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GEOCHEMICAL DISTRIBUTION OF SELECTED TRACE ELEMENTS IN VINEYARD SOILS FROM THE HUŞI AREA, ROMANIA

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Abstract: The aim of the present study is to highlight the amounts of eight trace elements (Cd, Co, Cr, Cu, Ni, Pb, Zn and As) determined in soils from one of the oldest and most famous wine-growing areas of Romania. Analyses were performed using energy-dispersive X-ray fluorescence spectrometry (ED-XRF). For each element the ranges of results are: 0.06 - 0.26 mg·kg^{-1} for Cd, 8.7 - 15.9 mg·kg^{-1} for Co, 91.0 – 299 mg·kg^{-1} for Cr, 26.8 - 282 mg·kg^{-1} for Cu, 22.0 – 51.9 mg·kg^{-1} for Ni, 14.1 – 26.7 mg·kg^{-1} for Pb, 43.1 -103 mg·kg^{-1} for Zn, 5.7 – 16.9 mg·kg^{-1} for As. The pH was determined in aqueous solution and data obtained describe a soil reaction from moderately acid (5.1) to moderately alkaline (8.4). To evidence the distribution and outliers presence, boxplot diagrams were used. The results have shown that the Cr, Cu, Ni and As contents exceed the normal reference values according to the Romanian legislative acts for the vineyard soils studied. The environmental background calculated for these four elements exceeds the normal value for soil regulated by the law in force, as well.

Keywords: distribution, vineyard soils, trace elements, XRF, boxplot, Huşi

1. INTRODUCTION

The accumulation of some elements can cause a reduction in soil functions, toxicity for plants and the contamination of the food chain. The source of these elements is either natural, namely an inheritance from the parental rock of the soil (geogenic source), or anthropogenic, including inputs resulting from the use of fertilizers, organic manures, industrial and municipal wastes (Hooda, 2010).

In viticulture, the use of metal-containing substances in order to sustain the crop production has increased significantly. To correct the micronutrient deficiencies, trace elements such as Cu, Zn, Fe, Mn and B, which are essential for plant growth, are applied. Other treatments with fungicides, pesticides and herbicides are also considered inputs into the vineyard soil.

The aim of the present study is to offer an overview of the content of vineyard soils regarding those trace elements normally useful for the vine which, under special circumstances, may become toxic. The trace elements found in the vineyard soils from the Huşi area represent only one focus point in a large study regarding the mobility within the system, which includes plant parts and wine.

In the present study, we focus on 8 elements (Cd, Co, Cr, Cu, Ni, Pb, Zn, As) and attempt to describe their distribution in relation to the references values established by Order no 756/1997 of the Romanian Ministry of Waters, Forests and Environment Protection (the law in force regarding the admissible values in soils), as well as a geochemical background. The Huşi area is one of the oldest and most famous wine-growing areas from Romania. There are numerous studies regarding the relief, the climatic conditions and the quality of the wine produced in the area, but none of them takes into account the trace elements.

2. MATERIALS AND METHODS

2.1. Study area

The Huşi area is situated in the eastern part of Romania, at the intersection of the 46°41' parallel with the 28°03' E longitude meridian.

The area is located in the basin bearing the same name, at the contact between the Moldavian

Central Plateau and the Hills of Fălciu, at an altitude of 120 meters.

The city is surrounded by hills that are not steep, but smooth, covered with vineyards. Its special position, as in a giant bowl, brought Huşi the name of "The town between the vineyards".

The European road E 581 passes through Huşi, connecting it to the Republic of Moldova through the Albița Customs.

Geologically, the study area is located in the eastern part of the Moldavian Platform, which is a continuation of the European Platform on Romanian territory (Fig. 1).

This unit is one of the oldest platform units of Romania, with a bedrock basement and a sedimentary cover.

The Lower Proterozoic metamorphic basement of the platform is intruded by gabbros, anorthosites and granites. The basement is covered by sedimentary formations developed during several sedimentary cycles: Vendian – Cambrian, Ordovician – Silurian, Devonian, Upper Jurassic – Cretaceous, Eocene and Oligocene (Ionesi et al., 2005).

2.2. Sampling

162 soil samples from 3 different types of soil (vertic chernozem, calcaro-calcic chernozems, and calcic chernozem), as well as 6 varieties of grapevine (Busuioacă de Bohotin, Aligoté, Fetească Regală, Tămâioasă Românească, Zghihară and Cabernet Sauvignon), were collected from the Huşi vineyard area.

The soil samples were collected systematically, from a network of points located at a distance of 50 meters (from one another). The sampling was carried out in 81 points, at two depths, 0-20 cm and 20-40 cm, respectively, from the topsoil.

The total sampling surface is 16.62 ha. A soil sample is composed of five sub-samples, gathered from four points found at a distance of 1 meter from the central sampling point.

The general characteristics of a sample were respected, each one being accurately located (a GPS device was used), representative for the study and the area, homogenous, and large enough for analyses to be performed on it. Moreover, any contamination after sampling was avoided.

The weight of the soil samples ranges between 1.5 and 2 kg. The soil samples were naturally air-dried after the organic debris was removed. The dry samples were further ground and homogenized in agate mortar, sieved through 1 mm mesh, and stored in zip-lock bags.

