ENIGMA 2nd INTERNATIONAL WORKSHOP

GIS-GEOINDUSTRY, s.r.o., Czech Republic CEI Know-how Exchange Programme

2nd INTERNATIONAL WORKSHOP

Environmental impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)

Prague, 16th May 2014

PROCEEDINGS

CEI CENTRAL EUROPEAN INITIATIVE CEI Know-how Exchange Programme (KEP)

Edited by: J. Šimek & H. Burešová

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CENTRAL EUROPEAN INITIATIVE
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ON THE PROJECT

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CONTENTS

TRACE ELEMENTS IN SOILS AND VINE FROM TIKVES AREA-REPUBLIC OF MACEDONIA

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Abstract: The paper presents the research of the presence of elements in traces Al, Ba, Ca, Cu, K, Mg, Mn, Na, Sr, As, Cd, Co, Cr, Ni, Pb, Zn in the soil of the Tikves area and the wine which is produced from the grapevine grown on those soil. The determination of the presence of elements in traces is made according to the method ICP-AES, ETASS. Due to the quantity in the graphic interpretation (maps of correlation between wine/soil) in the paper only the graphic interpretations for the elements NI, Cu, As are presented.

Key words: wine, soil, elements in traces, Tikves

Introduction

Vineculture and wine in Tikves area have a rich historical past and long tradition. They constitute the core industries of the population of the whole region.
The history of vines in this region goes back to more than two millennia, and that something can be seen from the numerous remnants of the past (archaeological artifacts in archeological sites such as: Stobi Eudarist, Belgrade, Antigone, Demir blackberry etc. .), written documents, photographs, stories, as well as folk songs, customs and other works (Cvijich, 1906).
Ancient Macedonians who lived in these areas with great love and piety cultivated this culture, and the god of wine was one of the most desirable deities. Grapes and wine were cult food items that are used during celebrations. Today in the area around Tikves can still be found numerous archaeological artifacts with representations of grapes and vines. But an even greater number of archaeological artifacts that were taken in the past of this region today are in the museums in Belgrade, Sofia and elsewhere.

Viticulture as an important branch of agriculture continued to flourish in the Middle Ages as witnessed by numerous entries from many historians and travel writers, but three miniatures from the middle of X century found in this region present the three stages of processing the grapevine. During the early Middle Ages in the cultivation of vines of great importance was the application of the "Codex Kotor " by which with the law it was regulated the cultivation of this crop , and non-compliance with these provisions was punishable by law . In the second half of the XVI century when the territory of Tikves was ruled by the brothers Dejanovik, twenty villages with fields and vineyards were donated to the Mount Athos monasteries Hilendar and Panteleimon. It should be noted that in the Middle Ages the best producers of grapes and wines were at the monastery property, and the method of preparing the wine was kept in an utmost secrecy. Today, when we talk about viticulture in Macedonia, it immediately reminds us of the Tikves area, the Tikves grapes and wine which is mentioned in numerous native Macedonian folk songs. Today the Tikvesh wine area is one of the most important, both in Macedonia and the Balkans (Elenov, 1986) .

Results which refer to the determination of the elements in tarces in the wine produces in the winetrade in Tikves area, as well as the rest of the wine regions in Republic of Macedonia can be found in the papers by: Julijana Cvetkovic, Sonja Arpadjanb, Irina Karadjova, Trajce Stafilov. (2002), Trajče Stafilov, Irina Karadjova (2009), Irina Karadjova, Julijana Cvetkovic, Trajce Stafilov, Sonja Arpadjan (2007), Irina Karadjova, Sonja Arpadjan, Julijana Cvetkovic and Trajce Stafilov (2004), Julijana Cvetković, Trajče Stafilov, Dragan Mihajlović (2001), Krste Tasev, Iirina Karadjova, Sonja Arpadjan, Julijana Cvetkovic, Trajce Stafilov (2004, 2006, 2005). Also, the results which refer to the geological, pedo-genetical and geo-chemical characteristics in the region Tikves and its surrounding can be found in the papers by: Blazo Boev *et all* (2005) and Trajce Stafilov *et all* (2008).

