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ASSESSMENT OF CHEMICAL ELEMENTS IN SOIL, GRAPES AND WINE FROM TWO REPRESENTATIVE VINEYARDS IN ROMANIA

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Abstract: Inorganic compounds from soil, grapes and wine have been measured in two Romanian vineyards (Ștefănești and Pietroasele vineyards). The analyses were carried out on macro- and microelements (Ca, K, Mg, As, Fe, Mn, Ni, Zn, Cd, Cr, Cu, Co, As, Se). In addition, the physical properties of the soil and the mineralogical content have been studied. The dominant elements in the soils, exceeding maximum limits allowed, are Cu, Ni, Zn, Pb and As. Calcium registered high values especially at Pietroasele vineyard, while magnesium and potassium at Ștefănești vineyard. The enrichment factor is high for Cd (12.95) and for As and Cu (> 6). Based on the geoaccumulation index, the analyzed soil is considered uncontaminated to moderately contaminated for most of the elements. The concentrations of K, Ca, Mg and Zn are higher in the white grapes than in the black grapes. Higher values of Zn, Pb and Fe have been identified in the red wine (Cabernet Sauvignon) than in the white wine (Riesling). The mobility ratio values are low for most of the analyzed elements except for K and Zn. The sources of the analyzed inorganic compounds are both natural and anthropogenic.

Keywords: enrichment factor - inorganic compounds – mineralogy - mobility ratio – Romania - vineyards

1. INTRODUCTION

The factors influencing growth and development of vine, as well as the taste of grapes and wine are natural and anthropogenic in character (Frank & Kowalski, 1984; Baluja-Santos & Gonzalez-Portal, 1992; Day et al., 1995; Tonietto & Carbonneau, 2004; Álvarez et al., 2007; Vystavna et al., 2014). Natural factors are referring especially to local geography, geology, and climate and soil type. Anthropogenic factors are represented by all types of pollution associated with soil and underground water contamination (Mihaljevič et al., 2006; Tariba, 2011; Botsou et al., 2016 a.o.). The application of various methods of soil conservation (e.g. the type of cover crop) can improve the vinestock productivity (Klik et al., 1998).

The natural presence of heavy metals in grapes and wine depends mainly on the mineralogical content of the soil developed on various types of rocks (Pohl, 2007) but locally can be strongly influenced by the fertilizers and fungicides used (e.g., Ramachandran & D'Souza, 1998; Lemos et al., 2002; Kment et al., 2005; Komárek et al., 2010; Geana et al., 2013; Wightwick et al., 2013) and by industrial pollution of the sites (Eschnauer & Neeb, 1988; Cvetković et al., 2006; Moreno et al., 2007; Pohl, 2007, Geana et al., 2013).

Romania has eight great wine regions (Fig. 1A), most of them being localized in hilly areas, with sandy soils in favorable regions for viticulture (Soare et al., 2010). Previous studies carried out on viticultural areas in Romania were generally focused either on the viticulture tourism (Nedelcu et al., 2015; Ungureanu, 2015) or on the identification of main micro-, macroelements and heavy metals into

