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

ENIGMA 2nd INTERNATIONAL WORKSHOP

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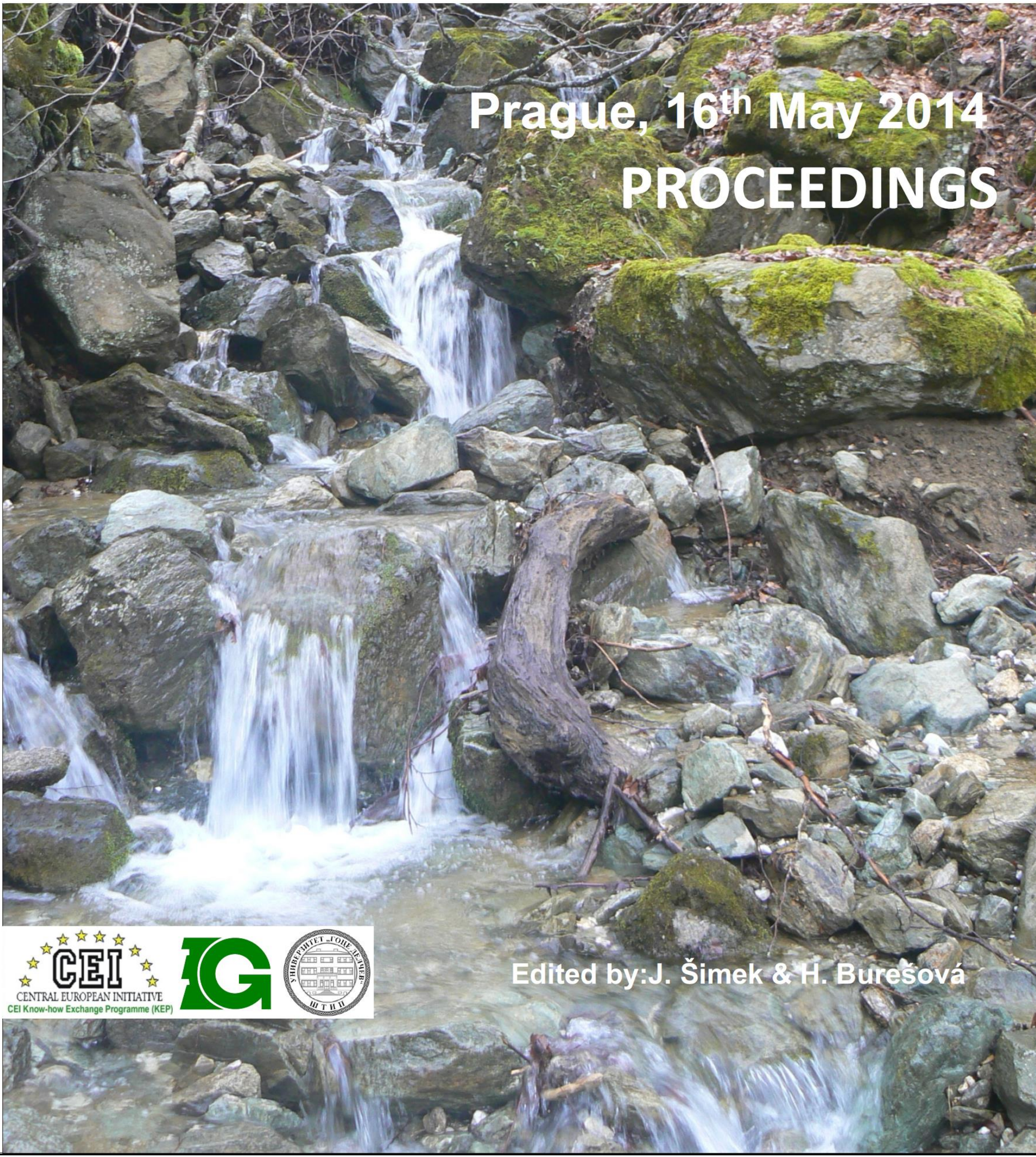
Environmental impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)



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PROCEEDINGS

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Edited by: J. Šimek & H. Burešová

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ON THE PROJECT

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TRACE ELEMENTS IN THE ONION ORIGINATED FROM THE TIKVES AREA (REPUBLIC OF MACEDONIA)

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Abstract: The paper presents the geochemical research for the presence of trace elements in onion produced in the Tikvesh area, Republic of Macedonia. The conducted research is made by the application of the method ICP-AES, ICP-MS. The following results for the presence of the trace elements are obtained: Li (0.037 ppm); B (8 ppm); Na (43 ppm); Mg (841 ppm); Al (17 ppm); P (2352 ppm); Ca (3747 ppm); Ti (5.1 ppm); As (0.033 ppm); Sr (23 ppm); Mo (0.457 ppm); Cd (0.043 ppm); Sb (0.008 ppm); Cs (0.018 ppm); Ba (18.5 ppm); Pb (0.348 ppm); V (0.040 ppm); Cr (0.848 ppm); Mn (9.2 ppm); Fe (148 ppm); Co (0.037 ppm); Ni (1.44 ppm); Cu (2.15 ppm), Zn (13 ppm); Ga (0.388 ppm).

Key words: onion, Tikvesh, geochemical, trace elements

Introduction

The absorption and accumulation of trace elements and heavy metals in the vegetable is a consequence of many factors, including: the concentration of trace elements and heavy metals in the soil, the content and the intensity of the aero sediment including the precipitation as well as phases of the development of the plant (Vontsa et all, [1]). Here should be add the sources which are generated from the agricultural technology like the irrigation and the quality of the water, the usage of the organic and mineral fertilizers which contain certain quantities of trace elements and the usage of pesticides (Sharma et al, [2]).

The urban industrial activity and the traffic lead to significant increase of the particles in the air which contain heavy metals that afterwards in the form of an aero sediment are input into the vegetative cycle of the plants (Lacatusu et al, [3]).

The quality of the environment today is an exceptional challenge for every society, considering the fact that the fast industrialization and the increased use of the fertilizers in the agricultural production influence a lot the conditions in the environment in terms of its quality (water, air, soil, food from the agricultural production) which leads to serious problems upon the human health.

Because of this preserving of the basic elements in the environments which provide its quality, and the environment on the other side provides conditions for the increase of the humanity (quality of water, air, soil, food from the agricultural production), there is a need for a serious and a scientific consideration for determination of the conditions in the environment.

Kavadarci, as a unit of the municipality (with over 40 000 citizens) is an exceptional area from an aspect of the potential in the agricultural production, considering the soil, climate and water potential in the Tikvesh area.

PHYSICAL- GEOGRAPHIC CHARACTERISTICS OF THE TIKVESH AREA

Among the valleys in Macedonia, which vary in their position, the Tikvesh Valley points as a separate geographic unity with its geo-morphological and anthropogenic characteristics. Spread on 2.120 km2, the Tikvesh area takes a significant part from the territory of the Republic of Macedonia. Tikvesh valley is limited by the following mountains: on the south-Mariovo Magellan Mountains, whose ranges are up to 1,700 meters. The mountain heights to the east and west a real so well expressed. On thewest side of the valley is Mount Borila which is 1,500 meters high, and on the south lies the mountain Balija with 1,400 m and Karadak with 750 meters height. This is how the Tikvesh valley is framed by mountains, and from thenorthsideit is cut by the river Vardar, and from the west side by the Crna River, whereas through the middle of the valley runs the river Luda Mara (Fig.1).

In a narrow geographic sense, the Tikves Valley spreads: on the north to the bed of the Bregalnica River towards the villages Vinicani and Nogaevci, then turns to the villages Gradsko and DolnoCicevo, then over the villages Sirkovo, Mrzen Oraovec, Farish, Raec, to the village Nikodin with the hill Nozot to the village Toplica.

The west border of the valley starts with the area Toplica thorugh the road Gradsko-Prilep to the villages Raec and Drenovo towards the Tikvesh Lake. It encompases the areas Suva Gora with the villages Begniste, Koshani and Dabnishte. On the south, the area continues towards the villages Vatasha, Moklishte and the plateau Vitachevo. This part encompasses the area Belgrad with the villages Gorni and Dolni Disan, Przdevo and Demir Kapija. The south side ends with the village Dren.

