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ACCUMULATION AND DISTRIBUTION OF HEAVY METALS IN THE CANES OF GRAPEVINE

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Abstract

Heavy metal pollution is a major environmental problem that can affect productivity, quality of the finished product and the quality of human health. Since the 1990s, heavy metal pollution proves to be a problem in some major wine regions. In recent decades several anthropogenic activities have caused a remarkable release of trace metals into agricultural soils. Some trace elements (copper, zinc and manganese) are essential to plant growth and are called micronutrients. These elements are also heavy metals, and are toxic to plants at high concentrations.
The objective of the present research is to evaluate Mn, Zn, Al, Cr and Cu (mg/100g) contents in the canes of grapevines of two local varieties, Royal Feteasca and Merlot grown in two private vineyards located near Craiova, namely Breasta and Simnic, an also their concentrations in soils. Canes and soil samples were collected in April and May 2014. For samples analyses were used the following equipments: mass spectrometer with inductively coupled plasma, flame atomic absorption spectrometer - Avanta, Milestone microwave digestion system.
Determined values for Royal Feteasca variety were higher for vines located in Breasta vineyard, except aluminum content which was higher in Simnic vineyard. For Merlot variety, the values measured were considerably higher for vines located in Simnic vineyard. Following the interpretation of the results obtained, it can be concluded that the results of all metal concentrations in analyzed soils are higher in Simnic vineyard than in Breasta.

***Key words**: accumulation, canes, grapevine, soil, heavy metals.*

INTRODUCTION

Heavy metals are naturally present in the environment. Heavy metals such as cooper and 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 and therefore on vines plants (Buzatu, 2014).
Grapevines are multiannual plants, hence the significant importance of the influence of the annual ecological offer over production, especially its quality (Costea et al., 2010). The absorption and transportation of mineral elements depend on on their concentration in soil (Vladulescu and Buse-Dragomir, 2009).
The objective of the present research is to evaluate Mn, Zn, Al, Cr and Cu (mg/100g) contents in the canes of grapevines of two local varieties, Royal Feteasca and Merlot grown in two private vineyards located near Craiova, namely Breasta and Simnic, an also to evaluate the Zn, Cr, Cu and Mn concentrations in vineyard soils.

MATERIALS AND METHODS

Analyses were performed using two varieties of vine canes: Royal Feteasca and Merlot. Samples were collected in April and May 2014, from the base and the middle part of each variety. For analyzing the samples was used the following equipment: mass spectrometer with inductively coupled plasma, ICP-MS, Perkin - Elmer Elan 9000, flame atomic absorption spectrometer Avanta PM, Milestone microwave digestion system. Calibration standards were made from stock solutions ICP-MS multi element calibration STD3, monoelement standard solutions 1000 ppm K, nitric acid 65% puris p.a. (Fluka), hydrogen peroxide 30% p.a. (Merck) and ultrapure water, grade 1 according to ISO 3696: 1987.
Amount of about 0.5g of sample, weighed accurately 0.0001g, 8 ml nitric acid 65%; 2 ml H_2O_2, 1 ml ultrapure water was placed in teflon

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vessels and were subjected to a heat treatment under pressure program: heating to 180°C with a gradient of 4.5°C/min and held for 20 minutes at 180°C. After cooling, liquid samples were transferred into flasks and were brought to volume of 50 ml using ultrapure water and analyzed according to the specific procedures of the two spectrometric instruments. Control sample (blank) was composed of 8 ml 65% nitric acid; 2 ml H_2O_2, 1 ml ultrapure water being processed under the same conditions as the samples analyzed.

On the field were taken three soil samples in seven repetitions on each depth; samples of the same depth were collected in a bucket and then were mixed well.

Soil samples collected from Breasta vineyard are notated with P1, P2 and P3, and represent mean values of collected samples, and samples from Simnic vineyard are denoted by S1, S2, S3.

RESULTS AND DISCUSSIONS

The results concerning samples from the aerial parts of Royal Feteasca and Merlot varieties are presented in Tables 1 and 2. At the Royal Feteasca variety, evolution of heavy metal content has the following dynamics: the highest concentrations of Mn, Zn, Cr and Cu are found in vine plants from Breasta vineyard compared with Simnic vineyard where concentrations were lower.

Only in respect of Al content are observed pronounced differences between the two vineyards, reaching a maximum of Al content (0.64 mg/100g) in Breasta vineyard and at the vineyard from Simnic were determined concentration of 8.54 mg/100g and 14.76 mg/100g (Table 1).

Within the same cane, belonging to Royal Feteasca variety from Breasta vineyard, the values measured were higher at the base compared to the middle part of the cane, with the following abundance: Mn> Zn> Al> Cr> Cu (Figure 1).

At the canes taken from the vineyard located in Simnic the concentration determined on the base of the canes is lower than the concentrations determined in the middle part. These canes are characterized by a very high concentration in aluminum, determined metals having the following abundance: Al>Zn>Mn>Cr>Cu.