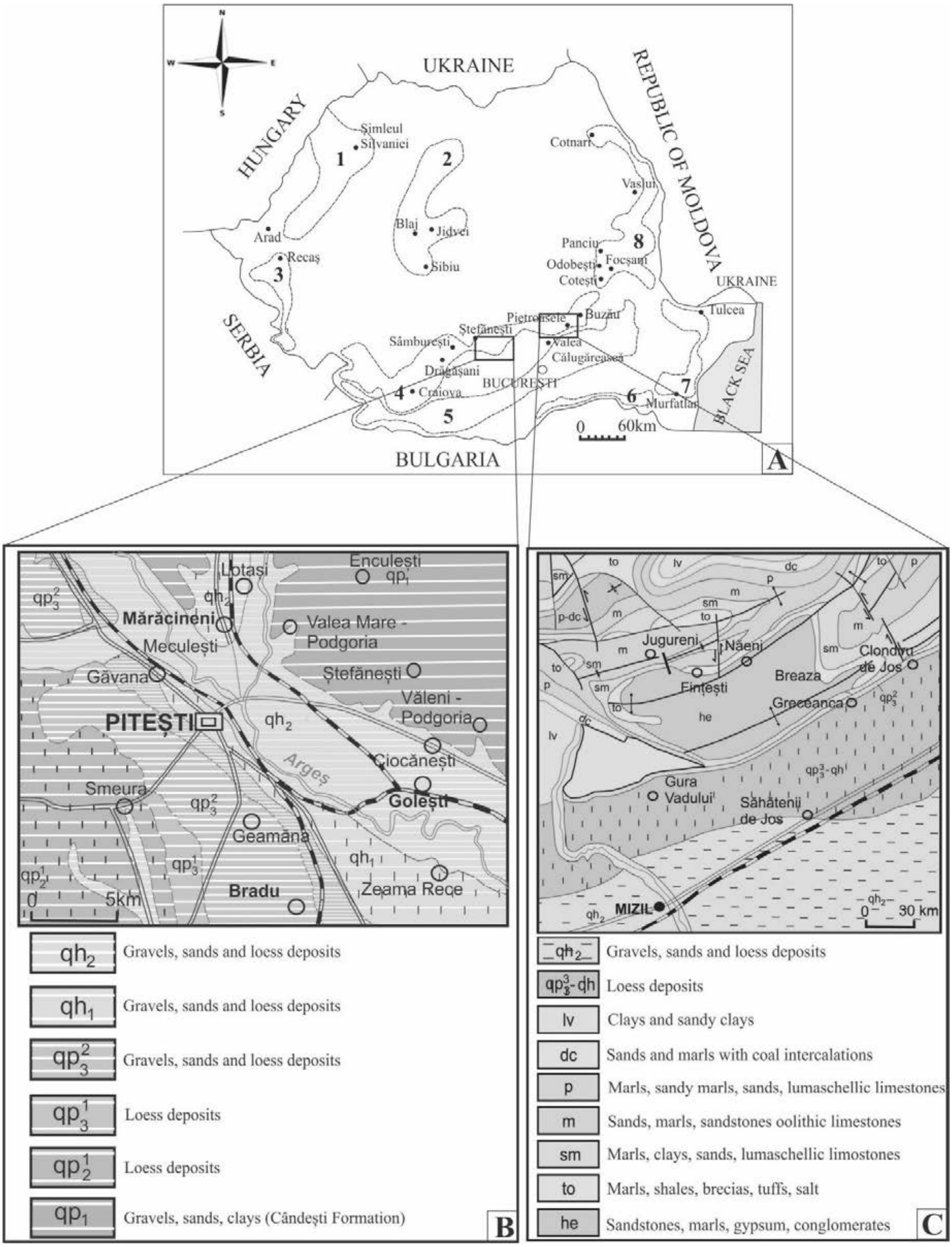

Figure 1. A - Geographical localization of the wine regions (simplified after Soare et al., 2010)(1 – Crișana and Maramureș; 2 –Transilvania; 3 – Banat; 4 – Muntenia and Oltenia; 5 – sands from southern part of Romania; 6 – Danube terraces; 7 – Dobrogea; 8 - Moldova), and position of the studied regions (in quadrants); B – geological map of the Ștefănești area (geological map 1:200 000, Pitești sheet, redrawn after Murgeanu et al., 1967a); C – geological map of Pietroasele area (geological map 1:200 000, Ploiești sheet, redrawn after Murgeanu et al., 1967b).

the soil, grapes and wine (Albulescu et al., 2009; Soare et al., 2010; Huzum et al., 2012; Lengyel et al., 2012; Bora et al., 2013, 2015; Geana et al., 2013, 2014, 2016; Cudur et al., 2014; Stegăruș et al., 2015; Dinca et al., 2016; Ungureanu et al., 2017). The aim of this study was to analyze the transfer of the metallic elements (As, Cd, Cr, Co, Cu, Ni, Pb, Se, Zn, Fe, Mn, Ca, Mg, K) from soil to grapes and wine. The objectives were to: i) analyze chemical elements (As, Cd, Cr, Co, Cu, Ni, Pb, Se, Zn, Fe, Mn, Ca, Mg, K) concentration, in four soil profiles from two vineyards in Romania (Ștefănești, Argeș and Pietroasele, Buzău) for two wine varieties (Riesling and Cabernet Sauvignon); ii) analyze the chemical elements in grapes and wine from the same two vineyards; iii) correlate the results in order to observe the transfer patterns of metallic elements from soil to grapes and wine.

2. STUDY AREAS

2.1. Ștefănești Vineyard

The Ștefănești Vineyard is located 5 km east from the city of Pitești, between 44°42' and 44°55' N, 24°54' and 25°15' E, at the contact between the Cândești Plateau and the Romanian Plain. It is a NW-SE-oriented staple strip, ca. 35 km long and 15 km wide, stretching between the Doamnei and Carcinov rivers. The plateau is characterized by the presence of alluvial - proluvial materials with the Cândești Gravels covered by clay. On the terraces and terminal plains, proluvial clay materials, weakly carbonated, prevail. The "Cândești Gravels" had been mentioned by Mrazec & Teisseyre (1901) around the namesake village, north of Buzău. These gravels have a large extension, stretching along the mountains, from the Eastern Carpathians to the western part of the Southern Carpathians. In the Carpathian area they reach hundreds or even thousands of meters in thickness (Liteanu, 1967; Damian, 2003), decreasing through the south, where the gravels are gradually replaced by sandstones and fine sandy clays (Liteanu, 1961) (Fig. 1B).

The Cândești Formation represents a predominantly coarse sedimentary cycle, revitalized by the tectonic movements which established new connections between the Middle Dacides (large tectonic components of the Southern Carpathians, in the northern part), considered as a source area, and adjacent sedimentary basins. This formation contains coarsely sorted ruditic, arenitic, siltic and lutitic components in various proportions, clearly separated. The Cândești Formation represents an epiclastic lithofacies accumulated in a hydrodynamic regime with a variable intensity (Anastasiu et al., 1987). The mineralogical assemblages are dominated by quartz, plagioclase and K-feldspar, hornblende and micas (as biotite and muscovite), with secondary minerals such as kyanite, garnet, staurolite, zircon, tourmaline, rutile, monazite, epidote, etc. Quartz and feldspar clasts or lithoclasts are embedded in calcitic and quartzitic cements (Mihăilă, 1971; Anastasiu et al., 1987; Iordache & Anastasiu, 1988).

Hydrogeologically, the Cândești Formation comprises two horizons: an upper one with local aquifers, free hydrostatic level and reduced flows; and a lower one, with significant reserves of exploitable underground water. Chemical composition of the underground water is as follows: anions (Cl^-, HCO_3^-) and cations (Na^+, Ca^{2+}, Mg^{2+}), with a pH of 7 (Liteanu, 1967).

