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STUDY OF RELATIONSHIPS BETWEEN THE METALS CONTENT IN NATIVE VEGETATION AND SOIL USING MULTIVARIATE ANALYSIS

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ABSTRACT. The aim of the present study was to assess the metals concentrations in native vegetation from Baia Mare city and to evaluate the relationships between the metals contents in vegetation and the soil chemical properties using multivariate statistical techniques. The metals concentrations in vegetation (mg kg^{-1} dry weight) in the studied areas ranged between: 0.35 – 18.3 for Cu, 2.30 – 120 for Zn, 0.05 – 2.58 for Cd, 0.02 – 15.0 for Pb, 0.21 – 4.09 for Ni, 0.08 – 2.03 for Cr, 1.65 – 389 for Mn, 5.20 – 278 for Fe and 12.0 – 398 for Al. The average content of Cd in vegetation from Ferneziu district exceeded the maximum level (1.0 mg kg^{-1}) allowed in animal feed set by the European Directive 2002/32/EC. Higher concentrations of Pb, Zn, Cr, Mn and Cd, were found in vegetation collected from the industrial part of the city, in the vicinity of smelting industrial units presently closed or partially closed, while the concentrations of Ni, Fe and Al were slowly higher in vegetation from the area considered unaffected by mining activities. By applying multivariate analysis it was found that soil pH is negatively correlated with all metals in vegetation and plays an important role in the soil-plant transfer. Generally poor correlations were found between pseudo-total metal contents in soil and metals content in vegetation.

Keywords: *native vegetation, soil pollution, heavy metals, Baia Mare, multivariate analysis*

INTRODUCTION

One of the main negative effects of mining related activities is the environment contamination with metals. Due to their non-biodegradability and their long biological half-lives, metals persist in soil for many years even after pollution ceases [1]. In addition, high concentrations of essential elements such as Mn, Fe, Cu and Zn along with the non-essential elements such as Cd, Cr, Pb, Al are hazardous for the ecosystems and human health [2, 3].

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Metals contents in vegetation reflect, usually, their concentrations in soil, water and in ambient air [4-8]. Even if vegetation has the capacity to select or limit the uptake of toxic elements, these processes are influenced by the geochemistry of growth media. Consequently, concentrations of metals in vegetation are often correlated with the abundance of these elements in soils [9], despite the fact that metals from soil can be adsorbed or retained by carbonates, organic matter, iron-magnesium oxides, primary or secondary minerals [10].

The city of Baia Mare, NW Romania, was the subject of many studies [11-15] regarding the soil pollution with metals caused by the non-ferrous mining activities developed in this area since ancient times. However, no data was found in the literature regarding the metals content in native vegetation from different parts of the city. The European Directive 2002/32/EC [16] established the maximum concentrations of toxic metals in vegetation used as animal feed in order to avoid its transfer and further accumulation in the higher trophic levels of food chain. The aims of this study were: (1) to evaluate the metals concentrations in native vegetation in the urban and peri-urban areas of Baia Mare, Romania; (2) to study the relationships between metal contents (Fe, Al, Cr, Mn, Cu, Zn, Ni, Pb, Cd) in vegetation and soil properties (pH, Total Organic Carbon (TOC)) using multivariate statistical techniques.

RESULTS AND DISCUSSIONS

The city of Baia Mare (Fig. 1) is located in the northwest Romania, at an altitude of 228 m above the sea level. The territory surface together with the peri-urban area is 235.7 km^2, of which 31.7 km^2 agricultural fields [17]. As a consequence of the non-ferrous mining activities developed in this area, Baia Mare was found to be one of the most polluted industrial centres with metals.

A total of 29 sampling points were randomly chosen from Ferneziu (A1), Săsar (A2), Baia Mare center (A3), and Dura (A4) districts. Surface soil samples (0-20 cm) and native vegetation (*Agrostis, Agropirum, Trifolium repens, Urtica dioica*) grown on these soils were sampled from each selected point. The locations of sampling points are presented in Figure 1.