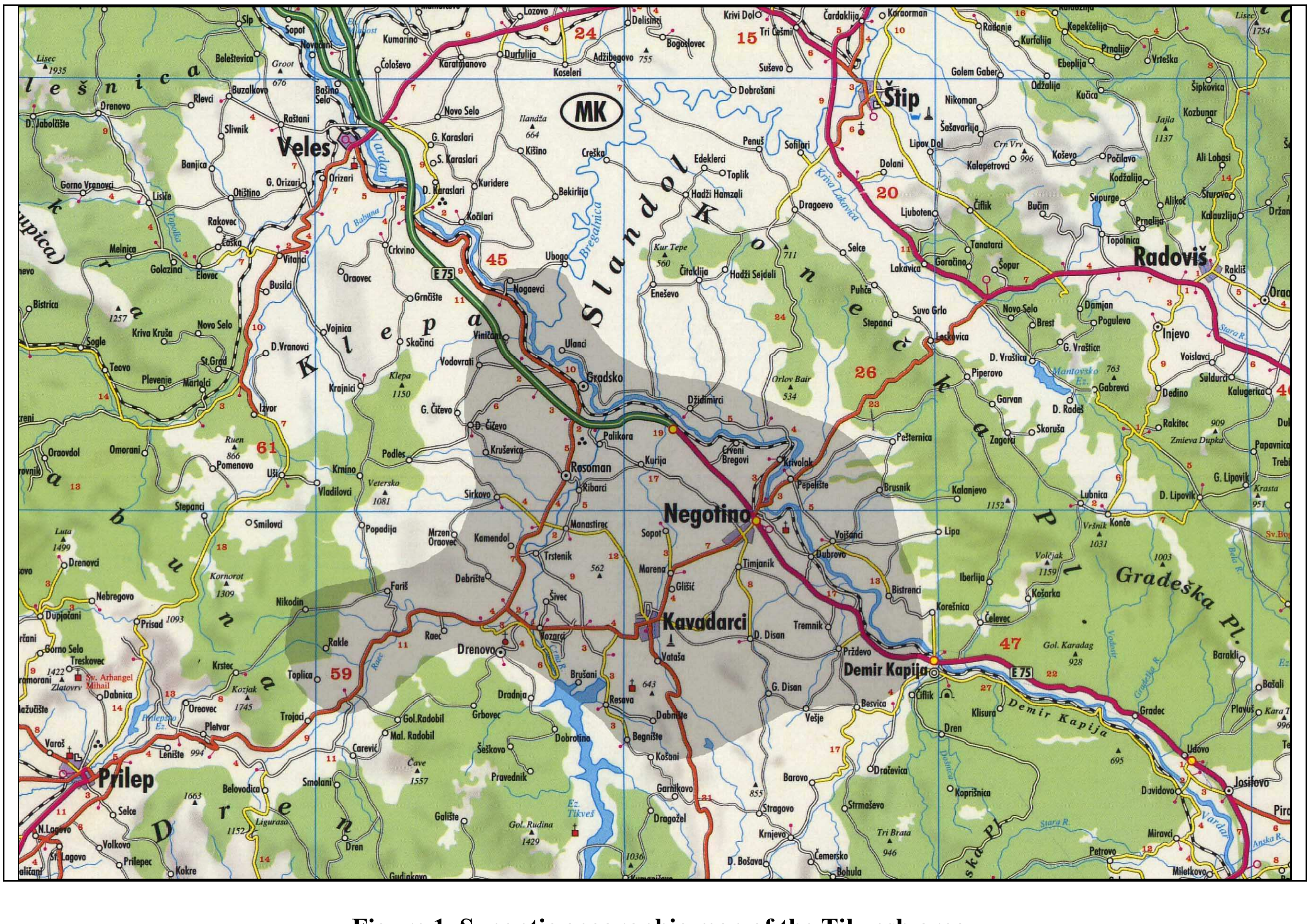

Figure 1. Synoptic geographic map of the Tikvesh area

The east side spreads trough the Vardar River towards the village Koreshnica, cuts the Lipkovska River and moves towards the villages Brusnik and Pepeliste via the Vardar River and the railroad Skopje-Gevgelija to the villages Ulanici and ends with the mouth of the Bregalnica River with Vardar River.

Climate

The climate has a great impact on the development of the grapevine in a sense of its quantity and quality of the grapes. As an important factor in the development of the grapevine the climate consists of the air temperature, the sun light, and the humidity of the air current which is 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 transform the grape into the vine.

The geography position and the relief of the Tikvesh area are the main factor which impacts the whole climate characteristics. The Tikvesh is an area of two intersected climates- continental and Mediterranean. The local mountain climate has less impact.

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

The Mediterranean climate comes from the Aegean Sea on the south along the valley of the Vardar River and it results in warm winters with a relatively high temperatures.

The influence of the local mountain climate is limited and it is highly felt at 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 Tikvesh 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 are the temperatures for the Tikvesh area. This region is classified in the warm places and this factor has an impact on the development of the vine growing. The middle annual temperature in Kavadarci is 18,9°C, and 19,5°C in Demir Kapija. The warmest month in Kavadarci is 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 Tikvesh region distinguishes itself with relatively high temperatures, especially during the summer months. On 22.07.1952 in the Republic of Macedonia is registered the highest air temperature of 44,5°C in Demir Kapija, whereas in Kavadarci it was 41°C. The absolute minimum of the air in Kavadarci is noticed on 27.01.1952 and it was -17°C, and in Demir Kapija it was -22°C.

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

Precipitation

The largest part of the Tikves region is characterized by small amounts of rainfall sand the territory around Gradsko is considered as the site with the least rainfall per square meter in the Republic of Macedonia. The average amount of rainfall is 484 mm in Kavadarci. In Kavadarci most arid summer months are July and August with average 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 rain of a rainy day.

Considering the exceptional physical- geographical characteristics of the Tikvesh area, the huge water potential (The Tikvesh Lake has a capacity of 500 million cubic meters of water) as well as the pedologic development of the soils, the protection of the environment is an imperative without alternative for the current and future generations.

Quality of the environment in the Tikvesh area

The following factors are differently positioned in time, but they directly influence and contribute to the quality of the environment in the Tikvesh area and the town Kavadarci:

- Industrialization of the area,
- Usage of fertilizers for protection of the agricultural production and usage of muck,
- Communal infrastructure

Because of the fact that this contribution to the quality of the environment is differently positioned in time, it should be emphasized that:

1. The quality of the environment in the Tikvesh area until 1980 year is upon influence of the two elements (usage of fertilizers in the agricultural protection, usage of muck, and communal infrastructure),
2. The quality of the environment in the Tikvesh area after 1980 is upon influence of the industrialization of the environment (putting into function the object for production of fero-nickel FENI- Kavadarci),

All these influences that took part in the past at the Tikvesh environment and the town of Kavadarci and its surrounding, are differently manifested today in some geo-chemical media like the soil, the water, the vegetation and the human population. Because of the variety of contributions upon the quality of the environment, a big effort is made with this research in order to determine the quantification of the contribution of a given source of influence upon the environment (in particular, the soils).

Usage of fertilizers for protection of the agricultural production and usage of muck

For a long period (over 60 years) the agricultural production cannot be imagined without the usage of a bigger amount of fertilizers and protection means which are used for the raise in the yield of the agricultural culture per unit of agricultural area. These protection means are product of the chemical technology which developed in different sequences of time and the various chemical matters which were used for the plant protection. Large part of these matters need different period to dissolve and to get eliminated from the soil where they were used. Big traces of these matters can still be found in the soil systems (residua) which basically change the primary characteristics of the soul substrates.

The large usage of fertilizers (in various forms in various time sequences) drastically modifies the soil structure, as well as the chemical basics for certain soil horizons. Considering the fact that on 1 ha of arable soil around 300 kg fertilizers are used, and if the arable soils in this region (around 20 000 ha) are added to this mathematical operation together with the time sequence of usage (over 60 years), then the result will show the quantity of the used fertilizers, and this result is quite big. These fertilizers in the soil systems bring the chemical- mineralogical substances, which in a longer time-frame can be immobile, but they can still change the element basics of the soil horizons.

The large usage of protection means for the plants and fertilizers also influences the underground and the flowing water in a longer period of time.

INDUSTRIALIZATION OF THE AREA

It is well known that the fast industrialization is a big pressure over the quality of the environment and all its elements, including the human population. Until the building of the object for fero-nickel FENI, the Tikvesh area was not considered as a place where the industrialization puts a pressure over the environmental systems. With the activation of FENI, the Tikvesh area was among the regions in the country which undergo significant anthropogenic influences over the environment.

The influences of this object for metallurgic over the environmental system are expressed through emission of the solid and gas phases which is emitted in the atmosphere (the liquid phase is relatively small and it does not influence the bigger systems, and the system for underground and flowing water). The emission of the solid phase is with complex chemical and mineralogical content, and it slowly makes layers in the surrounding around the object, so that its influence upon the environmental systems is basically determined with the quality of the eliminated solid phase and its stability in the supergene conditions. The gas phase is emitted through the atmosphere and it is fast spread in a wider aureole depending on the direction of movement of the air masses.

It has to be emphasized that the object FENI is a very complex technological aggregate which operates with a very good equipment and technology. This object also devotes its attention to the environmental protection since its functioning (FENI holds an A-integrated license for work, which means excellent implementation of the systems for environmental protection).

However, it should be noted that this object with its capacity and the manufacturing of various types of minerals (with different elemental basics), the usage of various chemicals, has its influence over the environmental systems in the Tikvesh area, and this influence needs to be determined and quantified.

Previous researches

The results which refer to the geological, pedo-genetical as well as the geo-chemical characteristics in the Tikves region and its surrounding could be found in the papers by Boev and Bermanec [4] and Stafilov et all [5]).

Methodology

Sample collection

The products are taken as

- mixed (roots and leaves) onion

The sample in quantity of 1 kg is gathered from the planned products and it is transported to the lab in a plastic bag.

Previous preparation of the products

The vegetative products are taken in quantity of 1 kg.

The vegetative products are washed in the lab with re-distilled water in order to be cleaned from the contamination with soil. For easier dryness and removal of the water, the products are cut in small parts. The vegetative products are dried in the drier on 800C, to a constant mass, so that the change of the mass after the drying is no higher than 5% from the starting mass of the product during the three cycles of drying and measuring.

The products are grinned in the mill for products of vegetative origin. The grinned products are kept in poly-ethylene bags.

Determination of the total contents of the elements

Dissolve of the samples from vegetative origin

Principle

The appropriately prepared sample, as described above, is divided with H2O2and HNO3acid. After the vaporization of the acid and the hydrogen peroxide to wet salts, the residue is dissolved in dissolved nitrogen acid. In order to minimize the danger from spattering due to the oxidation of the organic material with the hydrogen peroxide, the samples are treated with smaller portions from the reactants.

Reactants

Water, with cleanness level 2 according to ISO 3696

H2O2, p.a., w=   %

HNO3, p.a., ρ=1,41 g/mL

Equipment

Mill, for grinding the dried vegetative products without their contamination

Dryer, for drying the samples

Analytic scalewith precise level of 0,0001g

Glasses with capacity of400mL. After the usage the glasses are swamped in diluted nitrogen acid and they are put on a warm hotplate, and afterwards they are washed with re-distilled water.

Electrical hot plate with thermostat for temperature control of +/-100C

Digester

Measures from 50mL

Procedure

Dissolve

Exact 1,0 g is measured on an analytical scale, from the dried and grinned vegetative sample in glasses of 400mL. The glasses are covered with watch glass and 5 mLnitrogen acid and 5mL hyrdogen peroxid is added, then it is burned on electric hot-plate on 150^{0}C until the reaction starts. Afterwards, the glasses are removed from the hot-plate, and when the reaction ends, they are brought back to the hot-plate and warmed to wet salts. The procedure is repeated for three times in order to provide complete dissolve of the samples. 2,5 mL nitrogen acid and around 5 L water is added to the cold glasses with the samples after the third digestion, in order to alleviate the dissolve of the dissolved nitrogen salts. Finally the clear solution is put in measure of 50 mL, the measure is filled to the calibration line and it is mixed. The residue of the solid sample indicates uncompleted dissolve.

Determination

For determination of the examined elements Na, K, Ca, Mg the analytical method ICP-AES is applied (Table 1).

