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SELENIUM AND OTHER TRACE ELEMENTS IN THE SOILS OF THE TIKVES REGION

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Abstract

The paper presents the results obtained during the investigations carried out for the availability of selenium and trace elements (Ni, Cd, Cr, B) to the soils of the Tikves region. Examination by ICP-AES method were carried out on fifty samples taken in the vicinity of the villages of Begniste, Resava, Vozarci, Drenovo, Sirkovo, Manastirec, Sivec, Rosoman, Sopot, Vatasa, Kavadarci, the Beli Kamenja site as well as a number of samples collected between the places. The results obtained indicate high selenium quantities in the vicinity of Rosoman. Increased nickel concentrations, cadmium and boron along the Crna River course were also determined.

Introduction

The region of Tikves occupies the middle parts of the River Vardar valley. It includes the municipalities of Rosoman, Kavadraci, Negotino and Demir Kapija (fig. 1). The climate and soil in the region are favourable for viticulture and growing of vegetables. Most of the arable land is irrigated using the water of Lake Tikves. Annual production of grapes for making wine exceeds 100 million tons and those for eating 10 million tons. In that regard, investigations on the composition of the soil and the concentration of trace elements are of particular importance. Bearing in mind the anthropogenic activities in the region such as nickel and other non-ferrous industry, timber and furniture production, tobacco, metal and chemical industry as well as the use of motor oil, combustion of fossil fuels, the use of large amounts of mineral fertilizers and irrigation with polluted water indicate that examinations of this kind are essential.

Geology of the terrain

The Tikves area occupies the central parts of the Vardar zone. It is one of the largest geotectonic units in the Republic of Macedonia. The geology consists of rocks of various lithological composition and stratigraphy–from Paleozoic-Mesozoic to Quaternary formations. Igneous, sedimentary and metamorphic rocks have been determined. Igneous rocks have been found as an ophiolite series and as volcanic rocks. Sedimentary rocks are present as limestones, gravels, conglomerates, sands, sandstones, clays, whereas metamorphic rocks are present as marbles, quartzites, schists (fig. 2). The complex geological structure implies that the area consists of diverse soil types.

Fig.1. Panoramic view

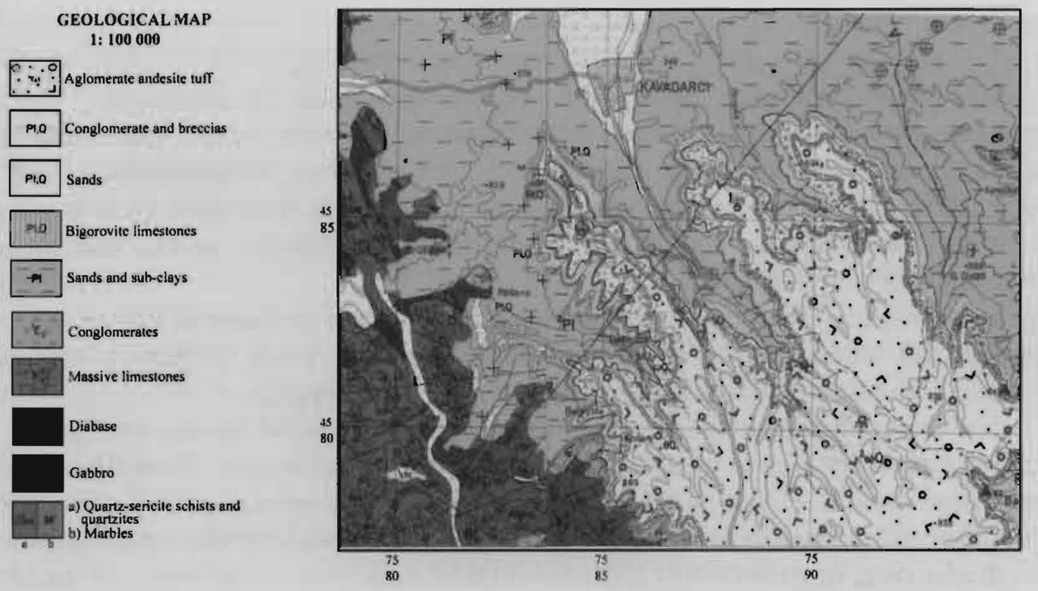

Fig. 2. Geological map of the Tikvesh region

Types of soils in the Tikves region

Examinations carried out so far have determined the following types of soils (Table 1):

Type of soil	In %
Alluvial eroded carbonate soils	44.41
Inundated alluvium	14.80
Chernozems	7.69
Brown carbonate	6.50
Carbonate deluvial	5.91
Eroded chernozems	5.22
Alluvial carbonate	4.82
Dark clays	4.64
Degraded chernozems	3.97
Other soil types	2.04

The most common type is alluvial eroded carbonate soil overlying the slopes used mostly for viticulture. The inundated alluvium, alluvial carbonate soils can be found along the Crna and Luda Mara River courses and are used for vegetable growing, orchards and vineyards.