Applied methodology

Terrain methods of research

Field research methods are very important research activity of which depends greatly on further research results, and of course the performance of the final conclusions. In this Master work these methods are renamed in full in order to:

- detailed insight on the field that is the subject of research,,
- drafting outreach activities,
- sampling of soils while GPS positioning, packaging and labeling samples,
- photographing the developed profiles in soil horizons from which the samples are collected,
- record owners of vineyards whose grapes are collected soil samples and samples of wines,
- sampling of wines are produced at home conditions, packinglabeling.

Collection of soil samples

The collection of soil samples was done in accordance with generally accepted methodologies for work, as the methodology FOREGS (methodology for the geochemical map of Europe). In line with this work the following was accessed:

• Making pedological profile for detailed analysis of the parameters of Pedological account. For this purpose a profile in depth of 1.5 meters was developed for a detail recognicion of all the elements that are necessary when taking soil samples from the aspect of determination of the presence of macroelements and trace elements (Fig. 1).

• Sampling of soils to a depth of 40 cm as the optimal horizon which is important for determination of the presence of macroelements and trace elements (Fig. 8).

• Each sample of soil is a set of five separate trials, taken at a distance of 10 meters from the central point.

Picture 1. Collection of individual soil samples

Laboratory methods of research

For the realization of the set goals, in the Master thesis the following methods of laboratory research were applied:

- Preparation of soil samples for geochemical and wine pursuits representation makroelementite and trace elements (ISO-14507);
- Preparation of samples of soil and wine, according to ISO-11466;
- Determination of the makroelements and trace elements by applying the methods of ICP-AES and ETASS.

Instrumentation

The researched elements are analysed by applying the atomic emission spectrometric method with double plasma (AES-ICP) and the method of electrothermal spectrometric atomic absorption (ETAAS). With the method of AES-ICP the following elements were simultaneously measured: Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V и Zn. The concentration of As, Cd, Co, Cr, Ni и Pb in the samples of wine were lower than the limitations of detection of AES-ICP and therefore they were analysed ETAAS. The instruments like: Varian 715-ES Series ICP Optical Emission Spectrometer (Varian, USA) and Zeeman ETAAS Varian SpectrAA-640Z were used for the analyses. The optimal instrumental parameters for the two techniques are presented in Tables 1 and 2.

Table 1. Instruments and conditions for work of ICP-AES system (Varian, 715ES)

RF Generator	
Operating frequency	40.68 MHz free-running, air-cooled RF generator
Power output of RF generator	700–1700 W in 50 W increments
Power output stability	Better than 0.1%
Introduction Area	
Sample Nebulizer	V- groove
Spray Chamber	Double-pass cyclone
Peristaltic pump	0-50 rpm
Plasma configuration	Radially viewed
Spectrometer	
Optical Arrangement	Echelle optical design
Polychromator	400 mm focal length
Echelle grating	94.74 lines/mm
Polychromator purge	0.5 L min^{-1}
Megapixel CCD detector	1.12 million pixels
Wavelength coverage	177 nm to 785 nm

Conditions for program			
RFG Power	**1.0 kW**	**Pump speed**	25 rpm
Plasma Ar flow rate	**15 L min^{-1}**	**Stabilization time**	30 s
Auxiliary Ar flow rate	1.5 L min^{-1}	Rinse time	30 s
Nebulizer Ar flow rate	0.75 L min^{-1}	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

Element	**Wavelength**	**Element**	**Wavelength**	**Element**	**Wavelength**
Al	396.152 nm	Cr	267.716 nm	Na	589.592 nm
As	188.980	Cu	324.754 nm	Ni	231.604 nm
Ba	455.403 nm	Fe	238.204 nm	Pb	220.353 nm
Ca	370.602 nm	K	769.897 nm	Sr	407.771 nm
Cd	226.502	Mn	257.610 nm	Zn	213.857 nm
Co	230.786 nm	Mg	279.553	V	292.401