Pedologically, the soils of Cândești Plateau are represented by luvisols, most of them affected by hydromorphic processes due to the stagnant water from the upper horizons or from the land surface, mainly in the rainy periods. On the slopes, eutric cambisols, anthroposols, regosols, and coluviosols are present (Tudor et al., 2013).

A temperate continental climate crossed by the Mediterranean air masses is characteristic for the Cândești Plateau. The mean annual temperature is 10-11°C, while precipitations reach 718 mm. During the vegetation period, insulation is 2177 hours/year, and the precipitation sum is 439 mm (Costescu, 2013).

2.2. Pietroasele Vineyard

The Pietroasele Vineyard, about 70 km long, is located in the central part of the larger Dealu Mare wine-producing region, between the Teleajen and Buzău river valleys. It occupies the southern part of Istrița Hill and part of the piedmont plain from its base. Istrița Hill is separated into three subunits: Nișcovului Hill (in the eastern part), Istrița Massif and Năienilor Hill.

The Istrița Massif consists of Sarmatian sandstone and carbonate formations. Toward the Romanian Plain, the contact is represented by faults and by the fall of the southern flank of the Ocnele Mari anticline. The Nișcovului Hill is formed by Quaternary and Levantine deposits containing sands, marls, clays and gravels in small amounts, while the Năienilor Hill is made up of Sarmatian limestones and sandstones (Fig. 1C). The Sarmatian deposits have different characteristics, depending on the outcrops: (a) in the Buzău Valley area the Sarmatian is represented by an alternation of clays and rhythmic sedimentary sands (Saulea, 1956); (b) at the contact with the Romanian plain, Sarmatian deposits have a neritic-coastal character, being represented by oolitic and coralligenous limestones; (c) in the eastern part, the dominant lithologies are brown marls, intercalated with marly limestones (Murgeanu et al., 1967b). Levantine deposits consist of sands, marls, clays, and rare gravels.

In the upper part of the Istrița Hill the soils have a skeletal-calcareous character, in the middle part the soils are skeletal-colluvial, while in the lower part, colluvial chernozem soils and typical chernozems occur.

The climate is characterized by a moderately drought microclimate, warm temperate with cold nights (Stroe et al., 2013).

3. MATERIALS AND METHODS

3.1. Sampling

The sampling campaign for soil, grapes and wine was carried out in the spring of 2014 – autumn of 2015. Soil sampling was conducted according the Order of the Ministry of Agriculture and Rural Development no. 278, published in the "Romanian Official Law Monitor" No. 928/28 December 2011 (OM 278/2011).

The soil samples were collected from Ştefăneşti and Pietroasele vineyards, down to 90 cm in depth, using a manual steel soil sampler. Sampling at the surface (0–20 cm depth) was performed after dust, roots, leaves or other residues from the surface were removed. 0.5 kg and 1.5 kg of each sample were collected for physical and respectively chemical analyzes. After that the samples were placed in labeled plastic bags, closed tightly. The grapes and wine cultivars sampled were Riesling and Cabernet Sauvignon from both vineyards.

3.2. Methods for soil analyzes

The soil physical parameters were determined according to the current national standard protocols, as follows: determination of organic matter - STAS 7107/1-76; determination of moisture - SR ISO 11465:1998; determination of grain size-sedimentation and sift method - STAS 1913/5-85 and SR EN 14688-2:2005; determination of bulk density using the immersion in fluid method - ISO 17892-2:2014, and determination of free swell index of soil - IS-2720-PART-40-1970. Please write information's about the instruments.

X-ray diffraction analyzes (XRD) were performed using a Bruker D8 Advance diffractometer with Bragg-Brentano geometry, CoKa1 with λ = 1.78897, Fe filter and a one-dimensional detector using corundum (NIST SRM1976a) as internal standard. Data were collected on a 5 - 64º 2θ interval, at 0.02º 2θ, with the measuring step of 0.2 seconds. Identification of the mineral phases was performed with Diffrac.Eva 2.1 (Bruker AXS), using the PDF2 (2012) database. XRD was done separately on bulk soil samples and oriented clay fraction (<2µm) which were subsequently treated with ethylene-glycol. 50 grams of homogenized samples were ground with an agate mortar and pestle and representative subsamples were studied by XRD. The clay fraction was separated by sedimentation in several rounds of distilled water and subsequently transferred to centrifuge tubes. Remaining carbonates were removed with 10% HCl. The samples were centrifuged and suspended in a small volume of distilled water, then placed on sample holders and allowed to dry at room temperature before being analyzed. The samples were then placed in ethylene-glycol saturated atmosphere for 24 hours and reanalyzed.

The physico-chemical parameters (electrical conductivity, salinity, pH, total dissolved solids) of the soil have been measured using a WTW Multi 350i multiparameter device.

For metal determination, samples were air-dried in a clean room and then milled with a Retsch RM 100 powder mill equipped with ceramic mortar and pestle. After grinding, the samples were sieved with a Fritsch Analysette 3 Spartan sieving system, retaining a granulation of less than 150 µm. The dry matter content was determined on 5-gram sub-samples for each soil sample.

Soil sample digestion was done in an open system, on a sand bath at temperatures below 200°C. About 1.5 g of soil added to a mixture of aqua regia (21 mL of 30% HCl and 60% HNO_3 7 mL) was allowed to digest in the sand bath for about 3 hours to rinse the mixture. The used acids were Trace type Select Fluka high quality. After cooling, the sample was filtered through filter paper with 14-18 µm porosity; further on, the quantitative solution was brought to 50 mL volumetric flasks by adding ultrapure water (Millipore Simplicity UV System).

