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# ACCUMULATION AND DISTRIBUTION OF HEAVY METAL IN PERENNIALS PARTS OF VINE IN FIVE LOCAL VARIETIES (RIZLING, SMEDEREVKA, HAMBURG, KRATOŠIA AND AFUS ALI ) FROM OVČE POLE (R. MACEDONIA)

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A b s t r a c t: This work was conducted in vinevards located in Ovče Pole. near the village of Krivi dol. in the eastern part of Macedonia, in order to assess the bio-accumulation and distribution of trace elements in perennial part of grape, in five local varieties (Rizling, Smederevka, Hamburg, Kratošia and Afus-Ali). For this purpose, the content of trace elements in soil and in the perennials parts of the vine: leaves, branches and grapefruit were measured, in all five local varieties. The content of Zn in soils varied from 75.7-96.33 mg/kg, Ni from 1.69 to 4.45 mg/ kg, Cu from 34.1- 53.6 mg/ kg, Ba from 65.8- 140.5mg/kg, Sr from 56,3-150,9mg/kg, As from 5.48 -13.59mg/kg, Mo from 1.99 to 3.1mg/kg, Pb from 14.19-26.9mg/kg, Ti from 119-239mg/kg, Fe from 2482-3080mg/kg, Mn from 722-1081mg/kg and Al from 2646-4012mg/kg, respectively. The content of Zn in plant varied from 154.8- 188.5mg/kg, Ni from 145.1 to 191.8mg/kg, Cu from 31.1 to 51.5mg/kg, Ba from 15.7 to 24.2mg/kg, Sr from 186.5 to 287.8mg/kg, As from 9.78-27.7mg/kg, Mo from 0.28 to 1.44mg/kg, Pb from 5.25 to 13.56mg/kg, Ti from3.73 to 7.38mg/kg, Fe from 345 to 464.5mg/kg, Mn from 352.3 to 400.2mg/kg and Al from 130.8 to 256.5mg/kg, respectively. The contents of Zn,Ba, As, Mo, and Pb not exceeded the maximum allowable content (MAC) in all soil (The Now Dutch list). The highest content of Cu and Ni (The Now Dutch list) were founded in all vineyard soil from Ovče pole. Considering the value for bioaccumulation factor (BAF), grape vine for Zn, Sr, Cu and As possessed the characteristics of hyper accumulator. Most of the accumulated metals are mainly concentrated in the leaves of the vine, with the exception of As, which are concentrated in the fruit of the vine.

Key words: grapevine, trace metals, bioaccumulation, distribution

#### **INTRODUCTION**

Heavy metals such as lead, cooper, zinc, in high concentrations, are toxic for plants, preventing their proper development. In recent decades several anthropogenic activities have caused a remarkable release of trace metals into agricultural soils. The most relevant of these include the application of fertilizers, liming materials, agrochemicals, the use of irrigation waters, and atmospheric deposition from industrial, urban and road emissions (Senesi, 1999). Wastewater may contain various heavy metals including Zn, Cu, Pb, Mn, Ni, Cr, Cd, depending upon the type of activities it is associated with. Continuous irrigation of agricultural land with sewage and industrial wastewater may cause heavy metal accumulation in the soil and plants (Sharma et al., 2007; Marshall et al., 2007). On the other hand, the total content of a trace metal in soil is generally of limited use for evaluating the amount of metal that can be absorbed by plants. An increase in the total metal content does not necessarily correspond to an increase in plant uptake. Bioavailability of trace metals in soil and its phytotoxicity associated with specific forms of metals in the soil, and to several soil properties, and variety of the plant (McBride et al. 1997).

