UDC 55 **CODEN – GEOME 2** **ISSN 0352 – 1206**

GEOLOGICA MACEDONICA

Geologica Macedonica	Год.	**24**	Број	2	стр.	73–116	Штип	2010
Geologica Macedonica	Vol.		No		pp.		Štip	

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Language editor	Лектура
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Address	Адреса
GEOLOGICA MACEDONICA	**GEOLOGICA MACEDONICA**
EDITORIAL BOARD	**РЕДАКЦИЈА**
Faculty of Natural and Technical Sciences	**Факултет за природни и технички науки**
P. O. Box 96	**пошт. фах 96**
MK-2000 Štip, Republic of Macedonia	**МК-2000 Штип, Република Македонија**
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400 copies	Тираж: 400
Published yearly	Излегува еднаш годишно
Printed by:	Печати:
2ri Avgust – Štip	2ри Август – Штип
Price: 500 den	Цена: 500 ден.
The edition was published in December 2010	Бројот е отпечатен во декември 2010

Photo on the cover: На корицата:

Argillitic alteration, Kadiica, Republic of Macedonia Аргилитска алтерација, Кадиица, Република Мекедонија

Geologica Macedonica	Год.	**24**	Број	2	стр.	73–116	Штип	2010
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aGeologica Macedonica, Vol. **24**, No. 2, pp. 75–86 (2010)
GEOME 2 ISSN 0352 – 1206
Manuscript received: June 15, 2010 UDC: 663.253 : 546(497.714)
Accepted: September 20, 2010

Original scientific paper

TRACE ELEMENTS IN WINES PRODUCED AT HOME IN THE TIKVEŠ AREA

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A b s t r a c t: In this paper the results of the geochemical research of the presence of trace elements (Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V и Zn) in the wines produced at home in the Tikveš area with the application of the methods of ICP-AES and (ETAAS) are shown. The paper also presents the correlations made on the basis the presence of certain trace elements in the soil on which the specified variety of grape wine is grown and the same elements in the wine which is produced from that type of grape. The correlations basically point to the fact that there is no great correlation between the presence of the determined trace elements in the soil and wine produced at home. Namely, these correlations for the determined geochemical pairs are the following: Al_{soil}/Al_{vine} (0.04); As_{soil}/As_{vine} (0.11); Ba_{soil}/Ba_{vine} (0.23); Ca_{soil}/Ca_{vine} (0.02); Cd_{soil}/Cd_{vine}(–0.06); Co_{soil}/Co_{vine} (–0.26); Cr_{soil}/Cr_{vine} (–0.04); Cu_{soil}/Cu_{vine} (0.04); Mg_{soil}/Mg_{vine} (–0.30); Mn_{soil}/Mn_{vine} (–0.40); Na_{soil}/Na_{vine} (0.11); Ni_{soil}/Ni_{vine} (0.03); Pb_{soil}/Pb_{vine} (0.27); The lack of significant correlations between the given geochemical pairs is a result of a few moments such as: (1) the presence of trace elements in the soil is determined up to the depthof 30 см. (2) trace elements in soils are present mainly in the silicate matrix from which the elements are not easily excreted into aqueous solutions. (3) the root system of the grape vine is at a much greater depth of 30 cm.

Key words: wine; geochemistry; elements in traces; correlations

INTRODUCTION

Wine is a drink that is an integral part of the human diet and it has played a significant role in the development of the society, religion and culture. Like any other skill, the production of wine was based on empirical findings, perception of some external phenomena, without getting into the essence of the process. This way of producing wine for centuries until Pasteur opened the doors of science for understanding the processes that occur while producing wine with his book, "Study on Wine" (1866).

The wine as a product of alcoholic fermentation of the must contains a number of compounds, some of which are in the must, while others occurred during the alcoholic fermentation, with the transformation of sugar into some other compounds. All of these compounds enter the geo-chemical composition of the wine, thus defining the quality that is manifested by the organolepthic properties of the wine. For the quality of wine not only qualitative composition is important, but also the quantification of compounds and elements in it. The determination of the geochemical analysis of the composition of wine is made by using analytical methods. Some of these analytical methods are simple and fast, and some are complex and require more time for analysis.

The results concerning the determination of the presence of trace elements in wines that are produced at wineries in the area Tikveš, as in other wine regions in the country, can be found in the works of: Cvetković et al. (2002a); Cvetković et al. (2002b); Cvetković et al. (2002c); Stafilov et al (2009); Karadjova et al. (2007); Karadjova et al. (2004); Cvetković et al. (2001); Tasev et al. (2004, 2006, 2005). Likewise, the results concerning the geological, pedo-genetical and the geochemical characteristics of the region of Tikveš and its wider surrounding can be found in the works of: Boev et al. (2005), Stafilov et al. (2008).

Physical-geographic characteristics of the Tikveš area

Among the valleys in Macedonia which by their position differ from one another, the Tikveš Valley stands out as a separate entity with its geographical, geomorphologic, and the anthropological-geographical features. With an area of 2120 km^2 the region Tikveš occupies a significant part of the territory of Macedonia. The Tikveš valley is constrainedin the southby the Mariovsko-Meglanski Mountains, whose ranges are up to 1700 meters. The mountain heights are also well expressed in the east and west. To the west of the valley is the mountain "Borila" of 1500 meters and in the south is the mountain "Ballina" with 1400 m and Karadak with 750 meters height. This Tikveš valley constrained with mountains is cut by the river Varda on the northern side, in the west by the river Crna Reka, while the river Luda Mara runs through the middle of the valley.

In a narrower geographical sense, the Tikveš valley lies: in the north by the river basin Bregalnica opposite the villages Viničani and Nogaevci and then turns above the villages Gradsko and Dolno Čičevo, then above the villages Sirkovo, Mrzen Oraovec, Fariš, Raec up to the village Nikodin, to the hill Nozhot and up to the village Toplice.

The western boundary of the valley begins from the locality Toplice across the road Gradsko–Prilep to the villages Raec and Drenovo towards the Tikveš Lake. It covers the localities Suva Gora with the surroundings of the villages Begnište, Košani and Dabnište. The area continues southward the villages Vataša, Moklište and the Vitačevo plateau. This section covers the villages of the locality Belgrade with the villages Gorni and Dolni Disan, Prždevo and Demir Kapija. The south side ends with the village Dren.

The East side moves across the river Vardar in the direction of the village Korešnica, cuts the Lipkovska river and goes toward the villages Brusnik and Pepelište, then passes the river Vardar and the railway line Skopje–Gevgelija to the village Ulanici and ends with the mouth of the rivers Vardar and Bregalnica.