Chernozems, eroded and degraded chernozems can be seen on the flat and slope parts. The soils are used for vegetable growing, orchards, viticulture, forage crops and wheat growing.

Methods of work

Various soil samples taken 10 cm at depth were dried, crushed and sieved. The concentration of trace elements was determined by ICP method (ISO-14869-2).

Sources and transport of selenium to the environment

Selenium is unevenly distributed in the geological environment. Volcanic emanations and metal sulphides related to magmatic activities are the major sources of selenium. Secondary sources are biological basins in which it accumulated over the history. About 50 Se minerals have been known. However, it is commonly associated with heavy metal sulphides occurring as selenide (Se^{-2}) or as an ion that replaces sulphur in the crystal lattice.

Soils containing selenium above the normal values can be found in arid or semi arid regions in the world such as those in Canada and the USA. Generally said, soils containing high selenium amounts can not be found in wet regions.

It has been calculated that about 6000 to 13 000 tons of Se are released to the atmosphere annually by natural sources, 60 to 80% of the values are the result of marine biogene processes. It is regarded that natural sources in the atmosphere release 7 000 to 18 000 tons of Se annually. From none to 400 t Se in the atmosphere come when wind blows the surface, from none to 1100 t by volatilization of sea salt, from 100 to 1800 t by volcanic activities, from non to 500 t from forest fires and from 600 to 14 300 t by biological processes.

Anthropogenic sources of selenium include coal and fossil fuel combustion, metal industry, waste (domestic, urban and industrial), and manufacture processes, mining, smelting, and refining. It has been calculated that annual anthropogenic transfer of selenium to the atmosphere amounts from 1700 to 5800 t. The major sources are coal combustion from 900 to 2800 t, oil combustion from 100 to 800 t, metal industry (mining, alloy production and that of Pb, Cu-Ni, Zn-Cd) from 700 to 2100 t, and waste dump from none to 100 t.

After transfer to nature, selenium like all other elements is transported by external factors. Selenium emission by volcanic emanations, magmatic processes, biological process, industry, coal and fossil oil combustion, waste and other sources is transported through the atmosphere and hydrosphere and the ultra thin layers of the lithosphere. Selenium particles from the atmosphere fall into waters and soils where they become available to plants and through food to animals and humans.

Selenium quantities in igneous rocks are low, less than 1 mg/kg. Similar quantities can be found in metamorphic rocks. Sedimentary rocks such as chalk, sandstones, limestones and gravels contain about 100 mg/kg Se.

Soils containing certain amount of selenium yield data about the origin of their material. For example in arid and semi arid areas, soils containing selenium were formed from sedimentary rocks, most often limestones and limestones. The chemical reactions of such soils are alkali and favour the formation of selenates, which are easily available to plants. The selenates are easily washed from the surface but rainfalls enhance their penetration to the deeper parts of the soil where they become available to plants. Thus, analysis of surface soils is not the right indicator for the possible development of vegetation containing toxic selenium amounts. From the air selenium enters the soil.

Selenium from waste also has the tendency to enter soils. When selenium does not come into contact with oxygen it remains rather immobile and does not pose risk for humans and plants. An increase in oxygen and acidity increases the mobility of selenium.

Increased selenium amounts are due to anthropogenic activities such as industry, coal and oil combustion, the use of pesticides, wastewaters etc. If selenium is more mobile, soils are more likely to become contaminated.

Soil temperature, dampness, the time period of the year, the content of organic material and activity of microorganisms are important factors for selenium mobility in the soil. Land cultivation will not only increase the content of selenium in the soil, but will increase its concentration in surface and drainage waters. Behaviour of selenium in soils depends on its interaction with other compounds and conditions in the environment at the time.

Coal contains unusually high selenium amounts, on average about 300 mg/kg. So, it is regarded as one of the greatest contaminants of soil. It is assumed that from coal selenium is released to the soil by erosion, washing, and biological activities.

Some soils yield products with selenium deficiency. Important factor in this probably is the chemical composition of soils, but also other factors such as rainfalls, climate, pH value and composite of the soil material.