Explaining the accumulation process of heavy metals in plant has led to wide research. The objective of the present research is to evaluate total trace element contents in grapes of five local varieties namely Rizling, Smederevka, Hamburg, Kratosia and Afus ali grown in a vineyard in Ovče pole (Eastern Macedonia) and to assess the Biological Accumulation Coefficient (BAC) of trace elements in the grapevine and distribution in perennial part of grape: leaves, branches and grapefruit, in five local varieties (Rizling, Smederevka Hamburg, Kratosia and Afus Ali).For this purpose, the content of trace elements in soil and in the pe-

#### Description of the sampling site

Research was carried out on a total area of 9 acres of arable agricultural land planted with vines, located in valley Ovče pole, in the eastern part of Macedonia (Fig. 1). Ovče Pole is a valley which is situated in the flow of Sveti Nikole's River, as a right tributary of the river Bregalnica, 41052, north latitude broadness and 19022, north latitude length,

rennial parts of the vine: leaves, branches and grapefruit were measured, in all five local varieties.

#### MATERIALS AND METHODS

eastern of Grinich. The climate of the plain is characterized by hot and dry summers and temperately cold winters, with occasional sharp lows. The highest registered temperature in the plain was  $44^{\circ}$ C and the lowest registered temperature was -23°C. The Ovče Pole plain is one of the driest areas in Europe and is plagued by frequent drought periods. The yearly average of rainfall is in the 400-500  $ml/m^2$  range.



Fig. 1. Location and number of sampling sites, around the village Krivi Dol, in eastern part of R. Macedonia

# Sample collection and preparation

Plant samples (leaves, branches and grapefruit) respectively of each vine variety, and corresponding soil samples were collected from five sampling sites around the village Krivi dol (figure 1). Soil samples were collected at a depth of 0-20 cm Sampling errors were minimized by collecting five soil cores combined as a single composite sample. All plant samples were collected, taking a representative sample of leaves, branches and grapefruit.

Soil and plant samples were collected and stored in polyethylene bags in the field, and transferred to the laboratory as soon as possible for analysis.

Leaves, branches and grapefruit of vine were thoroughly washed with tap water to remove dust and other particles, followed by Mili-Q water. The samples were dried in an oven for 48 h at 80°C, and finally ground to powder for chemical analysis.

The soil samples were air-dried at room temperature for two weeks, mechanically ground and sieved to <500 µm mesh diameter size.

#### Soil and plant analysis

The  $<500\mu m$  fraction soil samples were used todetermine the maximal environmentally available trace element in soil. This was done using aqua regia, in accordance with the ISO 11466 procedure (ISO, 1995).

Soil samples weredigested with a mixture of HCl (37%) and HNO3(70%), in a ratio of 3:1 (v/v), at room temperature for 16 h and, after, at 130 °C for 2 h, under refluxconditions. Each suspension was then filtered, diluted to 100 ml with 0.5 mol/L HNO<sub>3</sub> andstored at 4 °C until analysis.Plant samples were digested with HNO3 and HClO4 in 5:1 ratio until a transparent solution was obtained (Allen et al. 1986; Markert et al. 1996). The soil and plant digested solutions were cooled to room temperature, filtered, transferred quantitatively to 50 and 25 ml volumetric flasks, respectively, made up to volume with distilled water, and kept in clean plastic vials before metal analysis.Trace metal content in soil and plant extracts were determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES Liberty 110, Varian).

All chemicals were declared *pro analysis*, and all solutions were prepared with

double-distilled water. Standard working solutions were prepared from original certified stock solutions (MERCK), concentration 1000 mg/l in 1% (v/v) HNO3. All samples were analyzed at the Analytical laboratory of the University "GoceDelcev" of Stip. The quality control procedureconsisted of reagent blanks, duplicate samples and certified standard material (PS-3, COOMET № 0001- 1999 BG, COD № 310a 98) (Zapranova, 2006)

In order to assess the influence of soil properties on trace metal uptake by plants, the soil-to-plant transfer ratio were evaluated by calculating the biological absorption factor (BAF), i.e., the ratio of trace metal content in the plant ( $Me_{plant}$ ) to either the total metal content in soils ( $Me_{tot}$ ) according to (Chen et al, 2002)

$$BAF = \frac{Me_{plant}}{Me_{soil}}$$
(1)