Soil characteristics

The pH values were generally slightly acidic to neutral in the all studied areas, while the average TOC values were generally at higher levels in Ferneziu and Sasar than in Baia Mare center and Dura.

The *aqua regia* extractible metals (Fe, Al, Cr, Mn, Cu, Zn, Ni, Pb, Cd) concentrations, expressed in mg kg^{-1} dry weight, in soils sampled from the four studied areas from Baia Mare are presented in Table 1.

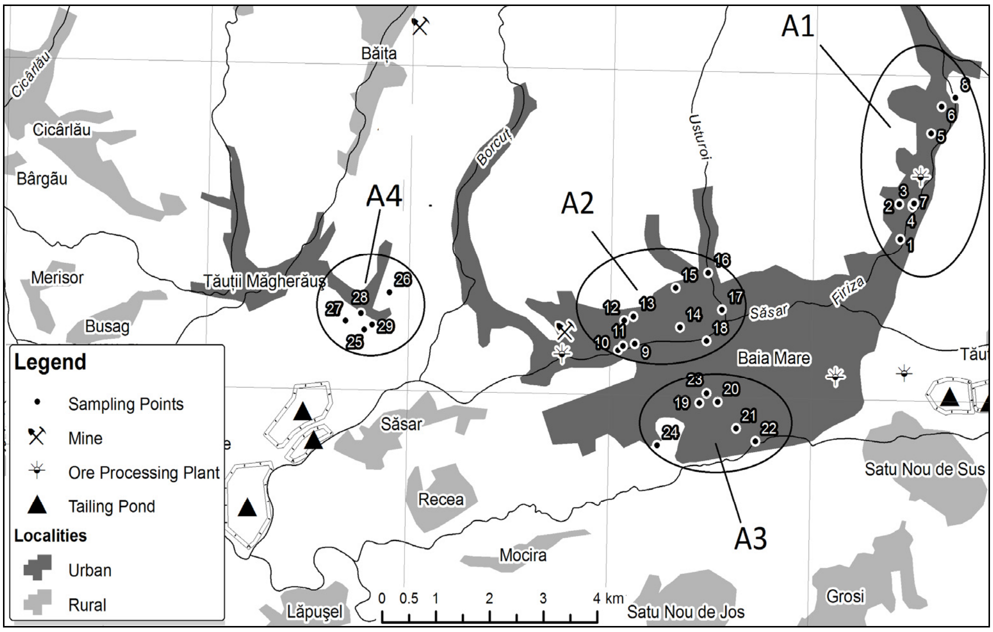

Figure 1. Sampling points and the main pollution sources from the four districts of Baia Mare: Ferneziu (A1), Săsar (A2), Baia Mare center (A3) and Dura (A4)

High concentrations of Pb, Cd, Cu and Zn were measured in soils sampled in the vicinity of Pb smelting plant (A1), with values that exceed the corresponding alert or intervention levels established by Romanian legislation [18]. The average concentration of Pb from this area exceeded of more than 30 times the intervention level. In area A2, the average concentrations of Cu and Pb exceeded 2.5 and 7 times respectively the intervention levels. The average concentration of Zn exceeded the alert level but was below the intervention level. The average concentrations of Cd and Zn in areas A3 and A4 were below the alert levels, whereas the average concentrations of Pb and Cu exceeded the corresponding alert levels. The concentrations of Ni and Cr did not exceed the corresponding alert or intervention levels. The concentration of Mn exceed the alert level only in three sampling points from A1, while for Fe and Al there are not established maximum admitted levels for soil.

The pollution with heavy metals as Pb, Cd, Cu and Zn are in accordance with the results obtained in previous studies conducted in Baia Mare area [19]. Also, in a previous study, it was showed that the concentrations of As exceeded the maximum admitted levels in areas from the industrial part of the Baia Mare [20].

