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Soil pollution

ANALYSIS OF HEAVY METALS CONTENT OF SOIL AND *Vitis vinifera* IN TWO VINEYARD AREAS OF THE CARAS-SEVERIN COUNTY, ROMANIA

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Abstract. Heavy metal pollution of agricultural soils is a major environmental problem that can affect agriculture, food quality and human health. Samples from vineyard soils in 2 locations (Tirol and Moldova Noua) situated in the Caras-Severin county, Romania, and corresponding samples of *Vitis vinifera* were analysed for the following heavy metals contents: Mn, Cu, Fe, Zn, Pb, Ni, Cr(VI) and Cd. The concentration of heavy metals was measured using a flame atomic absorption spectrophotometer, in conventionally cultivated soils from vineyards and in aerial parts of *Vitis vinifera*. The average content of heavy metals in soils from the Tirol vineyard decreased in the order: Fe > Mn > Cu > Zn > Pb > Ni > Cr > Cd, and in the case of private vineyards from Moldova Noua area, in the following order: Fe ≈ Mn > Zn > Cu > Pb > Ni > Cr >Cd. The average content of heavy metals in aerial parts of vines (*Vitis vinifera*) samples decreases in this way: Fe > Zn > Mn > Pb > Cu > Ni > Cd > Cr (Tirol) and Fe > Zn > Cu > Mn > Ni > Pb > Cd > Cr (Moldova Noua area). The metal accumulation in aerial tissue of *Vitis vinifera* was established by transfer factor. Surprisingly, the transfer factor is higher in the Tirol vineyard than in Moldova Noua area. These results indicate that the bioavailability of *Vitis vinifera* to heavy metals depends on other factors besides the metal concentration of heavy metals in soil.

Keywords: heavy metals, vineyard, *Vitis vinifera*, transfer coefficient, Romania.

AIMS AND BACKGROUND

The purpose of the present work was to make a comparison between 2 locations in Caras-Severin county, in which pollution was generated for many decades by the extractive and metallurgical industry. The chosen places were: Tyrol, well-known wine-growing area, and a vineyard in a private household, near the town Moldova Noua. We intend to determine the heavy metal content of soils and aerial parts of *Vitis vinifera*, to do a comparative study and to evaluate the results.

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy

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metals into the environment, such as energy and fuel production, metallurgy, iron and steel, mining and smelting of metalliferous, fertiliser and pesticide industry and application, etc. The major toxic metal ions hazardous to humans as well as other forms of life are Pb, Cd, Cr, Fe, Cu, Ni, Zn, Mn, etc. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency. Heavy metal pollution of agricultural soils is a major environmental problem that can affect plant productivity, food quality and human health[1].

In the Caras-Severin county the heavy metals concentration is high, in some areas out of the normal values; some of the metals are 1 to 5 times over the normal. High values were registered for cadmium, chrome, cobalt, lead, manganese, etc. The anthropical mining and metallurgical activities generate many materials with high content of metals such as dumps, cinder yards, etc. The pollutant migration gets along through air, surface water, phreatic water and opened transport outside the emplacement. The environmental balance indicates an overflow of heavy metals admitted in soil that shown a major possible pollution[2,3]. Heavy metal pollution of agricultural soils is a major environmental problem that can affect plant productivity, food quality and human health[4]. Therefore, the determination of heavy metals and their impacts to the environment have been broadly studied in the past years. Many latest studies investigated the heavy metal fractions of mine soils[5–7] and evaluated the phyto-toxic risk for human receptors[8].

The plants can accumulate significant quantity of heavy metals, as well. Metal accumulation in crops represents now one of the greatest problems of humanity[9]. Recent researches demonstrated that plant tissues accumulate a quantity of heavy metals directly proportional to the gradual addition of metal in soil. Accumulation speed depends on soil characteristics, on plant species, plant age, hydroclimatic condtions, type of tillage[10] .

Since the 90's heavy metal pollution turns out to be problem in some major viticulture regions. Comparative studies have been done in the region of Brestnik-Plovdiv (Bulgaria)[11], in Jordan[12], in France[13], in Greece[14] and Italy[15].