# **RESULTS AND DISCUSION**

# Trace metals in soil

The total content of Zn (75,7- 96,33 mg/kg), Ni (1,69-4,45 mg/kg), Cu (34,1-53,6 mg/kg), Ba (65,8-140,5 mg/kg), Sr (56,3-150,9 mg/kg), As (5,48-13,59 mg/kg), Mo (1,99-3,1 mg/kg), Pb (14,19-26,9 mg/kg), Ti (119-239 mg/kg), Fe (2482-3080 mg/kg), Mn (722-1081

mg/kg) and Al (2646-4012 mg/kg) in the selected vineyard soil in the Ovče pole region, are presented in Table 1. The content of Zn, Ba, As, Mo, and Pb, not exceeded the maximum allowable content (MAC) in all soil (Now Dutch list). The highest content of Cu and Ni (Now Dutch list), were found in all vineyard soil, on the Ovče pole region (Fig. 2).



Fig. 2. Total content of tracemetals and maximum permissible agricultural soil content in some European countries (The New Dutchlist)

# Distribution of trace metal in different part of grape vine

Total Zn (154,8-188,5 mg/kg), Ni (145,1-191,8 mg/kg), Cu (31,1-51,5 mg/kg), Ba (15,7-24,2 mg/kg), Sr (186,5-287,8 mg/kg), As (9,78-27,7 mg/kg), Mo (0,28-1,44 mg/kg), Pb (5,25-13,56 mg/kg), Ti (3,73-7,38 mg/kg), Fe (345-464,5 mg/kg), Mn (352,3-400,2 mg/kg) and Al (130,8-256,5 mg/kg) content in the selected variety of grapevine, obtained by summation of the levels in the examined organ of the vine: leaves , branches and grapefruit, are presented in T a b l e 1.

Iron: The content of Fe in plants is essential both for the health of plants and for the nutrient supply to humans and animals. The variation among plants in their ability to absorb Fe is affected by changing conditions of soil and climate and by stages of plant growth. Where Fe is easily soluble, plants may take up a very large amount of Fe. This is clearly shown by vegetation grown in soils derived from serpentine, where grass contained Fe within the range of 2127–3580 mg/kg (Johnston, 1977). Edible parts of vegetables contain Fe with in mean values from 33 to 65 mg/kg (Ensminger, et al. 1995). The average Fe contents of different cereals range from 31 to 98 mg/kg. Values above100 mg/kg are reported only for some countries, for example, 218 and 133 mg/kg, in barley from the United Kingdom and in oats from Canada, respectively (Kabata et al, 1979). It is a positive result that total Fe content in all the tested grapevine, in this work, has a high degree of bio-accumulation, but mostly accumulated in leaves and branches of grapevine.

Fig. 3 show distribution of Fe in the different parts of vine in the five selected variety of vine from Ovče pole. The Fe content in soil and grape plant did not differ significantly among the different species of grape. In terms of metals distribution in grape plants, the average content of Fe decrease in the order: leaves > branches > grape, with the exception of kratosia and rizling where the content of Fe in the branches were higher than those in the leaves. The highest content of Fe in the vine is measured in Hamburg (464 mg/kg), appropriate in this species of vine BAF has the highest value.