Climate

The climate has a great impact on the development of the grapevine in terms of quantity and quality of the grapes. As an important factor in the development of the grapevine, the climate consists of the air temperature, the sunlight, and the humidity of the air currents which are present in a given area. Each of these factors has its own influence upon the grapevine which is seen through the growth of the grapevine, the level of ripening of the fruit and the production of quality ingredients which from grapes pass into vine.

The geographical position and the relief of the Tikvešh area are the main factors which affect the totality of the climate characteristics. The Tikveš area is an area of two intersected climates – continental and Mediterranean. The local mountain climate has less impact.

The influence of the continental climate comes from the north along the Vardar River and the Bregalnica River. As a result, we have short and quite cold periods.

On the other hand, the Mediterranean climate comes from the Aegean Sea in the south along the valley of the river Vardar and it results in warm winters with relatively high temperatures.

The influence of the local mountain climate is limited and if there is any, it is highly felt in the mountain part of the area. Under the influence of these climates a special modification of the Mediterranean climate is produced in this region. As a result, the Tikveš region is rich in vegetation.

Temperature

The grapevine is a domestic plant which can vegetate and live in extremely high temperatures in the areas with warm climate, as is the case in the Tikveš area. This region belongs to very warm areas and this factor has a very favorable influence on the development of viticulture. The mean annual temperature in Kavadarci is 18.9 °C, and 19.5 °C in Demir Kapija. The warmest month in Kavadarci are July and August with an average temperature of 24.7 °C, and the coldest is January with an average temperature of 1,5 °C.

The Tikveš region is characterized by relatively high temperatures, especially during the summer months. The highest temperature of 44.5 °C in the Republic of Macedonia was registered in Demir Kapija on 22.07.1952 year, whereas in Kavadarci it was 41°C. The absolute minimum of the air in Kavadarci was noticed on 27.01.1952 and it was –17°C, and in Demir Kapija it was –22 °C.

The mean number of summer days when the air temperature is over 30 °C for Demir Kapija is 68, and it is a bit less for Kavadarci.

Rainfalls

The largest part of the Tikveš region is characterized by small amounts of rainfall and the territory around Gradsko is considered to be the site with the least rainfall per square meter in the Republic of Macedonia. The mean amount of rainfall is 484 mm in Kavadarci. July and August are the most arid summer months in Kavadarci with the mean monthly amount of 23 to 27 mm.

The average annual days with rainfalls in Kavadarci range from 63 to 112 days. If the total amount of rainfall is divided by the number of rainy days, the average is 5 mm of rain on a rainy day.

Geological characteristics of the Tikveš area

The geological characteristics of the area Tikveš have so far been the subject of research by a growing number of geologists, but the most complete description can be found in the works of Rakićević et al. (1965) and Hristov et al. (1965). Based on these studies made within the development of the basic geological map of the Republic of Macedonia in Tikveš area the litho-stratigraphic sequence has the following order (Fig. 1).

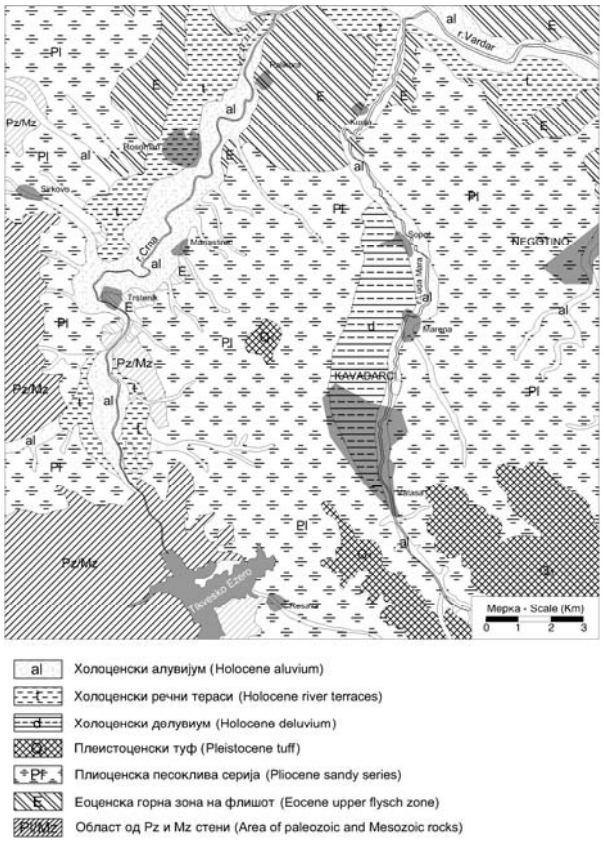

Fig. 1. Geological map of Tikveš area

The oldest formations have northwest-southeast direction delineation (NW-SE) and belong to the inner part of the Vardar zone. The lowest Paleozoic (Pz) metamorphic complex is represented by two series as follows: a series of amphibole and amphibole-chlorite schists with layers of marbles and a series of quartz-schist with quartz-sericite pro-layers of marble and filities. Along the rupture structures in the Vardar zone in the form of elongated tapes and interspersed lenses serpentinities appear. The furthest south-west of the area Tikveš is represented with marbles and dolomites, which are probably of Devonian age.

Through a series of Paleozoic metamorphic rocks developed the Mesozoic (Mz) formations, mainly from the Late Cretaceous age. The Turonian (K2) sandstones, massive conglomerates and limestone extend to the southwest and the west Tikveš of the area. The diabases and the submarines outbursts of spilites are common in the lower parts of this sequence, where also smaller masses of gabbros appear. The Paleozoic and Mesozoic rocks cover nearly 39 km^2 in the southwest and west part of the area Tikveš.

The complex of Tertiary and Quaternary sediments covers most of the Tikveš area. The Upper Eocene (4E3) flysch sediments and yellow sandstones occur along the valleys of the rivers Vardar, Crna River and Luda Mara, as well as in a fraction of the Tikveš basin. These sediments with depth to 3500 m cover about 34 km^2 mainly in the northern part of the Tikveš area.

The Tikveš basin is filled with Pliocene (Pl) sediments, bordering with the Vardar River in the north and the Paleozoic-Mesozoic formation which covers the north-west-southeast. This area is mainly represented by sandy series of different sands. These series are homogeneous, containing mostly yellow sands with low content of coarse sandy clay (pebble sandy clay) and fine-bean gray sandstone, poor in fossil remains. The Pliocene (Pl) sediments cover most (about 182 km^2) of the central part of the area Tikveš.

