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MAJOR AND TRACE ELEMENTS DISTRIBUTION IN MOLDAVIAN SOILS

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Abstract. The content of seven major and 26 trace elements were investigated by Epithermal Neuron Activation Analysis in a set of 17 samples of soil collected at a depth of 20 to 40 cm from Romanesti and Cricova vineyards. All data were interpreted within the Upper Continental Crust and Average Soil models as well as in accordance with sanitary norms concerning soil contamination. It was evidenced that the mineral material is very close to the Upper Continental Crust with a certain degree of chemical weathering and a prolonged process of sorting and recycling, which sustains the hypothesis of a mature, well developed soil. The content of Cr, Mn, Co, Zn and As, proved that, with excepting As, the soil have no traces of anthropogenic contamination. The As content, according to existing data, can be regarded as a characteristic of Moldavian soils, not related to any industrial polluting process.

Key words: Chernozems, Major elements, Trace elements, Activation Analysis.

1. INTRODUCTION

Viticulture, which exists in Moldova since antiquity, represents now an important agricultural practice which contribute with about 9% to Gross Domestic Product (GDP). At present, Moldavian vineyard cover an area of 148,500 hectares with a total production of wine estimated for 2016 at 1.7 Mhl [1]. The main wine growing zones in Moldova are: Balti (northern zone), Codru (central zone), Purcari (south-eastern zone), and Cahul (southern zone) (See Fig. 1), where the soil, typical for Eurasian steppe, consists of pure chernozem [2, 3].

To obtain a high quality wine, the vineyard soil plays a predominant role. At the same time, due to a secular exploitation, majority of the actual vineyard soils are

Fig. 1 – General map of the Republic of Moldova illustrating the location of Romanesti and Cricova vineyards.

usually degraded.

The soil, formed in thousands of years as a results of the interaction of living organisms with the material resulted from the physical and chemical weathering of the rocks contains almost all stable elements of the periodic tables in contents varying between tens of percent such as Al, Si, Ca or Fe to less than μg/kg such as platinum group. Such a diversity reflects not only the geochemistry of parent material but also the influence of century of anthropogenic activity [4–7]. Moreover, application of fertilizers and inorganic pesticides has resulted in an increased metal content of the soils. Contamination with metals and organic pollutants, together with erosion and tillage, reduces the quality of the soils and poses important environmental and toxicological threats [8]. Anthropogenically derived heavy metals are easily bound to the soil and could be easily transported *via* the root system into the plants where they accumulate into their different parts including fruits. It is also the case of wine grapes, where, as a result, the concentration of metals in wines increase, which, in the case of a continuous consumption may causes chronic poisoning. Hence, the study of the elemental content of soils is particularly useful to get information on the genesis of the soil as well as on the level of contamination [9].

To achieve this task, a variety of analytical techniques such as Instinctively-Coupled Plasma-Mass Spectrometry (ICP-MS) [10], X-ray Fluorescence (XRF) [11] allowing the determination of metal content in soil [12, 13] as well as other media [14, 15] were developed in the past decades. Among them, Instrumental Neutron Activation Analysis (INAA) distinguishes itself by the possibility to determine more than 40 elements in any solid sample with an accuracy better than 0.5 mg/kg [16–18].

In present study the INAA was used to determine the elemental composition of soil samples collected from two vineyards: Romanesti and Cricova in order to get more date regarding soil geochemistry as well as to estimate pollutants impact.

2. MATERIALS AND METHODS

For this study we have chose 17 samples of soil collected from two of the most representative vineyards of Moldova: Romanesti and Cricova. The vineyards situated at a distance of about 15 km one from the other belong to the Central (Codru) wine region, at an altitude of about 125 m. To avoid the top soil arising from the surrounding environment, all samples were collected at a depth varying from 10 to 20 cm. All samples were dried at 40 ^{o}C and homogenized in an agate mortar to avoid any contamination.

The homogenized soil samples were irradiated at the IBR-2 reactor JINR, Dubna. To increase the accuracy of measurements, from each sample, three aliquots were individually analyzed so that the final results represent the average value of three independent measurements. We have followed the standard procedure described in details in [19–21]. The validation of ENAA data were proved by inter-laboratory studies like Wageningen evaluating programs for analytical laboratories (WEPAL) for different types of samples [22].