Table 1. Instrument and instrumental conditions for the ICP-AES, Varian Liberty 110

Sample introduction						
atomizer			V-groove			
Atomizer chamber			Inert Sturman-Masters			
Peristaltic pump			12 rollers, 1 turn/min increment			
Conditions for the program						
Power of the plasma			1,0 kW			
Speed of the pump/rpm			25			
Flow ofArfor plasma			15 L/min			
Time for stabilization			30 s			
Flow of axial Ar			1,5 L/min			
Time for washing			30 s			
Pressure of the atomizer			200 kPa			
Time of lagging			30 s			
Correction of fon			dynamic			
Height of the plasma			Optimal according to SBR			
Conditions of elements						
element	Wave length/nm	Plasma height /mm	slit/nm	Time for integration/s	filter	Line of grating
Ca	396.847	20	0,02	5	1	1
Mg	279.553	20	0.02	5	6	2
Na	588.995	20	0.02	5	7	1
P	213.618	5	0.007	5	1	3
Fe	259.94	5	0.01	5	6	2
K	766.49	20	0.02	5	7	1

for determination of the examined elements, Li, Be, B, Al, Ti, V, Cr, Mn, Co, Ni, Cu, Z, Ga, Ge, As, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Cs, Ba, Tl, Pb, Bi, Th, U the ICP-MS is applied as analytical method (Table 2).

Table 2. Instrument and instrumental conditions for the ICP-MS Agilent 7500

Sample introduction			
atomizer		PEEK, Babington - type	
Atomizer chamber		Glass, doublepass, temperature of the automizer chamber2^{0}C	
Injector of ICP torch		Quartz, 2.5 mm	
Conditions of the program			
Power of the plasma		1500 W	
Speed of the pump/rpm		0,1 rps	
Aux flow ofArfor plasma		1,0 L/min	
Carrier gas flowAr		0,9 L/min	
Sampler cone		nickel	
Skimmer cone		nickel	
Sample depth		7.4	
Points/mass		3	
Time for integration		0,3 s	
Total time for acquisition/ replicates		8 s	
Replicates		3	
Total time for acquisition/ sample		24 s	
Element/mass			
Element	m/z	element	m/z
Li	7	As	75
Be	9	Sr	88
Al	27	Mo	95
Ti	48	Pd	106
V	51	Cd	111
Cr	53	Cs	133
Mn	55	Ba	137
Co	59	Tl	205
Ni	60	Pb	208
Cu	63	Bi	209
Zn	66	Th	232
Ga	69	U	238
Ge	72	Sn	120
Sb	121		

Results and discusion

The results obtained concerning the 23 locations where onion is grown in the Tikves area. Values obtained for the presence of rare elements in the tested samples of onion are shown in Table 3, the graphical interpretation is shown in Fig.2, and the Fig. 26th Hereinafter we give some interpretations concerning representation and spatial distribution of some rare elements that are present in onions that are grown in the Tikves area.

The contents of Li (Table 3) in the interval of 0.07-0.109 ppm with an average value of 0.037. The average content of Li in onions from various regions of the world is moving in the range of 0.06-1.6 ppm (Kabata-Pandias, [6]). From the displayed values it can be concluded that the content of Li in the onion from the Tikves area is within the prescribed limits. The spatial distribution of Li is shown in Fig.2 which can detect two separate zones of higher Li concentrations in the environment, the city and the surrounding of the village Rosoman.

The content of B (Table 3) in the interval of 2 -28ppm with an average of 8 ppm. The average content of B in onions from various regions of the world is moving in the range of 10 -381ppm (Kabata-Pendias, [6]). From the displayed values it can be concluded that the content of B in the onion of the Tikves area is within the prescribed limits. The spatial distribution of B in Tikves area is shown in Fig.3 , which can be seen in the western parts of the area are areas with very low concentrations of B, which in any case can be explained by the mode of formation of soils in this part of the field . These soils are developed on geological bases built of carbonate and metamorphic rocks.

Content of Na (3-201 ppm), the Mg (228-1402 ppm), the Al (2-84 ppm), the P (791-4859 ppm), of Ca (1728-8162 ppm), is within the published values for other regions of the world (Kaba-Pendias, [6]). The spatial distribution of these elements is shown in the pictures (4,5,6,7,8).It should be mentioned that the spatial distribution of Al and Na appear significant correlation with the occurrence of a pronounced zone of elevated concentrations in the northern part of the field. This zone can be explained by the genesis of soils in this region.

Table 3. Rare elements concentrations in the tested onion samples from the area of interest

y	x		mg/kg	Li	Be	B	Na	Mg	Al	P	Ca2	Ti	V	Cr	Mn	Fe2	Co	Ni	Cu	Zn
7579123	4599607	RI-1	0	0,083	<0,001	12	186	1380	125	1727	8503	10,842	0,053	0,31	46,2	229	0,124	1,4	1,8	7,419
7577866	4598618	RI-2	0	0,144	<0,001	10	547	1342	234	1710	5303	7,095	0,089	0,07	18,0	146	0,091	1,5	0,89	4,673
7577659	4596993	RI-3	0	0,119	<0,001	14	124	1464	**387**	2340	5844	7,609	0,071	0,32	14,6	142	0,060	1,2	1,0	7,068
7577689	**7595989**	RI-4	0	0,067	<0,001	**15**	**1025**	2047	49	1896	2686	3,585	0,028	0,31	**6,9**	72	0,031	1,2	1,1	6,806
7585381	4590800	KI-1	0	0,045	<0,001	10	55	763	**6**	2140	6406	8,279	0,015	0,80	12,2	168	**0,016**	1,1	1,4	7,267
7587599	4589811	KI-2	0	0,064	<0,001	12	40	1284	21	3278	8363	10,994	0,038	1,05	19,1	228	0,033	1,5	2,6	15,320
7587698	4588546	KI-3	0	0,069	<0,001	10	51	1317	22	2147	5039	6,664	0,030	0,99	11,0	192	0,016	1,2	1,5	11,449
7583820	4589000	KI-4	0	0,070	<0,001	14	84	1909	28	3779	9593	12,849	0,061	0,93	**55,8**	244	0,074	1,4	**7,9**	17,898
7585160	4586611	KI-5	0	**0,178**	<0,001	11	266	**2747**	11	2788	7700	10,070	0,028	0,93	22,2	213	0,021	1,4	2,9	14,951
7586131	4593208	MI-1	0	0,065	<0,001	11	118	1579	130	2939	5854	8,067	0,097	0,34	27,0	129	0,071	1,3	3,8	9,937
7584203	4593508	MI-2	0	0,035	<0,001	13	236	1502	185	4061	8839	12,033	0,138	0,57	20,8	175	0,079	2,2	3,9	19,867
7584863	4592172	MI-3	0	0,076	<0,001	14	127	2265	110	**4693**	**11954**	**16,339**	**0,280**	**1,21**	38,3	291	0,109	1,7	4,0	**27,446**
7586557	4596591	SI-3	0	0,076	<0,001	10	153	1695	276	3252	9204	11,945	0,073	0,72	42,4	206	0,073	**2,7**	5,2	11,864
7585657	4595594	SI-4	0	0,082	**0,0013**	10	171	1783	117	3962	8215	10,917	0,074	0,83	29,1	199	0,055	1,7	5,9	20,542
7576159	4591481	DI-2	0	0,026	<0,001	**4**	**23**	729	10	**816**	**1299**	**1,750**	0,015	0,20	12,1	**24**	0,103	**2,8**	**0,63**	**2,411**
7576172	4590477	DI-3	0	**0,012**	<0,001	8	52	**624**	23	1704	3082	4,067	0,034	0,21	8,0	151	0,055	0,9	1,2	3,503
7576068	4589470	DI-4	0	0,032	<0,001	9	44	1045	36	1898	6146	7,978	0,065	0,31	16,3	278	0,104	0,9	3,4	10,526
7575415	4592381	DI-5	0	0,036	<0,001	8	57	823	33	1918	6105	7,933	0,057	0,20	29,0	254	**0,138**	1,3	4,2	11,357
7578765	4589204	VI-1	0	0,082	<0,001	8	40	1073	61	2767	4644	5,970	**0,011**	0,89	23,7	146	0,071	2,4	4,1	12,517
7576929	4587864	VL-2	0	0,047	<0,001	8	129	1157	84	2679	4807	6,136	0,025	1,13	18,1	154	0,048	1,5	4,9	14,749
7580386	4587614	VL-3	0	0,016	<0,001	9	49	724	24	1345	3405	4,480	0,032	0,22	11,4	143	0,066	1,8	3,4	4,078
7580720	4590778	VL-5	0	0,029	0,001	13	158	1451	29	1992	9531	12,385	0,053	0,23	21,4	**343**	0,104	1,2	2,8	7,514
7581215	4592025	VL-5	0	0,023	<0,001	10	48	1017	42	2197	4280	5,636	0,043	0,21	11,9	161	0,062	**0,8**	1,4	10,309
Min				0,012	0	4	23	624	6	816	1299	1,750	0,011	0,07	6,9	24	0,016	0,8	0,6	2,411
Average				**0,062**	0	10	159	1348	85	2452	6171	8,141	0,059	0,54	21,8	180	0,068	1,5	2,9	10,912
Max				**0,178**	**0**	**15**	**1025**	**2747**	**387**	**4693**	**11954**	**16,339**	**0,280**	**1**	**56**	**343,248**	**0,14**	**2,832**	**8**	**27,446**