Table 2. Optimal instrumental parameters for ETAAS determination of Varian SpectrAA-604Z

Parameter	As	Cd	Co	Cr	Ni	Pb
Wavelength	193.7 nm	228.8 nm	242.5 nm	357.9 nm	232.0 nm	283.3 nm
Spectral width slit	0.2 nm	0.5 nm	0.2 nm	0.2 nm	0.2 nm	0.5 nm
Calibration mode	Peak area					
Lamp current	10.0 mA	4.0 mA	7.0 mA	7.0 mA	4.0 mA	5.0 mA
DRY						
Temperature	120 °C	120 °C	120 °C	120 °C	120 °C	120 °C
Ramp time	55 s	55 s	55 s	55 s	55 s	55 s
Hold time	-	-	-	-	-	-
PYROLYSIS						
Temperature	1400 °C	250 °C	750 °C	1000 °C	900 °C	200 °C
Ramp time	10 s	5 s	5 s	10 s	5 s	5 s
Hold time	37 s	22 s	22 s	30 s	22 s	22 s
ATOMIZING						
Temperature	2600 °C	1800 °C	2300 °C	2600 °C	2400 °C	2100 °C
Ramp time	0.6 s	0.8 s	1.1 s	1.2 s	1.1 s	1 s
Hold time	2 s	2 s	2 s	2 s	2 s	2 s
CLEANING						
Temperature	2600 °C	1800 °C	2300 °C	2600 °C	2400 °C	2100 °C
Time	2 s	2 s	2 s	2 s	2 s	2 s
Ramp time	-		-	-	-	-
SHEATH GAS	Argon					

Reagents and standars

Stock solutions (11355-ICP Multi Element Standard IV, Merck) of 23 elements with concentration of 1.000 mgL^1 was used for further dissolvement. The condtions for work are prepared according to the conditions for dissolvement of 1 molar nitrogen acid. All chemical reagents are of the analytical category: hydro-fluor acid p.a. (Fluka, Germany); perchloric acid p.a. (Alkaloid, Macedonia); hydro-chloric p.a. (MERCK, Germany) and nitrogen acid p.a. (MERCK, Germany). The used containers were previously washed by washing of 24 hours in proportion 1 part of HNO_3 and 3 parts HCl, followed by washing with double destilled water.

Sample of soil and preparation of soil sample

All soil samples were air dried . The whole material was spread in a layer not thicker than 15 mm, the surface that does not absorb moisture from the soil and causes contamination . It is important direct sunlight was avoided. If the samples are dried in lumps , it is necessary to be broken . Before crushing the rocks should be removed , the debris , glass and trash that are larger than 2 mm by sieving or manual . Care should be taken to minimize the portion of the material of the individual stones . After drying , the soil samples are crushed and broken .

Procedure for preparation of samples of soil for chemical

Exact weight of 0,500 g of the drained sample of soil and placed in a PTFE digestion vessel,with added 10 mL nitric acid. The container is placed on the asbestos plate 100 ˚ C and about 1 mL of the rest of the nitrogen acid is added. It is noticed that several successive passes of nitric acid may be necessary until the issue is no more distracting than the organic matter.

After the last addition of nitrogen acid, the container from the hot plate is removed and cooled to a room temperature prior to making the digestion. After the cooling 10 mL of hydrochloric acid and 3 mL of perchloric acid are added. The mixture is heated on a hot plate until it tickensi and stops evaporation of the perchloric acid and silicon tetrafluiorid. The mixture should not be dried completely. The container is lifted from the hot plate and cools, and 2 mL of hydrochloric acid and 2 mL of nitric acid are added and about 5 mL of water to balance rest. The solution is transferred quantitatively to 50 mL volumetric bottle and it is filled up to the labeling and stirred well.

