HEAVY METALS IN SOILS FROM THE HORTICULTURAL AREAS OF SÂRCA AND HUŞI (ROMANIA)

METALELE GRELE DIN SOLURILE UNOR AREALE HORTICOLE: SÂRCA ŞI HUŞI (ROMÂNIA)

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Abstract: *The present study aims at determining the geochemical contents of seven heavy metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn) in soils (haplic and calcaro-calcic chernozems) from the Sârca apple orchard and the Huşi vineyard area. The heavy metal contents were established using the AAS and EDXRF methods, the average values being between 0.12-0.88 mg/kg Cd, 11-12 mg/kg Co, 14-128 mg/kg Cr, 26-61 mg/kg Cu, 37-41 mg/kg Ni, 21 mg/kg Pb, and 67-71 mg/kg Zn. Measurements of the pH and the carbonate contents were also recorded, the dominant soil reaction being neutral to weakly alkaline, with an average content of 1.16% $CaCO_3$ for the soil sampled from the Sârca area, and 5.27% $CaCO_3$ for the Huşi vineyard area.*
Key words: heavy metals**,** AAS, ICP-MS, vineyard, apple orchard, Sârca, Huşi.

Rezumat *În cadrul acestui studiu au fost analizate concentraţiile a şapte elemente, Cd, Co, Cr, Cu, Ni, Pb, Zn din solurile utilizate în horticultură (cernoziomuri cambice şi calcarice) din cadrul bazinului pomicol Sârca şi arealului viticol Huşi. Conţinuturile de metale grele au fost determinate prin metodele AAS şi EDXRF obţinându-se valori medii între 0.12 -0.88 mg/kg Cd, 11-12 mg/kg Co, 14-128 mg/kg Cr, 26-61 mg/kg Cu, 37-41 mg/kg Ni, 21 mg/kg Pb şi 67-71 mg/kg Zn. De asemenea, a fost determinat pH-ul şi % de carbonaţi din sol, reacţia predominantă a solului fiind neutră spre slab-alcalină cu un conţinut mediu de 1.16% $CaCO_3$ pentru probele de la Sârca şi ceva mai ridicat (5.27% CaCO3) pentru solurile viticole de la Huşi.*
Cuvinte cheie: metale grele, AAS, ICP-MS, plantaţie viticolă, livadă de meri, Sârca, Huşi.

INTRODUCTION

Heavy metals are chemical elements with a specific weight higher than 5 g/cm^3 and an easily changing oxidation state, and which form hard-to-dissolve hydroxides and other chemical compounds with affinity for sulfides. Soil fertility and its pollution are contributing to an increase in the number of studies dealing with heavy metals in relation to their mobility as influenced by pedogenetic factors. The heavy metals in soils have sources that are either natural, deriving from the parental materials from which the soils formed and evolved, or anthropogenic, caused by industry and agricultural practices (Lăcătuşu R., 2000). In agriculture, the crop yields are influenced mainly by the fertility of the soil.

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The Sârca apple-growing area is located in the south-west of the Jijia hilly plain, at the boundary with the Iaşi Coast, being delimited by the Oilor Valley to the north, the Bahluieț Valley to the south, the Hârtop and Fandolica valleys to the west, and by the confluence of the Valea Oilor brook with the Bahluieț River to the east (Boronia G., 2010).

The Huşi area is located in the eastern part of Vaslui County, in the south-eastern part of the Huşi Depression. Geologically, the studied perimeters belong to the Moldavian Platform, which is part of the East-European Platform. The Sârca apple-growing area is located in the central-eastern part, while the Huşi vineyard area is located in the east of the Moldavian Platform. The lithology of the Sârca apple-growing area is represented by pelite deposits corresponding to the neritic lithofacies (clays with Cryptomactra) (Ionesi L. and Barbu N., 1996). Quaternary deposits consist of recent alluviums and terraces as results of a hydrographical network (Boronia G., 2009).