The enrichment factor (EF) and the geoaccumulation index (I_{geo}) of heavy metals into the soil have been calculated as follows: for EF the equation of Salomons & Förstner (1984) have been used, noting that Al was replaced by Fe as in other studies (Windom et al., 1989; Breslin & Sañudo-Wilhelmy, 1999; Abrahim & Parker, 2008; a.o); for

I_{geo} the formula proposed by Müller (1969) has been applied. For mobility ratio (MR) we used the equations proposed by Serbula et al., (2012).

3.3. Methods for grape and wine analyzes

The pretreatment of grape and wine samples was performed in a microwave oven, using a mixture of 65% HNO_3 and 30% H_2O_2 solution (both ultra-pure quality for trace metals analysis). 1 g of each sample was mixed with 5 mL 65% HNO_3 and 1 mL H_2O_2. After digestion, ultrapure water was added until the samples reached 25 mL.

The determination of total metal content was performed using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-EOS) with simultaneous determination. Calibration curves were obtained on a certified Certipur Merck (ICP multi-element standard solution IV) 1000 mg/L reference material. During the procedure, blanks, triplicates samples (n = 3) and Quality Control Standards (ME 21 and 7A Perkin Elmer type) were analyzed for quality control. The ICP-EOS method (SR EN ISO 11885:2009 standard) used as operational parameters: 1.5 mL/min nebulizer pump rate; 1400 W RF power; 15 L/min plasma flow; 0.7 L/min nebulizer flow; 0.2 mL/min auxiliary flow.

Metallic element analyses were performed in a laboratory accreditated according to ISO/IEC 17025:2005 Standard (General requirements for the competence of testing and calibration laboratories) using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-EOS) Perkin Elmer Optima 5300 DV with simultaneous determination.

4. RESULTS AND DISCUSSION

4.1. Micro-, macroelements and heavy metals in soil

All soil samples have a 1-2% humus content; at Ștefănești their absorption capacity is 70-100%, whereas at Pietroasele it varies between 60 and 90%. The soil texture is sandy clay for most of the samples, with two exceptions: at Pietroasele the 20-40 cm sample is silty clay with sand and at Ștefănești, the surface sample (0-20 cm) is clayey sand. The mineralogical content is similar for all soil samples. Quartz and muscovite are the main minerals, associated with plagioclase and K feldspars, chlorites and calcite (Fig. 2). An amphibole was identified only in sample C20 (20 - 40 cm deep) from Pietroasele, whereas dolomite only occurs in sample R60 (40 - 60 cm) from Pietroasele. The larger lithoclasts separated during sieving are usually pebble sized (fine to coarse gravel) and are made up of limestones, sandstones, quartzite and metamorphic rock fragments (micaschists and green schists) along with the odd brick or glass fragment. Consistent with the bedrock lithology, limestone pebbles are dominant in both sampled areas from Pietroasele, where sandstones also occur at various horizons and quartzites are rare. At Ștefănești, quartzite and schist lithoclasts make up most of the pebble fraction, along with a few limestone fragments. No sandstones were identified.

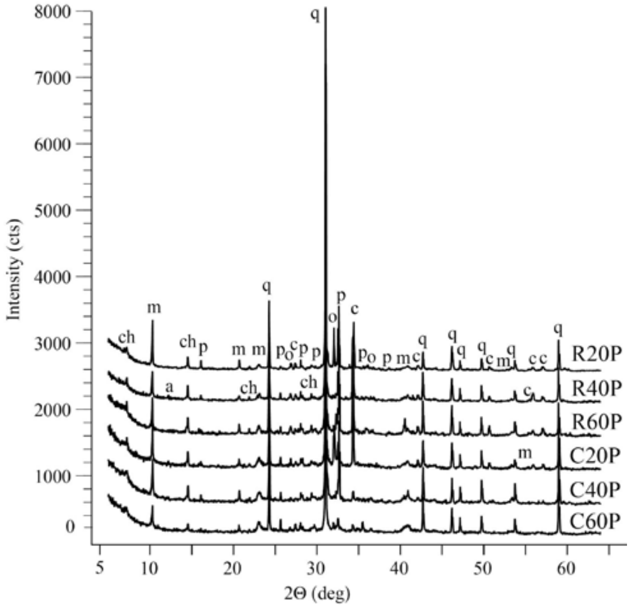

Figure 2. X-ray diffraction patterns of bulk soil samples from the Pietroasele vineyard (ch – chlorite, m – muscovite, a – amphibole, p – plagioclase feldspar, q – quartz, o – orthoclase, c – calcite).

Mineralogically, the clay fraction is fairly uniform in both sites, the exception being the presence - or absence - of montmorillonite and chlorite. At Pietroasele, XRD patterns of oriented and ethylene glycol - treated samples show that the <2 μm soil fraction contains mainly kaolinite, quartz, illite and chlorite; montmorillonite was found only in the upper soil samples taken from the Riesling cultivar area, lacking completely from the Cabernet Sauvignon area. At Ștefănești, montmorillonite was identified in all samples and chlorite in none. The other minerals participating in the association are kaolinite, illite and quartz, with vermiculite occurring in the two uppermost samples of the Riesling cultivated area. The soil from both vineyards is characterized by a pH ranging between 7.72 and 8.01, a low conductivity and TDS, and a value of salinity of 0‰.