Table 1

Column1	Fe (rizl)	Mn (rizl)	Al (rizl)	Zn (rizling)	Ni (rizling)	Cu (rizling)	Ba (rizling)	Sr (rizling)	As (rizling)	Mo (rizling)	Pb (rizling)	Ti (rizling)
grape	43,44	16,11	16,87	14,45	1,27	9,67	4,5	5,47	14,41	0,43	0,01	0,67
branche	215,6	126,2	55,12	47,16	0,05	14,31	8,55	79,23	9,49	0,396	10,55	1,33
leaf	196,5	253,5	125,9	98,49	1,31	7,06	5,82	136,33	3,52	0,62	2,3	4,06
sum	455,6	395,8	197,8	160,1	2,63	31,04	18,87	221,03	27,42	1,446	12,86	6,06
soil	3080	1081	4012	96,33	182,74	53,61	140,5	56,25	9	2,48	26,91	197
	Fe (Afusali)	Mn (Afusali)	Al (Afusali)	Zn (Afus	Ni (Afus ali)	Cu (Afus ali)	Ba (Afus ali)	Sr (Afus ali)	As (Afus ali)	Mo (Afus ali)	Pb (Afus ali)	Ti (Afus ali)
grape	80,73	24,36	18,24	39,02	0,44	10	4,35	9,73	1,13	0,56	7,42	3,17
branche	119,3	47,7	31,14	28,86	0,29	27,41	6,66	54,76	1,52	0,061	3,29	1,15
leaf	172,9	280,2	81,42	119,05	0,96	14,1	8,55	181,98	10,94	0,01	2,85	3,06
sum	372,9	352,2	130,8	186,93	1,69	51,51	19,56	246,47	13,59	0,631	13,56	7,38
soil	2482	772	3159	74,36	152,92	52,04	80,29	104,3	9	3,1	14,19	239
grape	Fe (smed) 54,83	Mn (smed) 16,05	Al (smed) 24,27	Zn (smed) 21,76	Ni (smed) 0,46	Cu (smed) 8,9	Ba (smed) 6,13	Sr (smed) 8,28	As (smed) 5,02	Mo (smed) 0,3	Pb (smed) 0,11	Ti (smed) 0,76
branche	120,36	106,11	42,06	34,78	1,01	14,5	6,81	98,39	3,07	0,215	3,1	0,93
leaf	169,91	265,27	69,05	98,31	2,98	9,97	6,77	91,71	2,79	0,175	2,04	2,04
sum	345,1	387,43	135,38	154,85	4,45	33,37	19,71	198,38	10,88	0,69	5,25	3,73
soil	2321	772	2646	72,34	145,11	37,61	65,86	120,85	6,18	1,99	14,54	197
	Fe (krat)	Mn (krat)	Al (krat)	Zn (kratosij	Ni (kratosija	Cu (kratosija	Ba (kratosija	Sr (kratosija	As (kratosija	Mo (kratosija	Pb (kratosija	Ti (kratosija

Content of heavy metals in soils and plants collected from Ovče pole

Accumulation and distribution of heavy metal in perennials parts of vine in five local varieties (Rizling, Smederevka, Hamburg,	5
Kratošia and Afus Ali ) from Ovče Pole (R. Macedonia)	

grape	59,95	23,7	29,62	20,53	1,03	8,88	4,62	16,19	5,39	0,95	0,89	0,84
branche	197,44	107,48	60,34	60,27	0,42	19,38	3,02	72,12	2	0,122	6,27	1,56
leaf	166,6	269,0	86,88	107,72	1,47	5,77	8,05	98,19	2,39	0,01	1,33	2,73
sum	424,0	400,2	176,8	188,52	2,92	34,03	15,69	186,5	9,78	1,082	8,49	5,13
soil	2932	929	3202	87,78	191,81	52,95	72,11	150,9	5,48	2,18	18,83	197
grape	Fe (ham) 73,41	Mn (ham) 15,77	Al (ham) 43,08	Zn (hambur 34,93	Ni (hambur 0,19	Cu (hambur 13,01	Ba (hambur 5,62	Sr (hambur 4,56	As (hambur 17,7	Mo (hambur 0,17	Pb (hambur 0,813	Ti (hambur 0,63
branche	154,2	100,2	53,6	28,41	0,19	15,41	8,91	158,13	2,13	0,097	2,11	1,05
leaf	237,1	269,1	159,8	101,55	1,9	12,78	9,68	125,19	7,87	0,019	3,27	3,02
sum	464,7	385,1	256,5	164,89	2,28	41,2	24,21	287,88	27,7	0,286	6,193	4,7
soil	2713	929	3413	75,76	157,1	44,72	87,66	74,1	12,5	2,78	21,57	119