Procedures for preparation of a wine sample

The sample of wine (15,0 mL) is placed in a quartz furnace and slowly ethanol is added until the sample reaches a volume of 8 mL. Then quantitatively it is placed in 25 mL volumetric bottle and stabilized with concentrated HCl.

Obtained results and comment

The results for the presence of trace elements in soils are shown in Table 3 and the results for the presence of trace elements in wine are shown in Table 4 th The results indicate an increased prevalence of correlativity between Ni in soils and wine (Fig. 2) , and Cu (Sl.3), and the content of As (Sl.4). The correlation with the contents of Ni and As in soils and wine can be explained by the large contamination of soils with arsenic and nickel due to metallurgical activity in the region , while the correlation with the contents of Cu can be explained by the long-lasting use of funds protection of grapevine which themselves have higher concentrations of copper .

Table 3. Concentratios of the trace elements in the soil fof Tikves area

Probe	Al (mg/kg)	As (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co(mg/kg)	Cr(mg/kg)	Cu(mg/kg)
1	29136	14,6	250,5	18912	0,1	21,2	144,3	31,0
2	21881	13,8	341,3	15755	0,1	17,3	99,8	22,8
3	39775	12,5	425,3	49579	0,3	15,9	68,0	35,5
4	29673	17,0	265,5	39903	0,1	17,3	130,0	27,7
5	24341	4,8	235,5	83053	0,3	12,5	97,2	36,9
6	35846	11,5	244,9	11531	0,1	37,6	442,4	25,1
7	37994	11,5	282,9	70535	0,1	13,4	59,6	11,3
8	32709	1,2	460,4	35912	0,2	14,9	77,4	27,5
9	27095	14,7	274,8	18722	0,2	16,6	93,3	26,9
10	31059	9,9	299,6	48398	0,2	12,2	76,3	12,8
11	18543	14,7	405,1	9140	0,2	14,4	76,2	22,4
12	17978	14,0	266,3	15108	0,5	11,0	71,9	18,5
13	39148	10,1	233,2	85519	0,4	15,5	105,8	17,5
14	39346	8,6	374,3	30745	0,1	17,1	70,5	30,2
15	44972	25,4	319,3	62644	0,1	18,7	107,0	29,5
16	32424	17,1	422,9	25952	0,1	14,6	61,6	13,4
17	41469	14,1	357,6	65030	0,0	16,3	69,9	18,2
18	20671	83,0	526,8	11124	0,1	13,2	69,9	21,7
19	42465	13,0	320,7	71886	0,1	17,7	88,5	36,2
20	23555	78,0	445,0	19955	0,1	11,4	69,2	25,5
21	19333	12,8	236,4	17513	0,1	18,4	182,2	43,8
22	30501	9,5	200,0	20254	0,0	25,8	155,2	27,5
23	30629	7,4	300,7	35033	0,0	14,4	65,8	20,5
24	25099	3,8	717,7	16734	0,0	11,1	30,6	12,8
25	39369	8,7	269,1	59715	0,2	16,1	71,8	19,8
26	40570	21,9	262,7	65629	0,1	15,5	74,7	16,3
27	26426	6,2	145,1	17179	0,0	26,9	166,8	30,2
28	28387	5,1	267,9	24982	0,0	21,9	127,9	26,6
29	35244	13,1	295,0	61618	0,1	15,4	67,7	31,8
30	37865	12,5	372,4	42831	0,0	19,0	77,5	27,2
31	31372	6,0	228,6	88862	0,1	13,3	91,8	12,8
32	31477	4,4	300,4	67769	0,1	17,4	72,1	46,3
33	24719	11,9	225,0	70201	0,1	17,4	104,6	18,9
Min	17978	1,2	145,1	9140	0,0	11,0	30,6	11,3
Average	30854	15,1	315,2	40790	0,1	16,8	99,9	24,6
Max	44972	83,0	717,7	88862	0,5	37,6	442,4	46,3

Table 3. Concentratios of the trace elements in the soil fof Tikves area (continue)