Southeast of Kavadarci there were Quaternary (Q) pyroclastic volcanites with tuffs, Brecias and agglomerates, which covered around 25 km^2.

The Quaternary period is represented by diluvium (d), river terraces (t) and alluvium (al). The diluvial sediments (12 km^2) contain coarse material from the surrounding rocks, mixed with sand and clay material. Along the rivers Vardar, Crna and Luda Mara terrace sediments are formed (23 km^2). The terraces contain gravel, sand and

clay. Alluvial sediments (40 km^2) cover the flooding plains of the rivers Vardar and Crna and Luda Mara and consist mainly of sand and clay.

Pedo-genetical characteristics of the Tikveš area

The pedo-genetical characteristics of the area Tikveš are shown based upon the detailed pedological description of the present types of soils (Fig. 2):

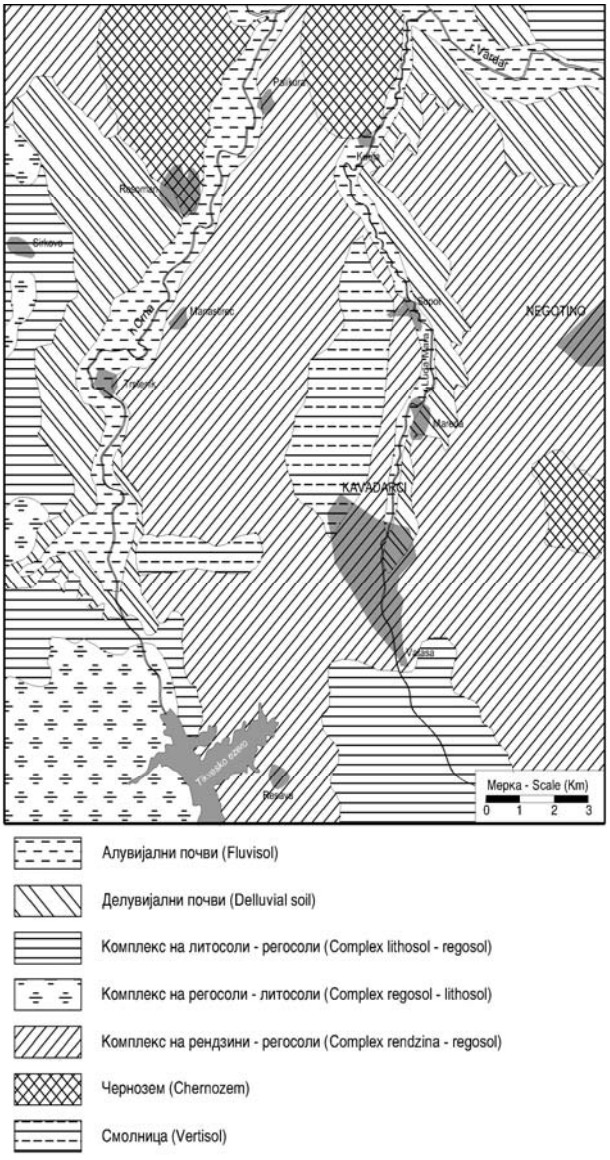

Fig. 2. Pedological map of Tikveš area

Automorphyc soils

Lithosols with the profile type (A)-R1-R2 are developed or poorly developed soils with a maximum depth of 20 cm of the solum, formed on a strong or weak cracked rock. These soils have low productive capacity due to the shallow solum, high skeleton content and low content of clay. These soils have no importance for the agricultural production.

Rogosols with the profile type (A)-C are formed on loose sediments. They are formed by accelerated erosion of the soil profile of previously developed soils with initial pedogenetical processes that lead to the creation of poorly developed horizon (A). These soils are prone to erosion, so we recommend anti erosive safeguards. Regosols are characterized by lower fertility than the neighboring soils from which they were made by erosion.

Soil complex from regosols and litosols in Tikveš appears on the terrains that are characterized by a greater slope, west of the Lake Tikveš in the areas of the villages Debrište, Kamen Dol and Kruševica and northwest up to the village of Dolno Čičevo.

The soil complex of litosols, regosols and renzines appears quite often. Litosols are noted on the highest parts of the ground. Very often on the surface where there is a presence of litosols solid rocks can be notised as well. Regosols appear on fields that are characterized by a slightly larger slope where erosion by the solum is progressively rejuvenating, whereas the rendzinas appear on flat fields and at the foot of the hills where there is an outbreak of frequent change of regosols at small distances. This soil complex is widespread in the area of the village Drenovo, then in the villages Sirkovo, Kamen Dol, Mrzen, Oreovec, Debrište and east of the district Gradsko on the left side of the river Vardar.

Soil complex litosols, regosols and rankers appears on the plateau Vitačevo near Kavadarci. Litosols and rankers are formed on the basis of compact volcanic tuffs, and the regosols are formed by erosion of the humus-accumulative horizon of the rankers.

Diluvial (coluvial) soils are defined as undeveloped and poorly developed soils with the possible (A) or Ar horizon. They have a simple construction of the profile of the type (A)-C. They are formed by erosion and transportation of substrates and soils from higher terrain by means of surface waters and water from torrential streams and modern sedimentation of the such eroded material in the foot parts of the ground. Horizon (A) contains a slightly larger amount of humus horizon than (C), but there are no visible signs of

the formation of structural aggregates. The diluvial soils have large horizontal and vertical (in depth profile) heterogeneity of all properties. In comparison with the alluvial bordering soils they have lower productive capacity.

Renzins are soils with profile of the type-A-AC-C. They are formed upon the bulk silicate-carbonate substrate with a mollic A horizon. The depth of humus horizon is 40 cm it has a dark gray, dark brown to black color with well-expressed structure. The carbonates emerge from the surface or at a certain depth. Most renzins are extensively used in the agriculture and one part of them is under pastures. On a map they are represented as a complex of rendzines and regosols, and a complex of litosols, regosols and rendzines. The complex of rendzines and regosols occupies the largest surface of the Tikveš area. In the vicinity of the village of Dolno Čičevo small areas of cinnamon forest soils and regosoli appear.

Vertisols are loamy soils formed on clay sediments with more than 30% of clay, which gives them a property of swelling (smektites) or on acidic rocks or ultra-acidic rocks whose decay provides larger quantities of clay. Vertisols in the Tikveš area are developed on tertiary clay sediments of a low wave relief with low inclination. They have the type of profile A-AC-C. The soil contains more than 30% of the clay horizon and has vertical properties: prismed cracks and distinctive structure. A horizon has a depth greater than 30 cm and AC horizon is typically 20–30 cm deep. In the Tikveš area thevertisols are isolated as an independent soil type. They prevail in the immediate vicinity of villages Ribarci, Trstenik and Vozarci and north of Kavadarci.