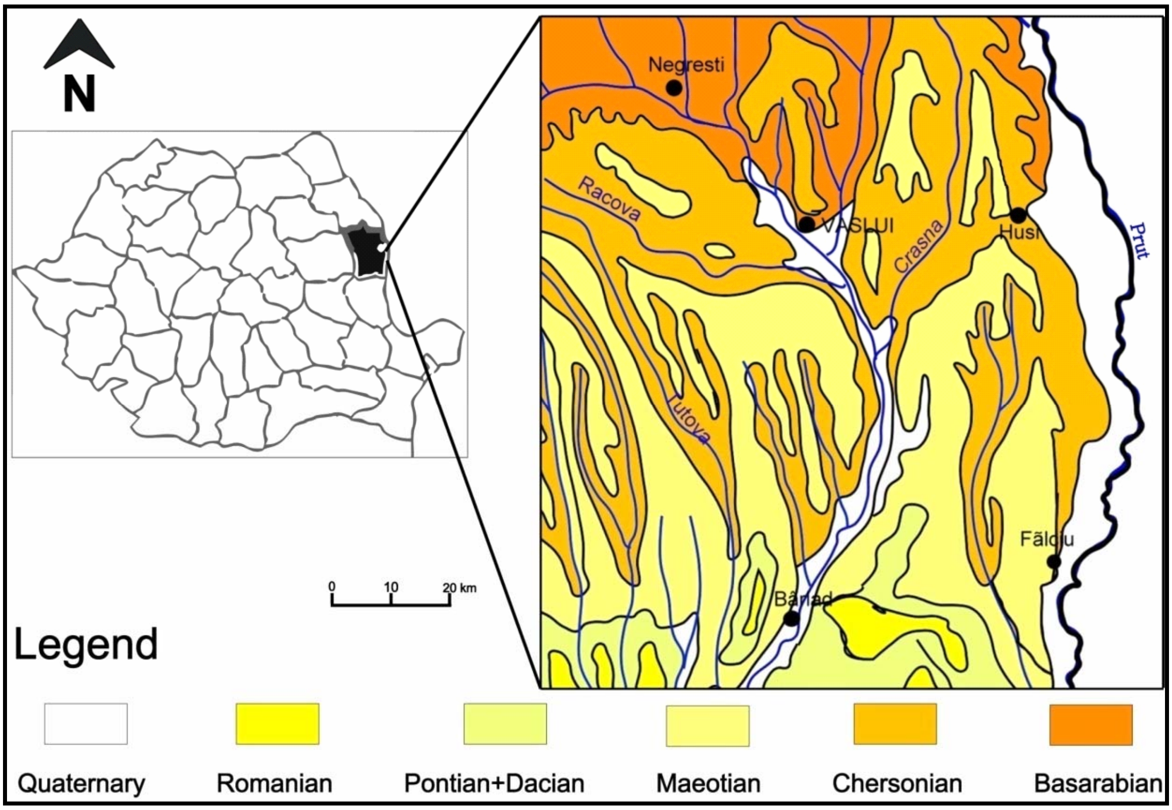


Figure 1. Geological map of the Huşi area - Moldavian Platform (modified from Ionesi et. al, 2005).

The total contents of trace elements (Cd, Co, Cu, Cr, Ni, Pb, Zn, As) were determined through energy-dispersive X-ray fluorescence spectroscopy (ED-XRF), using an ED-XRF Epsylon 5 Spectrometer.

In order to obtain the pellets (pressed-powder samples/disks) for ED-XRF analysis, an amount of soil and binder (synthetic raisin), at a ratio of 5:1, was mixed mechanically in an agate ball mill, for 15 minutes, at a constant speed of 180 rpm. For each sample, a pressed-powder disk (30 seconds at a force of 20 t/cm^2) weighing 9 g was obtained.

The standardization was performed by using 23 standards: 14 standards provided by Geological Survey of Japan (JA-1-3: andesite powder; JB-1-3: basalt powder; JLk-1: lake sediment powder ; JSd-1-3: stream sediment powder; JR-1-2: rhyoliye powder; JMs-1-2: marine sediment powder), 8 standards provided by CCRMP-CANMET-MMSL Natural Resources Canada (SO-1-4: regosolic clay soil, podzolic B horizon soil, calcareous C horizon soil and chermozemic A horizon soil; STSD-1-4: stream sediment powder) and 1 standard provided by USGS, United States Geological Survey, (RGM-1: rhyolite powder).

The exposure time was 60 s, with the exception of As and Cd, in which case the exposure time was 90 s. The detection limits for the elements analyzed are the following: Cd = 0.05 mg·kg^{-1}, Co = 1.14 mg·kg^{-1}, Cr =7.03 mg·kg^{-1}, Pb = 2.92 mg·kg^{-1}, Ni = 10.65 mg·kg^{-1}, Zn = 2.27 mg·kg^{-1}, As= 1.13 mg·kg^{-1}.

For each sample of soil, pH measurements were carried out using a WTW Inolab 730 pH-meter, through the potentiometric method, in aqueous solution, using a soil: water ratio of 1:2.5 (mass/volume).

The preparation of the samples for analyses, as well as the analyses themselves, was carried out at the University “Al. I. Cuza” of Iaşi, Romania, within the Department of Geology.

2.3. Data analysis

Statistical analyses were performed using the NCSS 2007 software and the Office 2007 package for Windows Vista.