3. RESULTS AND DISCUSSION

The final results concerning the content of the seven major, rock forming elements: Na, Mg, Al, Ca, K, Mn and Fe as well as of the other 28 trace elements: Sc, Ti, V, Cr, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th and U can be found in the Mendeley Repository at doi: 10.17632/g73xtfyjc3.1.

As expected, between the elemental contents of the soil of the two vineyards there are no significant differences, fact also confirmed by the results of a Principal Component Analysis as well as by the numerical values of the Spermans rank correlation coefficients which, for any pair of soil samples was all the time higher that 0.980 at $p<0.01$. In investigating soil elemental content, we have interested to get more information regarding two issues: i. - the soil geochemistry; ii. - a possible anthropogenic contamination.

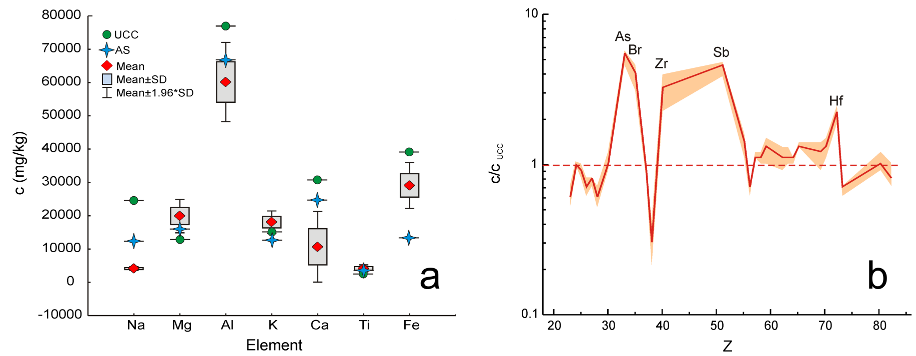

Fig. 2 – A Box-and-whiskers plot (a) illustrating the content of major elements (in mg/kg) and the spider diagram (b) illustrating the distribution of the trace element contents (UCC normalized).

In the case of first issue, the content major, rock forming elements was compared with those of the Upper Continental crust (UCC) [23] and average soil (AS) [24, 25]. We have noticed that, with respect to UCC and AS, the content of Na, Al, and Ca was lower, the content of Mg and K was slightly higher, the Fe content has an intermediary value between the UCC and AS (Fig. 2a) while the Ti content was almost the same with the UCC and AS ones. As INAA does not allow determining the total content of Si, we can only suppose a higher content of quartz while the increased content of Mg suggests the presence of a certain amount of dolomite.

Further, the content of the other 28 trace elements normalized to UCC are illustrated by the spider diagram reproduced in Fig. 2b. It can be remarked, that with the exception of As, Br, Sr, Zr, Sb and Hf, the content of all other trace elements dose not differ too much from the UCC.

Sr, an alkaline earth elements, due to its ionic radius close to Ca, substitutes Ca in Ca-rich minerals such as limestone, dolomite, plagioclase, hornblende, etc. while Rb, an alkaline metal coexist with Na and K rich minerals such as plagioclase, K-feldspars, different variety of micas, etc. The Ca-bearing minerals are more sensitive to chemical weathering than the K-rich one so, with the time, the Ca-Sr couple are depleted faster then K-Rb one which leads to higher Rb/Sr ratio [26]. Therefore, the Rb/Sr ratio can be used together with Chemical Index of Alteration [27] or with the Chemical Index of Weathering [28] as a proxy of the chemical weathering [29].

Accordingly, we have found for the vineyard soils a Rb/Sr ratio equal to 1.11 $\pm$ 0.34, significantly higher than the UCC one of 0.26 or AS of 0.33. This finding attests a significant chemical weathering which, at its turn, suggests a mature soil, but whose age, in the absence of a relevant geochronology could not be estimated with exactitude.