Table 1. Evolution of Mn, Zn, Al, Cr and Cu (mg/100g) content in the canes of Royal Feteasca

Sample canes		Mn		Zn		Al		Cr		Cu	
		April	May	April	May	April	May	April	May	April	May
Royal Feteasca Breasta	base	1.78	1.81	1.61	1.63	0.60	0.64	0.42	0.43	0.29	0.38
	middle	1.59	1.67	1.45	1.47	0.48	0.50	0.36	0.35	0.24	0.32
Royal Feteasca Simnic	base	0.83	0.82	0.88	0.90	8.50	8.54	0.37	0.34	0.33	0.21
	middle	0.89	0.90	1.33	1.35	14.16	14.76	0.16	0.14	0.56	0.28

Table 2. Evolution of Mn, Zn, Al, Cr and Cu (mg/100g) content in the canes of Merlot

Sample canes		Mn		Zn		Al		Cr		Cu	
		April	May	April	May	April	May	April	May	April	May
Merlot Breasta	base	0.83	0.84	1.37	1.40	0.31	0.30	0.34	0.36	0.31	0.27
	middle	0.77	0.78	1.57	1.61	0.26	0.25	0.36	0.37	0.26	0.24
Merlot Simnic	base	1.61	1.59	1.76	1.78	1.60	1.54	0.16	0.20	1.10	1.17
	middle	2.27	2.29	1.61	1.69	4.90	5.70	0.50	0.55	0.95	1.12

If at the Royal Feteasca variety the maximum concentration of Cu, determined in the canes of vines from vineyard Simnic, was 0.56 mg/100g, at the Merlot variety were recorded values of approximately two times higher in May.

Cr content of the canes belonging to Merlot variety was lower than the content determined in the canes of Royal Feteasca, a valid situation in both plantations analyzed.

The contents of heavy metals determined in the canes of Merlot variety are considerably higher in both April and May, compared to Royal Feteasca variety, in the case of Simnic vineyard. Only in respect of Al content, higher values are observed at canes of vine belonging to Royal Feteasca variety.

At Merlot variety, concentrations of Mn, Zn and Al determined in the canes of vine presents higher values for Simnic vineyard, remarking in this case the Al content of the canes that represents almost half of concentrations determined for the canes of Royal Feteasca (Table 1 and 2).

For Merlot variety located in Breasta vineyard, is observed a slight variation in the concentrations of these elements in the middle and basal canes.

The concentration of metal in the canes decreases as follows: Zn>Mn>Cr>Al>Cu (Figure 2).

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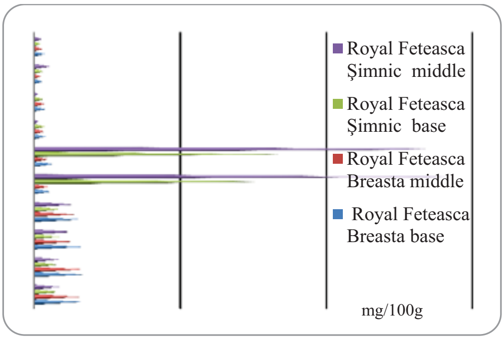

Figure 1. Evolution of Mn, Zn, Al, Cr and Cu (mg/100g) content at Royal Feteasca

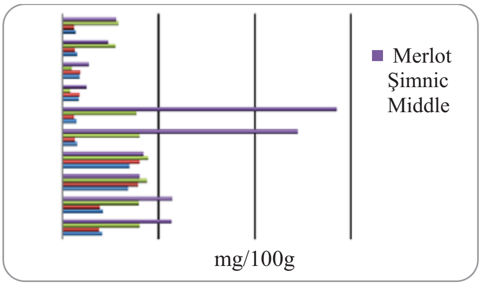

Figure 2. Evolution of Mn, Zn, Al, Cr and Cu (mg/100g) content at Merlot

According to Lindsay (1979) quoted by Vrinceanu et al., 2010, the average content of Cr in soil is 100 mg/kg, and the range of variation is 1-1,000 mg/kg; the average zinc content in soil is 50 mg/kg, and the range of variation is 10-300 mg/kg.

For manganese, the average content in soils is 600 mg/kg, with a range of variation between 20-3,000 mg/kg. Regarding the average content of Cu in soils, according to these authors, this is 30 mg/kg, and can range from 2-100 mg/kg.

The copper concentrations determined in Breasta vineyard have slight variations for P2 and P3 soil samples and the P1 sample, as determined by the depth of 20-40cm, is exceeding the threshold of 100 mg/kg both in April and May. On 0-20 cm depth, in April, Cu concentrations are at the limit of 200 mg/kg, which is the threshold limit intervention for sensitive use soils, and in May this threshold is exceeded (Table 3).

For manganese is specified in the Order 756/1997, as attention threshold, the value of 1,500 mg/kg and 2,500 mg/kg for intervention threshold.