Table 3 (continues). Rare elements concentrations in the tested onion samples from the area of interest

y	x		mg/kg	Ga	Ge	As	Sr	Mo	Pd	Ag	Cd	Sn	Sb	Cs	Ba	Tl	Pb	Bi	Th	U
7579123	4599607	RI-1	0	0,281492	<0,006	0,036598	33,31543	0,188713	0,001854	0,079421	0,046818	<0,058	0,022685	0,034771	9,246833	0,002796	0,88581	0,014043	0,004621	0,002327
7577866	4598618	RI-2	0	0,326762	<0,006	0,058365	29,67067	0,661375	0,003658	<0,006	0,103011	<0,058	0,00972	0,020331	10,74547	0,002063	0,300885	<0,002	0,006237	0,001774
7577659	4596993	RI-3	0	0,215501	<0,006	0,077373	31,45805	1,221952	0,003443	0,001006	0,084026	<0,058	0,020027	0,01648	5,992194	0,00114	0,873593	0,001836	0,003266	0,000501
7577689	7595989	RI-4	0	0,082315	<0,006	0,211617	20,43478	0,79219	0,00155	0,051666	0,060493	<0,058	0,015555	0,017061	2,095572	0,009736	0,735952	0,010796	0,003512	0,001103
7585381	4590800	KI-1	0	0,364298	<0,006	0,033047	28,45041	0,79173	-0,00126	<0,006	<0,007	<0,058	0,011124	0,015554	15,95468	<0,001	0,335762	0,00166	0,002279	-0,00053
7587599	4589811	KI-2	0	0,434192	<0,006	0,05164	42,22156	0,853186	0,000574	<0,006	0,027635	<0,058	0,007665	0,021998	18,38759	<0,001	0,372414	<0,002	0,006779	0,001466
7587698	4588546	KI-3	0	0,389811	<0,006	0,06047	49,9221	1,177696	-0,00085	<0,006	-0,00015	<0,058	0,016387	0,016868	16,49961	0,001553	0,353817	0,001514	0,004631	0,001165
7583820	4589000	KI-4	0	0,772172	0,007674	0,172124	63,05898	0,798531	0,013554	<0,006	0,342947	<0,058	0,007251	0,01944	33,08044	0,005731	1,890919	0,003041	0,007865	0,003828
7585160	4586611	KI-5	0	0,368174	0,007239	0,029753	61,307	1,57277	-0,00019	<0,006	0,013936	<0,058	0,006865	0,02135	16,63	0,001556	0,3591	0,004559	0,004831	0,000605
7586131	4593208	MI-1	0	0,534947	<0,006	0,058852	41,10855	0,65521	0,000228	0,393177	0,028553	<0,058	0,009265	0,020076	16,91542	0,001882	0,350651	<0,002	0,004318	0,00201
7584203	4593508	MI-2	0	0,372995	<0,006	0,066025	42,78292	1,387551	0,004945	<0,006	0,150123	<0,058	0,009112	0,021715	12,09617	0,005442	0,422932	<0,002	0,01	0,001586
7584863	4592172	MI-3	0	0,519238	<0,006	0,119272	63,40454	1,603272	0,005481	<0,006	0,105651	<0,058	0,011969	0,03254	16,96206	0,001984	0,337312	<0,002	0,023331	0,003523
7586557	4596591	SI-3	0	0,630066	<0,006	0,075133	57,14871	1,115334	0,000167	<0,006	0,023537	<0,058	0,014685	0,017854	21,06712	0,000959	0,438049	<0,002	0,004299	0,001854
7585657	4595594	SI-4	0	0,502764	<0,006	0,053965	55,55939	1,18353	0,000623	<0,006	0,031725	<0,058	0,013425	0,019722	17,60875	0,001941	0,412434	<0,002	0,003749	0,001664
7576159	4591481	DI-2	0	0,085468	<0,006	0,02198	7,372542	0,235479	0,000531	0,012298	0,037725	<0,058	0,010324	0,016635	3,187951	0,0022	-0,00888	0,001746	0,00334	0,0008
7576172	4590477	DI-3	0	0,107584	<0,006	0,025738	12,75855	0,218621	-0,00084	0,001265	<0,007	<0,058	0,003477	0,01717	2,823542	<0,001	0,049604	<0,002	0,00334	0,00103
7576068	4589470	DI-4	0	0,090693	<0,006	0,027795	16,15694	0,138026	-8,7E-05	0,000426	0,015935	<0,058	0,008768	0,018065	2,313843	<0,001	0,10907	<0,002	0,005306	0,001847
7575415	4592381	DI-5	0	0,070623	<0,006	0,01383	25,80726	0,171978	0,000469	0,0011	0,02342	<0,058	0,00267	0,016197	1,792035	<0,001	0,024761	<0,002	0,002249	0,001199
7578765	4589204	VI-1	0	0,461141	<0,006	0,048288	17,01343	0,199142	0,000947	<0,006	0,032365	<0,058	0,011323	0,016182	15,43962	0,000992	0,427395	<0,002	0,002152	0,001054
7576929	4587864	VL-2	0	0,255517	<0,006	0,02732	21,43025	0,196836	0,000132	0,003345	0,018232	<0,058	0,016238	0,016893	9,231185	0,003457	0,460232	0,005395	0,00306	0,001111
7580386	4587614	VL-3	0	0,124048	<0,006	0,030466	9,209537	0,149849	-0,00032	0,001862	0,00891	<0,058	0,00289	0,017112	3,185313	<0,001	0,070746	<0,002	0,003238	0,001406
7580720	4590778	VL-5	0	0,256664	<0,006	0,059321	31,13077	0,605584	0,000215	0,000515	0,01282	<0,058	0,007082	0,025851	10,12215	0,038676	0,035176	<0,002	0,006501	0,002309
7581215	4592025	VL-5	0	0,177965	<0,006	0,130609	16,15278	0,511486	0,001254	0,00084	0,038969	<0,058	0,004158	0,017922	6,741845	0,001919	0,061768	<0,002	0,005773	0,001852
Min				0,070623	0,007239	0,01383	7,372542	0,138026	-0,00126	0,000426	-0,00015		0,00267	0,015554	1,792035	0,000959	-0,00888	0,001514	0,002152	-0,00053
Average				0,312294	0,007384	0,062642	32,67699	0,690336	0,00145	0,042104	0,054842		0,010222	0,019722	11,24631	0,004721	0,387109	0,004611	0,005285	0,001456
Max				0,772172	0,007674	0,211617	63,40454	1,603272	0,013554	0,393177	0,342947		0,022685	0,034771	33,08044	0,038676	1,890919	0,014043	0,023331	0,003828

The content of Ti in the interval of 2.3-11.1 ppm with an average values of 5.1 ppm. The average Ti content in onions from various regions of the world is moving in the range of 1.6-197 ppm (Kabata-Pendias, [6]). The spatial distribution of Ti is shown in Fig. 9.