Fig. 3. Distribution of Zn, Ni, Cu, Ba, Sr, As, Mo, Pb, Ti, Fe, Mn and Al in vine from Ovče pole

**Manganese:** Manganese shows a particularly wide variation among plant species grown on the same soil, ranging from an average of 30 mg/kg in *Medicago trunculata* to around 500 mg/kg in *Lupinus albus*(Lonergan, 1975) Worldwide contents of Mn range from 17 to 334 mg/kg in grass and from 25 to 119 mg/kg in clover (Kabata et al, 2007.) The critical Mn deficiency levels for most plants ranges from 15 to 25 mg/kg, whereas the toxic concentration of Mn to plants is more variable, depending on both

plant and soil factors. Generally, most plants are affected by a Mn content at above 400 mg/kg. (Jones, 1972). In our study, the average content of Mn decrease in the order: leaves > branches > grape, in all variety of vine(figure 3). Mn as well as Fe, has a low phytotoxicity in grape vine, because in grape fruit is accumulated lowest part of Mn (15,77-24,36 mg/kg) (T a b l e 1).

Aluminum: Contents of this element in plants vary greatly, depending on soiland plant

factors. Some species of Al-accumulating plants may contain Al more than1000 mg/kg. (Adams, 1980). Aluminum has a lower bioaccumulation of manganese and iron, and almost equal distribution in all varieties of vine, with the exception of Hamburg where slight increase bio-accumulation factor (BAF) (figure 3).

Zinc: Zinc contents of plants vary considerably, reflecting the different factors of various ecosystems and of the genotypes. Mean values for Zn in cereals grains range from 24 to 33 mg/kg, in wheat and oats, respectively (Kabata et al, 2007) and did not show any clear differences between countries. The median Zn content (N = 5128) of wheat grains from France is 15.5 mg/kg (range 7-43 mg/kg) (Baize, 1999). Wheat grains (N = 14)from Serbia contain Zn within the range of 26.6-44.3 mg/kg, at the average value of 3.2 mg/kg (Škrbić, 2007) Mean total zinc content in all five variety of grapevine from Ovče pole valley, has high coefficient of bioaccumulation (figure 3), but these values do not exceed the minimum amd maximum limits of tolerance (27 - 150 mg/kg) (Kabata et al, 2007). In terms of metals distribution in grape plants, the average content of Zn decrease in the order: leaves (119-98 mg/kg) >branches (28-90 mg/kg) > grape (14-39 mg/kg).The highest part of Zn is accumulated in leaves.

**Nickel**: In food plants, Ni content varies from 0.1 to 5 mg/kg (Kabata et al, 2007) Average Ni contents of cereal grains from different countries varyfrom 0.34 to 1.28 mg/kg and is the highest in oat grains. Barley and wheat grains from Sweden contain Ni at mean values of 0.15 and 0.16 mg/kg, respectively (Eriksson, 2001). The mean Ni contentsof clover from various countries range from 1.2 to 2.7 mg/kg. A much higher Ni content has been reported formeadow grass (13–75 mg/kg) and forest grass (10–100 mg/kg) from taiga zone of Western Siberia (Niechayeva, 2002).

In vineyard soil from Ovče pole valley, were foundat the highest content of Ni (145-191mg/kg), but total content of Ni in grape vine (1,69-4,45 mg/kg) suggested not very high bio-accumulation index and the rate of low toxicity (Figure 3). The average content of Ni decrease in the order: leaves > branches > grape, with the exception of Afus-ali, content of Ni in the grape were higher (means 0,44-1,37 mg/kg) than those in the braches means (0,05-1,-5 mg/kg), in kratosia and riesling, respectively (figure 3).

