Research on the Chemical Composition of Soil with Pollutant Effect in Some Vineyards from Northwestern Transylvania

Florin Dumitru BORA.[1], Tiberia Ioana POP[1], Leonard MIHALY [2], Claudiu Ioan BUNEA[1], Nastasia POP[1]

[1] Faculty of Horticulture, USAMV Cluj-Napoca; boraflorindumitru@gmail.com
[2] Technical University of Cluj-Napoca, Baia Mare University Centre

Abstract. Soil pollution represents any unwanted change of its physical, chemical or biological characteristics, with direct implications on vegetation, animals and the human health. The chemical composition of soil affects the quality of grapes and wine. The research was conducted in Şimleul Silvaniei and Baia Mare, soil samples were collected from vineyards planted with Fetească, Fetească Regală and Italian Riesling. The quality of grapes, wine and the chemical composition of soil are closely interrelated. The chemical composition of soil analyzes the content of nutrient dynamics and their availability to plants. Samples were collected with the pedological drill, the sampling depths were 0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm, disaggregated in the Berghof MWS2 microwave and the chemical composition was determined through the AAS method. In Baia Mare, the highest concentrations of metals were found in the soil layer 0-60 cm (7802 mg/kg Na, 4024 mg/kg Ca, 10.87 mg/kg Cd, 100.32 mg/kg Ni, 52.53 mg/kg Co) in the area where there is a large mass of roots. Pb pollutes with high values (2605 mg/kg) in the 20-40 cm horizon. In Şimleul Silvaniei, only Ca has higher values (6381 mg/kg) than in Baia Mare in the same horizon (0-20 cm). All metals have lower values than in Baia Mare, due to the distance from the source of pollution. Through the genetic soil type, the parent rock influence and determining the chemical composition, it can be concluded that metals and heavy metals can lead to the pollution of vine.

Keywords: chemical composition, soil, vineyards, pollution

INTRODUCTION

At the national level, chemical pollution of soil affects about 0.9 million ha, of which 0.2 million ha are affected by excessive pollution. Pollution by heavy metals (especially Cu, Pb, Zn and Cd) and acid precipitation, due to SO_2, have aggressive effects upon soil and are present especially in areas like Baia Mare, Zlatna and Copşa Mică. Thus, it is very helpful to understand the content of heavy metals in urban soils to determine with precision the degree of soil pollution and take the possible measures to decrease the effects of pollution and rehabilitate the affected areas (Vaum, 2011).

In modern ecology, soil pollution is any action which results in disruption of the normal operation of the soil. The soil represents a support and a living environment in different natural or anthropogenic ecosystems. Disturbances are manifested by physical, biological or chemical degradation (Răuţă and Karst, 1984).

Soil, once polluted, becomes a source of pollution for plants and animals, and then, directly or indirectly, of man (Răuţă and Cristea, 1984). Therefore, the main objective of farmers is to avoid pollution of soil and transforming it into a source or reservoir of pollution (Paulette, 2004).

It is widely accepted that the determination of heavy metals or determination of macro and micronutrients in soil, above a certain level, based only on their total content, does not mean that these chemicals are toxic to vine growth and fructification. To know the potential risks of these heavy metals or non-metals to grapes, it is necessary to make an

analysis of the degree of mobility of the compounds and the free fraction available in the soil. The factors that affect the mobility of these compounds in the soil are: pH, temperature, oxidation-reduction potential, organic matter, ion exchange and microbial activity.

Mobility of heavy metals and non-metals is directly influenced by "chemical speciation" them. The chemical speciation of metals determines their behavior and toxicity in the environment, and some processes as: volatilization, photolysis, adsorption, atmospheric deposition, acid-base balance, polymerization, complexation, electron transfer reactions, solubility and precipitation equilibrium, changes made by microorganisms, diffusion (Fairbrother *et al.* 2007).

MATERIALS AND METHODS

Biological material

The research in this paper was conducted in two locations Şimleul Silvaniei and Baia Mare, soil samples were collected from vineyards planted with Fetească albă, Fetească regală and Italian Riesling.