Chernozem is a soil type of the semiarid steppe regions with typical molic A_0 horizon which is thicker than 40 cm and with a front horizon AC (25–0 cm). They contain $CaCO_3$ mostly from the surface and in the lower part of horizon A or AC. The horizon A has well expressed stable grain structure. In the Tikveš area chernozems often contain carbonates from the surface, and in some sections they are washed to some depth in solum. Chernozems were singled out as special pedological units (Fig. 2) north of the village Rosoman, whereas smaller areas are located east of the village Palikura and between the villages Timjanik and Dolni Disan.

Cinnamonic forest soils are soils with a profile of the type Ar-(B)-C or Ar-(B)C-C. They are characterized by the cambic horizon (B), which lies between A and C horizons. Cambic horizon (B) always contains more clay than the A horizon. It is more compact, with reduced capillary porosity, reduced stability of the structural aggregates and reduced presence of water. The production capacity of these soils is not great.

Hydromorphic soils

Alluvial soils are contemporary (recent) river or lake sediment layers, and they can have a horizon (A) or (Ar), and even G. Unlike the diluvial soils they are characterized by good assortment. The suspended materials from which these soils are formed have heterogeneous mineralogical-petro graphic composition. According to mechanical properties they are light soils. The macro structure is poorly expressed, and therefore the physical properties depend on the mechanical composition. They have good water, air and heat regime. They are a very fertile type of soil and they are used for intensive agricultural production. They are represented as an independent soil type along the rivers Vardar, Crna Reka and Luda Mara.

METHODOLOGY OF WORK

The sample of wine (15.0 mL) is placed in a quartz furnace and ethanol is slowly added until the sample reaches a volume of 8 ml, then quantitatively it is placed in 25 ml calibrated volumetric bottle and made up to the mark with concentrated HCl.

Instrumentation

The elements are analyzed through the application of atomic spectrometric method with dual plasma (AES-ICP) and the method of electro thermal spectrometric atomic absorption (ETAAS). With the method of AES-ICP the following elements were also measured: Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. The concentrations of As, Cd, Co, Cr, Ni and Pb in wine samples were below the detection limits of AES-ICP and therefore were analyzed by ETAAS. Instruments such as: Varian 715-ES Series ICP Optical Emission Spectrometer (Varian, USA) and Zeeman ETAAS Varian SpectrAA-640Z were used for the analysis.

OBTAINED RESULTS AND COMMENT

The results of the geo-chemical determination of concentrations of macro elements and trace elements in wines that are produced at home in the Tikveš area by applying the methods of ICP-AES and ETASS are shown in Table 1.

The spatial position of samples taken from the wines produced at home and the correlation between the presence of definite geo-chemical pairs of elements in wines/soils is shown in the images (Figs. 3–8), and statistical parameters are shown in Tables 2 and 3.

Table 1

Concentration of macro elements and trace elements in wines produced at home in the Tikveš area

Samp No.	Sort of vine	Region – attar	Samples of soils lattitude / longitide	Al	Ba	Ca	Cu	K	Mg
				mg/l					
I-1	Kratošija	Debrište-Ramnište	41.459362° / 21.895683°	0.11	0.17	62.23	0.046	851.7	102.87
I-2	Smederevka	Debrište-Ramnište	41.459362° / 21.895683°	0.22	0.11	39.77	0.318	582.6	88.86
I-3	Smederevka	Ljubaš		0.25	0.68	55.73	0.051	742.0	87.87
I-4	Kavadarka	Ljubaš		0.39	0.21	125.15	0.049	895.0	106.71
I-5	Burgundec	Glišicki atar	41.460129° / 22.014170°	0.10	0.06	19.77	0.036	431.0	23.92
I-6	Smederevka	Poroj (nad otpad)	41.453508°/ 21.997288°	0.17	0.08	34.11	0.093	636.8	57.14
I-7	Smederevka	Drenovo	41.432973°/ 21.881231°	0.96	0.15	99.74	0.036	868.0	70.15
I-8	Kratošija	Drenovo	41.432892°/ 21.889044°	0.27	0.10	51.57	0.127	897.2	96.18
I-9	Burgundec	Sirkovo	41.445288°/ 21.907220°	0.55	0.07	22.25	0.020	323.5	26.24
I-10	Rizling	Ribarci	41.507803°/ 21.976810°	2.43	0.10	105.16	0.277	698.5	95.27
I-11	Kratošija	Goligaz	41.445470°/ 21.986805°	0.29	0.22	49.02	1.081	442.1	116.22
I-12	Vranec	Ovcka Reka	41.436889°/ 22.054705°	0.89	0.19	82.09	0.051	983.4	88.19
I-13	Smederevka	Kurii-Lazarica	41.521023°/ 22.023823°	0.87	0.24	81.64	0.058	829.3	87.08
I-14	Kaberne	Sopotsko	41.483175°/ 22.043180°	0.78	0.34	78.40	0.065	1109.4	90.66
I-15	Smederevka	Krivi Dol Resava	41.403094°/ 21.977884°	1.08	0.22	32.12	0.127	748.8	81.15
I-16	Kratošija	Kalnica	41.421496°/ 22.021953°	0.81	0.47	35.66	0.077	819.8	113.34
I-17	Smederevka	Korija-Resava	41.409952°/ 21.977952°	0.26	0.12	43.40	0.009	1002.6	72.63
I-18	Kaberne	Sopot	41.508380°/ 22.006101°	0.44	0.34	85.01	0.034	1115.0	130.52
I-19	Belan	Kopacot	41.418623°/ 22.003520°	0.43	0.16	25.49	0.881	415.3	89.50
I-20	Kratošija	Kurii	41.527615°/ 22.005905°	1.38	0.20	36.99	0.043	1374.3	79.59
I-21	Šardone	Kurii	41.527615°/ 22.005905°	0.96	0.11	26.02	0.030	1253.2	93.60
I-22	Smederevka	Gradevica	41.393553°/ 21.986142°	0.29	0.14	57.67	0.029	606.0	74.54
I-23	Smederevka	Dabnište	41.384672°/ 22.006563°	0.27	0.22	37.81	0.085	813.2	78.53
I-24	Vranec	Begnište	41.358727°/ 21.994742°	0.65	0.09	60.66	0.023	956.1	86.18
I-25	Merlo	Krnjevo (Ploštovo)	41.310944°/ 22.125286°	0.27	0.25	57.87	1.389	805.5	83.90
I-26	Stanešina	Dabnište	41.384672°/ 22.006563°	0.34	0.27	44.87	0.115	824.7	100.37
I-27	Kratošija	Kruška	41.465574°/ 22.044982°	0.65	0.47	47.29	0.031	1174.3	122.32
I-28	Vranec	Moklište	41.387880°/ 22.046183°	0.16	0.38	49.47	0.090	1182.5	66.86
I-29	Smederevka+Kratošija	Rosoman (Konjarovec)	41.520796°/ 21.931591°	0.63	0.18	39.16	0.135	666.9	90.13
I-30	Kratošija	Dolni Disan	41.448101°/ 22.090495°	0.24	0.18	29.79	0.050	778.6	101.88
I-31	Rekaciteli	Krnjevo (Ploštovo)	41.313702°/ 22.125842°	0.19	0.17	35.37	0.184	397.2	87.53
I-32	Kaberne	Krnjevo (Poleto)	41.310946°/ 22.131133°	4.93	0.43	42.10	0.134	1626.4	88.97
I-33	Kratošija	Ljubaš	41.443418°/ 21.987745°	0.35	0.38	48.81	0.079	867.9	113.37
I-34	Smederevka	Belgrad	41.424559°/ 22.041539°	1.09	0.10	43.94	0.874	544.7	82.06
I-35	Belan	Sivec		1.55	0.25	37.59	0.873	571.2	73.03
I-36	Vranec	Palikura	41.527579°/ 21.975896°	1.05	0.16	62.65	0.045	1470.1	88.39
I-37	Smederevka+Temjanuga	Goligaz		0.27	0.10	25.92	0.490	454.5	82.53
I-38	Kratošija	Bel Kamen	41.430558°/ 21.997249°	1.27	0.38	32.85	0.319	883.5	114.85