K(mg/kg)	Mg(mg/kg)	Mn(mg/kg)	Na(mg/kg)	Ni(mg/kg)	Pb(mg/kg)	Sr(mg/kg)	Zn(mg/kg)
14433	12371	526	4879	112,0	13,8	53,0	61,2
13820	10357	651	7930	65,2	11,3	87,2	65,7
14092	7806	565	7956	50,6	22,0	204,0	43,6
14878	5579	539	4551	99,8	16,6	66,1	55,2
12308	3769	435	4532	64,2	10,2	109,6	40,2
10897	23195	794	4957	528,5	18,2	76,2	60,7
10924	7954	450	7214	42,0	15,3	137,0	37,7
13850	6645	492	8026	76,3	23,8	206,0	43,1
11774	9142	509	7373	66,0	1,9	54,3	48,7
10755	5093	439	6983	52,6	10,8	123,7	33,2
13627	8962	606	9420	50,3	24,2	135,1	57,5
12514	8174	516	7336	49,3	11,8	48,9	40,2
11120	7267	574	4669	71,1	12,8	100,6	37,7
14005	12606	660	8611	56,9	18,5	147,6	64,2
13472	10648	637	4596	78,4	9,7	94,6	55,1
13275	9520	616	8939	47,0	14,3	145,0	41,0
12862	13574	553	5741	57,6	15,5	188,8	46,6
14228	9289	547	10451	56,7	17,2	165,7	42,7
13761	10663	616	6564	65,5	15,6	131,8	58,3
16258	7857	397	11009	41,3	8,6	99,4	35,8
10147	8152	542	3385	139,1	13,4	40,9	72,4
4980	13387	700	6061	82,2	19,0	79,1	50,2
12302	8429	536	8427	52,5	4,6	85,8	42,6
19038	8291	480	13975	24,0	21,5	401,6	35,4
12975	17681	600	10088	50,4	20,0	185,8	49,4
11861	10510	568	9426	55,7	4,3	173,5	55,8
4187	10598	695	4031	96,1	24,9	65,7	49,8
8426	11764	646	7586	64,0	14,2	154,8	49,3
12617	10058	593	5637	57,2	10,0	124,9	54,1
14167	13121	651	6886	61,1	19,4	119,6	55,8
8778	5652	491	5990	65,9	4,7	198,2	36,1
13465	9965	703	6059	66,5	16,3	168,6	59,3
9079	9696	583	5446	104,9	13,3	190,3	43,3
4187	3769	397	3385	24,0	1,9	40,9	33,2
12031	9751	568	7003	78,7	14,1	129,5	48,7
19038	23195	794	13975	528,5	24,9	401,6	72,4