Table 3. Determination of Zn, Cr, Cu and Mn content (mg/kg) in Breasta vineyard

Sample soils	Zn		Cr		Cu		Mn	
	April	May	April	May	April	May	April	May
P1 (0-20 cm)	56.2	50.2	26.2	30.6	191.6	240.8	457.6	469.2
P1 (20-40 cm)	40.4	35.4	26.6	33.4	104.9	156.8	395.2	381.4
P2 (0-20 cm)	30.9	31.4	28.6	30.5	15.9	16.7	374.6	392.3
P2 (20-40 cm)	31.9	32.2	29.8	29.0	15.3	16.4	353.5	390.1
P3 (0-20 cm)	40.4	41.6	32.9	29.4	15.9	18.0	386.8	314.7
P3 (20-40 cm)	41.2	42.0	31.1	25.2	13.4	15.8	400.8	434.8

Determined concentrations of Mn has slight variations in both months of the study, there were recorded the highest concentrations of 457.6 mg/kg in April, and 469.2 mg/kg in May for soil sample P1.

Comparing the values obtained in this study with literature values it can be concluded that they are approximately 150 mg/kg lower for this research.

Zn concentrations determined in soil from vineyard located in Breasta have values between 30.9 to 56.2 mg/kg, being situated around average content of this element in the soil according to the literature. In this case, Zn content is not exceeded for sensitive use soils, which indicate as alert threshold the value of 300 mg/kg and 600 mg/kg for the intervention threshold.

The content of chromium presents the same trend for all the soil samples, the values being in the range from 26.2 to 33.4 mg/kg, determined concentrations being lower than the average content of 100 mg/kg referred to in the literature.

Also in this case, the Cr content is much lower than the alert threshold of 100 mg/kg normed for sensitive use soils (Table 3).

If in Breasta vineyard, the maximum concentration of Zn determined was 56.2 mg/kg, in Simnic vineyard were determined higher values for all samples, the maximum concentration of Zn being 181.62 mg/kg for sample S3, in April (Table 4).

In this research, the values obtained are higher than the average content specified in literature, being situated near the upper limit of the variation of Zn in soils, which is 300 mg/kg. However, the values obtained are situated and close to the alert threshold specified in Order no. 756/1997.

Table 4. Determination of Zn, Cr, Cu and Mn content (mg/kg) in Simnic vineyard

Sample soils	Zn		Cr		Cu		Mn	
	April	May	April	May	April	May	April	May
S1(0-20 cm)	70.5	99.49	48.0	47.2	196.47	252.89	576.6	675.7
S1 (20-40 cm)	71.84	96.2	46.2	44.7	162.23	248.37	565.8	630.7
S2 (0-20 cm)	106.19	86.11	36.7	38.9	113.46	196.47	592.2	757.1
S2 (20-40 cm)	85.4	88.78	42.4	41.7	106.19	162.23	623.2	844.1
S3 (0-20 cm)	181.62	115.04	54.0	52.2	111.41	302.68	780.1	805.9
S3 (20-40 cm)	168.8	92.7	55.7	55.7	100.94	211.46	796.8	898.2

Cr contents determined in Simnic vineyard have slightly higher values than those found in Breasta, but in this situation, the values measured are below the alert threshold of 100 mg/kg.

Cu and Mn concentrations are significantly higher in Simnic vineyard. It is also noted that in May were determined highest concentrations of Cu and Mn in soil. In April Cu concentrations are exceeding the alert threshold of 100 mg/kg, and in May concentrations are above the intervention threshold specified in Order no. 756/1997. The Cu content on 0-20cm depth is greater than the one determined on 20-40 cm depth, a fact confirmed by the results from the literature (Toselli et al., 2009). Although the concentrations of copper are high, this is common in vineyards, taking into account the application of copper-based fungicide treatments over time. The Mn content in Simnic vineyard is between 565.8 to 898.2 mg/kg. The Mn levels in Breasta vineyard are close to the average content of Mn in soil, 600 mg/kg as referred to in the literature.

CONCLUSIONS

At Merlot variety, concentrations of Mn, Zn and Al presents higher values for Simnic vineyard, pointing out, in this case, the content of Al which represents almost half of concentrations determined for Royal Feteasca. Cr content in Merlot was lower than contents determined for Royal Feteasca, in both analyzed vineyards. In May, Cu concentrations are higher at Merlot variety from Simnic compared to Royal Feteasca from Breasta. Based on the research conducted, we conclude that high concentrations of Cu accumulated are due to the use of copper-based fungicides. Copper concentrations are significantly higher in all soil samples in Simnic vineyard.

Following the interpretation of the results obtained, it can be concluded that the results of all metal concentrations in analyzed soils are higher in Simnic vineyard than in Breasta. Analyzed vineyard soils can be classified as unpolluted or slightly polluted soils, as most of the heavy metal concentrations are below the limits imposed by the Romanian legislation, except for the content of Cu in soils, which is greater than the alert threshold and threshold for intervention according to Order 756/1997.

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