Table 1. Continue

Sample No.	Sort of vine	Region – attar	Samples of soils lattitude / longitide	Co	Cr	Ni	Pb	Zn
						μg/l		
I-1	Kratošija	Debrište-Ramnište	41.459362° / 21.895683°	1.81	7.18	92.58	81.17	0.31
I-2	Smederevka	Debrište-Ramnište	41.459362° / 21.895683°	7.24	8.65	313.83	<5	0.15
I-3	Smederevka	Ljubaš		2.12	3.09	41.62	80.28	1.12
I-4	Kavadarka	Ljubaš		3.72	7.48	62.71	25.22	0.59
I-5	Burgundec	Glišicki atar	41.460129° / 22.014170°	0.48	1.37	22.18	15.56	0.23
I-6	Smederevka	Poroj (nad otpad)	41.453508°/ 21.997288°	0.84	6.48	60.46	28.09	0.57
I-7	Smederevka	Drenovo	41.432973°/ 21.881231°	2.24	19.70	119.95	53.18	0.23
I-8	Kratošija	Drenovo	41.432892°/ 21.889044°	5.58	13.52	108.52	21.55	0.66
I-9	Burgundec	Sirkovo	41.445288°/ 21.907220°	0.96	<1	23.02	16.42	<0.1
I-10	Rizling	Ribarci	41.507803°/ 21.976810°	10.57	15.06	26.68	36.92	0.35
I-11	Kratošija	Goligaz	41.445470°/ 21.986805°	3.86	8.90	58.19	103.57	0.70
I-12	Vranec	Ovcka Reka	41.436889°/ 22.054705°	3.50	9.81	9.35	18.33	0.78
I-13	Smederevka	Kurii-Lazarica	41.521023°/ 22.023823°	3.38	4.68	11.99	12.61	0.66
I-14	Kaberne	Sopotsko	41.483175°/ 22.043180°	1.39	4.46	17.98	59.09	0.12
I-15	Smederevka	Krivi Dol Resava	41.403094°/ 21.977884°	6.63	21.79	75.89	28.02	0.30
I-16	Kratošija	Kalnica	41.421496°/ 22.021953°	0.58	11.85	23.56	47.42	<0.1
I-17	Smederevka	Korija-Resava	41.409952°/ 21.977952°	0.38	4.84	16.44	<5	<0.1
I-18	Kaberne	Sopot	41.508380°/ 22.006101°	2.79	4.00	6.71	<5	0.13
I-19	Belan	Kopacot	41.418623°/ 22.003520°	1.70	3.21	12.39	22.29	0.26
I-20	Kratošija	Kurii	41.527615°/ 22.005905°	4.84	13.23	10.96	6.38	0.28
I-21	Šardone	Kurii	41.527615°/ 22.005905°	3.10	12.64	<5	<5	0.14
I-22	Smederevka	Gradevica	41.393553°/ 21.986142°	<0.1	22.06	37.19	37.15	<0.1
I-23	Smederevka	Dabnište	41.384672°/ 22.006563°	0.39	5.30	19.17	24.45	0.11
I-24	Vranec	Begnište	41.358727°/ 21.994742°	2.80	6.61	13.09	40.94	0.11
I-25	Merlo	Krnjevo (Ploštovo)	41.310944°/ 22.125286°	0.18	5.41	15.52	66.80	0.33
I-26	Stanešina	Dabnište	41.384672°/ 22.006563°	0.74	12.50	13.10	6.02	0.10
I-27	Kratošija	Kruška	41.465574°/ 22.044982°	3.33	19.82	31.73	218.34	0.77
I-28	Vranec	Moklište	41.387880°/ 22.046183°	<0.1	2.45	33.73	<5	<0.1
I-29	Smederevka+Kratošija	Rosoman (Konjarovec)	41.520796°/ 21.931591°	1.85	10.44	21.21	72.69	0.26
I-30	Kratošija	Dolni Disan	41.448101°/ 22.090495°	0.43	2.71	<5	<5	<0.1
I-31	Rekaciteli	Krnjevo (Ploštovo)	41.313702°/ 22.125842°	<0.1	1.87	<5	218.99	0.24
I-32	Kaberne	Krnjevo (Poleto)	41.310946°/ 22.131133°	2.02	99.53	56.05	26.89	0.04
I-33	Kratošija	Ljubaš	41.443418°/ 21.987745°	1.35	13.16	44.07	54.60	0.90
I-34	Smederevka	Belgrad	41.424559°/ 22.041539°	3.40	8.16	27.29	289.79	0.59
I-35	Belan	Sivec		6.73	30.09	93.29	156.75	0.37
I-36	Vranec	Palikura	41.527579°/ 21.975896°	0.78	12.49	31.84	25.44	<0.1
I-37	Smederevka+Temjanuga	Goligaz		<0.1	4.04	<5	90.70	0.32
I-38	Kratošija	Bel Kamen	41.430558°/ 21.997249°	1.50	18.46	37.26	49.56	0.18