At Baia Mare, soil samples were taken from the river valley Firiza, the predominant soil type in this location was alluvial soil, which is part of the protisol class (Damian *et al.*, 2008).

The type of soil from Şimleul Silvaniei is part of Luvisols class (LV). Sampling and sample preparation was performed in compliance with the rules of the applicable standards and laws of our country SR ISO 11464:1994, SR ISO 11047:1999, SR ISO 11466: 1999 (Bretan Laura, 2011). The sampling from 0-20 cm depth has been carried out by a preliminary removal of dust, roots, leaves and other residues found on the surface of the soil. The sampling was performed using a plastic shovel at the surface of the soil and at depths of 20-40 cm, 40-60 cm, 60-80 cm it was achieved with the pedological probe (Vaum Melinda Maria, 2011). Disaggregation was done with the Berghof MWS2 microwave.

Research methods

Soil analyses were processed in the laboratory of the University Research Center of Baia Mare, under the direction of PhD Leonard Mihaly.

In the first stage, the soil was passed through sieves with a maximum diameter of 2 mm and then it was dried in an oven at a temperature of $105^{o}C$ for 72 hours. Then pulverization and homogenization of soil samples was made using the automatic grinding mortar Resh 110.

For the disaggregation of the soil samples, an amount of 0.2-0.5 g of soil was measured and a volume of 12 ml of aqua regia (9 ml HCl+3 ml HNO_3) and after a waiting time of 15 minutes mineralization was made using the Berghof MWS2 microwave, with the parameters shown in Tab. 1. After the completion of the disintegration, the mineralized soil samples were filtered and brought to a volume of 100 ml with distilled water.

Tab. 1

Working parameters in disaggregation of soil samples in the microwave

Working steps	1	2
Temperature(^{o}C)	180	100
Power (%)	99	98
Time (min)	25	10

Atomic absorption spectrometry (Perkin Elmer Analyst 800, Shelton, USA) is to determine the concentration of a chemical in the sample by measuring the absorbance of electromagnetic radiation with a wavelength specific to each element, in its passage through the evenly distributed atoms of that item. The agent in which these atoms are issued is represented by the high temperature flame (about 2500°C) of a mixture of air-acetylene (Bretan Laura, 2011). Flame spray solution undergoes several transformations: water evaporates, minerals melt then they get volatilized (Bretan Laura, 2011).

Plotting the calibration curves

For the construction of the calibration curve, the device was brought to its optimum parameters listed in the operating manual. The absorbance of each standard solution was measured starting with the lowest concentration and the absorption was recorded for each standard. The results were used to draw the calibration curve (Bretan, 2011).

Tab. 2 shows the calibration curves for the non-metals and heavy metals analyzed.

Tab. 2

The operating conditions to determine the content of metals and heavy metals by atomic absorption spectroscopy (AAS)

No.	Element (nm)	Wavelength (nm)	Slit (nm)	Linear range (mg/L)	Correlation coefficent	Flame	Background correction
1.	Ca	422.7	0.7	5.0	1.000000	air-acetylene	-
2.	Mg	202.6	0.7	10.0	1.000000	air-acetylene	+
3.	Fe	248.3	0.2	6.0	0.999972	air-acetylene	+
4.	Zn	213.9	0.7	1.0	0.999999	air-acetylene	+
5.	Cu	324.8	0.7	5.0	0.999979	air-acetylene	+
6.	Ni	232.0	0.2	2.0	0.999920	air-acetylene	+
7.	Co	240.7	0.2	3.5	0.999900	air-acetylene	+
8.	Pb	283.3	0.2	3.5	0.999853	air-acetylene	+
9.	Cd	228.8	0.7	2.0	1.000000	air-acetylene	+
10.	Na	589.0	0.2	1.0	1.000000	air-acetylene	-

Determination of metals and heavy metals content from solutions obtained in the decomposition phase of soil samples was performed by AAS (flame absorption technique) using the Perkin Elmer Analyst 800, Shelton, USA atomic absorption machine.