Regarding the presence of macroelements into the analyzed soil it was noticed that the Ca values are higher in the Pietroasele vineyard (maximum 73387 mg/kg at 0-20 cm depth) than in Ștefănești vineyard (maximum 20224 mg/kg at 10-30 cm depth). Other investigated macroelements such as K (maximum value 2934 mg/kg in Ștefănești vineyard at 30-60 cm depth) and Mg (maximum 6771 mg/kg in Ștefănești vineyard at 0-10 cm depth) have relatively equal values in the studied vineyards for both analyzed varieties. The presence of these elements into the soil profile is strongly controlled by the parental material composition (Kment et al., 2005; Cuniglio et al., 2009) being intensively monitored due to their higher influence on the organoleptical properties of the wines (Lattore et al., 1994; Frias et al., 2001). Some of the minerals (calcite, plagioclases, micas) may release these cations through alteration processes such as hydrolysis and/or changing reactions (Lattore et al., 1994; Frias et al., 2001).

Several analyzed microelements have values which exceed the maximum limits allowed by Romanian legislation. Thus, for Cu the registered concentrations are significantly high in both vineyards with higher values in Ștefănești vineyard than in Pietroasele vineyard. The maximum value at the Ștefănești vineyard is 184 mg/kg at 60-90 cm depth for the Cabernet Sauvignon cultivar, whereas at the Pietroasele vineyard the maximum value is 87.9 mg/kg at 40-60 cm depth for the Riesling cultivar. These values exceed around nine times the maximum limits allowed and can be derived from used pesticides and/or fungicides (Merry et al., 1983; Kment et al., 2005; Komárek et al., 2010) affecting the growing process of the vine, even leading to the plant death (Romeu-Moreno & Mas, 1999).

Values over the maximum limits allowed by legislation have been recorded for Ni as well. The registered values are high in all the analyzed samples, with a maximum value around 32.5 mg/kg in the Ștefănești vineyard, at 0-10 cm in the batch cultivation of the Riesling grape variety. Generally, the values for Ni are higher at Ștefănești vineyard than at Pietroasele vineyard. The provenance of this metal into the soil can be linked to fungicide applications. For example, a widely used Bordeaux solution contains, in addition to $CuSO_4$, other elements such as Zn, Pb, Cr, Ni, and Cd (Mirlean et al., 2007). Aside from this anthropogenic source a geogenic source can be taken into account (Botsou et al., 2016) even if the studied samples are not containing serpentine, which is the main Ni and Cr mineral reported as a source for these elements into the soil (Massoura et al., 2006; Licina et al., 2010). Some other minerals such as pyroxene, olivine, biotite and chlorite can also be Ni-enriched (Massoura et al., 2006) and some of them have been identified in the studied samples.

In the Ștefănești vineyard, high values for Zn and Pb have been identified. These two elements exceed the maximum limit allowed (100 mg/kg and 20 mg/kg respectively) in the batch cultivation of grapes for the Cabernet Sauvignon variety. The maximum value for Zn is 161 mg/kg at 60-90 cm and can be attributed to many factors, such as agricultural practices and/or use of fungicides (Álvarez et al., 2007). For Pb, the maximum value is 39.4 mg/kg and was registered also at 60-90 cm depth. The presence of this metal into the upper part of the soil profile or into the uncontaminated soils can be linked to natural processes which are causing the degradation of the soil parental material (Hansmann & Köppel, 2000). However, the highest quantities of Pb into the soil also have anthropogenic origins (Mihaljevič et al., 2006) coming either from the combustion of coal (Novák et al., 2003) or from vehicle emissions (Monna et al., 1997; Novák et al., 2003), but also from the use of Pb-based insecticides (Merry et al., 1983). At 60-90 cm depth the presence of this metal is due to its migration towards the deeper soil horizons (Teutsch et al., 2001; Ettler et al., 2004).

Another element which registered an exceeding of the maximum limits allowed by legislation is As, with higher values in the samples from the Ștefănești vineyard (maximum 14.4 mg/kg). In the latter, the content of As is close to the maximum limits allowed by law. Products for insect control containing As have been widely used into the orchards and vineyards, especially into the first part of the last century until around 1970 when they were replaced by other products (Ajtonj et al., 2008). Still, the effects of this element on the growing processes of the plants have been highlighted by a number of studies (Merry et al., 1983 and references therein).

Generally, the values for some micro- and macroelements (e.g. Fe, Co, As, Mn, etc.) are higher in the Ștefănești vineyard (Tables 1 and 2) than in the Pietroasele vineyard (Tables 3 and 4). Calculating the EF, it can be observed that the highest values were registered for Cd, especially in the area where the grapes for Cabernet Sauvignon are cultivated. Cd was identified with the highest values in some other studies too (Mirlean et al., 2007; Sucharovà et al., 2012). The next elements are As and Cu, both having an enrichment factor (EF) higher than 6, excepting the samples prelevated from Pietroasele vineyard in the Cabernet Sauvignon cultivar area.

The EF for the other analyzed heavy metals is between 1 and 3 (Fig. 3). Based on calculated I_{geo} most of the analyzed soils are falling into the 0 class, indicating uncontaminated sites. Only for As, the I_{geo} is reaching the value 1, thus the analyzed soils are falling into 1st class, which means moderately contaminated with this heavy metal.