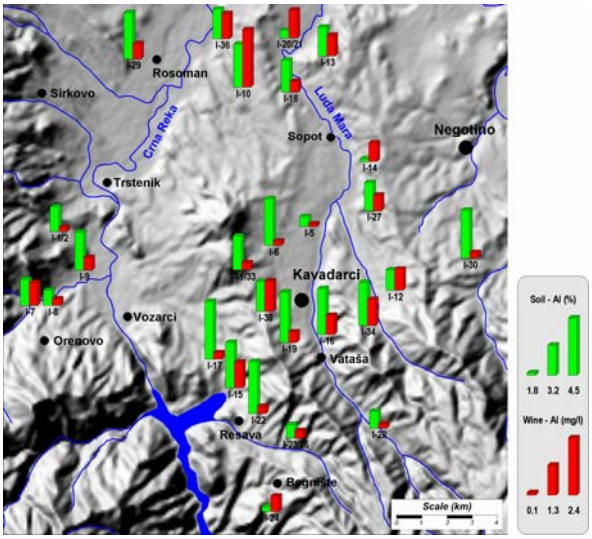

Fig. 3. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Al_{soil}/Al_{vines})

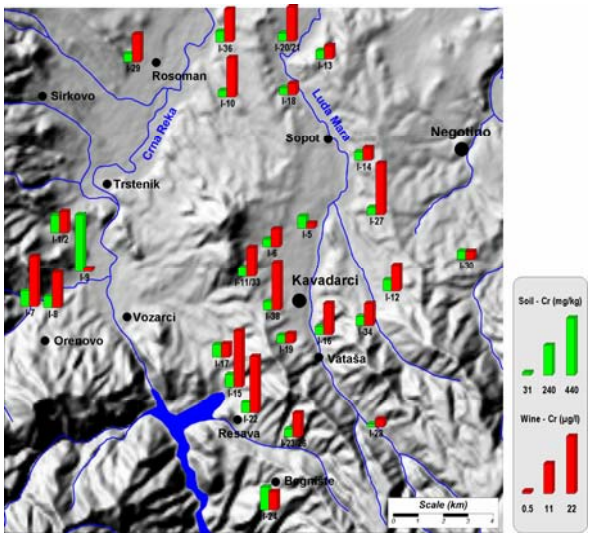

Fig. 6. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Cr_{soil}/Cr_{vine})

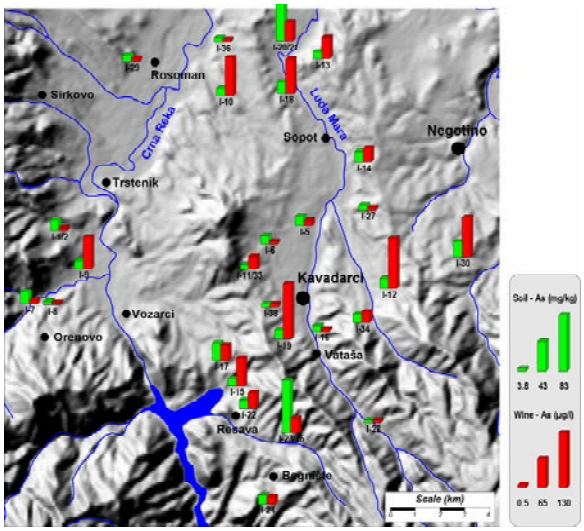

Fig. 4. Spatial position of samples taken from soils and wines and their geo-chemical correlation (As_{soil}/As_{vine})

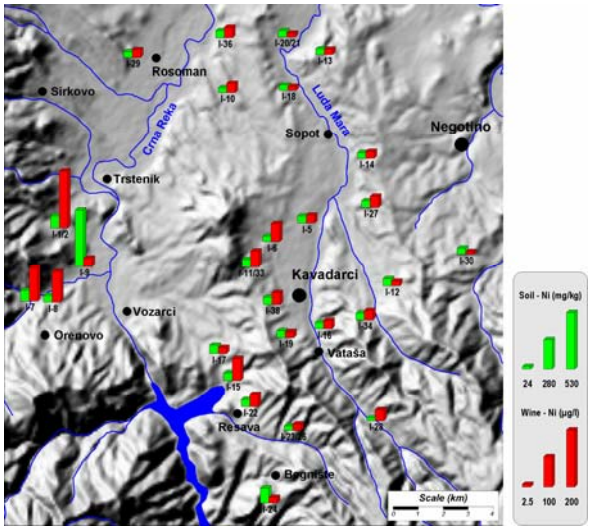

Fig. 7. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Ni_{soil}/Ni_{vine})

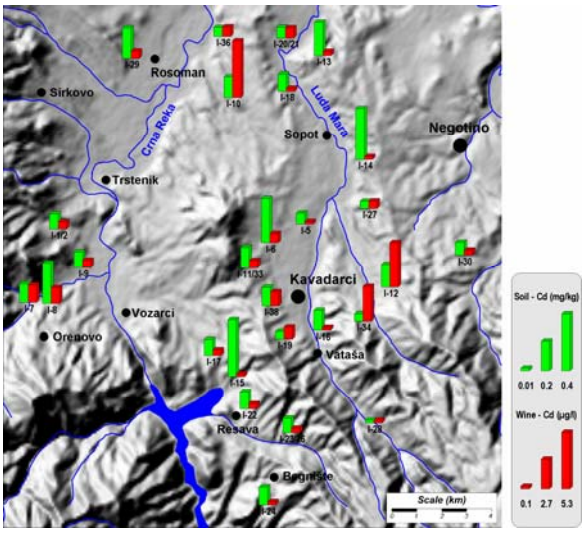

Fig. 5. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Cd_{soil}/Cd_{vine})