The operation was performed following two stages: a) the separation of metallic and nonmetallic cations from soil samples (stage of transition metals in ionic state), b) the determination itself. For each soil sample three readings were made and the final result given directly by the device represents the average of the three readings.

Among the characteristic factors influencing the metals and heavy metals mobility, in this paper were determined: soil pH (*SR ISO 10523/2009*), redox potential (*ORP*) and electrical conductivity (*SR EN 27888/1997*). The analysis was done using the *inoLab ® pH / Cond 720* device.

RESULTS AND DISCUSSIONS

Aluvisol soils from Baia Mare are defined by the presence of an A horizon (Am, Au, Ao) formed on parent materials consisting of fluvial, fluvial-lacustrine and newly formed lacustrine deposits of at least 50 cm thickness. Aluvisol soils have an Ao-C profile. Ao horizon is well-defined, has a thickness of 20-50 cm, has a brown-gray color, with

stratifications less obvious, different texture depending on the nature of deposits, from coarse to fine. It has a moderately weak structure, it can develop rust-colored stains due to the gleying process, and the transition to C horizon is done gradually. The C horizon parent material consists of stratified alluvial deposits of different thicknesses and different textures. Due to shallow groundwater, yellowish-brown spots appear frequently after the oxidation of iron compounds (Vaum Melinda Maria, 2011). They generally have a favorable aero-hydric regime, the humus content varies between 2-3%, the base saturation level of 80-100%, and the pH between 6.0 to 8.5 (Mihalache, 2006).

Luvisol soils from Şimleul Silvaniei are soils with an ocric A horizon (Ao), followed by eluvial E horizon and argic B horizon (Bt) with a high base saturation (V) over 53% at least in one subhorizon at the top, with no abrupt textural change (between E and Bt <7.5 cm). Those soils may present, in addition to those horizons, the O horizon, western horizon, intense stagnic properties (W) below 50 cm, sudden textural change (on 7.5 to 15 cm) or glossy crossing (albeluvic tonguing). Luvisols are poorly supplied with nutrients, the humus content is very low (1.5-2.5%), in the Ea horizon it can fall below 1%. It has a moderate acid reaction (5.0-5.5), the degree of base saturation is less than 60% and the Ea horizon can have values of 15-20% (Mihalache, 2006).

The chemical composition of the analyzed soils is shown in Tab. 3, Tab. 4, Tab. 5 and Tab. 6. Results represent the mean values of elements (metals and heavy metals) and standard deviation.

Accumulation of metals decreases with increasing depth in the soil profile, the level of accumulation was significantly reduced at depths of 20-40 cm, exception being cobalt, in the Baia Mare area and sodium in Şimleul Silvaniei area.

In Baia Mare, the highest concentrations of metals are: Na - 7802 mg/kg in the horizon 20-40 cm, high values being recorded also in the depth of the soil profile, Ca - 4024 mg/kg in the horizon 0-20 cm, Cd – 10.87 mg/kg in the 0-20 cm horizon, Ni – 100.32 mg/kg in the horizon of 20-40 cm, and Co – 52.53 mg/kg in the horizon 40-60 cm, where most of the roots mass is (Tab. 3). Total concentrations exceeded the maximum allowed by law.

With regard to heavy metals, Pb pollutes, being found in a high level concentration (2605.66 mg/kg) in the 20-40 cm horizon (Tab. 4), compared with the 0-20 cm horizon in which the concentration was lower (1774.14 mg/kg). The quantity was high also on the depth of the soil profile, where the mass of roots can be found. This may be due to the influence of the pollution source, which was represented by the mining in the area, or perhaps also the geological formations of soil. The concentration of Cu peaks in the 40-60 cm horizon (2895.22 mg/kg), well above the limit, and also the Fe and Mg in the 60-80 cm soil layer due the petrographic composition of the soil. Zn is found in the largest amount in the 0-20 cm from the soil surface, from pollution sources (2093.28 mg/kg, Tab. 4).