Table 1. *Aqua regia* extractible metals concentrations (mg kg^{-1}) in soils sampled from Baia Mare urban area

Sampling point	*Cu*	*Zn*	*Cd*	*Pb*	*Ni*	*Cr*	*Mn*	*Fe*	*Al*
A1									
1	823	1530	35.1	5520	27.6	47.9	2540	46200	33900
2	620	1570	56.5	5150	12.4	21.5	1100	55600	36600
3	295	1160	20.2	1860	8.50	19.6	652	41100	35100
4	15.3	247	0.50	105	1.20	0.75	14.2	11100	17200
5	12.9	105	0.53	154	1.55	0.70	3.70	11200	17400
6	10.0	147	0.49	166	1.20	0.95	14.7	9800	12800
7	1740	1180	30.2	5390	28.8	50.1	1800	9340	13200
8	660	426	17.9	3540	21.6	32.1	1620	25700	21100
A2									
9	137	431	1.45	916	0.60	7.10	1000	32000	32700
10	269	681	3.25	1330	5.05	15.8	1040	35700	35600
11	107	336	1.30	333	6.75	15.2	1350	31800	34200
12	105	247	1.15	230	7.45	17.9	748	29400	35500
13	59	271	0.40	125	8.25	17.4	509	23100	23500
14	1660	1200	7.45	778	12.4	14.8	1290	45300	19200
15	168	628	0.90	469	2.85	9.05	843	22800	20500
16	652	512	2.12	1130	2.66	8.65	584	21500	17600
17	73.5	241	1.00	326	3.20	7.25	730	36500	37700
18	189	428	1.50	532	3.80	17.4	1150	31800	28700
19	140	148	0.30	90.0	8.25	11.3	361	15000	11600
20	206	335	1.00	482	7.05	50.6	281	20300	30400
A3									
21	309	428	0.90	532	10.2	39.8	511	25200	28800
22	214	239	0.40	244	11.9	29.8	576	29900	37680
23	161	443	0.45	315	7.35	8.30	855	23200	29000
24	73.3	192	0.10	129	15.4	39.2	749	31700	39200
25	102	178	0.15	147	11.7	20.0	831	18100	20800
A4									
26	50.1	69.9	0.05	34.0	12.1	28.4	441	28200	25600
27	47.8	80.8	0.05	61.2	7.75	25.3	774	26500	24200
28	24.4	68.1	0.05	38.1	9.85	31.0	545	29900	28600
29	19.8	61.1	0.05	38.7	9.50	30.2	450	28100	28600
AL*	100	300	3	50	75	100	1500	-	-
IL**	200	600	5	100	150	300	2500	-	-

*Alert level for soil from sensitive areas, according to Romanian legislation [18]
**Intervention level for soil from sensitive areas [18]

Concentrations of metals in native vegetation

The metals (Fe, Al, Cr, Mn, Cu, Zn, Ni, Pb, Cd) concentrations, expressed in mg kg^{-1} dry weight, in native vegetation (*Agrostis, Agropirum, Trifolium repens, Urtica dioica*) sampled from Baia Mare urban area are presented in Table 2.

Table 2. Metals concentrations (mg kg^{-1}) in native vegetation sampled from Baia Mare urban area