In Moldova Noua the main economic activity of the village was long time mining, but the city has been strongly influenced by the masses of the mining sector restructuring, which considerably decreased the financial resources of the population, and the socio-economic activity in the area. The main activity is now transportation, agriculture and tourism. The other investigated area, Tirol, is situated at the west of the city Bocsa, a mining area until recently.

EXPERIMENTAL

Sample preparation. Soil and grape samples were collected in October 2008. In each of the 9 sites, 3 sub-sampling sites were randomly established. Samples from vineyard soils in 2 locations (Tirol and Moldova Noua) situated in the Caras-Severin county, Romania, and corresponding samples of aerial parts of vine (*Vitis vinifera)* were analysed for the following heavy metals contents: Fe, Mn, Cu, Zn, Pb, Ni, Cr (VI), and Cd. The soil samples were taken at 0 to 10 cm depth, after removal of the above-ground biomass. The samples have been noted with 1 to 6 for vineyards at Tirol and 7 to 9 for private vineyards beside Moldova Noua. Samples 7, 8 and 9 were taken at 12 km in the north, respectivelly south, and west of lake funnel that belonged to S. C. Moldomin and which contains sterile, with small amounts of copper, molybdenum, gold, uranium as a result of extracting of copper.

The soil samples were dried at the room temperature, then they were grinded, the average diameter of grain being approximately 2 mm. The next step was to bring them to a constant weight in the drying chamber at 100°C. The heavy metals were extracted from the soil samples (3 g, precise weight) by heating with aqua regia for 2 h, at reflux, in a nest, so that the black vapours would not exceed 1/3 of the refrigerant height. After interrupting the heat, the system was left in stand-by for 16 h. Then the samples were diluted in a flask with 0.5 N nitric acid to exactly 50 ml.

Plant tissues (leaves, stems) were thoroughly washed with running tap water and rinsed with deionised water to remove any soil particles attached to plant surfaces. The above ground and underground tissues were separated and oven dried (70°C) to a constant weight. Plant samples with precise weight were then brought to 600°C; to residual materials were added 5–10 ml of concentrated nitric acid, samples were maintained 30 min on the dry sand bath. After filtering them with a paper filter with small porosity were taken to a calibrated flask (20 or 25 ml) with nitric acid 0.5 N solution.

Equipment. A double-beam atomic absorption spectrometer 'Spectra AA-20 plus' manufactured by Varian was used. A delay of 2 s was employed both in reading and working time. Each reading was performed 3 times, the reproduction of readings being accurate. The RSD values ranged between 0.2 and 5.1, the majority being < 1. The parameters for each dosed metal are illustrated in Table 1.

Table 1. Equipment parameters for each dosed metal

Metal	Wavelength (nm)	Slit width (nm)	Acetylene flow (l/min)	Photomultiplier (V)	Lamp current (mA)
Cd	228.8	1	1.3	428	6
Pb	283.3	0.5	1.5	784.3	6
Zn	213.9	1	1.5	756.2	8
Cu	324.7	0.2	1.4	570.5	7
Cr(VI)	357.9	0.2	2.0	680.2	8
Ni	232.0	0.2	1.4	782.4	10
Fe	248.3	0.2	1.5	658.3	8
Mn	403.1	0.2	1.5	749.1	6

RESULTS AND DISCUSSION

The soil samples taken from the 2 regions have been analysed as described above in the determination of heavy metals. The experimental results are presented in Table 2 and the average content of heavy metals in analysed samples are illustrated comparatively in Fig. 1.

Table 2. Heavy metal content in vineyard soils, mg/kg soil (dry substance)

Sample*	Fe	Mn	Cu	Zn	Pb	Ni	Cr^{6+}	Cd
1	375.45	277.50	47.28	46.8	38.38	24.55	13.32	1.77
2	377.08	295.00	36.63	50.1	21.73	24.30	16.78	1.85
3	345.37	394.58	53.83	55.6	21.63	20.90	12.20	1.82
4	360.63	296.25	63.17	53.9	23.03	23.42	12.13	1.95
5	364.80	260.00	112.00	37.2	25.30	20.92	12.73	1.80
6	334.25	270.83	107.00	29.1	25.59	13.82	4.57	1.28
7	287.50	325.17	59.50	199.0	30.10	27.17	7.18	3.22
8	337.50	279.17	43.02	294.0	47.08	31.18	5.92	2.87
9	309.25	306.83	61.00	121.8	46.21	22.70	6.95	2.03

* Samples 1–6 were taken in the Tirol area and samples 7–9 near Moldova Noua town.