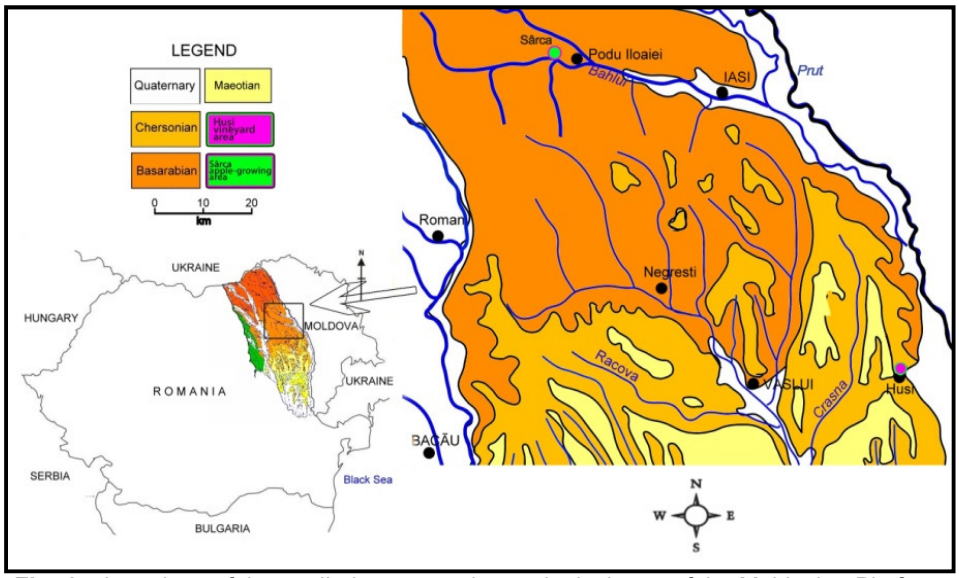

Fig. 1 – Locations of the studied areas on the geological map of the Moldavian Platform (modified after Ionesi et al., 2005)

The soil samples from the Sârca apple-growing area were collected from the surface of Farm no. 6, on which haplic and calcaro-calcic chernozems are found. In the Huşi vineyard area, the sedimentary cover is represented by sand with sandstones layers, sometimes with oolitic texture, and argillaceous sands of Chersonian age. The soil type from the vineyard sampling area of Farm no 16, the Galbena Hill, is calcic chernozem (OJSPA Vaslui, 2006).

MATERIAL AND METHODS

The soil sampling was carried out using telescoping augers. Samples with weights between 1.5-2 kg were stored in zip-locked bags, clearly marked with the

corresponding identification tag. A soil sample was composed of 5 sub-samples, resembling a square, collected from 4 points one meter away from the center.

From the Sârca apple-growing area, 12 topsoil (0-20 cm) samples were collected from points located in the middle of the apple tree rows, on a sampling grid of 300 m. In the Huşi area, the soil was sampled using a 50 m grid, 14 samples being collected from the grape-vine rows and inter-rows, at depths of 0-20 cm.

After drying and the removal of vegetal parts, the samples were ground and sieved through 1 mm mesh. A 1:5 ratio mixture of soil and resin was used to obtain the pressed powder pellets.

The soil and resin mixture was homogenized for 10-12 minutes at 180 rpm, using an agate ball mill. After mixing, 9 g weighted in aluminum capsules were kept for 30 seconds under a 20 t/cm^2 pressure. The pressed pellets were analyzed using an Epsylon-5-type energy-dispersive XRF spectrometer (EDXRF), within the Geology Department of the "Al. I. Cuza" University of Iaşi.

The total contents of heavy metals from the Sârca apple-growing area were obtained using flame atomic absorption spectrometry (AAS) at the National Institute of Research and Development for Pedology, Agrochemistry and Environment Protection, Bucharest, after sample digestion, in an open system, with a mixture of HNO_3 and $HClO_4$.

For all 26 samples, the pH measurements were performed using the potentiometer method, in aqueous solution, with a 2.5:1 water:soil ratio. The carbonate percentages were determined using a Bernard calcimeter.

RESULTS AND DISCUSSION

In order to obtain the statistical parameters (minimum, maximum, mean, standard deviation, median, and geometric mean), the Statistica 8 software was used (tab. 1). Central statistical parameters (mean, median and geometric mean) are representative for the sets of data which have similar values centered between minimum and maximum limits. This suggests a normal distribution of the two data sets (Reimann et al., 2008).