All plants take up selenium from soils depending on the type, degree of development and availability. The factors affecting availability to selenium are pH value and iron content.

Different plants contain variable selenium amounts. Certain plants, selenium accumulators, contain selenium quantities that are toxic for animals. In the USA domestic animals fed on Astragalus plant from areas with increased selenium concentrations were poisoned. On the other hand sheep in areas with selenium deficiency got “decease of white muscles”. Selenium, via the food chain, enters humans and animals, which calls for permanent check ups for possible concentration of selenium and other toxic materials in plants that are used for food by people and animals.

Results and discussion

The results obtained during the examinations are given in Table 2. It can be seen from Table 2 that the mean Se value in soils ranges within 1.7 mg/kg (from 1.10 to 6.30). The highest Se value was found near the village of Sopot (5 to 6.30). The map of distribution (fig.3) also shows that significant anomalies occur in the region of Sirkovo and Rosoman.

The results show that the soils in the Tikves region contain elevated selenium contents compared with those in the world (Ure at all., 1979; Frank, et al., 1979; Lag, 1974, Steinnes, 1980). The increased amounts are due to the combustion of fossil fuels in the FENI processing plants in the vicinity of Vozarci. It is of note that the increased amounts of selenium are due to the dry climate that enhances the increase of selenium in the soil and the use of fertilizers in vineyards.

Investigations carried out for the presence of nickel in the soils of the Tikves region indicate that its mean value amounts to 83.2 mg/kg (from 27 to 195 mg/kg). A comparison with the values found in some countries in the world indicates that in the area of Sirkovo and Rosoman there are increased contents of nickel (fig.4)(Bradley, 1980; Aubert et al., 1977; McKeague et al., 1974; Tjell et al., 1972). The increased contents of nickel are similar to the values published for some region in the world in which contamination comes from local sources, mostly industry (mainly non-ferrous industries, iron, steel and chemical industries), agriculture, use of mineral fertilizers, especially phosphates, road traffic etc. (Cox et al., 1981).

Table 2: Concentration of Se, Ni, Cr, Cd, B in soils of the Tikves region (mg/kg)

	Coordinates			Concentration				
	x	*y*	z	**Ni** *(ppm)*	**Cr** *(ppm)*	**Cd** *(ppm)*	**B** *(ppm)*	**Se** *(ppm)*
1	458000	758200	320	77	108	3.61	41	1.50
2	458000	784000	400	79	106	3.25	40	1.30
3	458200	758200	400	80	102	4.61	45	1.60
4	458200	758400	400	85	115	4.50	42	1.30
5	458200	758600	500	88	110	4.20	41	1.50
6	458400	758000	230	78	100	4.10	45	1.20
7	458400	758200	250	80	110	3.90	38	1.30
8	458400	758400	300	85	105	4.50	41	1.20
9	458600	758000	280	80	92	5.34	45	1.40
10	458600	758200	270	85	98	5.50	46	1.10
11	458600	758600	400	60	70	3.5	31	1.10
12	458700	757880	380	85	93	4.41	45	1.30
13	458700	758000	270	84	98	4.50	46	1.20
14	458700	758200	290	83	100	4.30	41	1.30
15	458700	758400	260	67	51	4.87	31	1.50
16	458700	758600	260	65	50	4.60	30	1.30
17	458700	758800	560	40	45	3.70	30	1.20
18	458800	757600	260	78	77	4.75	45	1.20
19	458800	757800	200	80	81	4.80	46	1.10
20	458800	758200	300	81	90	4.60	45	1.20
21	458800	758400	300	35	27	1.69	25	1.10
22	458800	758600	240	33	28	1.50	24	1.20
23	458800	758800	400	27	25	1.20	21	1.10
24	459000	757600	200	80	85	3.90	39	1.50
25	459000	757800	280	85	90	3.95	41	1.30