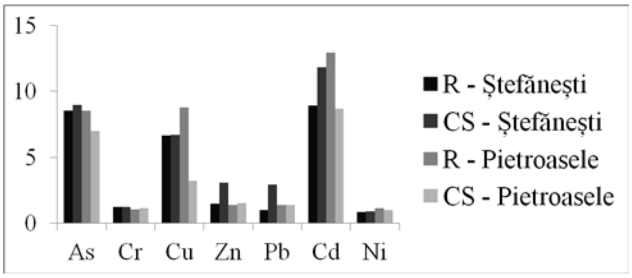

Figure 3. Enrichment factors for trace metals in soil; R – white wine (Riesling); CS – red wine (Cabernet Sauvignon).

4.2. Micro-, macroelements and heavy metals in grapes and wine

The most abundant major element into the analyzed grapes is K (maximum value 2265 mg/kg) followed by the Ca and Mg. A big difference can be observed in the case of Ca which has a maximum value of 792 mg/kg in white grapes, and a maximum value of 288 mg/kg in the black grapes from the Ștefănești vineyard. This succession of elements (K>Ca>Mg) has been also mentioned by Kment et al., (2005) in a study of samples from Czech Republic and by Acuña-Avila et al., (2016) which studied the Cabernet Sauvignon variety from Mexico.

Table 1. The concentration of macro-, microelements and heavy metals in soil from Ștefănești area (Riesling cultivar)(mg/kg)

	Macroelements				**Microelements/heavy metals**									
Depth (cm)	**MAL - Ca**	**MAL - K**	**MAL - Fe**	**MAL - Mg**	**MAL 1 Se**	**MAL 15 Co**	**MLA 30 Cr**	**MAL 20 Cu**	**MAL 900 Mn**	**MAL 100 Zn**	**MAL 20 Pb**	**MAL 1 Cd**	**MAL 20 Ni**	**MAL 5 As**
0-10	10843.0	2703.0	29819.0	6771.0	12.9	12.1	28.4	148.0	1031.0	69.8	12.2	0.6	32.5	10.9
10-30	10620.0	2362.0	28184.0	6368.0	13.5	11.3	27.7	124.0	932.0	63.2	11.1	0.58	30.6	9.2
30-60	9602.0	2248.0	27771.0	6142.0	14.4	11.5	28.3	77.9	904.0	58.4	10.6	0.58	30.0	8.2
60-90	8800.0	2086.0	28787.0	6233.0	13.3	11.9	28.0	81.3	976.0	58.6	11.3	0.58	31.0	9.3
Average														
x	9966.2	2349.7	28640.2	6378.5	13.5	11.7	28.1	107.8	960.7	62.5	11.3	0.59	31.0	9.3
(30-90)	9674.0	2232.0	28247.3	6247.6	13.7	11.5	28.0	94.4	937.3	60.0	11.0	0.58	30.5	8.8
Minimum values														
	8800.0	2086.0	27771.0	6142.0	12.9	11.3	27.7	77.9	904.0	58.4	10.6	0.58	30.0	8.2
Maximum values														
	10843.0	2703.0	29819.0	6771.0	14.4	21.2	28.4	148.0	1031.0	69.8	12.2	0.65	32.5	10.9

MAL – maximum allowed limits

Table 2. The concentration of macro-, microelements and heavy metals in soil from Ștefănești area (Cabernet Sauvignon cultivar)(mg/kg)

	Macroelements				**Microelements/heavy metals**									
Depth (cm)	**MAL - Ca**	**MAL 20 K**	**MAL - Fe**	**MAL - Mg**	**MAL 1 Se**	**MAL 15 Co**	**MAL 30 Cr**	**MAL 20 Cu**	**MAL 900 Mn**	**MAL 100 Zn**	**MAL 20 Pb**	**MAL 1 Cd**	**MAL 20 Ni**	**MAL 5 As**
0-10	14802.0	3394.0	25444.0	5933.0	13.1	10.2	26.7	116.0	833.0	113.0	23.1	0.75	31.5	10.6
10-30	20224.0	2904.0	25576.0	5642.0	10.3	9.45	24.9	103.0	782.0	94.6	19.7	0.72	29.5	9.25
30-60	16197.0	2934.0	28121.0	6263.0	10.8	10.4	28.9	76.6	829.0	98.5	34.7	0.66	31.7	8.72
60-90	16167.0	2657.0	22096.0	4690.0	8.24	8.03	22.5	184.0	710.0	161.0	39.4	0.68	24.5	6.74
Average														
x	16847.5	2972.2	25309.2	5632.0	10.6	9.52	25.7	96.7	788.5	116.7	29.2	0.70	29.3	8.82
(30-90)	17529.3	2831.6	25264.3	5531.6	9.78	9.29	25.4	121.2	773.6	118.0	31.2	0.68	28.5	8.23
Minimum values														
	16167.0	2657.0	22096.0	4690.0	8.24	8.03	22.5	76.6	710.0	94.6	19.7	0.66	24.5	6.74
Maximum values														
	20224.0	2934.0	28121.0	6263.0	13.1	10.4	28.9	184.0	833.0	161.0	39.4	0.75	31.7	10.6

MAL – maximum allowed limits

Table 3. The concentration of macro-, microelements and heavy metals in soil from Pietroasele area (Riesling cultivar)(mg/kg)