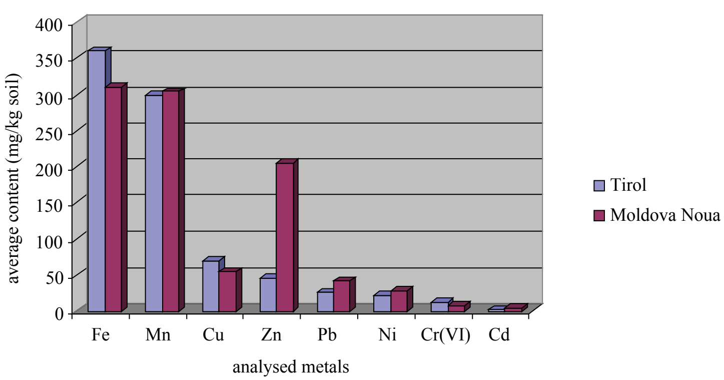

Fig. 1. Comparative average content of heavy metals in vineyard soils

The average contents of heavy metals in soils from the Tirol vineyard decreased in the order: Fe > Mn > Cu > Zn > Pb > Ni > Cr > Cd, and in the case of private vineyards from Moldova Noua area, in the following order: Fe ≈ Mn > Zn > Cu > Pb > Ni > Cr > Cd. There are significant differences between the 2 regions in the content of Zn which is much higher in Moldova Noua. Can be noted that soils of Moldova Noua are richer in Mn, Zn, Pb, Ni and Cd than those of the Tirol area. The past metalliferous industry in the area of Noua Moldova may be an explanation for the higher content of these metals in soil and the trace element composition of soil is influenced by pedogenic and anthropogenic processes. Hydrated metaloxides mainly of Fe, Mn and Al and organic matter are considered to be the most important soil components contributing to competition for the substitution of trace elements.

In Table 3 are presented data regarding the accumulation degree level of heavy metals in the aerial parts of grape (*Vitis vinifera*) and in Fig. 2 – the average content for analysed metals, comparatively in the 2 mentioned locations.

Table 3. Heavy metal content in aerial part of *Vitis vinifera*, mg/kg plant

Sample*	Fe	Mn	Cu	Zn	Pb	Ni	Cr^{6+}	Cd
1	68.11	3.89	1.48	3.57	3.92	1.21	0.29	0.27
2	91.13	8.17	5.45	7.87	2.36	2.58	traces	0.25
3	48.36	13.24	2.16	4.24	3.53	1.37	traces	0.20
4	35.78	3.27	2.38	3.53	3.36	1.01	traces	0.11
5	107.70	3.65	3.21	21.11	5.42	1.21	0.08	0.70
6	89.70	4.69	2.37	4.82	6.56	2.32	0.43	1.10
7	6.88	0.55	1.06	1.89	0.18	0.49	0.08	0.11
8	4.67	2.14	0.97	5.08	0.23	0.64	0.10	0.10
9	13.35	2.17	3.49	1.93	0.32	0.37	traces	0.12

* Samples 1–6 were taken in the Tirol area and samples 7–9 near Moldova Noua town.