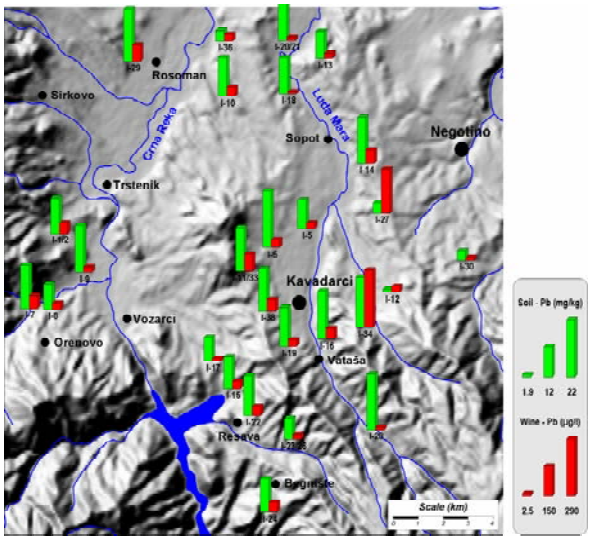

Fig. 8. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Pb_{soil}/Pb_{vine})

Table 2

The statistical parameters of the vine geochemistry

Basic statistical parameters

	X	Xg	Md	min	P10	P25	P75	P90	max	*s*	A	E
Al	0.7700	0.5100	0.5500	0.1000	0.1700	0.2700	0.9600	1.2000	4.9000	0.9100	3.5200	14.9200
As	34.0000	9.9000	28.0000	0.5000	0.5000	0.5000	53.0000	87.0000	130.0000	36.0000	1.0300	0.3800
Ba	0.2200	0.1900	0.1800	0.0580	0.0920	0.1200	0.3400	0.3800	0.4700	0.1200	0.7800	–0.5500
Ca	51.0000	47.0000	47.0000	20.0000	30.0000	34.0000	61.0000	82.0000	110.0000	22.0000	0.9500	0.2800
Cd	0.8700	0.3800	0.4600	0.0500	0.0500	0.1200	0.9200	1.5000	5.3000	1.2000	2.5200	6.3700
Co	2.3000	1.2000	1.7000	0.0500	0.1800	0.5700	3.4000	4.5000	11.0000	2.3000	1.8000	4.4100
Cr	12.0000	7.6000	8.9000	0.5000	2.4000	4.5000	14.0000	20.0000	100.0000	17.0000	4.4800	22.7400
Cu	0.2200	0.0930	0.0790	0.0087	0.0290	0.0360	0.1800	0.8700	1.4000	0.3500	2.3800	4.8700
K	840.0000	790.0000	820.0000	320.0000	430.0000	637.0000	1000.0000	1200.0000	1600.0000	310.0000	0.5300	0.2600
Mg	87.0000	83.0000	88.0000	24.0000	67.0000	81.0000	96.0000	120.0000	130.0000	23.0000	–0.9200	1.9900
Mn	1.4000	1.3000	1.2000	0.4800	0.7400	1.1000	1.5000	1.9000	3.0000	0.5400	1.1300	2.0300
Na	9.5000	5.5000	3.6000	1.0000	2.0000	2.5000	11.0000	20.0000	64.0000	13.0000	3.0700	11.4600
Ni	38.0000	24.0000	24.0000	2.5000	6.7000	13.0000	44.0000	76.0000	200.0000	42.0000	2.5800	7.8600
Pb	53.0000	27.0000	28.0000	2.5000	2.5000	16.0000	55.0000	100.0000	290.0000	68.0000	2.4300	5.6200
Sr	1.1000	0.8200	0.9500	0.1500	0.3500	0.4400	1.4000	2.4000	2.9000	0.7400	0.9700	0.0900
Zn	0.3000	0.1900	0.2300	0.0360	0.0500	0.0500	0.5700	0.7000	0.9000	0.2600	0.9300	–0.4400

Table 3

The statistical parameters of the vine geochemistry

Correlation coefficients

Al	1.00															
As	0.18	1.00														
Ba	0.28	–0.10	1.00													
Ca	0.18	0.11	0.04	1.00												
Cd	0.44	0.37	–0.23	0.44	1.00											
Co	0.33	0.20	–0.17	0.42	0.59	1.00										
Cr	0.88	0.01	0.37	0.01	0.18	0.12	1.00									
Cu	–0.06	0.14	–0.05	–0.08	0.09	0.05	–0.09	1.00								
K	0.50	–0.12	0.50	0.28	–0.01	0.01	0.51	–0.34	1.00							
Mg	0.11	0.04	0.60	0.26	0.05	0.25	0.13	0.14	0.32	1.00						
Mn	0.21	–0.03	0.12	0.55	0.43	0.64	0.10	0.15	0.11	0.52	1.00					
Na	0.03	0.18	0.19	0.26	0.02	0.01	–0.07	–0.09	0.11	0.38	–0.02	1.00				
Ni	0.01	–0.38	–0.11	0.10	0.01	0.31	0.20	–0.03	–0.03	0.01	0.24	–0.30	1.00			
Pb	–0.03	–0.25	0.08	–0.07	0.19	0.04	–0.03	0.35	–0.24	0.20	0.07	0.16	–0.04	1.00		
Sr	0.07	–0.11	0.51	0.28	–0.09	0.19	0.01	–0.05	0.39	0.72	0.44	0.39	–0.19	0.07	1.00	
Zn	–0.14	0.02	0.03	0.17	0.33	0.37	–0.10	0.24	–0.16	0.26	0.27	0.02	0.12	0.37	0.09	1.00
	Al	**As**	**Ba**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Sr**	**Zn**

From the presented results concerning the correlation between the presence of the macro elements and trace elements in soils and wines that are produced at home in Tikveš we can conclude that there is no marked correlation in certain element pairs. The lack of significant correlation between analyzed soils analysis and analyzed wines should be explained by the small number of samples that are the subject of the research, as well as through the very processes of concentration of the micro-elements in wines.

On the other side, another interesting part are the correlations which refer to the concentration of respective trace elements in the wines produced at homes, and the wines produced at the wineries in the Republic of Macedonia.

The pictures 9 and 13 show the concentrations of As (Fig. 9) and the concentrations of Pb (Fig. 13) from where it can be noted that there are higher concentrations of these two elements in the wines produced at home in relation to the wines produced at the wineries (Tašev et al. 2005, Karadzova et al. 2007) with an exception of the wine vranec and the content of Pb which is nearly identical to both wine types.

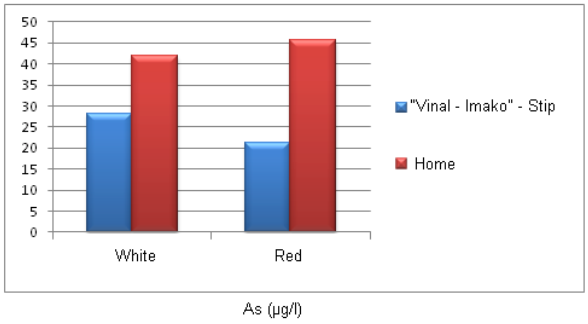

Fig. 9.