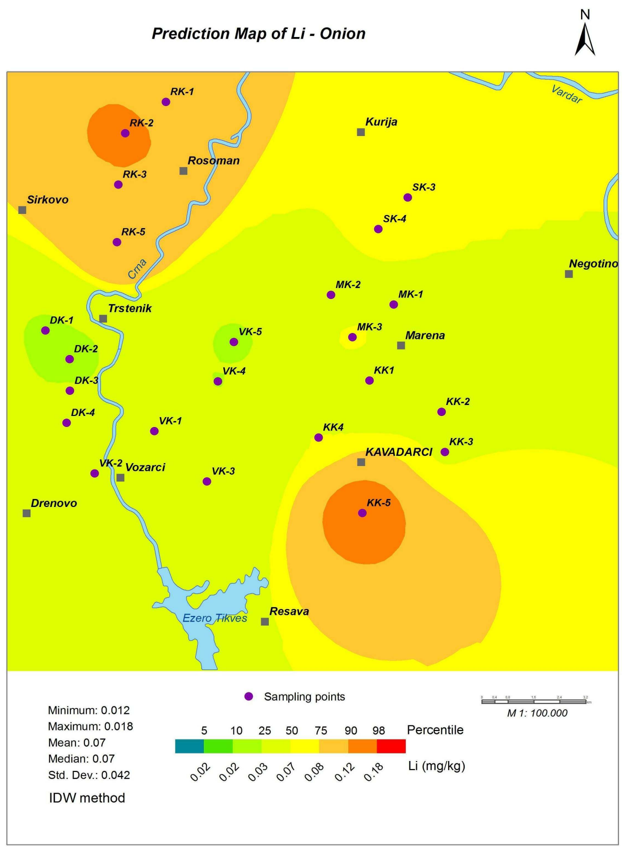

Figure 2. Spatial distribution of Li in the onion in the Tikves area

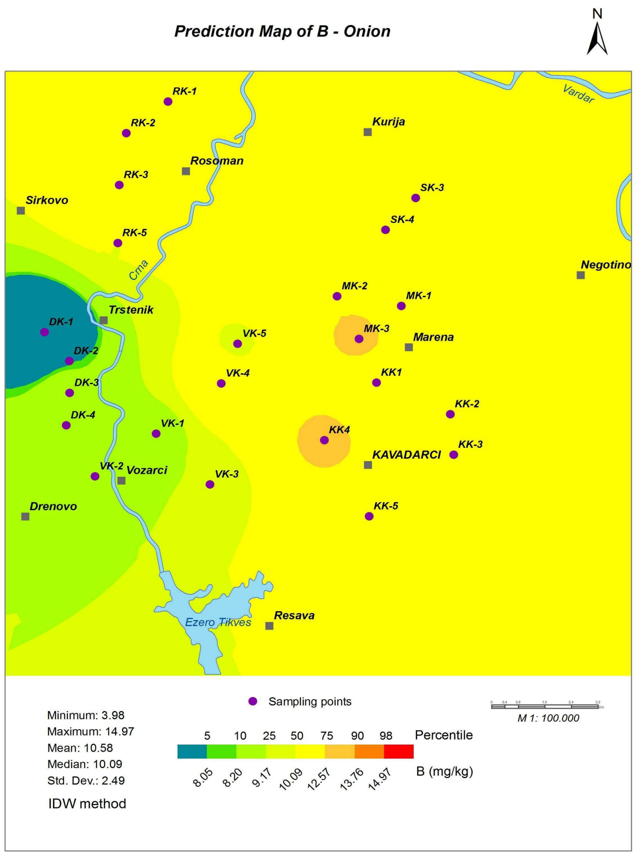

Figure 3. Spatial distribution of B in the onion in the Tikves area

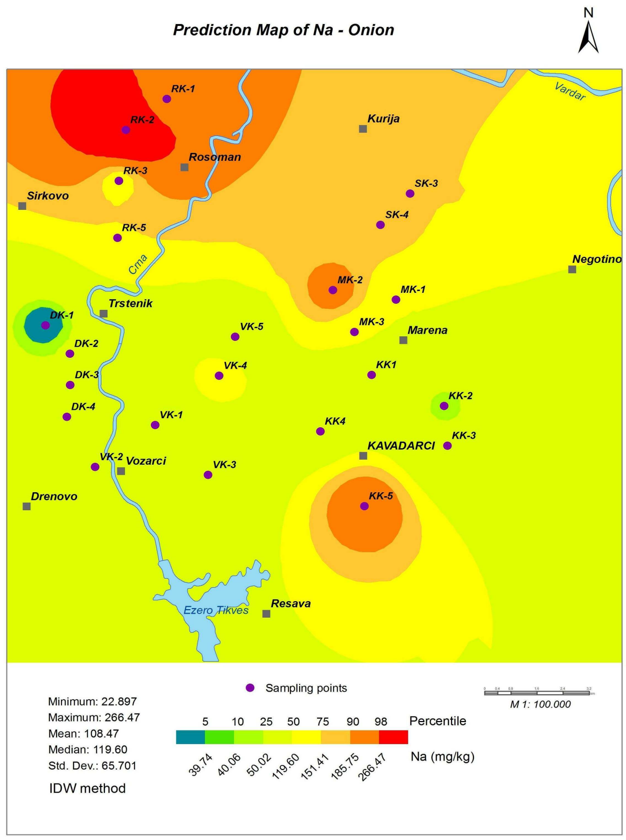

Figure 4. Spatial distribution of Na in the onion in the Tikves area

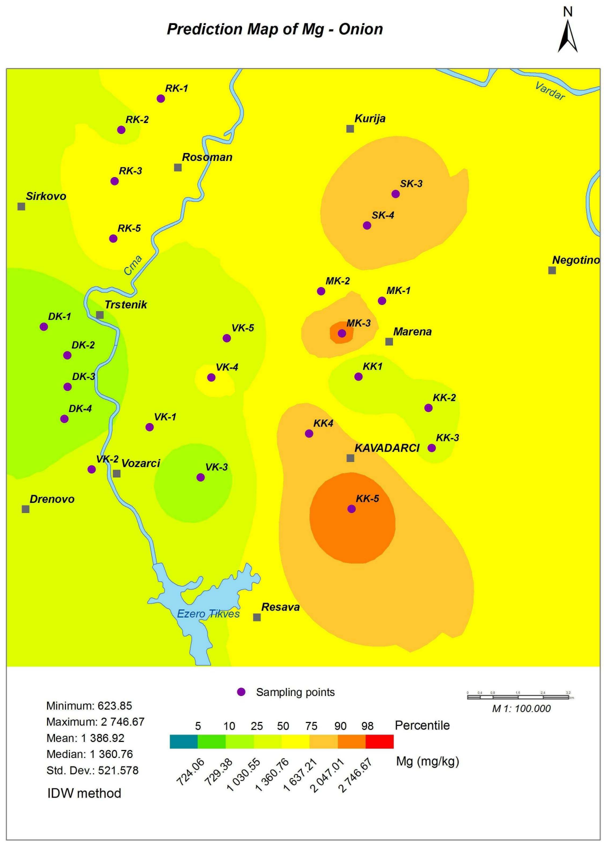

Figure 5. Spatial distribution of Mg in the onion in the Tikves area

The content of As in the interval of 0.008-0.085 ppm with an average value of 0.033 ppm. The average content of As in onions from various regions of the world amounts to 4.5 ppm (Kabata-Pendias and Piotrowska [7]).

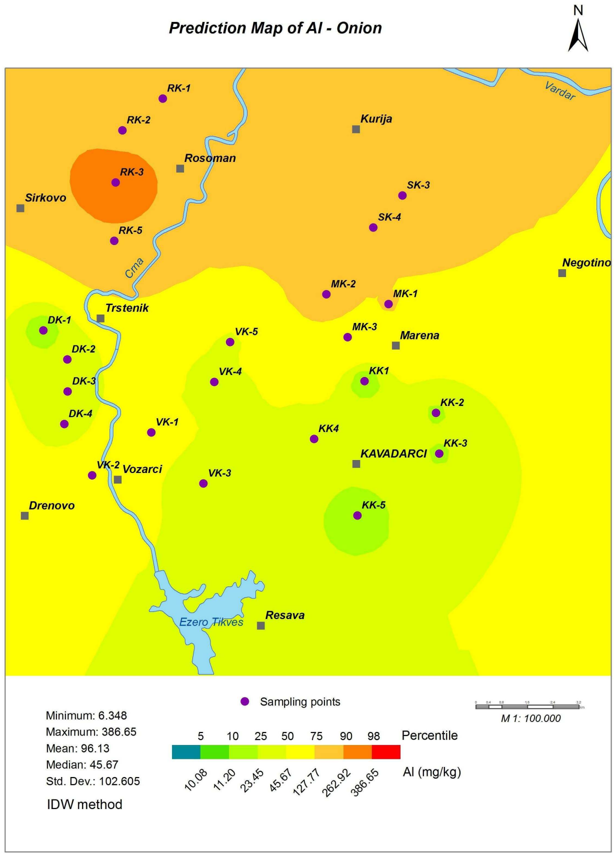

Figure 6. Spatial distribution of Al in the onion in the Tikves area

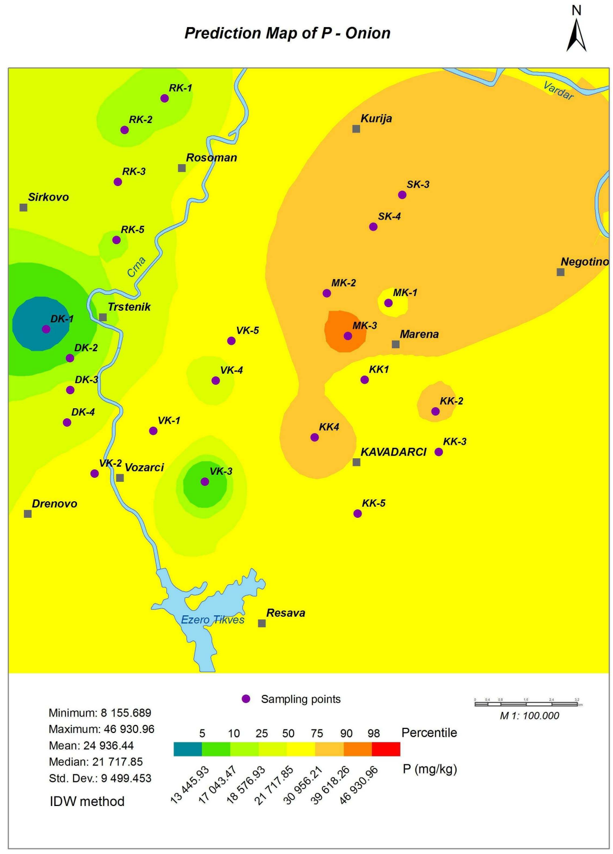

Figure 7. Spatial distribution of P In the onion in the Tikves area

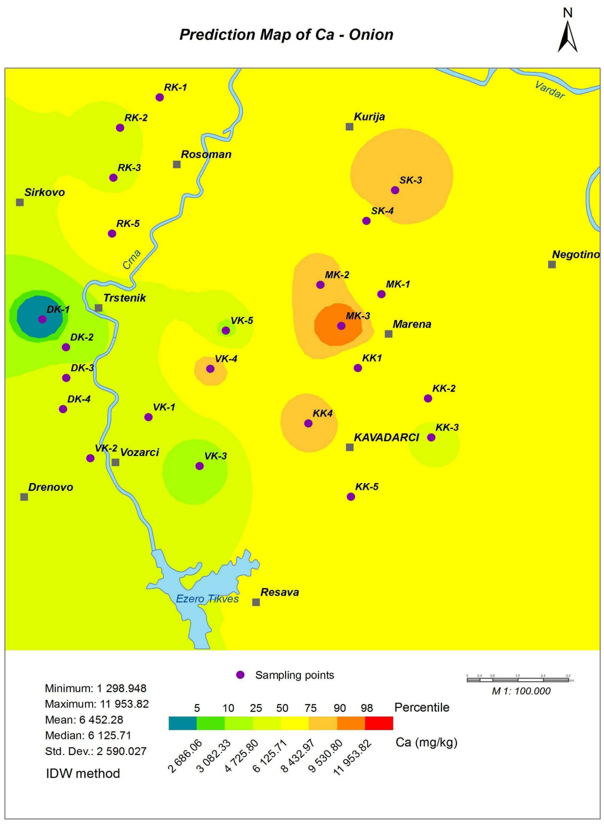

Figure 8 Spatial distribution of Ca in the onion in the Tikves area

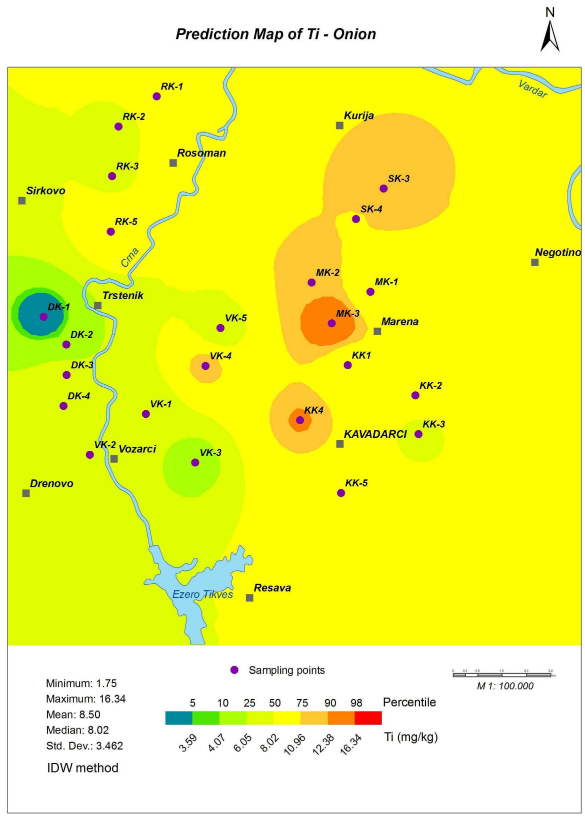

Figure 9. Spatial distribution of Ti in the onion in the Tikves area

Spatial distribution of As in the onion fields of winery shows the Fig. 10 and it can be seen that higher concentrations of As in onions produced in the vicinity of, the city. This in any case can be explained by the increased intensity of traffic in this part of the valley. The content of Sr in the interval of 6-37 ppm with an average value of 23 ppm. The median Sr in onions from several regions in the world is 50 ppm (Chapman, [8]). The spatial distribution of Sr in the onion fields of Tikves area is shown in Fig.11.