The concept of a global standard for the background value is often criticized because of considerable differences of a regional and even a local character.

Many factors influence the natural concentration of elements whose spatial distribution is not equal (Reimann & Garrett, 2005). The geochemical background was calculated using the methods suggested by Ouellette (2009) and Reimann & Garret (2005) and Reimann et al., (2005).

A comparison between the results obtained using these two methods, included in table1, clearly indicate that the values are close.

Tabel 1. The upper limit of environmental background calculated using the two methods (mg·kg^{-1})

Element	*Reimann & Garret, 2005; Reimann et al., 2005*	*Ouelette, 2009*
Cd	0.19	0.24
Co	14	14
Cr	139	139
Cu	79.3	79.3
Ni	45.0	51.8
Pb	22.9	25.6
Zn	85.2	103

The establishment of background concentrations in the surface environment is important for at least two reasons: (1) it allows the distinction of contaminated or polluted areas from uncontaminated or unpolluted ones, and (2) it enables modeling of the anthropogenic influence on the mobilization, migration, and deposition /uptake of substances in the environment (Galuszka, 2007).

The first objective may be useful for setting environmental quality standards, whereas the second one is useful for assessing the extent of human activities and their influence on the cycling of elements.

For a normal distribution, all four parameters (mean, geometric mean, median and module) will, theoretically, have the same value, though there may be slight differences depending on the actual data (Reimann et al., 2008).

Only Co, Cu and Cr follow a normal distribution of lognormal transformed data, respecting the general rule of trace element distribution in soils.

Boxplot diagrams are used to present and compare analytical data. The diagram displays a summary of five statistical data: median –line inside the box, upper and lower quartiles –borders of the box, the distribution and skewness of the inner fence, which contain 50% of the data set, minimum and maximum values – marked as the end of the “whiskers” and outliers – marked with green circles (higher than 1.5 x the hinge spread) and red circles (higher than 3 x the hinge spread).

In the present study, we chose boxplot diagrams to compare the two sets of data regarding the two sampling depths. For each element, the boxplot diagrams highlight the distribution of elements and the two comparative reference values: background and normal values for soils.

3. RESULTS AND DISSCUSION

The total trace element contents of the soils are summarized in table 2 and figure 2.

The distribution of chemical elements in rocks or any natural formations is a defining characteristic. Statistically, the frequency contents of an element are governed by a law of distribution, characterized by a proper set of statistical parameters: arithmetic mean, variance, standard deviation.

The mean contents of Cd, Co, Cr, Ni, Pb, Zn and As are between the range of lower and upper quartiles. When the value is out of this range, like in the case of Cu average content, then the geometric mean is taken into account.

The variance values of Ni, Zn, Cr and Cu are very large, which means on average that the data are more scattered from mean value.

Taking into account that the variance is a measure of the "spread" of a distribution about its average value, the smaller is the variance value then the individual values of the random variable tend to be closer to the mean (case of Cd, Co, Pb, As).

The Pb, As and Ni negative values of skewness suggests a close to normal distribution with a left skewed distribution, most values being concentrated on the right of the mean, with extreme values to the left.

The positive values show right skewed data, most values being concentrated on left of the mean, with extreme values to the right.

Positive values of skewness are increasing with a slight degree starting from Zn and continue to Co, Cd, Cu and Cr.

Kurtosis value under 3, the case of Cd, shows a positive value of excess or a much higher density of values around the mean value.

The kurtosis values bigger than 3, shows a negative value of excess or a wider spread around the mean- case of Zn, Pb, Ni, Co, As, Cu and Cr.

The geochemical background was calculated in order to distinguish between the soil reference values established by the law in force, and the natural background.

The vineyard soils from the Huşi area display a homogeneous concentration, which can be explained as a result of leaching, poughing and agricultural practices (Mîrlean et al., 2007).

The small diferences between the 0-20 and 20-40 depths are illustrated in Fig. 3.

The abundances of the selected trace elements in the soil are described by the following increasing sequence: Cd < As < Co < Pb < Ni < Zn < Cu < Cr.

For 162 samples collected from the research area, the average pH value is 7.2, ranging from 5.1 – moderately acid, to 8.4 – moderately alkaline (Fig. 4). The results can be divided into two sampling depths:

- for the soil samples collected from depths between 0-20 cm: 3.7% display a pH from 5.1 to 5.8, describing soils with weak moderately acid reaction; 37.04% display a pH from 5.9 to 6.8, describing soils with weak acid reaction; 11.11% display a pH from 6.9 to 7.2, describing soils with neutral reaction; 48.15% display a pH from 7.3 to 8.4, describing soils with weak alkaline reaction;
- for the soil samples collected from depths between 20-40 cm: 3.7% display a pH from 5.1 to 5.8, describing soils with weak moderately acid reaction; 35.80% display a pH from 5.9 to 6.8, describing soils with weak acid reaction; 7.41% display a pH from 6.9 to 7.2, describing soils with neutral reaction; 53.09% display a pH from 7.3 to 8.4 describing soils with weak alkaline reaction.