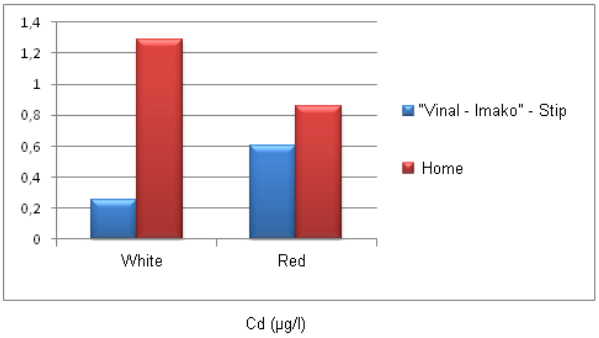

Fig. 10

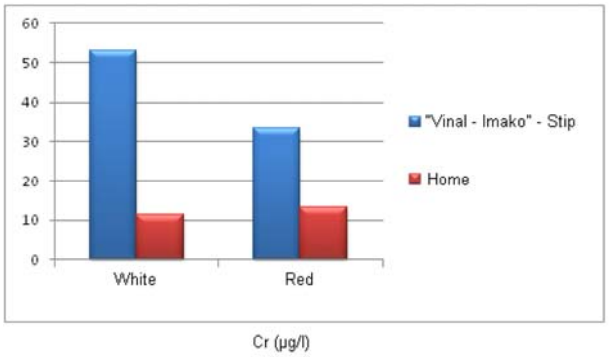

Fig. 11

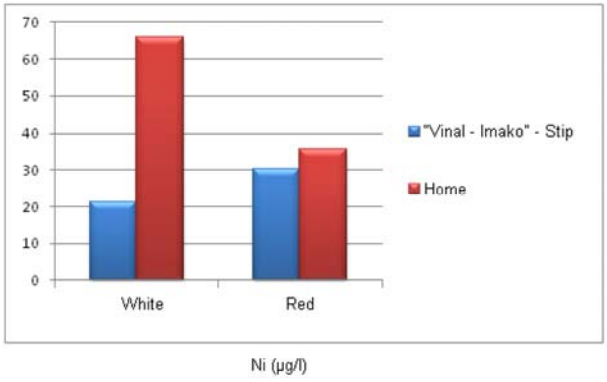

Fig. 12.

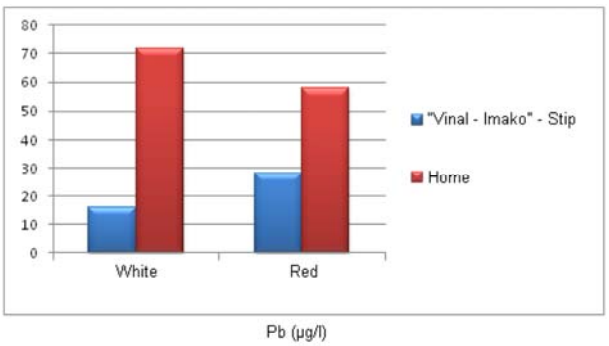

Fig. 13

Fig. 9–13. Correlationsof trace elements concentration in the wines produced at homes, and the wines produced at the wineries in the Republic of Macedonia

Figure 11, 12, 13 shows the relation of the contents of Cd, Ni, Cr in the white and red wine produced in home conditions and in the conditions at the Tikveš winery. From this picture it can be concluded that we have bigger concentrations of Cd and Ni in the white and red wine produced in home conditions in relation to the wines produced in the winery. It should be noted that this trend of bigger concentrations of the elements in the wines produced in home conditions does not follow the concentration of Cr.

CONCLUSION

The studies made about the presence of trace elements in wines produced at home in Tikveš suggest the following conclusions:

– The presence of trace elements such as As, Pb, Cd, Ni is higher in wines produced in home conditions in relation to the presence of these trace elements in wines produced in industrial conditions.

– There are no correlations between the presence of trace elements in wines produced at home and the elements that are present in soils.

The non-existence of correlations between element pairs (N_{soil}/N_{vine}) is the result of: the small depth at which samples are taken from the soil (30 cm): the presence of trace elements in soil is mainly in the silicate structure from which it is very difficult to perform the excretion the elements: the root systems of grape vine are very deep.

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Р е з и м е

МИКРОЕЛЕМЕНТИ ВО ВИНАТА ПРОИЗВЕДЕНИ ВО ДОМАШНИ УСЛОВИ ВО ТИКВЕШКО

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Кеs њордс: вино; геохемија; микроелементи; корелации

Во овој труд се прикажани резултатите од геохимиските истражувања на присуство микроелементи (Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V и Zn) во винаta произведени во домашни услови во Тиквешко со примената на методите на ICP-AES и (ETAAS) Во трудов се прикажани и корелациите направени врз основа на присуство на некои микроелементи во почвата на која се одгледува одредената сорта на грозје и истите елементи во виното кое се произведува од таков вид на грозје. Корелациите во главно укажуваат на фактот дека не постои голема поврзаност помеѓу присуството на одредени микроелементи во почвата и виното произведено во домашни услови. Имено, овие корелации за испитувањето на определена геохимиски парови се следните: $Al_{почва}$ / $Al_{вино}$ (0.04); $As_{почва}$ / $As_{вино}$ (0.11); $Ba_{почва}$ / $Ba_{вино}$ (0.23); $Ca_{почва}$ / $Ca_{вино}$ (0.02); $Cd_{почва}$ / $Cd_{вино}$ (–0,06); $Co_{почва}$ / $Co_{вино}$ (–0,26); $Cr_{почва}$ / $Cr_{вино}$ (–0,04); $Cu_{почва}$ / $Cu_{вино}$ (0.04); $Mg_{почва}$ / $Mg_{вино}$ (–0,30); $Mn_{почва}$ / $Mn_{вино}$ (–0,40); $Na_{почва}$ / $Na_{вино}$ (0.11); $Ni_{почва}$ / $Ni_{вино}$ (0.03); $Pb_{почва}$ / $Pb_{вино}$ (0.27); што укажува на дека отсуството на значајни корелации помеѓу дадените геохимиски парови е резултат на неколку моменти како што се: (1) присуството на микроелементи во почвата на длабочина до 30 cm. (2) микроелементите во почвата се присутни претежно во силикатна матрица од која елементи не можат лесно да се издвојуваат во водни раствори. (3) на кореniот систем на винова лоза кој е во многу поголема длабочина од 30 cm.