Sampling point	*Cu*	*Zn*	*Cd*	*Pb*	*Ni*	*Cr*	*Mn*	*Fe*	*Al*
A1									
1	5.49	47.1	0.89	6.52	0.42	0.55	5.65	79.1	22.4
2	18.3	59.1	1.81	15.0	3.22	2.54	10.5	89.0	20.7
3	0.75	120	1.22	6.42	0.41	1.85	7.65	18.6	19.1
4	0.45	75.8	0.58	3.93	0.22	0.17	2.80	7.12	28.9
5	0.35	90.5	1.03	1.04	0.23	0.19	7.95	23.9	39.5
6	1.12	65.5	1.12	1.12	0.21	0.15	5.50	26.6	49.1
7	3.50	70.2	1.11	1.09	0.24	0.19	6.31	29.9	57.0
8	2.30	30.1	1.12	2.96	0.81	0.25	11.2	68.3	65.1
A2									
9	10.0	87.9	0.25	1.45	1.11	1.3	26.6	86.7	50.2
10	16.1	70.5	0.44	2.11	1.81	2.63	22.4	97.0	63.1
11	6.71	44.4	0.25	1.14	1.62	10.2	60.0	101	74.0
12	4.93	19.5	0.10	0.05	0.28	0.08	6.50	22.3	12.0
13	14.6	105	0.11	2.24	1.30	3.55	35.1	119	77.1
14	9.30	109	0.41	2.05	2.32	2.35	59.4	92.1	44.3
15	7.95	115	0.72	1.05	1.91	1.03	86.0	68.2	32.2
16	15.9	93.1	2.58	11.7	1.84	6.75	202	110	94.1
17	10.8	94.5	0.89	1.32	2.27	5.60	110	119	47.4
18	16.7	104	1.05	1.85	3.02	3.04	107	164	75.0
19	6.11	38.5	0.15	1.45	1.85	6.05	21.4	171	54.1
20	6.60	57.1	0.21	5.10	1.33	1.75	13.8	117	120
A3									
21	2.95	23.3	0.11	2.34	0.61	0.50	19.2	93.9	68.0
22	1.05	2.30	0.10	0.02	0.65	0.85	1.65	5.20	37.9
23	2.45	26.5	0.15	0.75	1.68	0.72	18.3	12.4	31.8
24	2.95	13.6	0.05	1.52	0.78	0.59	29.5	118	93.0
25	1.06	9.21	0.08	1.13	0.46	1.37	10.8	83.0	76.0
A4									
26	2.50	18.7	0.09	1.73	3.36	10.3	106	278	398
27	1.45	21.4	0.08	1.51	3.16	10.3	227	206	255
28	0.45	25.1	0.22	2.12	3.35	5.95	389	136	101
29	9.45	13.6	0.24	1.48	4.09	8.55	92.8	168	162

The metals concentrations in vegetation (mg kg^{-1} dw) in the studied areas ranged between: 0.35 – 18.3 for Cu, 2.30 – 120 for Zn, 0.05 – 2.58 for Cd, 0.02 – 15.0 for Pb, 0.21 – 4.09 for Ni, 0.08 – 2.03 for Cr, 1.65 – 389 for Mn, 5.20 – 278 for Fe and 12.0 – 398 for Al.

The average content of Cd in vegetation from Ferneziu exceeded the maximum level (1.0 mg kg^{-1}) established by the European Directive 2002/32/EC allowed in animal feed. Also the maximum level for Cd was exceeded in several samples from Sasar district. The maximum admitted level for Pb (10 mg kg^{-1}) was exceeded in only one vegetation sample from Ferneziu district.

According to the data from the literature [9], the critical concentrations of metals in plant tissues, that affects the vegetation growth (especially for sensitive vegetation species) are in the range of 5-10 mg kg^{-1} for Cd, 1-2 mg kg^{-1} for Cr, 15-20 mg kg^{-1} for Cu, 20-30 mg kg^{-1} for Ni and 150-200 mg kg^{-1} for Zn. As presented in the Table 2, the found values in the analysed vegetation were generally below the critical concentrations, except for Cr and Cd, in several samples from Sasar and Ferneziu districts. Although the vegetation growth is not affected, metal concentrations are high enough to consider the vegetation contaminated, and unsuitable to be used as animal feed.

Generally, higher concentrations of metals such as Pb, Cd, Zn and Cu were found in vegetation collected from industrial part of the city. Thus, the average Pb concentration in A1 was approximately 1.7 times higher than in A2 and 2.5 times higher than in A3 and in A4, explained by the presence of a Pb smelter in that area. Also, the average of Cd concentration was found to be higher in A1 (2 times higher than in A2 and 10 times than in A3 and in A4), while the averages of Zn concentration in vegetation from industrial districts A1 and A2 were approximately 3 times higher than in A3 and in A4. The Cu concentrations were found to be higher in vegetation collected from the vicinity of the Cu smelter, A2 (2 times higher than in A1 and 3 times higher than in A3 and A4). The highest concentrations of Cr were found in the analysed vegetation from A2, while the concentrations of Ni, Mn, Fe and Al were higher in the vegetation from the area A4, situated far from the industrial smelting facilities.