26	459000	758000	350	70	80	3.80	38	1.30
27	459000	758200	560	50	60	2.50	25	1.20
28	459000	758400	280	38	29	1.80	25	1.10
29	459000	758600	270	40	30	1.60	28	1.10
30	459200	757600	220	80	90	4.50	45	1.30
31	459200	757800	230	85	98	4.60	42	1.10
32	459200	758000	320	60	70	3.80	38	1.30
33	459200	758200	540	45	55	2.60	31	1.10
34	459200	758400	230	46	48	4.67	38	3.12
35	459200	758600	230	47	50	4.70	33	3.50
36	459400	757600	250	80	90	4.60	45	1.70
37	459400	757800	160	85	98	4.50	47	1.20
38	459400	758000	230	77	85	3.90	39	1.10
39	459400	758200	300	60	70	3.80	35	1.20
40	459400	758400	300	50	60	3.90	38	1.20
41	459400	788600	200	44	46	4.19	35	1.10
42	459600	757400	300	190	197	4.88	50	1.30
43	459600	757600	250	180	170	4.70	45	1.70
44	459600	757800	220	190	198	4.80	46	1.90
45	459600	758000	250	100	130	4.50	38	1.70
46	459800	757600	220	198	183	6.90	48	6.30
47	459800	757800	230	190	180	6.70	45	5.80
48	459800	758000	210	195	178	6.30	42	4.90
49	459800	758200	230	100	110	5.80	41	4.70
50	459800	758400	240	60	70	4.50	35	2.00

Cr contents in the soils of Tikves are within the 25 – 198 mg/kg interval (mean value of 90.62 mg/kg).

The highest chromium concentrations have been found near the villages of Sikovo and Rosoman (fig.5). A comparison between the results obtained for chromium concentrations in Tikves with those published for some countries in the world (Naidenov et al., 1977; McKeague et al., 1980; Kitigashi et al., 1981; Ure et al., 1979) shows that chromium concentration in Tikves are similar to those found in other countries in the world.