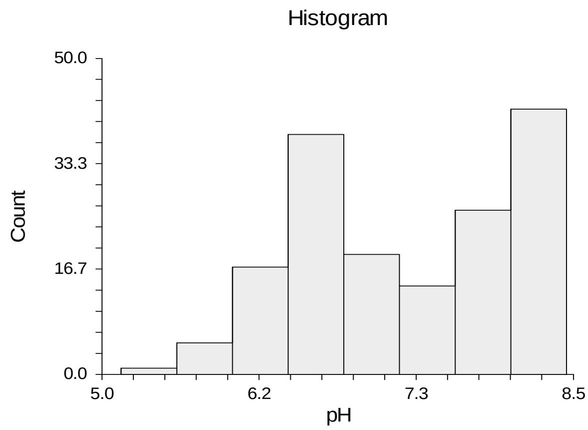


Figure 4. Histogram of soil pH

The matrix of the correlation coefficients for the selected trace elements from the Huşi vineyard area (Table 3) indicates the predominance of positive correlations over negative ones. Co-Ni, Co-Pb, Co- Zn, Ni-Pb, Ni-Zn and Pb-Zn display good positive correlations, while Co-Cr, Cr-Ni, Cr-Pb and Cr-Zn display slight negative correlations.

In the investigated soils, the Cd concentrations range between 0.06 and 0.26 $mg \cdot kg^{-1}$, with an average of 0.13 $mg \cdot kg^{-1}$. In the present study, the highest value of Cd belongs to the plot cultivated with the "Cabernet Sauvignon" variety, where the soil type is vertic chernozem. The lowest concentration is also associated with the "Cabernet Sauvignon" vine variety. The explanation lies in the slope of the terrain and the washing away of the soil by precipitation.

Adriano (2001) presents a background of 0.40 $mg \cdot kg^{-1}$ for world soils, and 0.3 - 11 $mg \cdot kg^{-1}$ as the largest amount of soils derived from sedimentary rock.

Tabel 2. Statistical parameters for the vineyard soils from the Huşi area

Element/ Parameter	Cd ($mg\cdot kg^{-1}$)	Co ($mg\cdot kg^{-1}$)	Cr ($mg\cdot kg^{-1}$)	Cu ($mg\cdot kg^{-1}$)	Ni ($mg\cdot kg^{-1}$)	Pb ($mg\cdot kg^{-1}$)	Zn ($mg\cdot kg^{-1}$)	As ($mg\cdot kg^{-1}$)	pH
Arithmetic mean	0.13	12.0	146	84.9	38.9	19.9	73.9	10.5	7.2
Geometric mean	0.13	12.0	143	75.4	38.5	19.7	72.8	10.3	7.2
Harmonic mean	0.12	11.9	141	67.3	38.1	19.6	71.8	10.1	7.2
Median	0.13	11.9	138	76.6	39.2	20.0	72.2	10.7	7.3
Mode	0.10	-	-	-	39.0	-	-	-	-
Standard deviation	0.04	1.4	29.2	44.6	5.4	2.4	12.2	2.0	0.79
Variance	0.00	2.1	852	1989	29.1	5.7	148	3.9	0.62
Skew	0.42	0.36	1.8	1.7	-0.23	-0.13	0.2	-0.14	-0.21
Kurtosis	2.86	3.5	8.3	7.0	3.4	3.2	3.1	3.9	1.8
Variation coefficient	0.32	0.12	0.2	0.53	0.14	0.12	0.2	0.19	0.11
Lower quartile	0.10	11.2	128	55.0	35.9	18.5	66.1	9.4	6.5
Upper quartile	0.16	12.6	157	76.6	41.9	21.4	81.6	11.9	8.1
Range	0.21	7.2	208	256	29.9	12.6	60.1	11.2	3.3
Minimum	0.06	8.7	91.0	26.8	22.0	14.1	43.1	5.3	5.1
Maximum	0.26	15.9	299	283	51.9	26.7	103	17.4	8.4
Count	162	162	162	162	162	162	162	162	162
Distribution	normal	log-normal	log-normal	log-normal	normal	normal	normal	normal	-
Background	0.19	14.0	140	79.3	45.0	22.9	85.2	13.2	-
NVS*	1	15	30	20	20	20	100	10	

**NVS - normal values for soils, Order no. 756/1997 of the Romanian Ministry of Waters, Forests and Environmental Protection*

Tabel 3. The matrix of correlation coefficients for the selected trace elements

	Cd	***Co***	***Cr***	***Cu***	***Ni***	***Pb***	***Zn***	***As***
Cd	1							
Co	0.13	1						
Cr	-0.04	-0.37	1					
Cu	-0.09	-0.07	-0.05	1				
Ni	0.07	0.68	-0.32	-0.03	1			
Pb	0.09	0.56	-0.26	0.18	0.72	1		
Zn	0.12	0.75	-0.33	0.29	0.73	0.74	1	
As	0.05	0.10	0.02	-0.12	0.34	0.24	0.12	1

Other studies conducted on vineyard soils suggest the following values in the case of Cd:

- a total mean content of 0.358 $mg\cdot kg^{-1}$ in the Castelon region, Spain (Peris et al., 2007);

- based on 4 depths – 0-10, 10-20, 20-30 and 30-40 cm – the following means: 1.9; 1.6; 1.4 and 1.1 $mg\cdot kg^{-1}$ are obtained for the Brestnik village, Bulgary (Angelova et al., 1999). In this case, it can be easily noticed that the concentration decreases with depth.