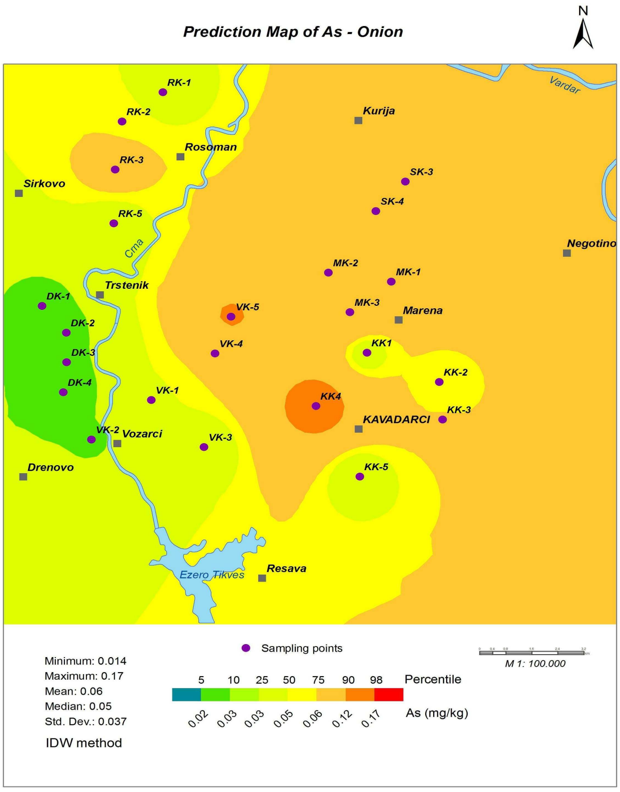

Figure 10. Spatial distribution of As in the onion in the Tikves area

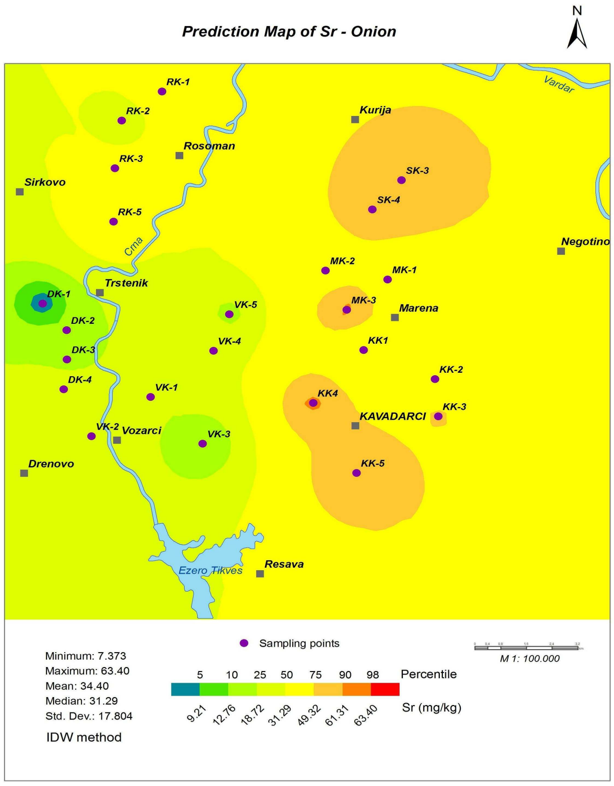

Figure 11. Spatial distribution of Sr in the onion in the Tikves area

The content of Mo (0.117-1.652ppm) and the content of Cd (0.002-0.176ppm) are shown in Fig. 12-13.

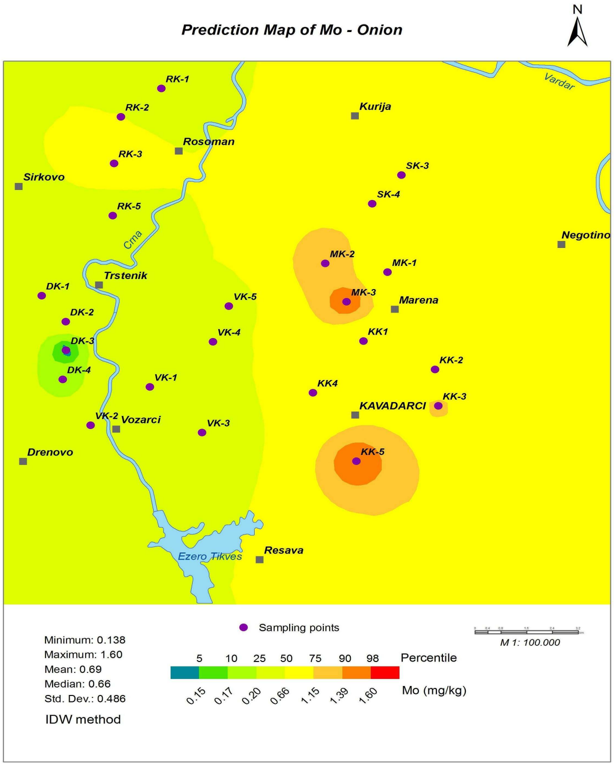

Figure 12. Spatial distribution of Mo in the onion in the Tikves area

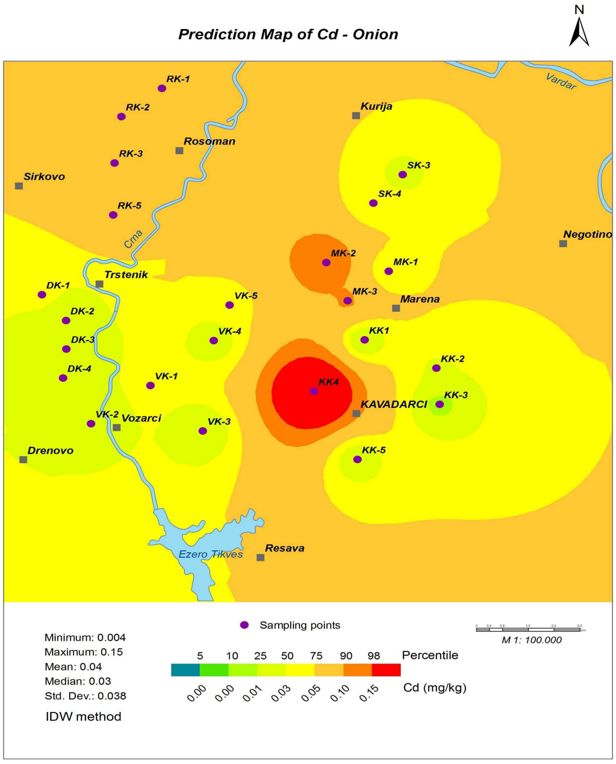

Figure 13. Spatial distribution of Cd in the onion in the Tikves area

Content of Sb (0.001-0.020ppm), the content of Cs (0.016-0.025ppm), the content of Ba (3.4-43.8ppm), the contents of Pb (0.028-0.974ppm), the content of V (0.004-0.129ppm) in onion fields of Tikves area are within the published values for other regions of the world (Schaklette, [9]), (Schaklette, et al, [10]) . The spatial distribution of these elements is shown in Fig. 14-18.