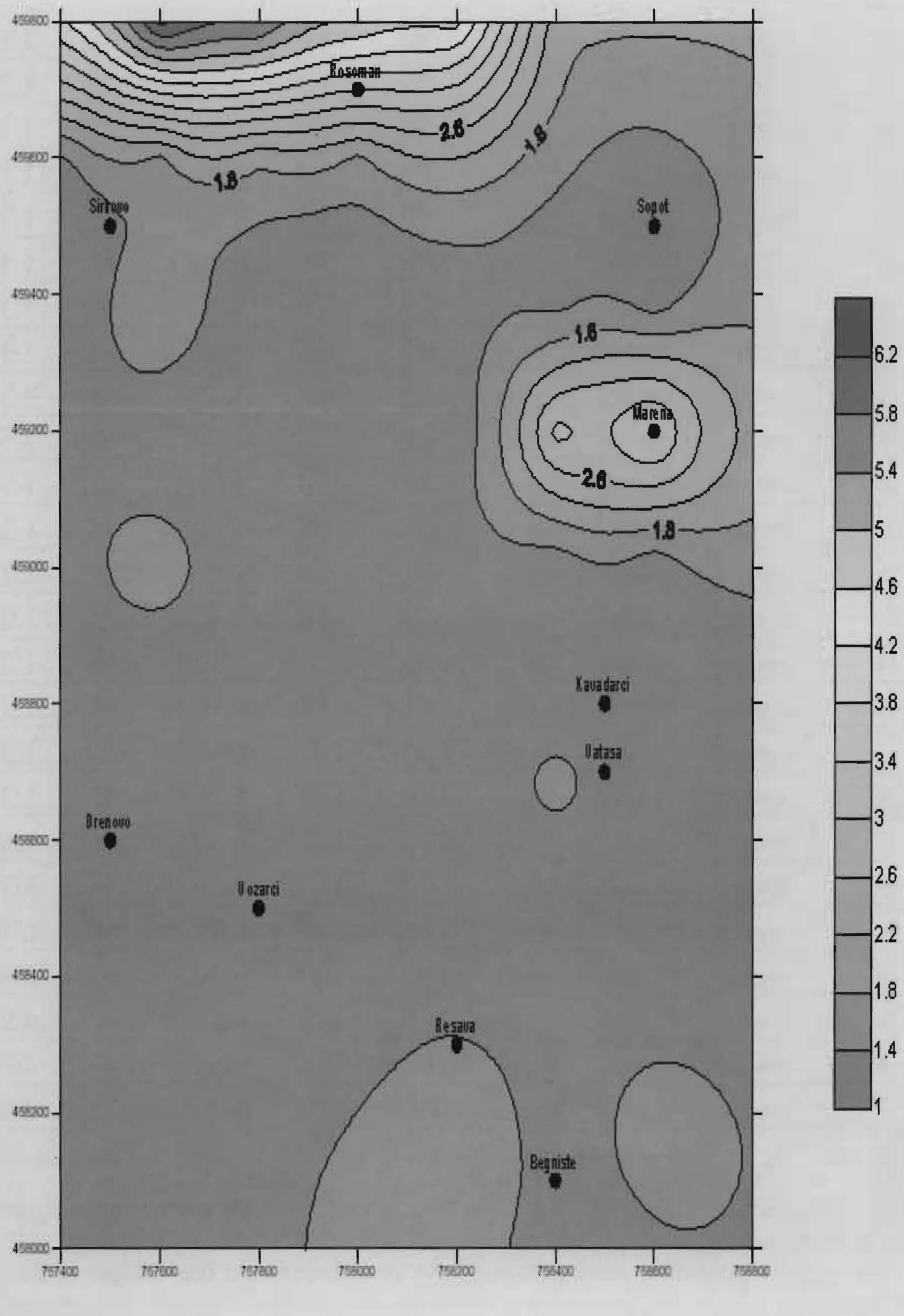

Fig. 3. The map of distribution of selenium

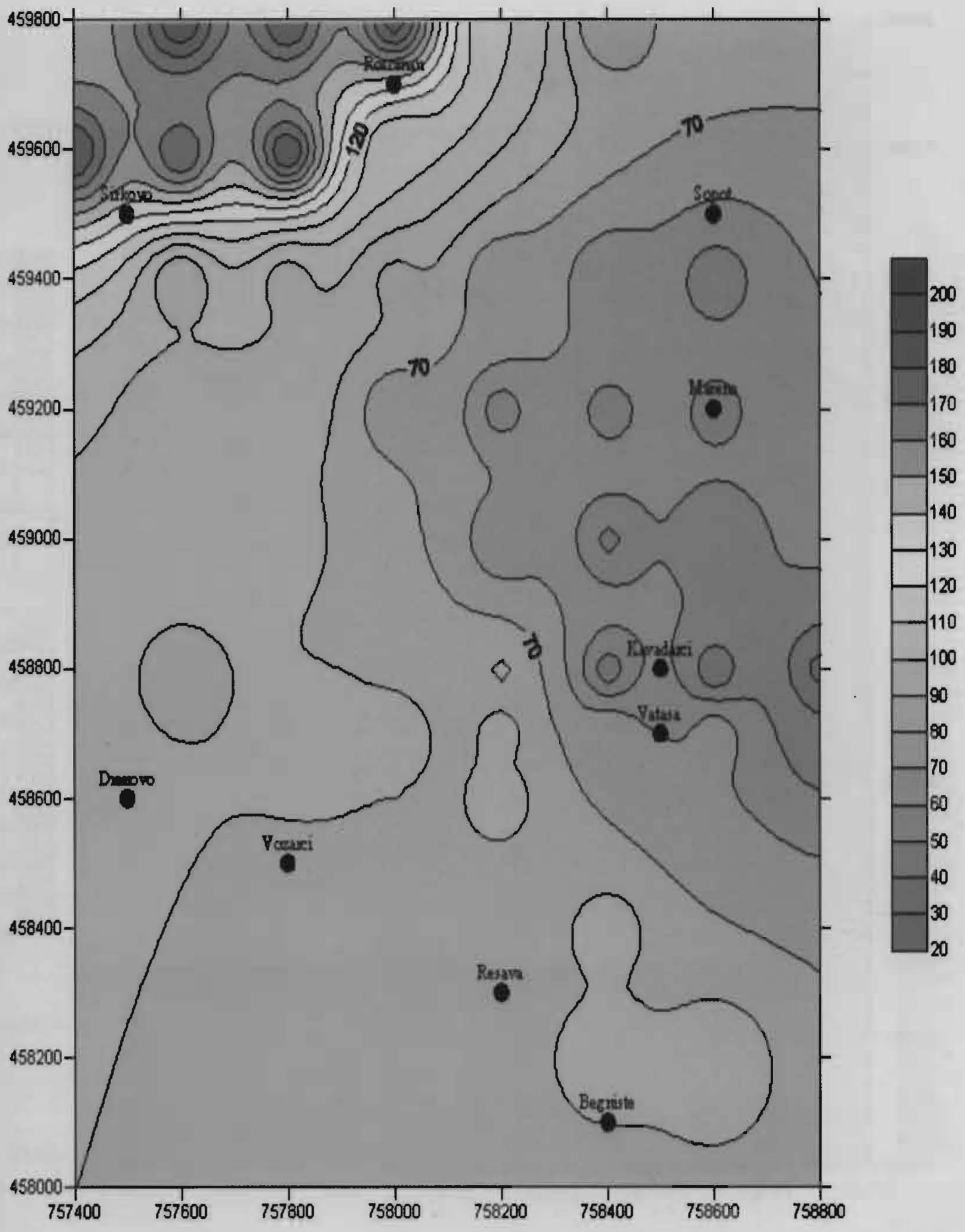

Fig.4. The map of distribution of nickel

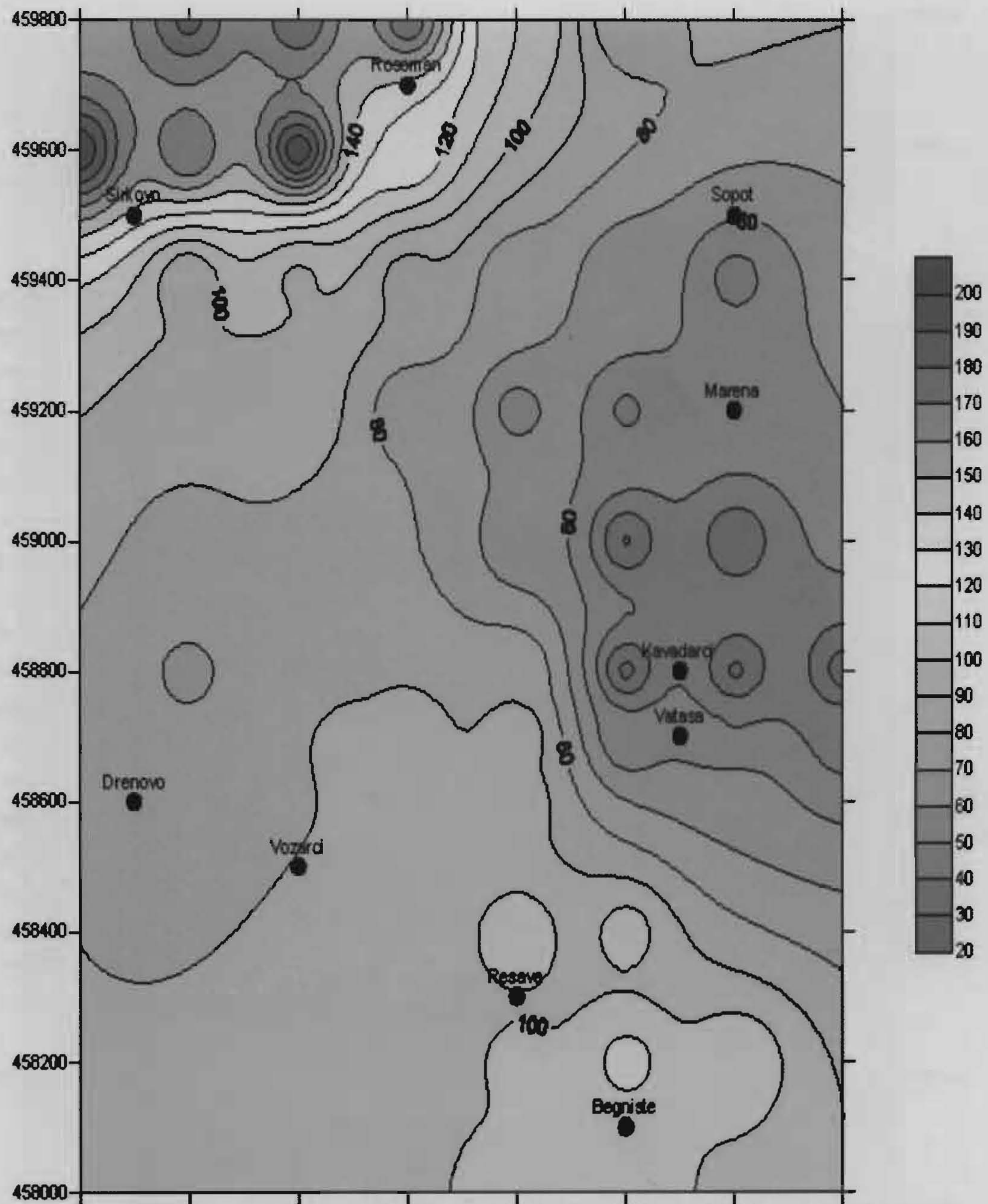

Fig. 5. The map distribution of chromium

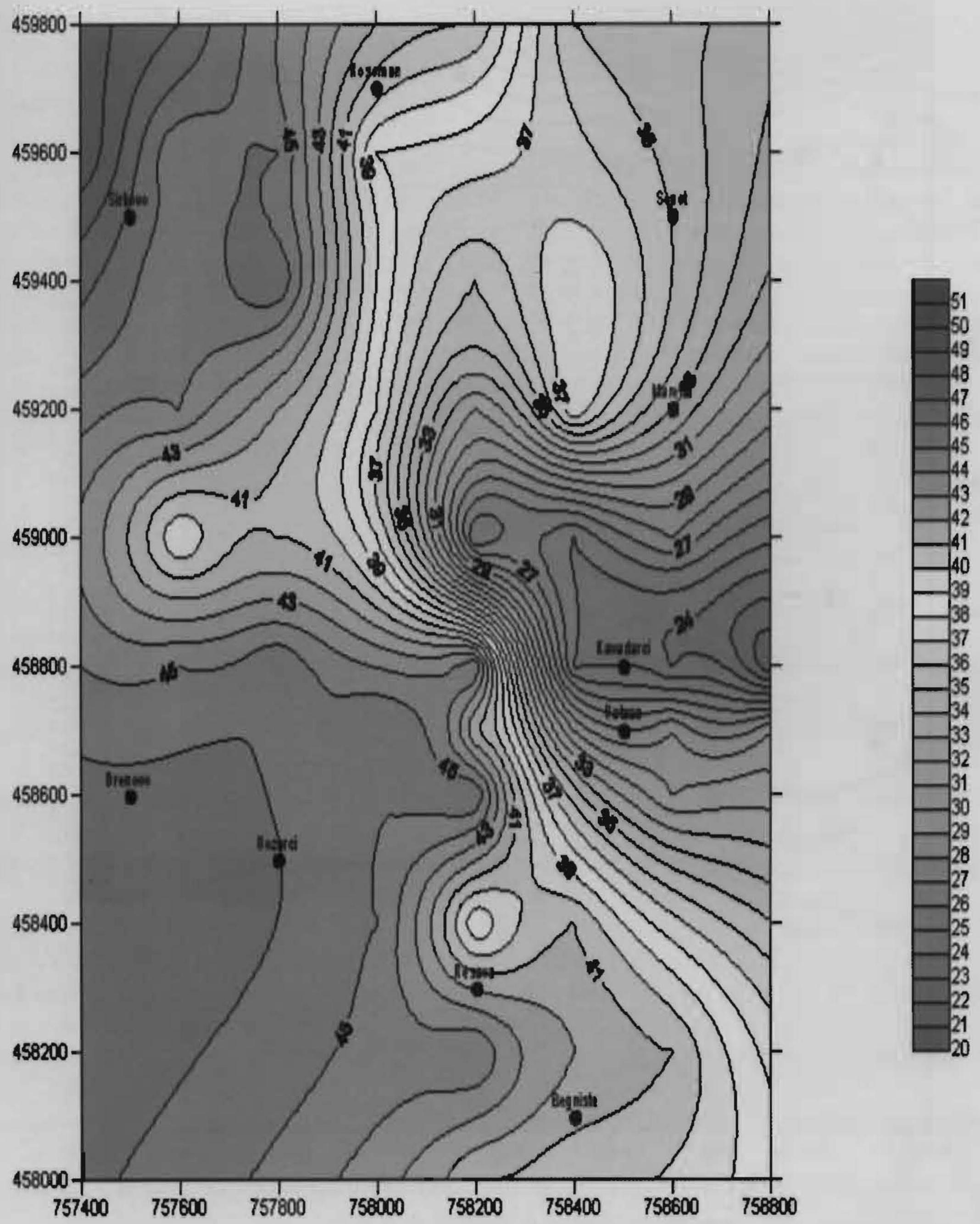

Fig. 6. The map of distribution of boron

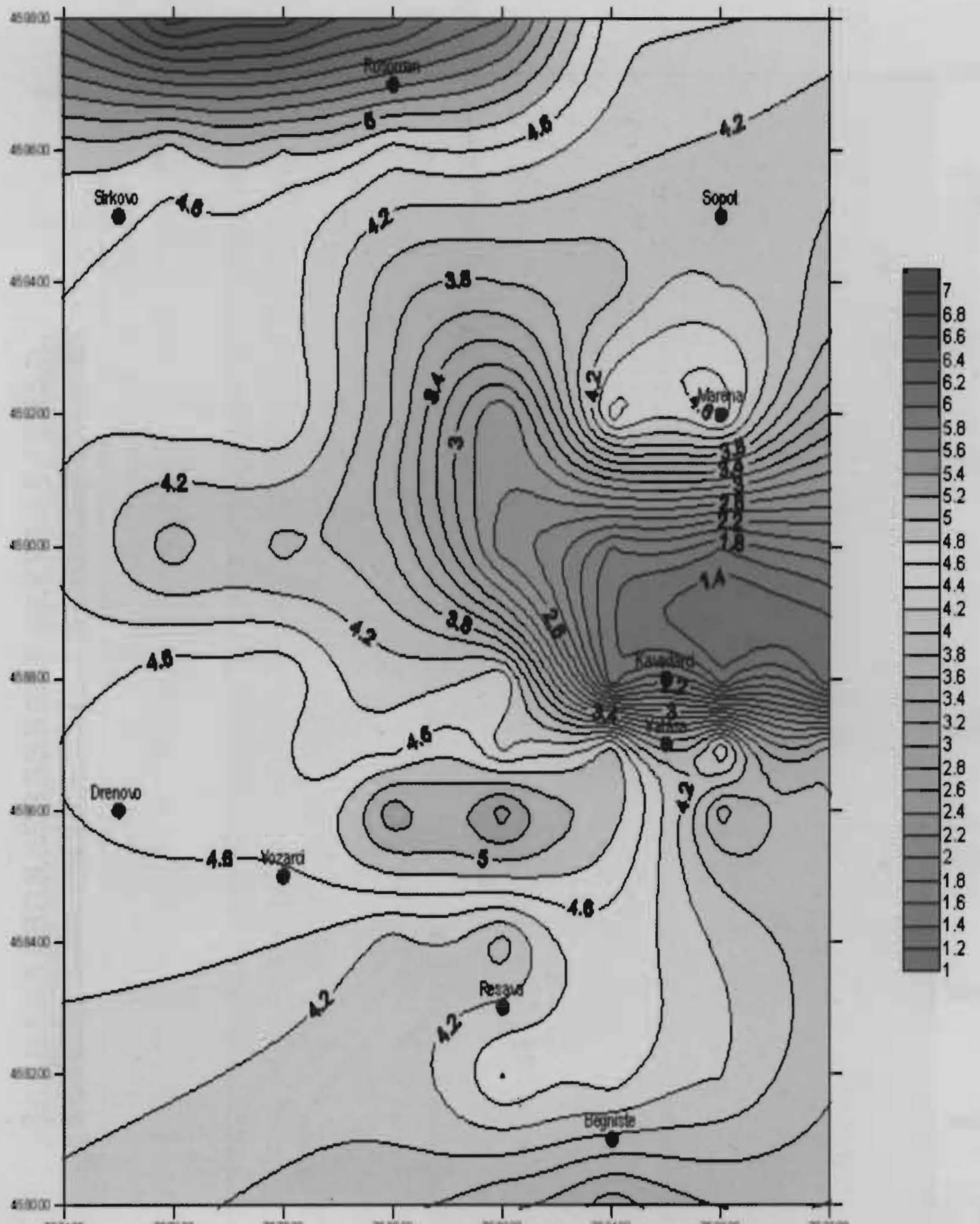

Fig.7. The map distribution of cadmium

Content of B in the soils of the region under consideration is within the 21 – 47 mg/kg interval or mean value of 38.72 mg/kg. The map of