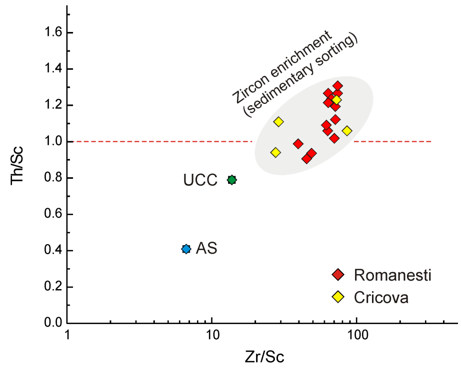

Fig. 3 – Th/Sc *versus* Zr/Sc bi-plot illustrating a repeated sorting and recycling of the mineral soil material.

The presence of Zr and Hf is mainly due to the mineral zircon, which due to its resilience to weathering and lack of reactivity persists in various sedimentary deposits including soils. For this reason, the Zr content is regarded as a proxy for weathering and material recycling [30]. Indeed, in the case of both Romanesti and Cricova soils, the average value of the Zr/Sc ratio of 57 $\pm$ 18 is significantly higher than those of 6.7 and 13.8, corresponding to the AS and UCC respectively, this peculiarity suggesting a repeated sorting and recycling of the mineral soil material (see Fig. 3), in agreement with the hypothesis of a mature soil as previously proposed. The Hf/Zr ratio of 1.43 $\pm$ 0.04 is very close to 2.07 reported for the UCC.

To get more information, we have represented the relative distribution of three incompatible and immiscible elements Sc, La and Th [31] by the means of a ternary discriminating diagram (Fig. 4a). As it can be remarked, all points are concentrated around the UCC which indicates a primary continental origin of the soil material. The same conclusions is confirmed by a La/Th radios close, within the total uncertainties, to 2.52 and 2.73 for the AS and UCC respectively. The same conclusion is sustained by the chondrite-normalized REE diagram (Fig. 4b) which shows a good similarity with the UCC distribution. In this regard it should be remarked that the Eu/Eu* anomaly presented in all soil sample is characterized by an average value of 0.46 $\pm$ 0.06, very close to the UCC and AS values of 0.45 and 0.5 respectively.

In the case of the second issue, we have noticed that excepting As, whose content in the soil of all vineyards was about 8 mg/kg, the content of all possible industrial pollutants: Co, Ni and Zn were close to UCC [23] and AS [24, 25]. In this regard, Sb also considered a toxic element had an average content of 0.9 $\pm$ 0.1 mg/kg, higher then the UCC value of 0.2 mg/kg and 0.7 mg/kg for average soil [32, 33] but about five time lower that the 5 mg/kg, the value considered normal according to

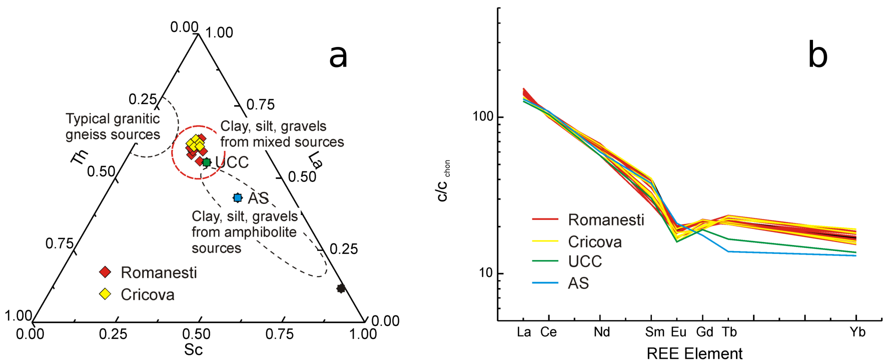

Fig. 4 – Sc-La-Th discriminating ternary diagram (a) as well as chondrite-normalized REE diagram (b) of investigated Moldavian soils. For a better description, the corresponding data of UCC and AS are illustrated too.

Romanian Norms [34]. Br is the last element whose presence, in high amount, could be related to human activity. In this case, the Br content of 8 ± 2 mg/kg, although overpass four times the UCC value of 2 mg/kg, is still compatible with the world soil values ranging between 7.9 and 130 mg/kg for different types of soil [33] and significantly lower than the 50 mg/kg, the alert threshold as defined in [34].