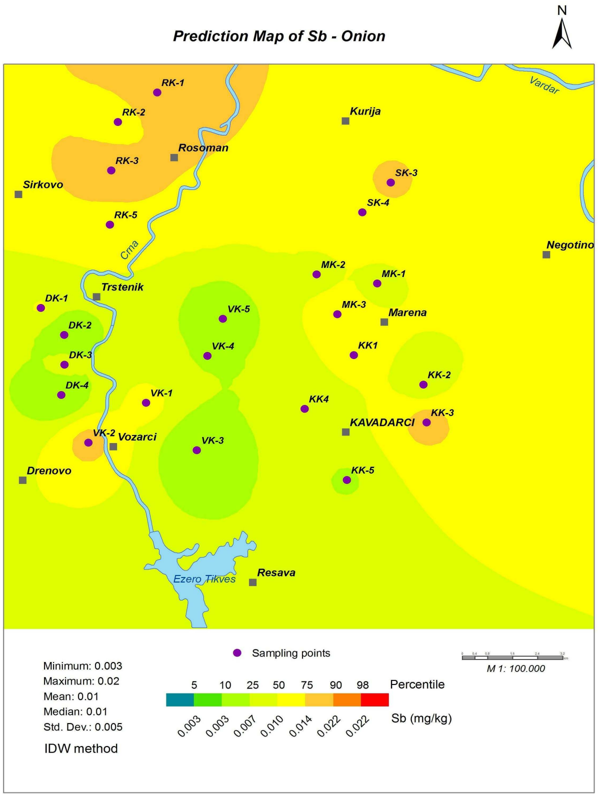

Figure 14. Spatial distribution of Sb in the onion in the Tikves area

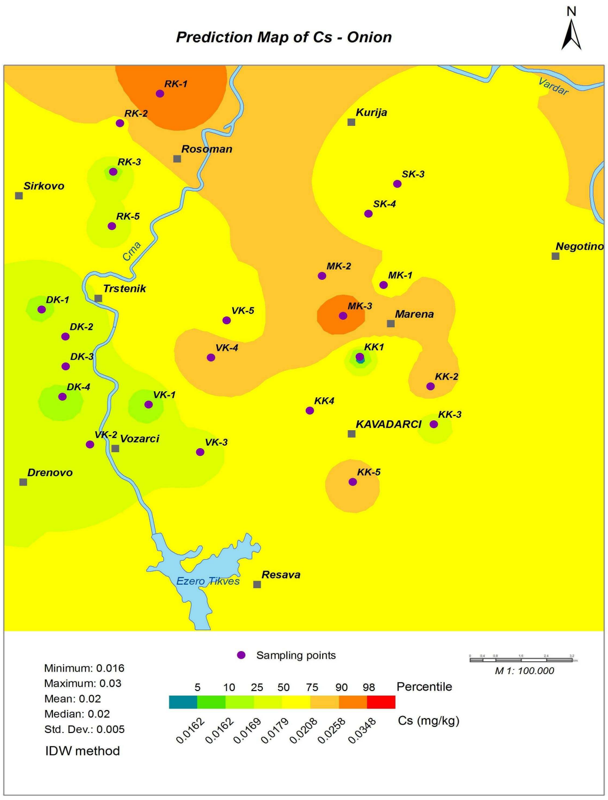

Figure 15. Spatial distribution of Cs in the onion in the Tikves area

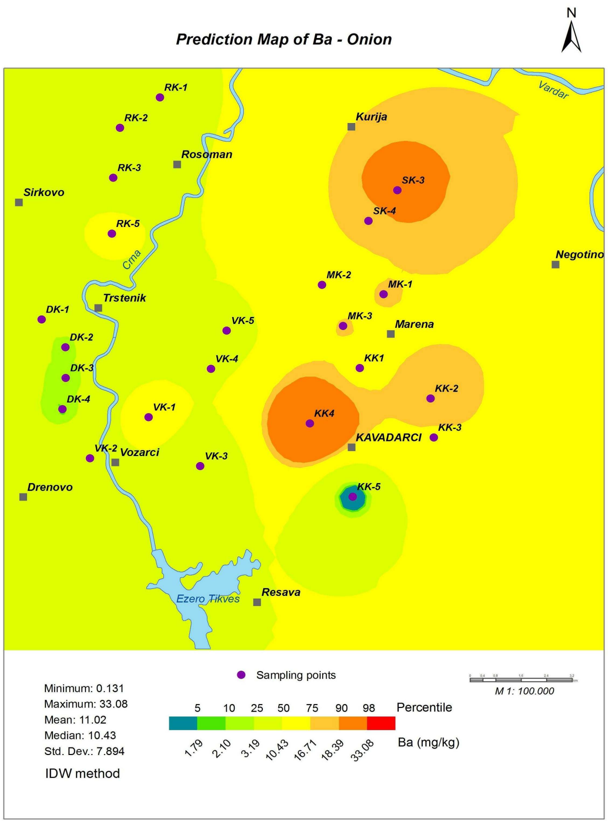

Figure 16. Spatial distribution of Ba in the onion in the Tikves area

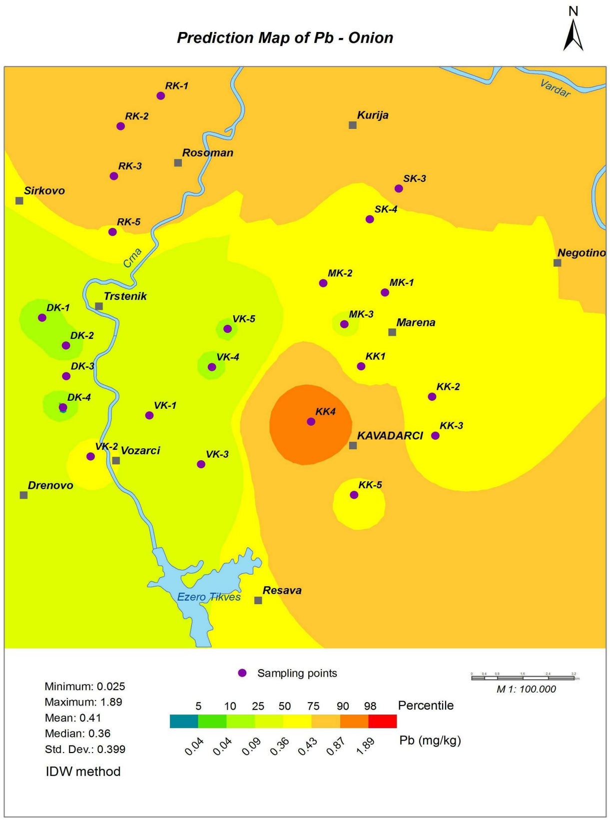

Figure 17. Spatial distribution of Pb in the onion in the Tikves area

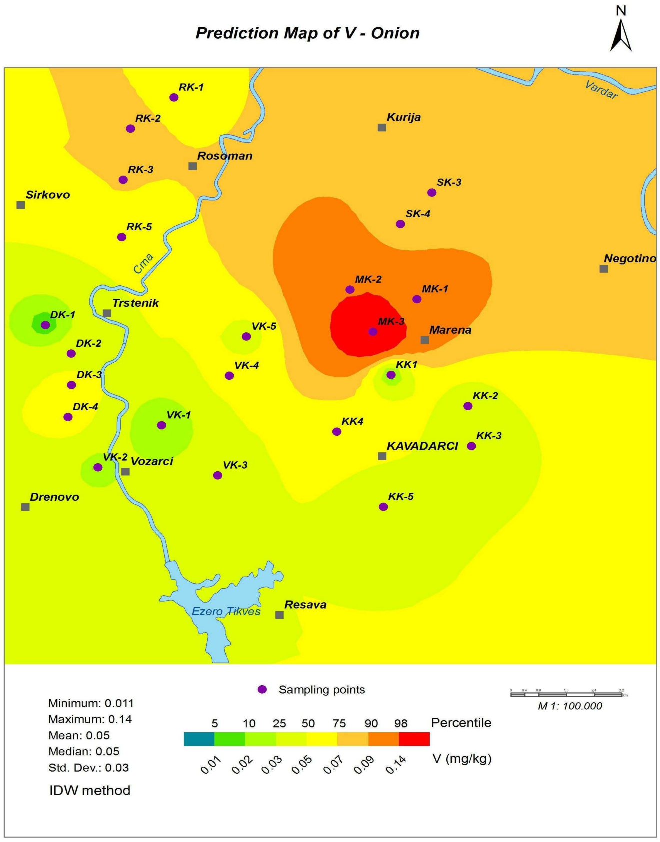

Figure 18. Spatial distribution of V in the onion in the Tikves area

The content of Cr (0.086-1.476 ppm), the Mn (4.2-52-9ppm), the Fe (74-192ppm), the Ni (0.40-4.93ppm), a Cu (0.58-8.47ppm), the Zn (8-29ppm) shows a slight increase over the contents of the published values (Schaklette, [9]), (Schaklette, et al, [10]) (Chapman, [8]), (Jasiewicz, [11]) is shown in Fig. 19-24.