distribution shows that (fig.6.) boron is almost evenly distributed. Boron concentrations in the soils of Tikves are similar to those in certain parts of the world (Kosanovic et al., 1962; Ravikovic et al., 1961; Cumakov, 1988).

The content of Cd in the area ranges from 1.20 to 6.90 mg/kg or mean value of 3.5 mg/kg (fig.7.). It is obvious that the content of cadmium is relatively high compared to the content of the element in other parts of the world (Kabata – Pendias, 1981; Frank et al., 1979; Rauta et al., 1985). Increased concentrations of cadmium have been found in other regions of the Republic of Macedonia, which points out the possible anthopogenic emission of cadmium in the wider region.

Conclusion

The investigation carried out on the presence of Se, Ni, Cd, Bo, Cr in the soils of the Tikves region indicated high concentrations of nickel, cadmium and selenium in some parts. The increased amounts are due to anthopogenic influences such as increased industrial activity and the use of fertilizers in viticulture. The investigations pointed out the need of further detailed investigations for the possible presence of trace elements in the soils. Because of the variety of soil pollutants and concentrations, impacts are not very well known. Strategies to tackle the problems concerned with sources of pollution require prevention and cleaning up of polluted soils. Unfortunately, very few countries have elaborated legislation with respect to the registering and cleaning up of polluted soils. Whether or not such operations have been undertaken, polluted soils raise a number of legal and administrative issues.

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