Cd concentrations range between 0.09-1.88 mg/kg for the samples collected from Sârca (S), while for the samples from the Huşi vineyard (H) the range is narrower: 0.06-0.20 mg/kg.

For Co, the contents display similar values for the studied areas, with small variations between 10-13 mg/kg (S), and 11-12 mg/kg (H), respectively.

Greater differences between the two areas regard Cr values: 11-17 mg/kg for (S) and 112-158 mg/kg for (H). This gap is not mainly due to a natural and/or anthropogenic influence. Instead, it is more likely an effect of the two different methods used for concentration measurements and the possible interferences during the EDXRF analyses.

The situation is similar for the Cu contents, where the 19-33 mg/kg range for (S) is clearly below that for (H): 34-104 mg/kg. The differences can be explained by the intensive Cu-based treatments applied to vineyard soils ($Ca(OH)_2$+$CuSO_4$ – Bordeaux mixture).

Table 1

Statistical parameters of heavy metals contents, pH and $CaCO_3$

Statistical parameter	Location	Cd	Co	Cr	Cu	Ni	Pb	Zn	pH	$CaCO_3$
		mg/kg								%
min	Sârca apple-growing area (n=12)	0.09	10	11	19	31	10	60	6.51	0.56
max		1.88	13	17	33	51	35	88	8.04	2.52
mean		0.88	11	14	26	37	21	71	7.25	1.16
σ		0.60	0.90	1.93	4.22	5.59	6.52	7.78	0.44	0.52
G		0.64	11	14	26	37	20	71	7.24	1.07
Me		0.91	11	14	26	36	21	71	7.20	1.09
min	Huşi vineyard area (n=14)	0.06	11	112	34	37	19	63	7.73	1.02
max		0.20	12	158	104	43	22	77	8.35	10.1
mean		0.12	12	128	61	41	21	67	8.09	5.27
σ		0.05	0.47	11.8	20.7	1.72	1.14	3.66	0.14	2.81
G		0.11	12	128	57	41	21	67	8.09	4.44
Me		0.13	12	127	59	41	20	67	8.12	5.05
NV*		1.00	15	30	20	20	20	100		
AT*		3.00	30	100	100	75	50	300		

x_{min}- minumum, x_{max} – maximum, σ – standard deviation, G – geometric mean, Me – mean, NV – normal value in soil, AT – alert threshold for soil with sensitive use, * - Order no 756/1997 emitted by the Romanian Ministry of Waters, Forests and Environmental Protection.

No significant differences arise in the case of the Ni concentrations, which range between 31-51 mg/kg for (S), and 37-43 mg/kg for (H).

The comparison of the two sets of data yields only slight variations in the case of Pb. However, the range is wider for (S): 10-35 mg/kg than for (H): 19-22 mg/kg.

The same is valid for Zn, which displays a wider range of 60-88 mg/kg for (S), and a narrower one, of 63-77 mg/kg, for (H).

The sequence order for the mean contents for the two studied areas is the following: Cd<Co<Cr<Cu<Pb<Ni<Zn for (S), and Cd<Co<Pb<Ni<Zn<Cu<Cr for (H). The pH values describe a neutral soil reaction, with a mean content of 1.16 % $CaCO_3$, for (S), and a weakly alkaline one, with an average of 5.27 % $CaCO_3$, for (H).

The mean values of Cd are 0.88 mg/kg for (S), and 0.12 mg/kg for (H), both under the normal reference value in soil, of 1 mg/kg (Fig.3). For Co, the normal reference value in soils is 15 mg/kg (Order no 756/1997), while the mean Co concentrations obtained are under this threshold (11 mg/kg for (S), 12 mg/kg for (H)).

The Pb mean of 21 mg/kg is equal for both sets of data, slightly higher than the normal reference value in Romanian legislative acts. By comparing it with an average continental crust of 11 mg/kg (Rudnick R.L. and Gao S., 2003), one notices an enrichment in the case of the soils studied (fig. 2).