Table 4. Concentration of the trace elements in vine from Tikves area

Probe	Al, mg/l	Ba, mg/l	Ca, mg/l	Cu, mg/l	K, mg/l	Mg, mg/l	Mn, mg/l	Na, mg/l
1	0,11	0,17	62,23	0,046	851,7	102,87	1,09	1,09
2	0,22	0,11	39,77	0,318	582,6	88,86	1,31	3,70
3	0,10	0,06	19,77	0,036	431,0	23,92	0,69	1,05
4	0,17	0,08	34,11	0,093	636,8	57,14	1,19	3,49
5	0,96	0,15	99,74	0,036	868,0	70,15	2,39	2,93
6	0,27	0,10	51,57	0,127	897,2	96,18	1,95	1,82
7	0,55	0,07	22,25	0,020	323,5	26,24	0,51	2,04
8	2,43	0,10	105,16	0,277	698,5	95,27	3,00	6,39
9	0,29	0,22	49,02	1,081	442,1	116,22	2,22	1,71
10	0,89	0,19	82,09	0,051	983,4	88,19	1,15	10,62
11	0,87	0,24	81,64	0,058	829,3	87,08	1,04	25,35
12	0,78	0,34	78,40	0,065	1109,4	90,66	1,23	5,79
13	1,08	0,22	32,12	0,127	748,8	81,15	1,34	3,20
14	0,81	0,47	35,66	0,077	819,8	113,34	1,88	2,83
15	0,26	0,12	43,40	0,009	1002,6	72,63	1,20	2,13
16	0,44	0,34	85,01	0,034	1115,0	130,52	1,84	63,91
17	0,43	0,16	25,49	0,881	415,3	89,50	1,11	2,24
18	1,38	0,20	36,99	0,043	1374,3	79,59	1,38	11,82
19	0,96	0,11	26,02	0,030	1253,2	93,60	1,05	9,23
20	0,29	0,14	57,67	0,029	606,0	74,54	0,95	2,54
21	0,27	0,22	37,81	0,085	813,2	78,53	0,46	5,77
22	0,65	0,09	60,66	0,023	956,1	86,18	1,21	3,60
23	0,27	0,25	57,87	1,389	805,5	83,90	1,23	3,20
24	0,34	0,27	44,87	0,115	824,7	100,37	1,97	12,90
25	0,65	0,47	47,29	0,031	1174,3	122,32	1,90	4,28
26	0,16	0,38	49,47	0,090	1182,5	66,86	0,74	2,62
27	0,63	0,18	39,16	0,135	666,9	90,13	1,12	19,88
28	0,24	0,18	29,79	0,050	778,6	101,88	1,46	3,46
29	0,19	0,17	35,37	0,184	397,2	87,53	0,48	31,09
30	4,93	0,43	42,10	0,134	1626,4	88,97	1,13	9,04
31	0,35	0,38	48,81	0,079	867,9	113,37	1,37	11,77
32	1,09	0,10	43,94	0,874	544,7	82,06	1,41	19,62
33	1,05	0,16	62,65	0,045	1470,1	88,39	1,28	10,40
Min	0,10	0,06	19,77	0,009	323,5	23,92	0,46	1,05
Average	0,71	0,20	49,64	0,196	835,9	85,06	1,32	8,90
Max	4,93	0,47	105,16	1,389	1626,4	130,52	3,00	63,91

Table 4. Concentration of the trace elements in vine from Tikves area (continue)

Sr, mg/l	As, µg/l	Cd, µg/ml	Co, µg/l	Cr, µg/l	Ni, µg/l	Pb, µg/l	Zn, µg/ml
0,85	<1	0,12	1,81	7,18	92,58	81,17	0,31
0,44	1,28	0,86	7,24	8,65	313,83	<5	0,15
0,21	5,99	<0.1	0,48	1,37	22,18	15,56	0,23
0,25	<1	0,70	0,84	6,48	60,46	28,09	0,57
0,35	<1	1,50	2,24	19,70	119,95	53,18	0,23
0,38	<1	1,37	5,58	13,52	108,52	21,55	0,66
0,15	71,23	0,46	0,96	<1	23,02	16,42	<0.1
1,38	86,91	5,32	10,57	15,06	26,68	36,92	0,35
2,44	7,26	0,20	3,86	8,90	58,19	103,57	0,70
1,03	114,54	4,15	3,50	9,81	9,35	18,33	0,78
1,16	46,13	0,20	3,38	4,68	11,99	12,61	0,66
1,17	27,04	<0.1	1,39	4,46	17,98	59,09	0,12
1,04	60,85	<0.1	6,63	21,79	75,89	28,02	0,30
1,98	<1	<0.1	0,58	11,85	23,56	47,42	<0.1
0,54	30,92	0,33	0,38	4,84	16,44	<5	<0.1
2,88	76,71	0,09	2,79	4,00	6,71	<5	0,13
0,45	128,74	0,92	1,70	3,21	12,39	22,29	0,26
1,04	79,62	0,49	4,84	13,23	10,96	6,38	0,28
0,93	<1	1,11	3,10	12,64	<5	<5	0,14
0,48	31,44	0,29	<0.1	22,06	37,19	37,15	<0.1
0,39	18,90	0,39	0,39	5,30	19,17	24,45	0,11
1,77	10,16	0,12	2,80	6,61	13,09	40,94	0,11
0,43	48,17	<0.1	0,18	5,41	15,52	66,80	0,33
1,01	37,51	<0.1	0,74	12,50	13,10	6,02	0,10
2,45	<1	0,44	3,33	19,82	31,73	218,34	0,77
0,82	<1	<0.1	<0.1	2,45	33,73	<5	<0.1
1,25	<1	0,51	1,85	10,44	21,21	72,69	0,26
0,95	88,18	0,30	0,43	2,71	<5	<5	<0.1
0,44	35,35	0,73	<0.1	1,87	<5	218,99	0,24
0,73	52,67	1,55	2,02	99,53	56,05	26,89	0,04
1,24	44,44	0,76	1,35	13,16	44,07	54,60	0,90
0,44	20,56	3,20	3,40	8,16	27,29	289,79	0,59
2,39	<1	0,72	0,78	12,49	31,84	25,44	<0.1
0,15	1,28	0,09	0,18	1,37	6,71	6,02	0,04
0,99	46,91	1,00	2,56	11,98	43,92	58,53	0,35
2,88	128,74	5,32	10,57	99,53	313,83	289,79	0,90