Multivariate statistics

The Pearson's correlation matrix revealed strong positive correlations between the pseudo-total (*aqua regia* extractable) concentrations of Cu, Zn, Cd and Pb in soil, metals that can be attributed to the pollution generated by the mining activities. Also, strong positive correlation between the pseudo-total concentrations of major element in soil, Al and Fe, was found, while moderate correlations between Fe and Zn, Cd and Cr concentrations in soil were observed. In case of metals contents in soil and vegetation, low correlations were found for Zn, Cd and Pb, while for Cu, Ni, Cr, Mn, Fe and Al no significant correlations were observed. The poor correlations between pseudo-total contents of metals in soil and in vegetation revealed that the accumulation in vegetation is not directly influenced by the total metal contents of soil, but mainly by the metals mobility and plants uptake mechanisms.

The varimax rotated factor loadings of principal components (PCs) for metal concentrations in vegetation and soil and chemical properties of soil are presented in Table 3. The loadings in bold face correspond to variables that dominantly influence the selected latent factor. Four PC's with eigenvalues higher than 1 explains about 76% of the total variance of the system. The first component (PC1) exhibits 30% of the total variance with positive loadings on pseudo-total (*aqua regia* extractable) content of Cu, Zn, Cd, Pb, Ni, Cr and Mn, and reflects the influence of anthropogenic sources on metal contents in vegetation. Generally, poor correlations were found between total metal content in soil and metal content in vegetation since many factors control the availability of metals from soil [21].

The second component (PC2) explains about 20% of the variability and contains the metals (Ni, Cr, Mn, Fe, Al) accumulated in vegetation and negatively correlated with soil pH. The elements from this group are metals that can be transferred to plants as free ions resulted from dissolution of soluble species, such as carbonates, under influence of soil pH. Additionally, at the soil-roots interface, the pH may vary by up to 2.5 pH units from that of the bulk soil solution as a result of roots exudates of organic acids with influence on the availability of metals [22].

Table 3. Factor loadings after Varimax rotation

	PC1	PC2	PC3	PC4
Cu soil	**0.771**	-0.111	0.281	-0.186
Zn soil	**0.736**	-0.270	0.399	0.302
Cd soil	**0.790**	-0.154	0.276	0.279
Pb soil	**0.884**	-0.183	0.240	0.109
Ni soil	**0.896**	0.004	-0.324	-0.070
Cr soil	**0.677**	0.181	-0.467	0.053
Mn soil	**0.776**	-0.033	0.033	0.238
Fe soil	0.334	0.151	0.152	**0.835**
Al soil	0.013	-0.003	-0.219	**0.871**
TOC	0.084	-0.002	**0.756**	-0.215
pH	0.102	**-0.554**	**-0.495**	-0.148
Cu vegetation	0.028	0.217	**0.616**	0.453
Zn vegetation	-0.101	-0.220	**0.735**	0.010
Cd vegetation	0.284	-0.064	**0.830**	-0.097
Pb vegetation	0.375	0.082	**0.620**	0.260
Ni vegetation	-0.074	**0.821**	0.108	0.299
Cr vegetation	-0.158	**0.858**	0.004	0.045
Mn vegetation	-0.147	**0.725**	0.133	-0.064
Fe vegetation	-0.038	**0.887**	-0.123	0.068
Al vegetation	-0.045	**0.807**	-0.277	-0.180