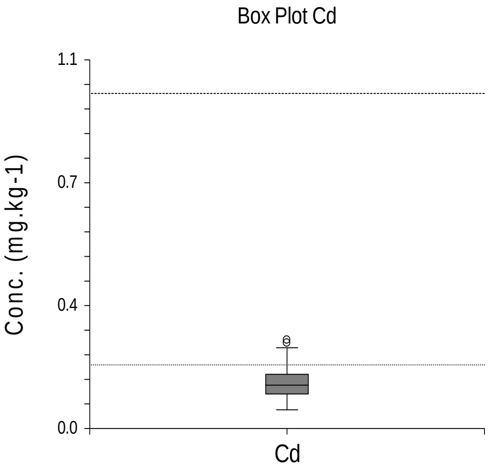
- higher values are obtained for the southern part of Brazil, as part of a study which takes into consideration the age of vineyards, discovering that the concentration increases with the age, from 0.03 $mg\cdot kg^{-1}$ (less than 20 years) to 1.4 $mg\cdot kg^{-1}$ (100 years) (Mîrlean et al., 2007).

- an average of 0.24 $mg\cdot kg^{-1}$ was suggested for the vineyard soils from the Douro river basin in Portugal (Reis et al., 2007)

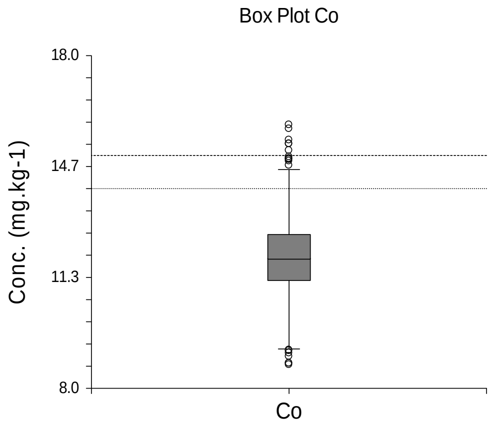
- a study regarding the vineyards in the Caraş-

Severin county, located in the south-west of Romania, was carried out at a soil depth of 0-10 cm. In this case, Cd varied between 1.28 and 3.22 mg·kg^{-1}. These values are higher than normal because of the mining and metallurgical activities that have been carried out for several decades in the area (Albulescu et al., 2009).

The Co content from the Huşi area varies between 8.7 and 15.9 mg·kg^{-1}, with an average of 12.0 mg·kg^{-1}. The plot with the highest Co value belongs to a calcic chernozem soil type cultivated with the "Fetească Regală" vine variety.



(a)



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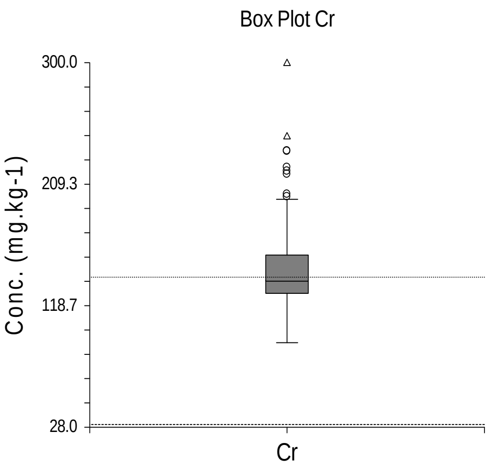

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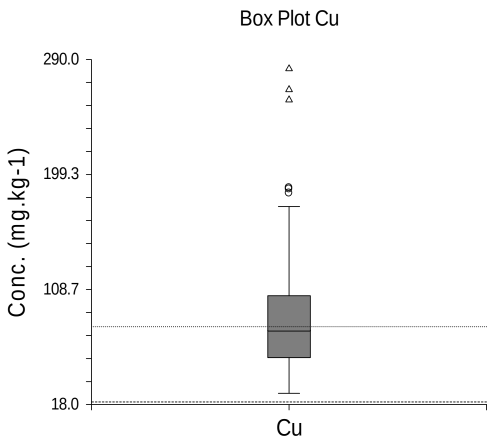

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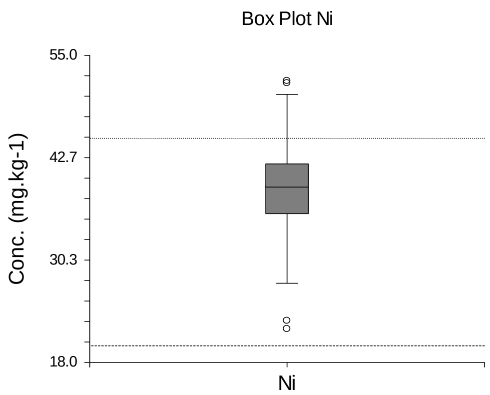

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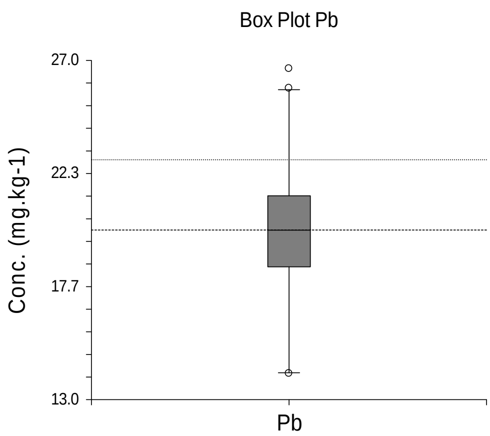