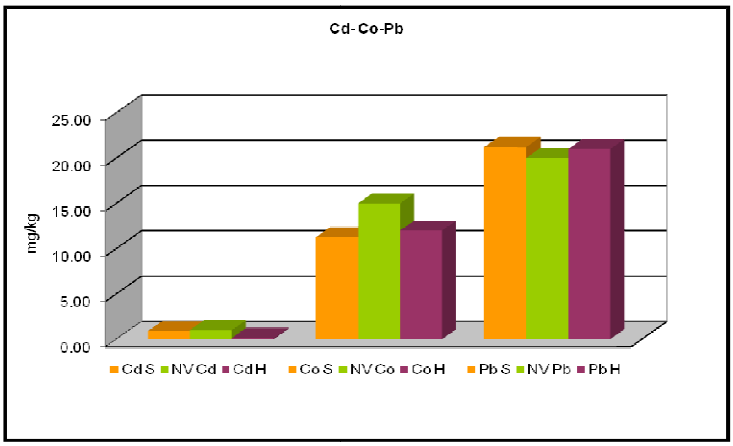

Fig. 2 – The distribution of Cd, Co and Pb in the Sârca and Huşi areas, compared to the normal reference values in soils (Order no 756/1997). S – Sârca fruit-growing area, H – Huşi vineyard area, NV – normal values in soils.

The mean contents obtained for Cu are 26 mg/kg for (S) and 61 mg/kg (H), both over the normal reference value (20 mg/kg). Given the differences in the application of Cu-based fungicides, an increase in the Cu concentrations occurs in the case of vineyard soils, where the maximum value exceeds the alert threshold for soil with sensitive use (100 mg/kg).

Due to the two different analysis methods, the Cr contents for the Huşi area should be treated carefully when considering a comparison with the Romanian legislation. Regarding the (S) area, the mean value of 14 mg/kg is lower than the normal limit in soil.

The mean values of Zn and Ni are similar for both sets of data: 71 mg/kg (S) - 67 mg/kg (H) Zn and 37 mg/kg (S) - 41 mg/kg (H) Ni, the normal limit in soil being exceeded only by Ni (fig. 3).

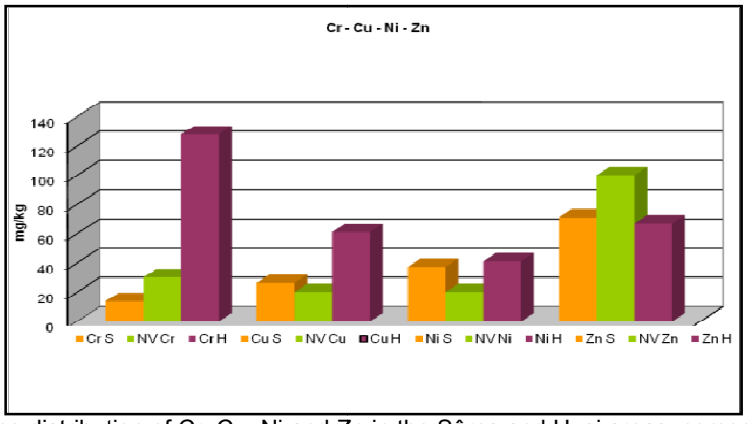

Fig. 3 – The distribution of Cr, Cu, Ni and Zn in the Sârca and Huşi areas, compared to the normal reference values in soils (Order no 756/1997). S – Sârca fruit-growing area, H – Huşi vineyard area, NV – normal values in soils.

The present study presents the contents of seven heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) in the topsoils from the Sârca apple-growing (Farm no. 6) area and the Huşi vineyard area (Farm no. 16).

Although two different analysis methods were used, namely AAS and EDXRF, similar results were obtained, the only difference being registered in the case of Cr.

CONCLUSIONS

The average Cu concentrations are over the normal reference limit provided by national regulations. An increased accumulation can be observed for the soils sampled from the Huşi vineyard area, caused by intensive foliar-spray treatments.

The chernozems from the two studied areas display similar concentrations for Cd, Co, Ni, Pb and Zn. Only Ni and Pb exceed the normal limit in soils.

The soil reaction ranges from neutral to weakly alkaline, with a mean $CaCO_3$ content of 1.16 – 5.27%.

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