Copper: Some plant species have a great tolerance to increased content of Cu and can accumulate extremely high amounts of this metal in their tissues. The content of Cu in plant tissues seems to be a function of its level in the nutrient solution or in soils. The pattern of this relationship, however, differs among plant species and plant parts. Cu in ash of a variety of plant species, growing under widely ranging natural conditions, is reported to range from 5 to 1500 mg/kg (Shacklette, 1978) However, Cu contents of whole plant shoots do not often exceed 20 mg/kg, and thus values from 20 to 100 mg/kg are usually considered to indicate the threshold of excessive contents (Kabata et al, 2007).

In grapevine from Once pole valley, copper (33,37-53,6 mg/kg) along with zinc, arsenic and strontium have the highest level of bio-accumulation and the total content is equally distributed between the organs of the grapevine. The average total content of Cu in grape vine is very high (31,4- 52,0 mg/kg), but the greatest partis contained in the branches of grapevine (14,3- 27,4mg/kg). In the grape fruit content of Cu range from 8,88mg/kg in kratosia to 13,01mg/kg in hamburg.

Molybdenum: Mo is an essential micronutrient, but the physiological requirement for this element is relatively low.Its mobility and phytoavailability increases with soil pH. (Sardans et al., 2008) observed that drought affects the Mo uptake by plants and depending on plant species its concentration may increase ordecrease. The Mo content in the five selected variety of grape in the Ovče pole region is were ranged between 0.28 in hamburg and 1,44 mg/ kg in rizling, which is quite low with respect to the needs for animal and human nutrition (Kabata et al, 2007). The average content of Mo in different part of vine in all variety of grape vine decrease in the order: grape (0,95-0,17 mg/kg) >branches (0,39-0,61 mg/kg)>leaves (0,01- 0,62 mg/kg).

Lead: The total lead content in grape vine, obtained by summation of the levels in the examined organ, (5,25-13,56 mg/kg) suggests a low phytotoxicity in grape vine (Kabata et al, 2007) with exception of rizling (12,8 mg/kg) and hamburg (13,56 mg/kg).

The total lead content in grape vine, obtained by summation of the levels in the examined organ, range between 5,25 mg/kg in smederevka, to 13,56 mg/kg in Afusali. In the examined organ of grape vine, the greatest part of Pb is contained in the branches (2,11-10,5 mg/kg) and leaves (8,49-2,3 mg/kg), with exception of Afusali were greatest part of Pb is contained in the grape fruit. This result suggested high risk of phytotoxicity grape variety Afusali.

**Barium**: Although Ba is reported to be commonly present in plants, it is apparently not an essential component of plant tissue. Ba mean contents in most plants range from 2 to 13 mg/kg, with an exception of blueberries in which highly elevated Ba levels are reported (Anke et al. 2002). The highest contents of Ba are reported for Brazil nuts, depending on the location of growth, from about 3000 to 4000 mg/kg (Kabata et al, 2007)

In all five varieties of vines collected from Once pole were no significant variations between the barium content in the soil (65,8-140,5 mg/kg) and vines (15,7-24,2 mg/kg). Ba in leaf ((5,82- 9,68 mg/kg), branches (3,02-8,91 mg/kg) and fruit (4,35-6,13 mg/kg), of the vine is equally distributed, with the exception of kratosia where the content of Ba in the grapefruit (4,62 mg/kg) were higher than those in the branches (3,02 mg/kg). This result suggests a low phytotoxicity in grape vine (Kabata et al, 2007)

Arsenic: Content of As in plants grown in uncontaminated soils vary from 0.5 to 80 µg/kg (Queirolo et al. (2000).Gough et al. reviewed findings on the As phytotoxicity and reported that its content of injuredleaves of fruit trees ranged from 2.1 to 8.2 mg/kg. In general. the tolerance for As of agronomiccrops is established at 0.2 mg/kg and in other plants at >5 mg/kg (Kabata et al, **2007)**. However, the critical value in rice plants is as high as 100 mg/kg in plant tops and 1000 mg/kg in roots. (Kitagishi et al, 1981).