The values in bold face show the highest loadings

The third component (PC3) explains approximately 17% of the total variability, and contains the metals (Cu, Zn, Cd and Pb) negatively correlated with soil pH and positively correlated with soil TOC. As expected, soil pH plays an important role in the mobilization of metals, while TOC has a different effect on the metals mobility and their transfer to plants. The different metal mobilization patterns are explained by the type of complexes that are formed between each metal and organic matter. It is recognized that elements such as Cu, Zn and Pb forms strong complexes with dissolved organic matter that facilitates metal transport through soils in the form of organic complexes [23]. These complexes are not dissolved even at low pH, but are absorbed by vegetation particularly if they have low molecular weight. Previous studies showed that the addition of the fertilizers can increase the metals uptake by vegetation [24]. For the elements attributed mainly to the natural background such as Al, Mn, Fe, Cr and Ni, no correlation was found between soil TOC and metals contents in vegetation, explained by theirs initial complexation by organic matter with low molecular weight which, in time, are converted into compounds with higher molecular weight (humic substances) [25].

The fourth factor (PC4) contains the major elements (Al and Fe) related to the natural conditions from soil. This factor explains only 9% of the total variability.

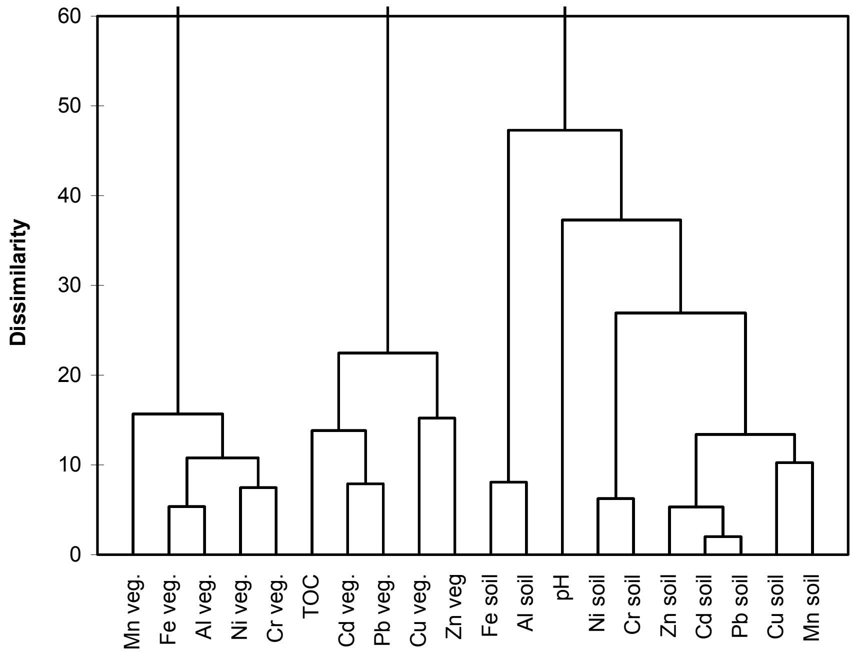

Figure 2. Dendogram showing the clustering of metals in vegetation, soil and chemical soil properties

The dendrogram resulting from AHC (Agglomerative Hierarchical Clustering), created by using Ward method and the Euclidian distance for dissimilarity, presented in Figure 2, shows 3 major clusters: cluster 1 (Mn, Fe, Al, Ni, Cr from vegetation), cluster 2 (soil TOC and Pb, Cd, Cu and Zn accumulated in vegetation), cluster 3 (soil pH and aqua regia extractable metal concentrations), and confirm the results obtained by the PCA.

CONCLUSIONS

The obtained results showed high concentrations of some metals (Pb, Cd, Cu and Zn) in soil, exceeding the corresponding maximum admitted levels, established by the Romanian legislation. In vegetation, higher concentrations of Pb, Zn, Cr, Mn and Cd, were found in the industrial parts of the city, while the concentrations of Ni, Fe and Al were slowly higher in the vegetation from the area situated far from smelting facilities. Multivariate statistical analysis showed poor correlations between metals concentration in soil and in vegetation. The study revealed that pH plays an important role in the metals mobilization, with influence in the soil-plant transfer, while TOC from soil is a lower indicator for metals transfer to vegetables, in the studied area.

