PC1) contributed 20% of the total variance and the second component (PC2) contributed 15%. Fig. 3(a) depicts the result of the PCA of wine samples with the individual variables projected onto the PC1–PC2 plane. It is apparent that lith-

Table 4
Correlation coefficients for variables in wines

Na	Mg	K	Ca	Mn	Fe	Cu	Zn	P	Be	Al	V	Cr	Co	Ni	As	Sr	Ag	Cd	Sb	Ba	Tl	Pb	U	Li	Rb	Cs	pH	acidity
Na	0.041	-0.259	**0.485**	0.104	-0.175	-0.294	-0.100	-0.057	0.218	0.405	0.351	0.236	-0.038	0.213	0.078	-0.455	0.129	-0.010	0.389	0.170	-0.097	0.232	0.108	0.456	-0.053	-0.117	-0.192	-0.107
	Mg	0.380	0.117	**0.635**	-0.018	-0.339	0.069	0.070	0.105	0.039	**-0.633**	**0.594**	0.123	**0.475**	-0.157	**0.627**	**0.538**	0.061	**-0.559**	**0.484**	**0.577**	-0.459	-0.259	0.278	0.395	**0.815**	**0.546**	-0.134
		K	0.185	0.134	0.162	-0.020	0.060	-0.182	-0.371	**-0.480**	-0.210	0.016	-0.166	0.300	-0.184	**0.637**	0.300	-0.002	-0.382	0.210	0.195	**-0.557**	0.039	0.040	0.103	0.249	0.534	-0.101
			Ca	-0.002	-0.123	-0.451	-0.191	-0.233	-0.286	0.012	-0.044	-0.095	0.022	0.183	-0.169	-0.102	0.455	-0.025	0.102	0.202	0.064	-0.163	-0.185	0.392	-0.197	-0.207	-0.282	**0.468**
				Mn	**0.500**	-0.326	-0.107	0.206	0.216	0.055	**-0.632**	**0.755**	0.188	0.259	-0.275	0.275	**0.588**	0.030	-0.306	**0.613**	0.356	-0.147	-0.157	-0.026	0.085	**0.571**	**0.495**	-0.360
					Fe	0.313	-0.285	0.034	-0.054	-0.158	-0.355	0.278	0.041	-0.149	-0.018	0.108	0.168	-0.161	0.088	0.167	-0.061	0.196	0.009	-0.229	-0.263	-0.199	**0.515**	**-0.499**
						Cu	0.291	0.097	0.172	0.059	0.516	-0.381	0.307	-0.352	**0.574**	0.036	-0.413	0.197	0.323	-0.123	-0.130	**0.532**	0.376	-0.164	0.027	-0.433	-0.049	-0.254
							Zn	0.092	-0.206	-0.271	0.040	-0.179	0.361	0.001	-0.137	0.087	-0.242	0.425	-0.221	-0.017	0.313	0.128	0.239	0.065	0.257	0.318	-0.232	-0.091
								P	0.357	0.267	0.006	0.161	**0.519**	0.080	-0.101	0.129	-0.189	0.247	0.233	0.208	0.330	0.281	0.053	-0.175	0.110	0.215	0.067	-0.192
									Be	**0.670**	0.216	0.437	0.239	-0.074	**0.560**	-0.125	-0.036	0.093	0.321	0.213	-0.044	0.340	0.164	-0.008	0.318	0.015	-0.026	-0.128
										Al	0.323	0.201	0.139	-0.071	0.368	-0.151	0.005	0.230	0.124	0.315	-0.233	**0.487**	-0.063	0.331	0.242	-0.235	-0.237	0.117
											V	**-0.546**	0.002	-0.164	0.474	**-0.570**	-0.474	0.223	0.490	-0.329	-0.513	0.437	**0.602**	-0.009	-0.135	**-0.682**	-0.411	-0.010
												Cr	0.063	0.312	-0.097	0.171	**0.456**	-0.016	-0.162	**0.467**	0.262	-0.147	-0.184	-0.058	0.086	0.618	**0.518**	-0.451
													Co	0.007	0.021	0.181	0.032	0.338	0.178	0.282	**0.525**	0.262	0.243	0.050	0.138	0.251	-0.250	-0.035
														Ni	-0.236	0.343	0.310	0.034	-0.059	0.374	0.267	-0.400	-0.091	0.219	0.097	**0.585**	0.404	-0.033
															As	-0.043	-0.288	-0.105	0.444	-0.040	-0.162	0.280	0.156	0.178	0.242	-0.358	-0.130	0.042
																Sr	0.289	0.065	-0.417	0.445	0.446	-0.415	-0.199	0.367	0.391	**0.566**	**0.507**	0.035
																	Ag	0.185	-0.321	**0.480**	0.226	-0.417	-0.254	0.247	-0.113	0.358	0.218	0.092
																		Cd	-0.097	0.364	0.285	0.212	0.084	0.113	0.141	0.214	-0.202	-0.001
																			Sb	-0.025	-0.147	0.461	0.256	-0.044	-0.201	-0.429	-0.298	-0.009
																				Ba	0.352	-0.044	-0.198	0.234	0.243	0.447	0.278	-0.003
																					Tl	-0.338	-0.047	0.088	0.169	**0.798**	0.206	-0.100
																						Pb	0.227	0.065	0.038	-0.511	-0.401	-0.120
																							U	0.080	-0.029	-0.128	-0.034	-0.255
																								Li	0.263	0.050	-0.142	0.286
																									Rb	0.435	0.090	0.058
																										Cs	0.391	-0.192
																											pH	**-0.566**

$p < 0.01$.
$p < 0.001$.
$p < 0.0001$.