The distribution of As, is drastically varied with variety of vine. kratosia, riesling,

hamburg and smederevka contained the highest content.

As in all five varieties of vines has a high degree of bio-accumulation (9,8-27,7 mg/kg) and most of it is accumulated in the fruit of the vine (5,0 mg/kg in smederevka; 5,3 mg/kg in kratosija; 14,4 mg/kg in rizling; 17,7 mg/kg in hamburg), with the exception of Afus Ali where most of the arsenic is accumulated in the leaves (3,5-10,8 mg/kg). These results indicate an increased risk to the health of all five varieties of grapevine.

**Strontium**: Although Sr is apparently not a plant micronutrient, it is absorbed following the plant's metabolicrequirements for Ca and is related to both the mechanisms of mass flow and exchange diffusion (Kabata, 2011).

The content of Sr in plants is highly variable (Shacklette, 1978) and seems to be the lowest in grains (means 1.5–2.5 mg/kg) and the highest in vegetable leaves (means 45–74 mg/kg) and in tops of legume feedplants (means 219–662 mg/kg).

In all five varieties of vines from Once pole, Sr has a high degree of bioaccumulation, but most of it is lowest in grapefruit (means 4,56–16,19 mg/kg) and the highest in leaves (means 91,7-198,4 mg/kg). This value indicated that Sr is likely to be accumulated in leaves.

**Titanium:** Contents of Ti in grain crops from Kazakhstan range from 1.2 to 7 mg/kg and in wheat fl our, from 0.4 to1.0 mg/kg (Grabanov, 1970). In Swedish cereal grains, mean Ti concentrations are 0.17 and0.25 in wheat and barley, respectively (Eriksson, 2001). Some weeds, especially horsetail and nettle are known to accumulatemore Ti, up to 80 mg/kg. In vines from Ovče pole, the phytoavailability of Ti (4,7-7,4 mg/kg) is low, and is not a danger to the environment (table 2).

# Bio-accumulation factor of trace metals

The bio-accumulation factor (BCF) values of total trace metal contents in vineyard soils are shown in Figure 4 for leaves, branches and grapefruit.

Cu and Ni, Fe, Mn, Al, Mo, Pb, Ba and Ti have a low BAF value. Considering the value for bio-accumulation factor (BAF), grape vine for Zn, Sr, As and to a lesser extent Cu, possessed the characteristics of hyper accumulator. Most of the accumulated metals are mainly concentrated in the leaves of the vine, with the exception of As and Sr (Fig. 4), which are concentrated in the fruit of the vine, in rizling and homburg. This may indicate that a leaves tends to uptake trace element from soil to a greater degree than a other parts of grapevine (Lee, 1998), except As and Sr.

BAF=c(plant)/c(soil)	4,50 4,00 3,50 3,00 2,50 2,00 1,50 1,50 1,00 0,50												
	0,00	Fe	Al	Mn	Cu	Ва	Мо	Pb	As	Sr	Zn	Ti	Ni
<b></b>	grape	0,15	0,05	0,37	0,58	0,13	0,58	0,48	3,05	3,93	1,66	0,03	0,01
<b>t</b>	oranches	0,15	0,04	0,46	0,99	0,24	0,20	0,96	1,51	2,36	2,51	0,03	0,01
	eaves	0,15	0,05	0,50	0,89	0,30	0,35	0,36	1,76	1,64	2,14	0,02	0,03
S S	sum	0,14	0,06	0,43	0,64	0,22	0,50	0,45	1,78	1,24	2,15	0,03	0,02
<b>S</b>	soil	0,17	0,08	0,41	0,92	0,28	0,10	0,29	2,22	3,89	2,18	0,04	0,01

Fig. 4. Bio-accumulation factor (BAF) for Fe, Al, Mn, Cu, Ba, Mo, Pb, As, Sr, Zn, Ti and Ni

# CONCLUSION

The results showed that in all the vineyard soil, the region winery, measured high content of Cu and Ni (The New Dutchlist), but if we take into account that the bio-accumulation index for nickel is very low, then you can say that nickel, does not present a potential hazard for all vine species. On the other hand, total content Cu in some organs of grapevine is higher than the content in the soil, suggested the high BAF value.