In the case of Şimleul Silvaniei soil, the total concentration values of Pb and Zn are under the maximum allowed by law, with higher values in the deeper soil layer (60-80 cm). The exception is Cu (728.62 mg/kg) in the 0-20 cm soil layer, and also on the depth of the soil profile, probably because of the influence of treatments on vine with copper based products. The Fe and Mg are found in high concentrations, increasing from the surface horizon to the depth of the soil profile (Tab. 6).

From the point of view of the content in metals, at Na and Ca (Tab. 5), we can observe a very high concentration throughout the depth of the soil profile, higher values being found in Na in the 60-80 cm layer (3344.39 mg/kg) and Ca in the 0-20 cm (6381.02 mg/kg).

Tab. 3

Chemical composition of aluvisol from Baia Mare (mg/kg)

Depth (cm)	pH (H₂O)	Redox potential (mV)	Conductivity (µS/cm)	LMA* Na	LMA* Ca	LMA* Cd	LMA* Ni	LMA* Co
				-	-	1 mg/kg	20 mg/kg	15 mg/kg
				Na *(Sodium)*	Ca *(Calcium)*	Cd *(Cadmium)*	Ni *(Nickel)*	Co *(Cobalt)*
0-20	6.33	326	191.8	5674.74±342.69	4025.22±291.59	10.87±1.64	75.94±1.51	24.43±0.44
20-40	6.19	332	196.0	7802.03±460.23	3225.14±254.44	8.19±0.49	100.32±6.74	31.05±1.88
40-60	6.05	358	173.8	7246.27±468.08	3138.96±251.21	6.48±0.09	83.67±5.43	52.53±1.52
60-80	5.91	357	186.4	6638.62±562.91	3668.46±201.53	7.95±0.01	88.61±3.30	45.22±2.41
Minimum values				*5674.74±342.69*	*3138.96±251.21*	7.95±0.01	*75.94±1.51*	*24.43±0.44*
Maximum values				7802.03±460.23	4025.22±291.59	10.87±1.64	100.32±6.74	52.53±1.52

LMA*=maximum allowed, Ord. MAPPM no. 756 from 3rd November1997

Tab. 4

Chemical composition of aluvisol from Baia Mare (mg/kg)

Depth (cm)	pH (H₂O)	Redox potential (mV)	Conductivity (µS/cm)	LMA* Pb	LMA* Cu	LMA* Zn	LMA* Fe	LMA* Mg
				20 mg/kg	20 mg/kg	100 mg/kg	-	-
				Pb *(Lead)*	Cu *(Copper)*	Zn *(Zinc)*	Fe *(Iron)*	Mg *(Magnesium)*
0-20	6.33	326	191.8	1774.14±95.42	2434.68±108.37	2093.28±201.52	12299.37±2115.29	2288.17±90.88
20-40	6.19	332	196.0	2605.66±237.57	2642.07±92.45	1939.07±143.87	14933.55±1236.24	1822.24±46.62
40-60	6.05	358	173.8	2591.54±207.49	2895.22±109.11	2042.97±263.29	10638.67±1548.93	2028.51±63.90
60-80	5.91	357	186.4	2449.88±88.32	2432.46±14.07	1967.04±387.03	17455.15±610.54	2654.62±240.90
Minimum values				*1774.14±95.42*	*2432.46±14.07*	*1939.07±143.87*	*10638.67±1548.93*	*1822.24±46.62*
Maximum values				2605.66±237.57	2895.22±109.11	2093.28±201.52	17455.15±610.54	2654.62±240.90

LMA*=maximum allowed, Ord. MAPPM no. 756 from 3rd November1997

Tab. 5

Chemical composition of luvisol from Șimleul Silvaniei (mg/kg)