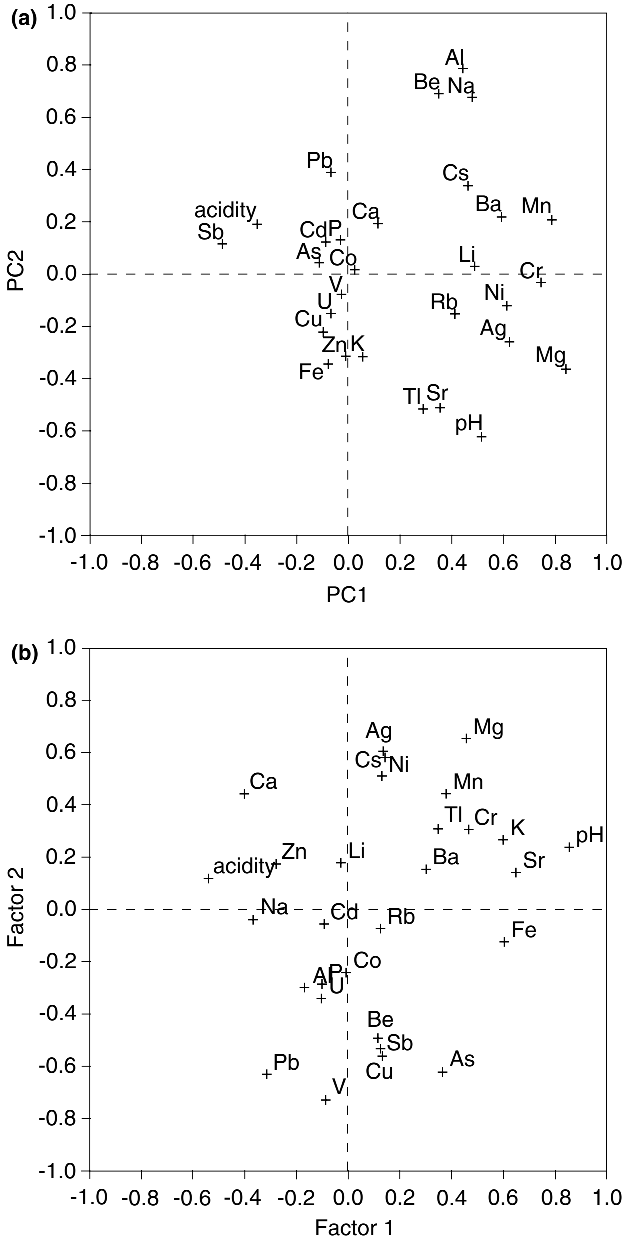

Fig. 3. (a) Loading plot for principal components analysis in wines; (b) Loading plot for first two factors in wines after varimax rotation.

ophile elements, such as Mg, Mn and Ba, predominate in the positive values of PC1. Others, such as Ag, Cs, Li, Sr and Tl, also contribute here which is caused by significant correlations among them (Table 4). On the other hand, the elements from anthropogenic sources (As, Cd, Cu, Pb, V and Zn) show considerably negative values in the PC1, caused by their negative correlations with the mentioned lithophile elements. The greatest effect on PC2 is exerted by Be and Al, which are significantly correlated. It appears that the values of PC1 separate elements that have a single or dominant source in the soil (positive PC1 values) from elements whose sources are affected by human activity (negative PC1 values). However, it is not possible to determine a fact-forming basis for the distribution of the variables according to their contribution to PC2.

The basic structure of the variables in wines was determined using factor analysis (FA). The first four factors explain 55% of accumulated variance of the 29 original variables. Fig. 3(b) depicts the results of factor analysis of the samples of wine at the plane factor 1(F1)–factor 2(F2). The first factor contributes 16% of the total variance and the second factor contributes 12%. It is apparent that the above-mentioned group of lithophile elements (Mg, Mn, Cs and others) are grouped in the positive F1–F2 plane. Factor analysis assigned K, and also pH, to the group of lithophile elements. This indicates that the contents of major lithophile elements (prevalently K and Mg) can also be affected by pH of original must and consequently the pH of wine.

The values of pH and total acidity exhibited opposite extreme values at F1, caused by their decreasing dependence (Fig. 3(b)). On the other hand, Pb and V are located in the negative F1–F2 plane. While positive values of F2 are exhibited by lithophile elements, negative F2 values are exhibited by contaminants derived from atmospheric pollution (Pb, V) or from application of pesticides (Cu, As).

4. Conclusions

Although a statistically significant dependence between the contents in the vineyard soil and wine is exhibited only for Mg, similar transport mechanisms are probably also valid for other lithophile elements (K, Mn, Cs, Cr, Ba, Sr). This group affected the amounts of elements with the lowest contents (Tl, Ag). It was also observed that contents of K and Mg could be affected by the pH of wine.

Principal component analysis and factor analysis indicated that the given data structure may be differentiated according to elements derived from the vineyard soil or elements derived from human activity. Thus, the group of lithophile elements had a single or predominant source in the vineyard soil. Cu and As probably originated from application of pesticides or similar operations. The presence of other trace elements (Cd, Pb) can be attributed to anthropogenic pollution, as also can the V content.

The application of multivariate analyses is essential for treatment of such an extensive data set. It has been shown, in the Czech wine/soils system, that a combination of chemical analysis and statistical treatment is a suitable tool for differentiating sources of elements in wines.

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