The contents of Zn, Ba, As, Mo, and Pb not exceeded the maximum allowable

content (MAC) in all soil (The Now Dutch list), but the highest content of zinc, copper and strontium, has been measured in the some organs of the grapevine. Most of the accumulated metals are mainly concentrated in the leaves of the vine, with the exception of arsenic, which are mostly concentrated in grape fruit. A significant amount of manganese is also accumulated in the plant, while the other metals have a significantly higher content in the soil.

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#### Резиме

# АКУМУЛАЦИЈА И ДИСТРИБУЦИЈА НА ТЕШКИ МЕТАЛИ ВО ЕДНОГОДИШНИ ДЕЛОВИ ОД ЛОЗАТА ВО ПЕТ ЛОКАЛНИ СОРТИ (РИЗЛИНГ, СМЕДЕРЕВКА, ХАМБУРГ, КРАТОШИЈА И АФУС АЛИ) ОД ОВЧЕ ПОЛЕ (Р. МАКЕДОНИЈА)

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Ова истражување беше спроведено во лозарски парцели лоцирани во котлината Овче поле, во близина на селото Криви Дол, источна Македонија, со цел да се процени биоакумулацијата и дистрибуцијата на елементите во траги во едногодишни делови на лозата (стебло, гранки и гроздов плод), во пет локални сорти (Ризлинг, Смедеревка, Хамбург, Кратошија и Афус Али). За таа цел, беше извршена хемиска анализа на елементите во траги во почвата и во одделните делови од лозата од сите пет локални сорти на винова лоза. Вкупната содржина на Zn во почвата варира од 75.7-96.33 mg/kg, Ni од 1.69 to 4.45 mg/ kg, Cu од 34.1- 53.6mg/kg, Ba од 65.8- 140.5mg/kg, Sr од 56,3-150,9mg/kg, As од 5.48-3.59 mg/kg, Мо од 1.99 to 3.1mg/kg, Рb од 14.19-26.9mg/kg, Ті од 119-239mg/kg, Fe од 2482-3080mg/kg, Mn од 722-1081 mg/ kg и Al од 2646-4012mg/kg, соодветно. Вкупната содржина на Zn во лозата варира од 154,8-188.5mg/kg, Ni од 145,1 до 191.8mg/kg, Си од 31,1 до 51.5mg/kg, Ва од 15,7 до 24.2mg/kg, Sr од 186,5 до 287.8mg/kg, As од 9.78-27.7mg/kg, Mo од 0,28 до 1.44mg/kg, Pb од 5.25 to 13.56mg/kg, Ti од 3,73 до 7.38mg/kg, Fe од 345 до 464.5mg/kg, Mn од 352,3 до 400.2mg/kg и Al од 130,8 до 256.5 mg/kg, соодветно. Содржината на Zn, Ba, As, Мо, и Рb не ја надминува максимално дозволената содржина на овие метали почвата (The Now Dutch list). За Си и Ni беше измерена повисока содржина од максимално дозволената (The Now Dutch list) во почвата од Овче поле. Со оглед на добиените вредности за био-акумулациониот фактор, виновата лоза, од сите испитувани сорти, за Zn, Sr и As поседува карактеристики на хипер-акумулатор. Повеќето од акумулираните метали се главно концентрирани во листовите на лозата, со исклучок на As, кој е концентриран во плодот на лозата.