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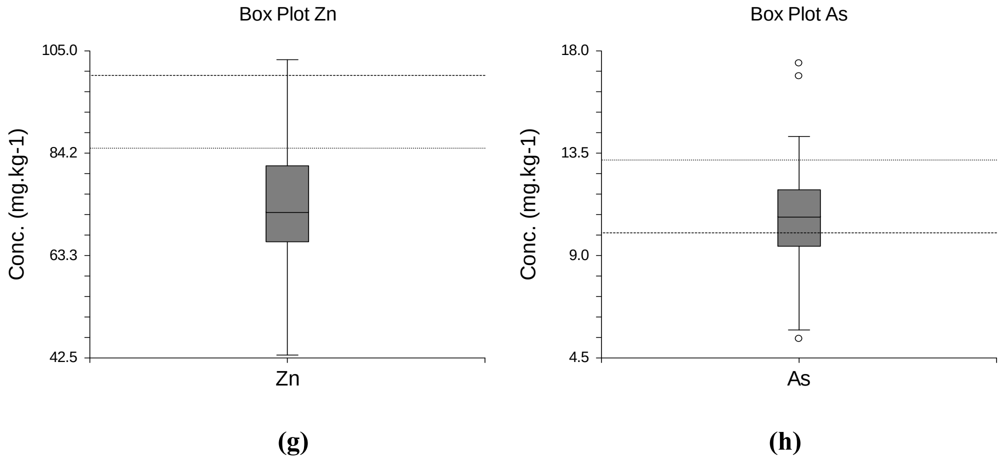

Figure 2. Boxplot for each element, showing the geochemical background limit and the line of NVS: (a) Cd; (b) Co; (c) Cr; (d) Cu; (e) Ni; (f) Pb; (g) Zn; (h) As.
--- Geochemical background; - - - NVS, ○ transition population; △ anomalous population.

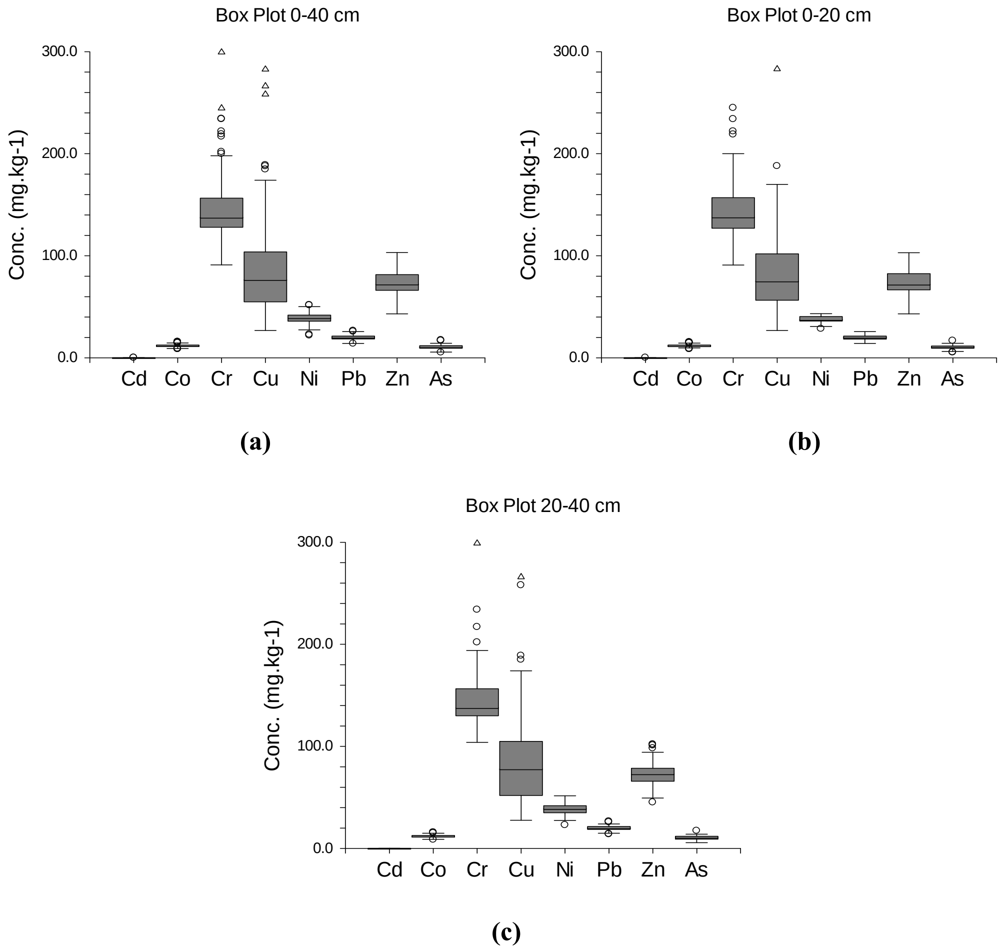

Figure 3. Boxplot for the comparison of trace elements at the following depths: (a) 0-40; (b) 0-20; (c) 20-40 cm; ○ - Transition population; △ Anomalous population.