EXPERIMENTAL PART

Site description and Sampling

Soil samples at 0-20 cm depths and vegetation from the spontaneous flora (*Agrostis, Agropirum, Trifolium repens, Urtica dioica*) grown on these soils were sampled from each selected point (presented in Fig. 1). The coordinates of sampling points recorded with a 310 Magellan GPS.

Materials and methods

Instrumentation

The content of all metals in soil and Al, Fe, Mn, Zn and Cu in vegetation extracts were measured by inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 5300 DV (Perkin Elmer, USA), while Cd, Pb and Ni in vegetation extracts were measured by inductively coupled plasma mass spectrometer (ICP-MS) ELAN DRCII (Perkin Elmer, USA). Total Organic Carbon content was measured by using the Multi N/C 2100S Analyser (Analytic Jena, Germany). The pH was measured with Consort 2000 pH-meter equipped with a combined pH electrode. A mortar grinder PM 100 (Retsch, Germany) and a sieve shaker Analysette 3 Spartan (Fritsch, Germany) were used for samples grinding and sieving.

Reagents, Standard Solutions and CRMs

Stock multielemental standard solutions containing all the analysed elements (1000 mg L^{-1}) Merck (Darmstadt, Germany) were used for ICP-OES calibrations. For all dilutions ultrapure water (18 MΩ cm^{-1}) obtained from a Direct Q3 (Millipore, France) system was used. A soil certified reference material SRM 2709 San Joaquin Soil (New York, USA) and two vegetable certified reference materials NCS ZC85006 Tomato (Beijing, China) and IAEA-359 Cabbage (Vienna, Austria) were used for the internal quality control of metals determination.

Laboratory Analysis

The pre-treatment of soil samples were made according to SR ISO 11466:1999 [26]. Samples were ground to a fine powder and sieved through 100 µm sieve. The vegetables were intensely rinsed with tap water and ultrapure water, to eliminate soil and dust from the roots and shoots, and then dried at 40°C, grounded and the sieved through the 100 µm sieve. All the soil and plant samples were kept in sealed plastic bags until analysis.

The total metal concentrations of soils were determined after *aqua regia* digestion according to SR ISO 11466:1999 [26]. An amount of 1 g soil was heated with 21 mL of 12 M HCl and 7 mL of 15.8 M HNO_3, then filtered and diluted to 100 mL with 0.5 M HNO_3. The vegetables were digested using a microwave digestion system. Approximately 1.0 g of sample was digested with 6 mL of HNO_3 and 2 mL of H_2O_2 and then diluted to 50 mL with ultrapure water.

Quality assurance included CRMs analyses and replicate analyses. The recovery degrees (%) of Fe, Al, Cr, Mn, Cu, Zn, Ni and Pb in soil CRM, SRM 2709, calculated using the average of five replicates and relative standard deviation at a 0.05 significance level, were 96±11%, 90±12%, 102±10%, 109±9%, 95±9%, 99±12%, 93±11% and 92±12%, respectively. The recovery degrees (%) of Al, Mn, Cu, Zn, Ni, Cd and Pb in NCS ZC85006 tomato CRM, calculated using the average of five replicates and relative standard deviations at a 0.05 significance level, were 105±14%, 100±12%, 92±15%, 88±13%, 96±16%, 93±13% and 107±16%, respectively. For IAEA-359 cabbage CRM, the recovery degrees (%) of Fe, Mn, Cu and Zn, calculated using the average of five replicates and relative standard deviations at a 0.05 significance level, were 108±10%, 96±14%, 103±15% and 86±17%, respectively.

Statistical Analyses

The XLStat Microsoft Excel plug-in (Addinsoft) was used for the statistical processing of the data.