Depth (cm)	pH (H₂O)	Redox potential (mV)	Conductivity (µS/cm)	LMA* Na	LMA* Ca	LMA* Cd	LMA* Ni	LMA* Co
				-	-	1 mg/kg	20 mg/kg	15 mg/kg
				Na *(Sodium)*	Ca *(Calcium)*	Cd *(Cadmium)*	Ni *(Nickel)*	Co *(Cobalt)*
0-20	6.51	339	110.5	2313.17±196.41	6381.02±723.53	0.26±0.16	20.19±1.68	14.00±1.16
20-40	6.62	353	132.1	3019.95±148.08	5264.34±682.15	0.18±0.01	17.94±0.97	13.82±3.09
40-60	6.58	327	143.0	2927.37±240.28	4652.16±324.21	0.33±0.03	16.75±2.21	10.18±0.79
60-80	6.53	321	156.7	3344.39±301.59	5392.61±841.26	0.19±0.03	16.70±3.32	9.67±0.57
Minimum values				*2313.17±196.41*	*4652.16±324.21*	*0.18±0.01*	*16.70±3.32*	*9.67±0.57*
Maximum values				3344.39±301.59	6381.02±723.53	0.26±0.16	20.19±1.68	14.00±1.16

LMA*=Maximum allowed, Ord. MAPPM no. 756 from 3rd November 1997

Tab. 6

Chemical composition of luvisol from Șimleul Silvaniei (mg/kg)

Depth (cm)	pH (H₂O)	Redox potential (mV)	Conductivity (µS/cm)	LMA* Pb	LMA* Cu	LMA* Zn	LMA* Fe	LMA* Mg
				20 mg/kg	20 mg/kg	100 mg/kg	-	-
				Pb *(Lead)*	Cu *(Copper)*	Zn *(Zinc)*	Fe *(Iron)*	Mg *(Magnesium)*
0-20	6.51	326	110.5	15.65±3.39	728.62±59.45	94.25±5.11	1392.99±162.63	3705.19±196.63
20-40	6.62	353	132.1	13.22±3.23	698.55±41.55	77.97±4.01	1519.23±178.75	3019.27±84.92
40-60	6.58	327	143.0	17.74±2.05	500.79±45.94	81.76±3.48	1905.87±228.59	3931.59±417.71
60-80	6.53	321	156.7	19.68±1.01	440.55±22.18	92.26±4.42	2042.09±160.49	4194.46±193.90
Minimum values				*13.22±3.23*	*440.55±22.18*	*77.97±4.01*	*1392.99±162.63*	*3019.27±84.92*
Maximum values				19.68±1.01	728.62±59.45	94.25±5.11	2042.09±160.49	4194.46±193.90

LMA*=Maximum allowed, Ord. MAPPM no. 756 from 3rd November 1997

The Cd and Co values fall within the maximum allowed by law (1 mg/kg and 15 mg/kg). Instead, Ni is over the maximum allowed of 20 mg kg with 0.19 mg/kg.

Retaining large quantities of heavy metals in the upper horizon is due to the presence of organic matter, the mineralogical composition of the fine fraction of the soil, and the acidifying effect of the emissions of pollution sources (Vaum Melinda Maria, 2011).

Previous studies conducted by Răuţă *et al.* (1984) and Lăcătuşu *et al.* (1991) established that the heavy metals in Baia Mare area that could cause significant pollution are: Pb, Cu, Zn. Furthermore, Bretan Laura (2011) highlights that Fe could also be considered a metal with pollutant character in the Baia Mare area.

CONCLUSIONS

The results of the research conducted in the areas Baia Mare and Şimleul Silvaniei lead to the following conclusions:

-Accumulation of metals decreases with increasing depth in the soil profile, the level of accumulation was significantly reduced at depths higher than 20-40 cm, exception were cobalt at Baia Mare and sodium at Şimleul Silvaniei.

-Soils of Baia Mare are more vulnerable to pollution because of their reaction, which was acid or moderately acid.

-Among the heavy metals accumulated in the soils of the two sites, the highest concentrations were found in the soil from Baia Mare. The Cu concentration was higher than Pb, which was higher than Zn, the values of these heavy metals exceeding the maximum allowed by law. At Şimleul Silvaniei, the soil concentration in heavy metals is very low compared to Baia Mare, lower than the maximum allowed by law, except Cu, whose concentration exceeds this limit.

-The content of Cu is high both at Baia Mare and Şimleul Silvaniei, one explanation could be the frequency of using plant protection products based on Cu, soil pollution by mining and geological influence of soil structure.

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