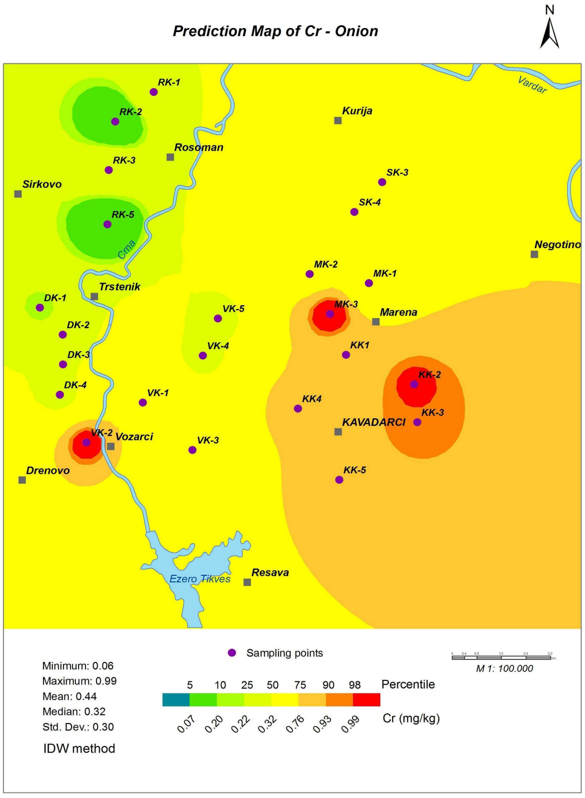

Figure 19. Spatial distribution of Cr in the onion in the Tikves area

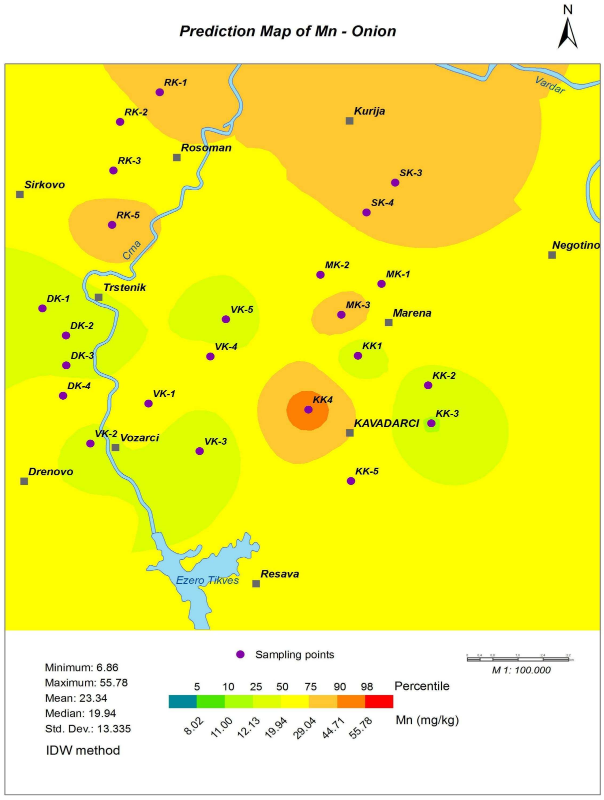

Figure 20. Spatial distribution of Mn in the onion in the Tikves area

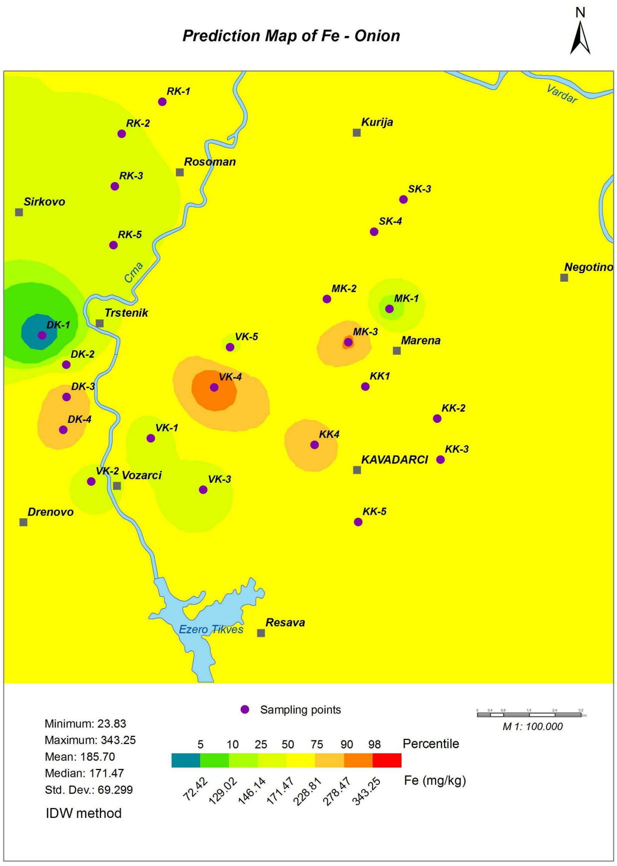

Figure 21. Spatial distribution of Fe in the onion in the Tikves area

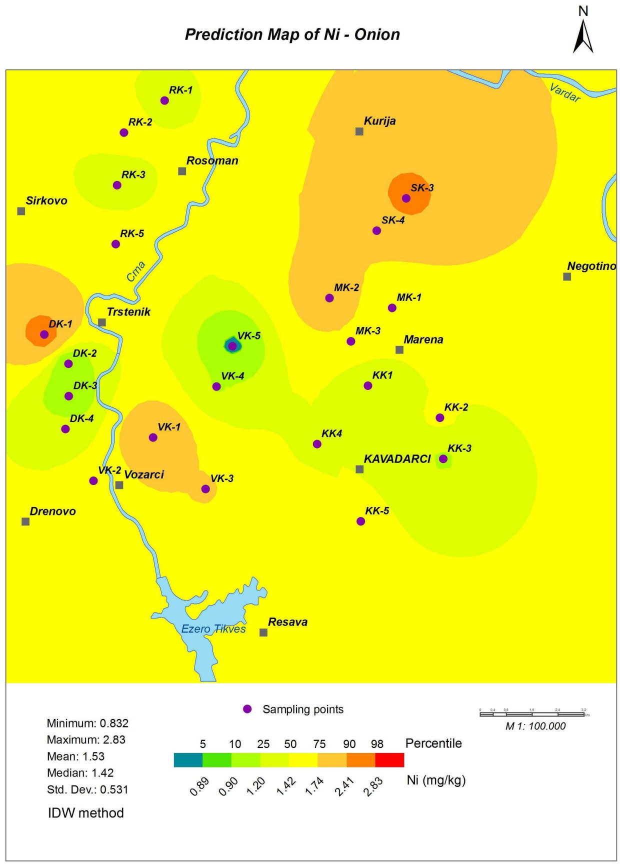

Figure 22. Spatial distribution of Ni in the onion in the Tikves area

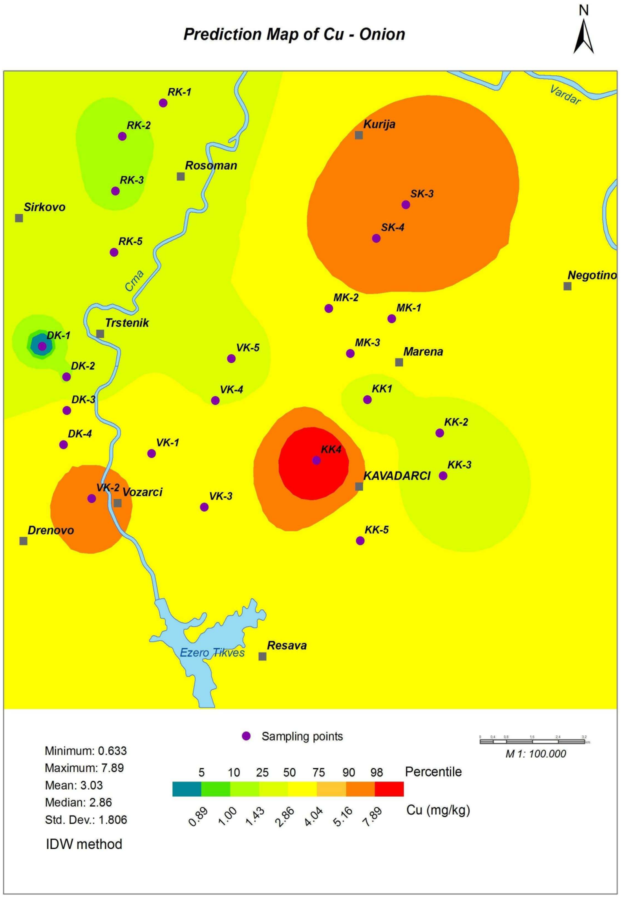

Figure 23. Spatial distribution of Cu in the onion in the Tikves area

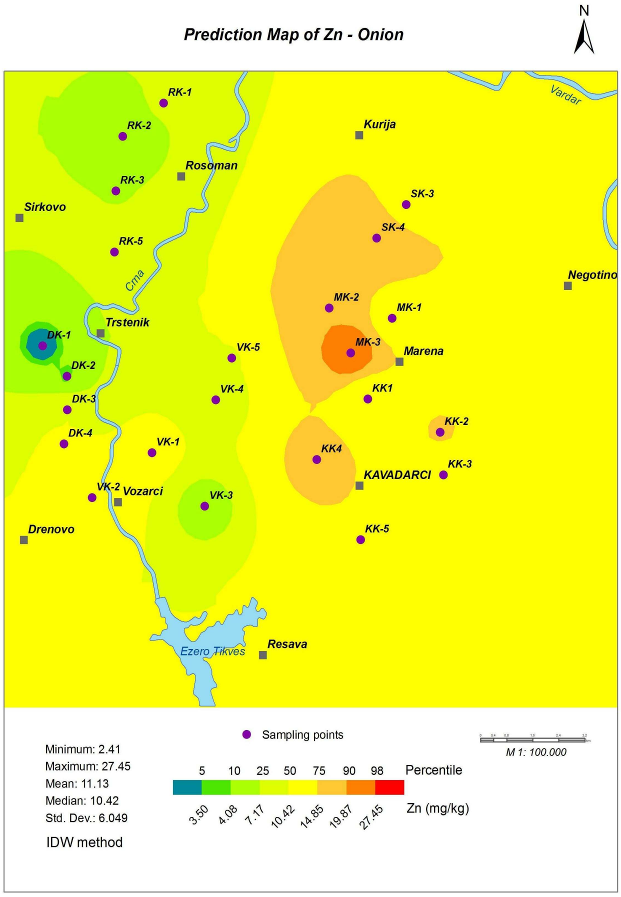

Figure 24. Spatial distribution of Zn in the onion in the Tikves area

Slight increase in the concentrations of these elements is the result of the work of the metallurgy of iron and nickel that is present in this area, the increased intensity of traffic and the increasing use of protective equipment used in the production of agricultural crops.

On the Fig.25, 26 are presented the distribution of the Co and Ga.

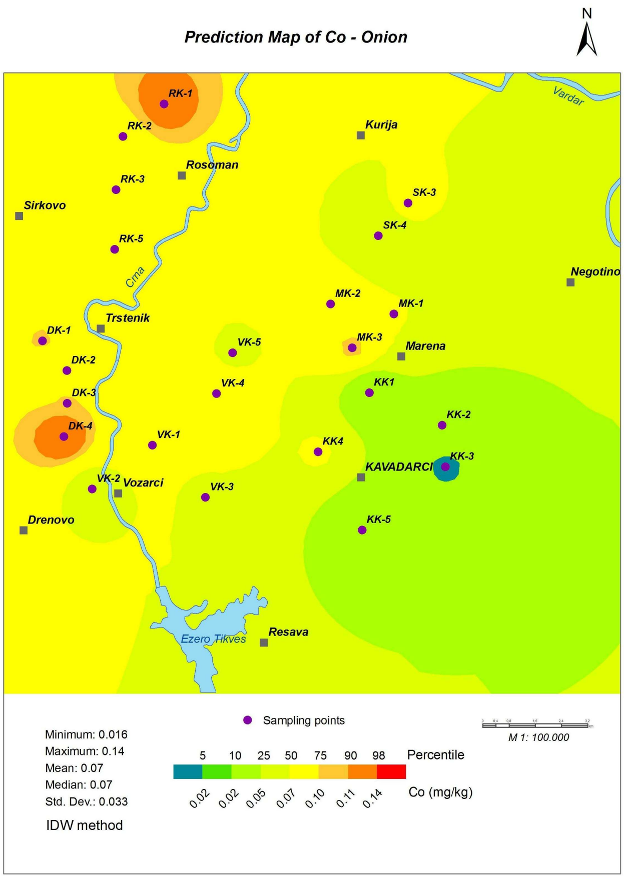

Figure 25. Spatial distribution of Co in the onion in the Tikves area

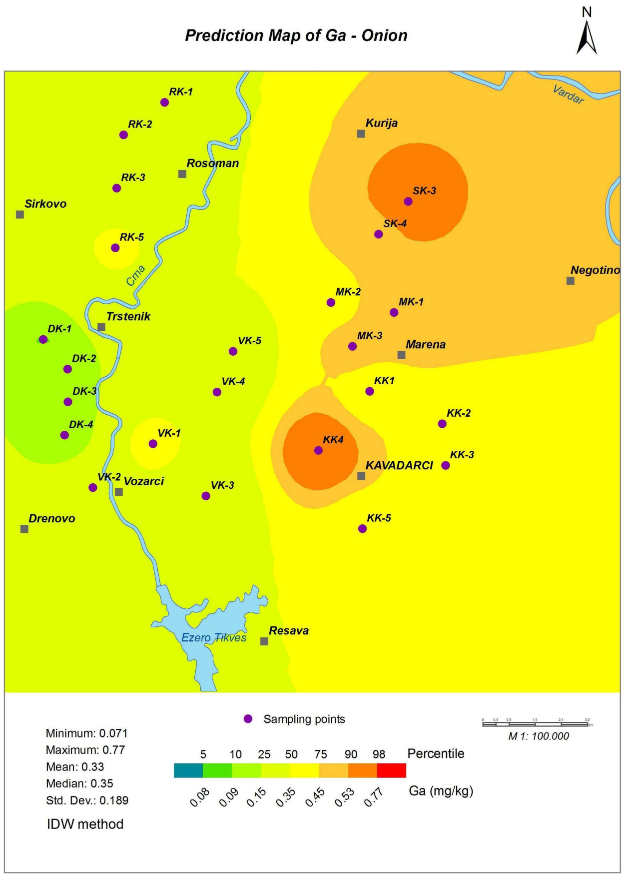

Figure 26. Spatial distribution of Ga in the onion in the Tikves area

Conclusion

The conducted geochemical research for the presence of the rare elements in the onion which is produced in the Tikves area point to the following: the contents of the elements Li, B, Na, Mg, Al, P, Ca, Ti, As, Sr, Mo, Cd, Sb, Cs, Ba, Pb, V, is within the frames of the publishes levels whereas the contents of Cr, Mn,Fe, Ni, Cu, Zn shows a slight increase in reference to the published levels. This slight increase in a consequence of the industrial activity in the area (production of fero-nickel) the increased intensity of traffic and the increased usage of agricultural staff in the production of agricultural products. It should be noted that the biggest increase in the marks is in the content of the copper which is due to the long-term usage of protection staff in the grape production.

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