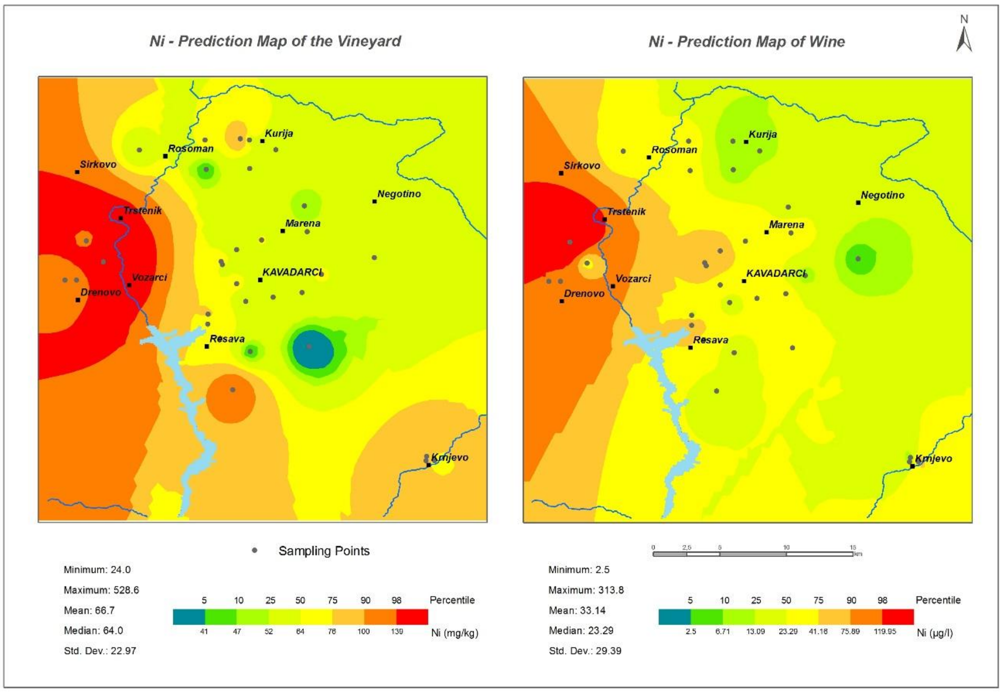

Fig.2. Map distribution of Ni in the soil/vine

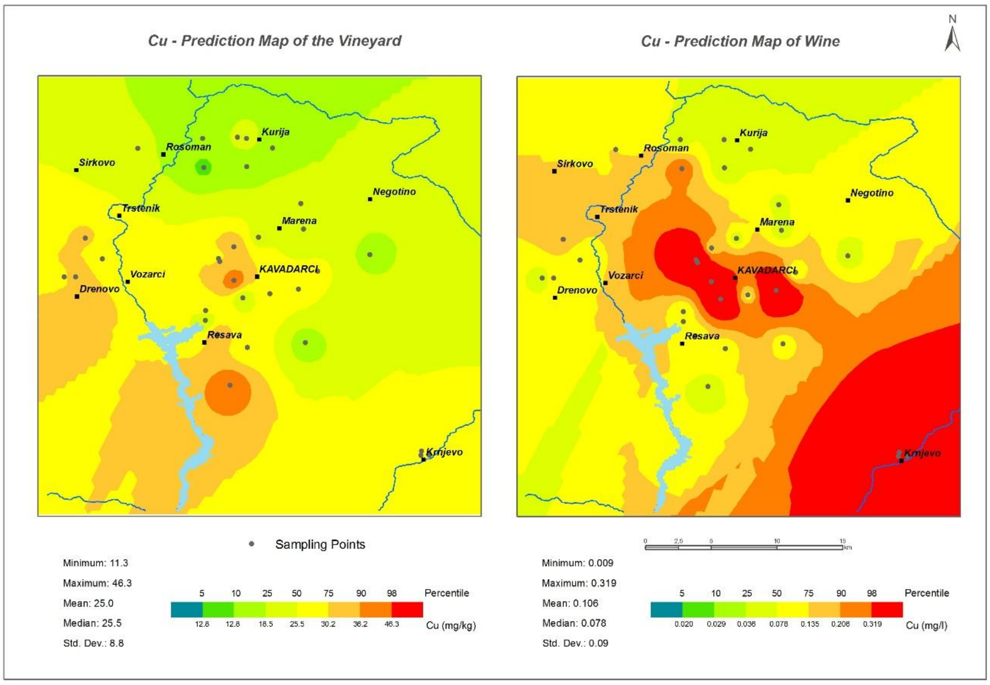

Fig.3. Map distribution of Cu in the soil/vine

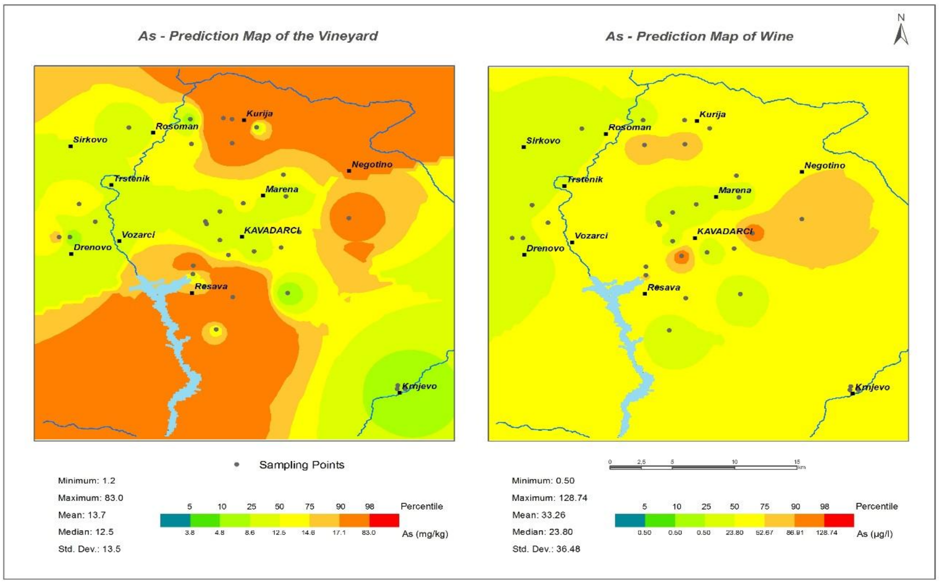

Fig.4. Map distribution of As in the soil/vine

Conclusion

From the surveys on the presence of trace elements in soils and in the wine of Tikves region winery expressed correlative relationships among elements Ni, As and Cu can be concluded.

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