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REFERENCES

1. J. Gal, J. Markiewicz-Patkowska, A. Hursthouse, P. Tatner, *Ecotoxicology and Environmental Safety*, **2008**, *69*, 139
2. N. Massa, F. Andreucci, M. Poli, M. Aceto, R. Barbato, G. Berta, *Ecotoxicology and Environmental Safety*, **2010**, *73*, 1988
3. D. Desideri, M.A. Meli, C. Roselli, *Microchemical Journal,* **2010**, *95*, 174
4. S.R. Oliva, A.J.F. Espinosa, *Microchemical Journal,* **2007**, *86*, 131
5. M.N. Rashed, *Journal of Hazardous Materials*, **2010**, *178*, 739
6. M. Malandrino, O. Abollino, S. Buoso, A. Giacomino, C. La Gioia, E. Mentasti, *Chemosphere*, **2011**, *82*, 169
7. S. Muhammad, M.T. Shah, S. Khan, *Microchemical Journal,* **2011**, *99*, 67
8. G. Nabulo, C.R. Black, S.D. Young, *Environmental Pollution*, **2011**, *159*, 368
9. A. Kabata-Pendias, “Trace Element in Soils and Plants”, Third edition, *CRC Press*, **2001**, chapter 4
10. F.J. Gallagher, I. Pechmann, J.D. Bogden, J. Grabosky, P. Weis, *Environmental Pollution*, **2008**, *156*, 699
11. E. Cordos, C. Roman, M. Ponta, T. Frentiu, R. Rautiu, *Revista de Chimie –Bucharest*, **2007**, *58*, 470
12. T. Frentiu, M. Ponta, E. Levei, M. Senila, M. Ursu, E. Cordos, *Journal of Optoelectronics and Advanced Materials,* **2007**, *9*, 3505
13. E. Levei, M. Senila, C. Roman, M. Ponta, T. Frentiu, E. Cordos, *Studia UBB Chemia,* **2008**, *3*, 51
14. M. Miclean, E. Levei, M. Senila, B. Abraham, C. Roman, E. Cordos, *Studia UBB Chemia,* **2008**, *3*, 57
15. M. Senila, E. Levei, M. Miclean, L. Senila, L. Stefanescu, S. Marginean, A. Ozunu, C. Roman, *Environmental Engineering and Management Journal*, **2011**, *10*, 59

16. Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on undesirable substances in animal feed
17. E. Levei, T. Frentiu, M. Ponta, M. Senila, M. Miclean, C. Roman, E. Cordos, *International Journal of Environmental Analytical Chemistry*, **2009**, *89*, 635
18. Ministerial Order 956:1997, *Official Gazette of Romania*, 303/bis/06.11.1997
19. E. Levei, M. Miclean, M. Senila, O. Cadar, C. Roman, V. Micle, *Journal of Plant Development*, **2010**, *17*, 139
20. G. Oprea, A. Michnea, C. Mihali, M. Senila, C. Roman, S. Jelea, C. Butean, C. Barz*, American Journal of Environmental Sciences*, **2010**, 6, 33
21. H. Deng, Z.H. Ye, M.H. Wong, *Environmental Pollution*, **2004**, *132*, 29
22. E. Oburger, G.J.D. Kirk, W.W. Wenzel, M. Puschenreiter, D.L. Jones, *Soil Biology & Biochemistry*, **2009**, *41*, 449
23. K.G.J. Nierop, B. Jansen, J.A. Vrugt, J.M. Verstraten, *Chemosphere*, **2002**, *49*, 1191A
24. M.S. Mendes, G.P. Duda, C. W. Araujo do Nascimento; M.O. Silva, *Scientia Agricola*, **2006**, *63*, 328
25. R. Clemente, D.J. Walker, M.P. Bernal, *Environmental Pollution*, **2005**, *138*, 46
26. SR ISO 11466 – 1999. Soil quality - Extraction of trace elements soluble in aqua *regia*. *International Organization for Standardization, Geneva, Switzerland*