For a better description, Table 1 presents the average values of the content of Cr, Mn, Co, Ni, Zn and As together with the corresponding threshold value as defined by the National Authorities of Moldova and neighboring Romania and Russian Federation [34–36]. Moreover, we have calculated for each element the Enrichment Factor *EF* [37], Geo-accumulation Index I_{geo} [38, 39] as well as Pollution Index *PI* [40] (Table 2). According to [37], an *EF* less then unit attests an uncontaminated environment while a value between one and three characterize a minor contamination. In the case of I_{geo}, a negative value shows an uncontaminated environment, a value between one and two is attributed to an environment uncontaminated to moder-

Table 1

Average numerical values (± St. Dev.) of the content of Cr, Mn, Co, Zn and As considered as possible contaminants together with the corresponding limits between normal and alarm level as defined buy the Moldavian [35], Russian [36] and Romanian [34] authorities.

Element	Soil content	Moldova	Russian Federation	Romania
Cr	91 ± 9	–	–	30 - 100
Mn	678 ± 56	–	–	900 - 1500
Co	13 ± 1	–	–	15 - 30
Ni	35 ± 7	75	20 - 80	20 - 75
Zn	72± 10	300	55 - 220	100 - 300
As	8.7 ± 1.1	–	2 - 10	5 - 12.5

Table 2

Average numerical values ($\pm$ St. Dev.) of the Enrichment Factor (*EF*) [37], Geo-accumulation Index (I_{geo}) [38, 39] as well as of the Pollution Index *PI* [40] of the investigated soils. Due to an increased content of As, the Pollution Index has a value which apparently classifies soils as low contaminated (see the text for explanations).

Element	*EF*	I_{geo}	Pollution index
Cr	1.29 ± 0.12	-0.62 ± 0.15	
Mn	1.18 ± 0.13	- 0.75 ± 0.12	
Co	1.01 ± 0.06	- 0.97 ± 0.13	
Ni	0.84 ± 0.10	- 1.24 ± 0.24	
Zn	1.33 ± 0.14	-0.58 ± 0.22	
As	7.14 ± 0.47	1.85 ± 0.16	
			1.15 ± 0.11

ately contaminated while a value between two and three characterizes a moderately contaminated medium. At its turn, PI which is restrained only to those elements considered as contaminants, in our case Cr, Mn, Co, Ni, Zn and As, suggests a weak polluted environment for values greater than unit [40].

As data provided in Table 1 show, the contents of Cr, Co, Ni, Zn and As are higher then the corresponding values for normal, uncontaminated soils, but lower than the minimum threshold to be considered as contaminants. On the other hand, due to the increased content of As with respect to UCC, the numerical values of the *EF,* I_{geo} and *PI* provided in Table 2, points towards, a low degree of anthropogenic contamination only in the case of As.

The apparent discordance between the official norms and the contamination proxies is mainly due to the fact that national regulations are more permissive so that an environment is considered as polluted only if the contaminant contents overpass two to three time the normal levels (see Table 1). Therefore, according to [35], the Moldavian vineyards soils could be considered as uncontaminated, although *EF*, I_{geo} and PI suggest a moderate contamination with As. But if we take into account that an increased content of As represents a general peculiarity of Moldavian soils as reported by [41] and not a result of certain industrial process, we can consider that the soil horizon where samples were collected is uncontaminated.

4. CONCLUSIONS

Epithermal Neutron Activation Analysis was used to determine the investigate the distribution of seven major, rock forming, and 28 trace elements in 17 samples of soil of two renowned Moldavian vineyards: Romanesti and Cricova.

All data, interpreted within the Upper Continental Crust model, showed first of all that within experimental uncertainties, the soil of both vineyards is identical and close to the average composition of the UCC. A more detailed analysis of the distribution of Rb, Sr, and Zr evidenced a significant degree of chemical weathering as well as a prolonged process of sorting and recycling of the mineral.