The lowest value of Co overlaps the same grape variety as in the case of the highest value, only that the soil type is different, namely a vertic chernozem.

In the literature, a value of 2-40 mg·kg^{-1} is suggested for world soils (Adriano, 2001), a total content of 7.9 mg·kg^{-1} for Spain (Peris et al., 2007), and a average of 12 mg·kg^{-1} for the Douro river basin in Portugal (Reis et al., 2007).

In the present study, the Cr content displays a distribution range between 91.0 and 299 mg·kg^{-1}, with an average of 146 mg·kg^{-1}.

According to Adriano (2001), based on most of the data from the literature, the values vary within a large range, from 5 to 1000 mg·kg^{-1}, with a world soil average of 55 mg·kg^{-1}.

In their study, Mîrlean et al., (2007) suggest a variation between 8.2 (young plantation) and 77.9 mg·kg^{-1} (40 years). For Portugal, Cr displays an average of 31 mg·kg^{-1} (from a minimum of 3 to a maximum value of 243 mg·kg^{-1}) (Reis et al., 2007), while the values for Spain are quite close: a total content mean of 32.2 mg·kg^{1} (Peris et al., 2007).

Cu is one of the most studied element in wine-growing regions, because of the well-known treatment and prevention of vine downy mildew using the Bordeaux mixture ($Ca(OH)_2$ + $CuSO_4$).

The average value of Cu for the soils investigated is 84.9 mg·kg^{-1}, with a minimum of 26.8 mg·kg^{-1} and a maximum of 283 mg·kg^{-1}. For the present study, the minimum value of Cu corresponds to the "Tămâioasă Românească" vine variety and the calcic chernozem soil type, while the maximum value corresponds to the "Busuioacă de Bohotin" vine variety, cultivated on a vertic chernozem.

Soil pH has an influence upon the speciation and solubility of Cu. In uncontaminated soil, at neutral pH, Cu is easily mobile and thus is not available for plants (Kabata-Pendias, 2011).

The world average for soil is 30 mg·kg^{-1} (from 2 to 250 mg·kg^{-1}) (Adriano, 2001). Studies carried out in Spain indicate a mean of 35.4 mg·kg^{-1} (Peris et al., 2007), in Portugal one of 24 mg·kg^{-1} (from 1 to 111 mg·kg^{-1}) (Reis et al., 2007), in France one of 227 mg·kg^{-1} for the deep horizon (Chopin et al., 2008), while in Brazil it ranges between 50.1 mg·kg^{-1} (20 years) and 2197 mg·kg^{-1} (100 years) (Mîrlean et al., 2007). The background value for central Taiwan ranges between 1.4 and 5.6 mg·kg^{-1} (Lai et al., 2010).

The total average of Ni for the Huşi area soils is 38.9 mg·kg^{-1}, ranging between 22.0 and 51.9 mg·kg^{-1}. The lowest Ni content for the soils in the Husi vineyard area overlaps the vine variety of "Tămâioasă Românească", and the highest content – with the "Aligoté" vine variety, both being cultivated on calcic chernozem soil. The world soil average value for Ni is 40 mg·kg^{-1} (Adriano, 2001).

The Ni values for different countries are the following: a total content mean of 19.9 mg·kg^{-1} in the Castelon area, Spain (Peris et al., 2007), a mean value of 28 mg·kg^{-1} (with a minimum of 2 mg·kg^{-1} and a maximum of 539 mg·kg^{-1}) in the Douro basin, Portugal (Reis et al., 2007), and a variation from the youngest to the oldest vineyard from 4.1 to 58.04 mg·kg^{-1}(Mîrlean et al., 2007). In the SW of Romania, the Ni content ranges between 13.82 and 31.18 mg·kg^{-1} for a 0-10 cm depth (Albulescu et al., 2009).

In the vineyard soils studied, Pb displays a total average of 19.9 mg·kg^{-1}, varying from a minimum value of 14.1 to a maximum value of 26.7 mg·kg^{-1}. Regarding the minimum and maximum values of Pb in the soils studied, these correspond to the "Aligoté" vine variety and the calcic chernozem soil, respectively.

No value range is provided for world agricultural soils, given the fact that such a range would be very wide, depending on parent material and anthropogenic inputs (< 1.0 mg·kg^{-1} to over 10% Pb in ore materials) (Adriano, 2001). From the large literature regarding trace element concentrations in different vineyard soils, we have extracted some for the purpose of comparison:

- the total content mean of Pb in the Castelon region, Spain, is 56.1 mg·kg^{-1} (Peris et al., 2007);
- in the Champagne region of France, Pb ranges from 76 (deep horizon) to 141 mg·kg^{-1} (topsoil) (Chopin et al., 2008);
- in the case of the soils from the Brestnik village, Bulgary, values range from 72.6 mg·kg^{-1} for a 0-10 cm depth, to 61.4 mg·kg^{-1} for a 10-20 cm depth, to 46.3 mg·kg^{-1} for a 20-30 cm depth, down to lower values of 42.1 mg·kg^{-1} for a depth of 30-40 cm (Angelova et al., 1999);
- for the vineyard soils of the region in Portugal studied by Reis et al., (2007), a mean value of 28 mg·kg^{-1}, with a minimum of 4 and a maximum of 171 mg·kg^{-1}, was suggested for Pb. Regarding the studies which take into account the age of vineyards, in the case of Pb the rule of the values being higher (17.4 mg·kg^{-1}) for older plantations, compared to younger ones (2.0 mg·kg^{-1}), is also followed.
- in the SW of Romania, the study suggests a distribution range for concentrations from 21.63 to 47.08 mg·kg^{-1} (Albulescu et al., 2009).