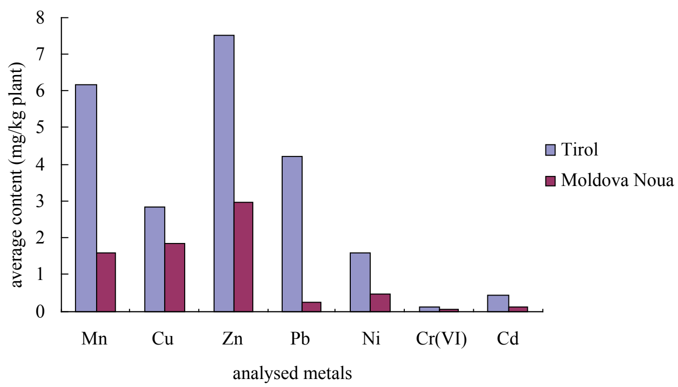

Fig. 2. Comparative average content of heavy metals in *Vitis vinifera* (aerial parts)

Because of excessive quantity of iron found in plants in the area Tirol (average value 73.46 mg/kg plant) than the area Moldova Noua (average value 8.30 mg/kg plant,) the iron content it is not represented in Fig. 2, to make possible a comparative representation of other metals content. The average content of heavy metals in aerial parts of vines (*Vitis vinifera*) samples was in order: Fe > Zn > Mn > Pb > Cu > Ni > Cd > Cr (Tirol area) and Fe > Zn > Cu > Mn > Ni > Pb > Cd >Cr (Moldova Noua area). In both regions, the order differs from that of metals in soils. These results indicate that the bioavailability of *Vitis vinifera* to heavy metals depends on other factors besides the metal concentration of heavy metals in soil. The traditional use of metal-based fungicide in vineyards may have led also to the accumulation of trace metals.

For assessing the pollution with metals from soil by plants and the accumulation of them in different parts of the plant tissue are used different indices as is the transfer factor (TF) defined by Freytag in 1986 as:

$$TF = (Q_p/Q_s) \times 100\%,$$

where Q_p is the metal quantity accumulated in plant, mg/kg; Q_s–metal quantity accumulated in soil, mg/kg.

The comparative representation of metal accumulation in aerial tissue of *Vitis vinifera* is shown in Fig. 3.

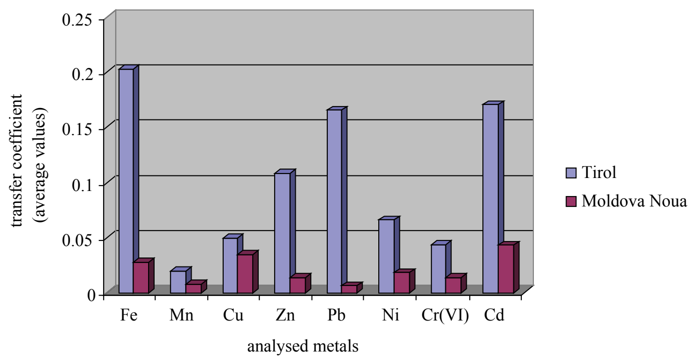

Fig. 3. Calculated transfer coefficients for aerial parts of *Vitis vinifera* in 2 locations of the Caras-Severin county: Tirol and Moldova Noua

There were found differences between the transfer coefficients soil/plant of the 2 investigated regions: surprisingly, for all the heavy metals, the transfer coefficients are higher in the Tirol vineyard than in the Moldova Noua area, although here the exploitation industry was very powerful few decades before. The explanation can be given by several other factors that control metal bioavailability, including pH, redox potential, alkalinity and hardness, cations and anions, as well as interaction with organic compounds that must be included in further research. As well, the high transfer coefficients found in the vines in the area Tirol for some toxic heavy metals such as Fe, Pb, Cd, Zn, determine us to consider in future research the analysis of wines produced here.

CONCLUSIONS

There are no significant differences between soils of the 2 regions in terms of content of Fe, Mn, Cd, Cr, but soils of Moldova Noua contain a larger quantity of Zn and Pb.

Plants (*Vitis vinifera*) accumulate in aerial parts different amounts of heavy metal: those in the area of the vineyard Tirol have a higher content of Fe, Mn, Zn, Pb, Ni, Cr, Cd than those from the vineyards in households, in Moldova Noua area.

The average values of transfer coefficients are much higher in the area Tirol, although pollution soil is not much different from those of the Moldova Noua area. The bioavailability of *Vitis vinifera* to heavy metals depends on other factors besides the metal concentration of heavy metals in soil. Investigating causes and a possible contamination of wines is the subject of further research.

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