	Macroelements				Microelements/heavy metals									
Depth (cm)	**MAL - Ca**	**MAL - K**	**MAL - Fe**	**MAL - Mg**	**MAL - Se**	**MAL 15 Co**	**MAL 30 Cr**	**MAL 20 Cu**	**MAL 900 Mn**	**MAL 100 Zn**	**MAL 20 Pb**	**MAL 1 Cd**	**MAL 20 Ni**	**MAL 5 As**
0-20	73387.0	1826.0	17505.0	6088.0	13.9	8.30	13.4	86.3	1003.0	35.2	9.36	0.57	25.6	6.17
20-40	55198.0	1903.0	17734.0	6201.0	13.8	8.23	13.3	85.6	805.0	34.9	9.28	0.57	25.4	6.12
40-60	55767.0	2025.0	18734.0	6424.0	8.94	7.87	17.4	87.9	674.0	38.2	9.18	0.44	24.9	4.89
Average														
x	61450.0	1918.0	17991.0	6237.6	12.2	8.13	14.7	86.6	827.3	36.1	9.27	0.52	25.3	5.72
(20-60)	55482.0	1964.0	18234.0	6312.5	11.3	8.05	15.3	86.7	739.5	36.5	9.23	0.50	25.1	5.50
Minimum values														
	55198.0	1826.0	17505.0	6088.0	8.94	7.87	13.3	85.6	674.0	34.9	9.18	0.44	24.9	4.89
Maximum values														
	73387.0	2025.0	18734.0	6424.0	13.9	8.30	17.4	87.9	1003.0	38.2	9.36	0.57	25.6	6.17

MAL – maximum allowed limits

Table 4. The concentration of macro-, microelements and heavy metals in soil from Pietroasele area (Cabernet Sauvignon cultivar)(mg/kg)

	Macroelements				Microelements/heavy metals									
Depth (cm)	**MAL - Ca**	**MAL - K**	**MAL - Fe**	**MAL - Mg**	**MAL - Se**	**MAL 15 Co**	**MAL 30 Cr**	**MAL 20 Cu**	**MAL 900 Mn**	**MAL 100 Zn**	**MAL 20 Pb**	**MAL 1 Cd**	**MAL 20 Ni**	**MAL 5 As**
0-20	37969.0	2405.0	17608.0	5165.0	8.04	6.95	16.3	43.0	652.0	42.3	10.3	0.36	22.8	5.27
20-40	29199.0	2673.0	19581.0	5161.0	7.82	7.65	17.9	32.3	673.0	42.1	10.2	0.39	25.6	5.57
40-60	46656.0	2321.0	18479.0	5610.0	7.39	7.00	16.5	26.3	646.0	39.5	9.62	0.37	22.8	3.98
Average														
x	37850.3	2466.3	18556.0	5312.0	7.75	7.20	16.9	33.8	657.0	41.3	10.0	0.37	23.7	4.94
(20-60)	37927.5	2497.0	19030.0	5385.5	7.60	7.32	17.2	29.3	659.5	40.8	9.9	0.38	24.2	4.77
Minimum values														
	29199.0	2321.0	17608.0	5161.0	7.39	6.95	16.3	26.3	646.0	39.5	9.6	0.36	22.8	3.98
Maximum values														
	46656.0	2673.0	19581.0	5610.0	8.04	7.65	17.9	43.0	673.0	42.3	10.3	0.39	25.6	5.57

MAL – maximum allowed limits

Other major elements present the tendency Na>Fe>Mn, the same succession as the one described by Kment et al., (2005). Regarding the heavy metal content, the most abundant element is Zn, which registered 174 mg/kg in white grapes and 68.7 mg/kg in the black grapes from the Ștefănești vineyard. The amount of this element into the grapes from the Pietroasele vineyard is much lower, not exceeding values of 1 mg/kg. Other chemical elements with higher values are Cu, Cr and Se, identified also in Ștefănești vineyard. Other studies (Chopin et al., 2008; Acuña-Avila et al., 2016) show the Zn>Cu>Pb succesion for chemical elements. In our study the Pb values recorded for grapes are not exceeding the value of 0.05 mg/kg.

Most of the analyzed elements present higher values in the wine from Pietroasele vineyard than in the wine from Ștefănești vineyard (Fig. 4). Comparing the white wine with the red wine it can be observed that the higher values are registered in the red wine. The higher level for Zn (7.42 mg/l) an Fe (13.82 mg/l) are identified in the Cabernet Sauvignon wine from the Ștefănești vineyard and for Ca (338.7 mg/l) and Mg (129.2 mg/l) in the same variety from the Pietroasele vineyard. The element succession in the analyzed wines are Ca>Mg>Fe>Zn>Mn>Pb>Cu>Cr. All the other elements have concentrations under 0.15 mg/l. Based on the Romanian legislation (HG 512/2016) the values for Pb (0.65 mg/l in white wine and 0.25 mg/l for red wine at the Ștefănești vineyard) and Zn (7.42 mg/l for red wine, Ștefănești vineyard) exceed the maximum limits allowed, which are 0.2 mg/l and 5.0 mg/l, respectively.