The Zn content from the Huşi vineyard area varies between 43.1 and 103 mg·kg^{-1}, with an average of 73.9 mg·kg^{-1}. As in the case of the Pb content, the minimum and maximum values for Zn correspond to the vine variety "Aligoté" and a calcic chernozem soil, respectively.

The world soil average for Zn is 50 mg·kg^{-1} (Adriano, 2001). Compared with the data from the literature, the values obtained for Zn are the following: 76.8 mg·kg^{-1} for the Castelon region, Spain (Peris et al., 2007); from 318 mg·kg^{-1} in the topsoil to 208 mg·kg^{-1} in the deep horizon in the Champagne region of France (Chopin et al., 2008); a mean of 75 mg·kg^{-1}, with a minimum value of 14 mg·kg^{-1}, and a maximum value of 344 mg·kg^{-1} for the vineyard area in Portugal (Reis et al., 2007).

Regarding the depths from the Brestnik area, the Zn content increases from the surface to the deep horizon, namely from 243 mg·kg^{-1} to 187 mg·kg^{-1} (Angelova et al., 1999). In the case of vineyard soils from southern Brazil, the Zn values range from 17.5 mg·kg^{-1} for young plants, to 211.2 mg·kg^{-1} for older plants (Mîrlean et al., 2007).

In the present study, As varies from 5.3 to 17.4 mg·kg^{-1}, with an average value of 10.5 mg·kg^{-1}. The lower value corresponds to a plot cultivated with the "Tămâioasă Românească" vine variety on a calcic chernozem, while the highest value corresponds to the "Zghihară" vine variety on a calcaro-calcic chernozems soil.

Regarding As, among the studies previously mentioned, only one takes into account this element. Thus, Reis et al., 2007 suggested a mean value of 28 mg·kg^{-1}, with a minimum of 2 mg·kg^{-1} and a maximum of 257 mg·kg^{-1}. These values surpass the normal limit for soils, but Adriano, 2001 suggested a mean of 10 mg·kg^{-1} for world soils. Because of the wide range given for soils, the value of 4.8 mg·kg^{-1} can also be used to estimate the composition of As in the upper continental crust (Rudnick & Gao, 2003).

In terms of reporting to the law, the soils in the Huşi vineyard area can be considered polluted with Cr, Cu and Ni, whose contents are, on average, about 1.5 higher than those imposed by the Order no 756/1997. Regarding the background values and any excessive use of fertilizers and pesticides in the vineyard, we can describe both as normal for the area investigated.

The source of these concentrations above the normal values lies in the excessive use of fertilizers and pesticides in the vineyard, in order to achieve high yields of grapes per hectare, as well as in the use of the former over a long time (due to the long biological life of the vine).

4. CONCLUSIONS

In the present study, the selected trace elements follow the normal and lognormal distribution.

The boxplot diagrams were used to evidence the distributions and the presence of outliers.

The small differences between the concentrations of trace elements with depths are given by the soil homogeneity, caused by the agriculture practices.

The concentrations of Cr, Cu and Ni are higher than the normal values for soils according to the Romanian law in force. The environmental backgrounds for those elements are higher in the area than the normal values according to the Romanian legislative acts.

From the total count of Zn, Co, Pb, and As results, the values of 3.09 %, 3.7 %, 50.62 % and 55 % respectively are higher than the legislative normal values. The only element with values under this limit imposed by the legislation is Cd.

Because of the unknown history of the treatments applied to the Huşi agrosystem, the contents of the 8 trace elements selected were highlighted per vine varieties and soil type, but correlations cannot be made.

The origin of higher Cu concentrations from analysed soils can be explained through the intensive application of Cu-based fungicides, such as $Cu(OH)_2$, copper oxychloride $3Cu(OH)_2$-$CuCl_2$, $CuSO_4$ and Cu_2O, which are allowed in European organic viticulture, comparing with synthetic organic fungicides that are banned (Komárek et al., 2010).

Beside vineyards, fertilizers and pesticides are extensively used for different crops (Komárek et al., 2010). It is known that beside principal components, the fertilizers and pesticides contain various residual metals and thus their significant contribution to the total concentrations could be justified.

The same explanation used by Prundeanu & Buzgar (2011) to orchard soils for the Cu, Pb and As high contents, can be available in case of using the $PbHAsO_4$ (lead arsenate) as pesticide.

Another little increase for Pb content probably, can be caused by the mechanized equipment used for all works made in the vineyard.

The foliar spraying micronutrients as well as compost applications to the soil are not anthropogenic neglected inputs to the total amount of soil trace elements (Ni, Zn, Co, Cr, As).

The abundances of elements in studied soils are described by the following increasing sequence: Cd < As < Co < Pb < Ni < Zn < Cu < Cr.

As expected, the results are comparable with data from other wine-growing areas from Romania or abroad, being included in the same range.

A correlation between soil concentrations cannot be made in the case of the present study because of the longer period over which the different treatments were applied; most of the time, these treatments differ from a vine variety to another and also from year to year.

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