At the same time, the soil content of Cr, Mn, Co, Zn and As, the possible anthropogenic contaminates proved, with the exception of As, the absence of any systematic heavy element pollution. In this regard, although the As content overpasses few times the UCC value of 1.5 mg/kg, almost reaching the alarm threshold according to some national regulations, its increased content can be regarded, according to literature data, as a characteristic of Moldavian soils, without any traces of anthropogenic contamination.

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REFERENCES

1. IOVW, World Viticulture Situation, International Organization of Vine and Wine, (2016), http://www.oiv.int/public/medias/5029/world-vitiviniculture-situation-2016.pdf.
2. A. Ursu, A. Overenco, I. Marcov *et al*., Chernozem: Soil of the Steppe, in: Soil as World Heritage, Ed. D. Dent, (Springer, 2014) pp. 3-8.
3. Anonymous, Soil map of Moldavskoi SSR (Moldava), Joint Rsearch Center, European Soil Data Center (ESDAC), http://eusoils.jrc.ec.europa.eu/images/Eudasm/MD/russ_x80.jpg. (Title in Russian.)
4. P.S. Hooda, Trace elements in Soils, (Wiley, 2016).
5. J.V. dos Santos, W. de Melo Rangel, A. Azarias Guimaraes *et al*., Soil biological attributes in arse nic-contaminated gold mining sites after revegetation, Ecotoxicology **22**, 1526-1537 (2013).
6. I. Sherameti, A. Varma, Heavy Metal Contamination of Soils-Monitoring and Remediation, (Springer, 2005).
7. C. Su, L.Q. Liang, and W.J. Zhang, A review on heavy metal contamination in the soil worldwide situation, impact and remediation techniques. Environ. Skeptics and Critics, **3**, 24-383, (2014).
8. M. Komarek, E. Cadkova, V. Chrastnyc *et al*., Contamination of vineyard soils with fungicides: A review of environmental and toxicological aspects. Environ. Int. **36**, 138-151 (2010).
9. M. Bettinelli, G.M. Beone, S. Spezia *et al*., Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis, Anal. Chim. Acta **424**, 289-296 (2000).
10. J.S. Becker, Inorganic Mass Spectrometry: Principles and Applications, (Wiley-Interscience, 2007).
11. B. Kanngiesser, N. Langhoff, R. Wedell *et al*., (Eds.), Handbook of practical X-Ray fluorescence analysis, (Springer, 2006).
12. I.D. Dulama, E.D. Chelarescu, and O.G. Duliu, Heavy metal contents of *Brassica oleracea* as bioindicator determined by XRF and AAS analytical methods, Rom. Rep. Phys. **68**, 1221-1226 (2016).