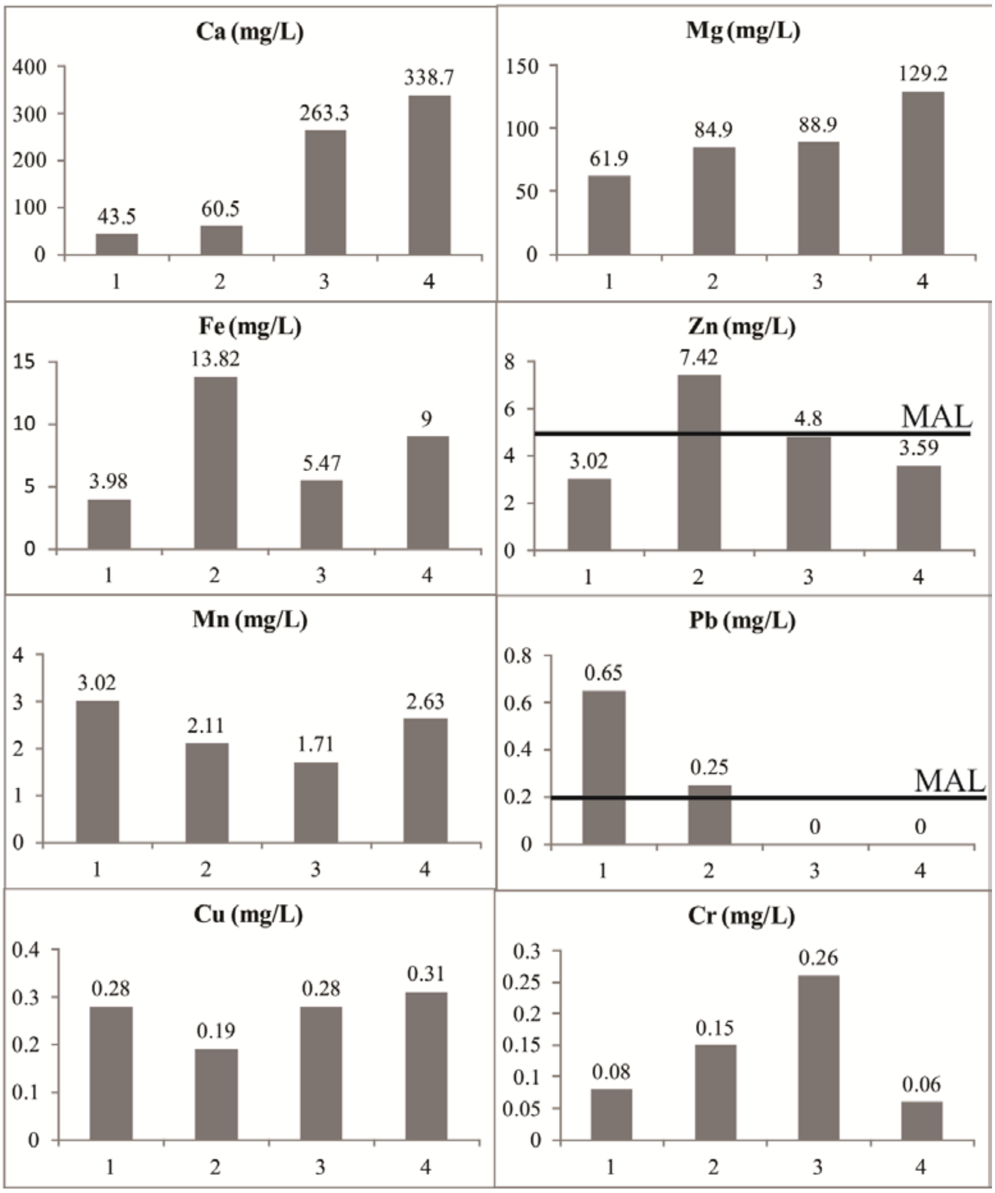

Figure 4. Concentration of macro-, microelements and heavy metals in wine (mg/L); 1 – Ștefănești white wine (Riesling); 2 –Ștefănești red wine (Cabernet Sauvignon); 3 – Pietroasele white wine (Riesling); 4 – Pietroasele red wine (Cabernet Sauvignon); MAL – maximum allowed limits

According to the mobility ratio, all the analyzed plants show a low metal translocation from soil, since the values of this index are generally lower than 1. This result, together with the high EF values for Cd and As, indicates that the plants generally have a low metal uptake and an indifferent behavior toward these elements. Two exceptions can be observed regarding the mobility ratio value and they are for K and Zn. Both elements present a mobility ratio >1 in the white grapes from Ștefănești vineyard.

5. CONCLUSIONS

The concentrations of chemical elements into the soil, grapes and wine from two Romanian vineyards have been investigated. The soil samples analyzed fall mostly in the sandy clay category, with little variation. The soil mineralogy is fairly uniform and largely reflects the underlying lithology. Based on the results obtained, the following conclusions can be outlined:

1. The chemical element (K, Mg, Cu, Ni, Zn, Pb, As) concentrations in the soil samples from the Ștefănești vineyard are higher than at Pietroasele vineyard. At the latter, only Ca values are higher than at Ștefănești. All these elements mentioned exceed the maximum limits settled by the Romanian legislation.

2. The presence of macroelements into the investigated soil samples can be related to the presence of some minerals identified through the X-ray diffraction. These minerals are: plagioclase, K

feldspar, illite, chlorite and calcite.

3. The values recorded for Ca, Zn, Cr, and Se are higher in the white grapes from both vineyards. The only element that showed higher concentration in the black grapes was Cu.

4. The values for the analyzed macroelements (Ca and Mg) are higher in the Riesling wine samples than in the Cabernet Sauvignon ones, who however seem to accumulate higher amounts of heavy metals (Zn and Fe).

5. Based on the geoaccumulation index, most of the soil is classified as uncontaminated to moderately contaminated for most of the elements excepting As.

6. The apparent correlation between the enrichment factor and the mobility ratio is an argument in favor of the natural sources of Cd and As in the soils. Although As seems to exceed the maximum allowed limits in soil, there is no correlation with its amount in the plant samples; vine samples have a positive uptake only for K and Zn, being indifferent to other elements.

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