13. L.C. Tugulan, J. Gradinaru, and O.G. Duliu, An EDXRF and WDXF intercomparison case study: major elements content of Dobrogea loess, Rom. J. Phys. **61**, 1626-1634 (2016).
14. I.D. Dulama, C. Radulescu, E.D. Chelarescu *et al.*, Determination of heavy metal contents in surface water by inductively coupled plasma-mass spectrometry: a case study of Ialomita river, Romania, Rom. J. Phys. **62**, 807 (2017).
15. D. Dunea, S. Iordache, C. Radulescu *et al.*, A multidimensional approach to the influence of wind on the variations of particulate matter and associated heavy metals in Ploiesti City, Romania, Rom. J. Phys. **61**, 1354-1368 (2016).
16. M.D. Glascok, Activation Analysis in: Instrumental Multi-Element Chemical Analysis, Ed. Z.B Alfassi, (Springer, 1998).
17. A. Srivastava, G.S. Bains, and R. Acharya, Study of seleniferous soils using instrumental neutron activation analysis, Appl. Rad. Isot. **69**, 818-821 (2011).
18. N. Zaim, C. Dogan, and Z.J. Camtakan, Neutron Activation Analysis of Soil Samples from Different Parts of Edirne in Turkey, J. Appl. Spec. **83**, 271-276 (2016).
19. S.S. Pavlov, A.Y. Dmitriev, and M.V. Frontasyeva, Automation system for neutron activation analysis at the reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia, J. Radioanal. Nucl. Chem. **309**, 27-38 (2016).
20. O.A. Culicov, O.G. Duliu, and I. Zinicovscaia, Study of elemental grouping in moss-bags as a function of height and location of the exposure site, Rom. Rep. Phys. **68**, 736-745 (2016).
21. I. Zinicovscaia, O.G. Duliu, O.A. Culicov *et al.*, Geographical Origin Identification of Moldavian Wines by Neutron Activation Analysis, Food Anal. Meth. **10**, 3523-3530 (2017).
22. Anonymous, Wageningen Evaluating Programs for Analytical Laboratories. International plant-analytical exchange. Quarterly report 2013.1, Environmental Sciences, (Wageningen Agricultural University, 2013) the Netherlands, p 98.
23. R.L. Rudnick and S. Gao, Composition of the Continental Crust, in: Treatise in Geochemistry, Ed. H. Holland and K. Turekian, (Elsevier, 2004).
24. A.P. Vinogradov (1959) The geochemistry of rare and dispersed chemical elements in soils, 2nd ed., revised and enlarged, (Consultants Bureau Enterprises, New York, 1959), pp. 209.
25. H.T. Shacklette and J.G. Boerngen, Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States, US Geological Survey professional paper, 1270, (1984), 105 pp.
26. E.J. Dasch, Strontium isotope in weathering in profiles, deep sea sediments and sedimentary rocks. Geochim. Cosmochim. Acta **33**, 1521-1552 (1969).
27. H.W. Nesbitt and G.M. Young, Early Proterozoic climates and plate motions inferred from major element chemistry of lutites, Nature, **299**, 715-717 (1982).
28. L. Harnois, The CIW index: a new chemical index of weathering. Sedim. Geol. **55**, 319-322 (1988).
29. C. Yang, C. Jun, L. Lianwen *et al.*, Spatial and temporal changes of summer monsoon on the Loess Plateau of Central China during the last 130 ka inferred from Rb/Sr ratios, Sci. China - Earth Sci. **46**, 1022-1030 (2003).
30. S.M. McLennan, S. Hemming, D.K. McDaniel *et al.*, Geochemical approaches to sedimentation, provenance, and tectonics. Geological Society of America, Special paper, 284, p. 20, (1993).
31. S.R. Taylor and S.M. McLenan, The Continental Crust: Its Composition and Evolution, (Blacwell, 1991).
32. T. Tchan, B.H. Robinson, and R. Schulin, Antimony in the soil-plant system - a review, Environ. Chem. **6**, 106-115 (2009).
33. A. Kabata-Pendias, Trace Elements in Soils and Plants, (CRC Press, 2010).

34. Anonymous, Order nr. 756 of 03.11.2017 of the Minister of Waters, Forests and Environmental Protection: regulations concerning environmental evaluation, Official Monitor of Romania Nr. **303 bis** of 6.11.2017 (1997).
35. Anonymous, Soil protection procedures during agricultural practice, Decision nr. 1157/13.10.2008 of the Government of the Republic of Moldova, Official Monitor of Moldova, **193-194** of 28.10.2008 (2008).
36. Anonymous, Hygienic Norm 2.1.7.2511-09. Tentatively Permissible Concentrations of Chemical Substances in Soil, Moscow (2009).
37. K.J. Puckett and E.J. Finegan, An analysis of the element content of lichens from the Northwest Territories, Canada, Canad. J. Botany, **58**, 2073-2089 (1980).
38. G. Müller, Index of geoaccumulation in sediments of the Rhine River, Geol. J, **2**, 109-118 (1969).
39. M. Nowrouzi and A. Pourkhabbaz, Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Hara Biosphere Reserve, Iran, Chem. Spec. & Bioavail. **26**, 99-105 (2014).
40. D.L. Tomlinson, J.G. Wilson, C.R. Harris *et al*., Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index, Helgoländer Meeresunters. **33**, 566-575 (1980).
41. G. Jigau, M. Motelica, M. Lesanu *et al*., Heavy Metals in the Anthropogenic Cycle of Elements, in: Soil as World Heritage, Ed. D. Dent, pp. 61-68 (Springer, 2014).