

HEAVY METALS IN SOIL-PLANT SYSTEM AROUND BAIJA MARE CITY, ROMANIA

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Abstract: A field survey was conducted to investigate the metal contamination in soils and vegetables, and to evaluate the possible health risks to local population through food chain transfer near two processing of non-ferrous ore deposits in Baia Mare, northwestern Romania. Contamination levels in soils and vegetables with cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) were measured, Pearson correlations and transfer factors (TF) from soils to vegetable plants were calculated accordingly. Results showed that both soils and vegetables from villages near the contamination area were heavily contaminated, compared to a village 38 km from the smelter (Mara). The values for heavy metals in soil are between 9.1- 2593 mg.kg⁻¹ for Cu, 1.1- 27 mg.kg⁻¹ for Cd, 83-8040 mg.kg⁻¹ for Pb and between 60-11445 mg.kg⁻¹ for Zn. The values for Cu, Cd, Pb and Zn concentrations in vegetables for 20 samples are between 5.8-196 mg.kg⁻¹ Cu, 0.3-5.2 mg.kg⁻¹ Cd, 0.5-15 mg.kg⁻¹ Pb respectively, 21-126 mg.kg⁻¹ Zn (on dry weight basis). The transfer factor (TF) has lower values such as 0.04-1.07 for Cu, 0-1.19 for Cd, 0-0.04 for Pb and 0.01-0.43 for Zn, which means that the heavy metals are retained by plants from atmospheric emissions and highlight that the heavy metals are strongly retained in soil. Pearson coefficients correlations are well assured for Cd 0.53 at 0-10 cm and 0.46 at 20-40 cm. The complexity of metal contamination and their health risks are also discussed. The final results illustrated that the environment has been polluted by industrial activities.

Keywords: soil, heavy metal, carrote roots, transfer factor, Pearson correlation

1. INTRODUCTION

The studied region, Baia Mare, is an important urban center in northwestern Romania and is located in the western part of the Maramureș County, in the depression Baia Mare, on the middle of Săsar River. The altitude is 228 m above sea level, ranging geographical coordinates 47°39'-47°48' north latitude and 23°10'- 23°30' east longitudinal.

Baia Mare lies almost entirely over northern peaks of the Eastern Carpathians. It is a town that is constantly submissively to the pollution existed by mining, extraction and processing of non-ferrous ore deposits. The major pollutants in the Baia Mare area are: copper and lead smelters (*S.C. Cuprom S.A.* and *S.C. Romplumb S.A.* Fig.1), the ponds located in this area, the mine dumps resulting from mining

activities and the mine water discharged from the existing galleries in the area.

Climate of Maramureș County falls in both moderate continental climate section and in the mountain climates. In Baia Mare, as well as throughout Maramureș County, there is a large amount of precipitation (976 mm/year). Wind regime is conditioned by the airflow in the western sector, with an average annual rate of 13.7% and the eastern sector with an average annual rate of 10.8%.

Heavy metal concentrations of the soils are different due to the soil processes formation or as the degree of contamination (Oluwatosin et al., 2008). Soil can accumulate high amounts concentrations of heavy metals. Other researches demonstrated that the heavy metal concentrations exceed the normal concentrations and the allowable maximum limit, especially for Pb, Zn and Cu for the area from the

south part of the Cuprom metallurgical smelter (Lăcătușu et al., 1996a, Damian et al., 2010).

The main components of soil that can affect retention and bioavailability of heavy metals are: pH, soil texture, redox potential, clay content, organic matter, the presence of other metals in soil, temperature and soil moisture and cation exchange capacity (CEC), (Kugonič & Grčman 1999, Jung 2008, Dube et al., 2001, Kalbitz & Wennrich, 1998). Also the toxicity of the heavy metal in soil is influenced by the metal specie and availability, (Yuan-peng et al., 2007).

The general soil characteristics, (pH, CEC, humus content, total nitrogen) influences the heavy metals concentration in soil (Kobza, 2005) by specific mechanisms and the quantity of these metals that can be transferred into edible plants (the TF) (Lăcătușu et al., 1996b, 2008, Puschenreiter & Horak, 2000).

The way for the pollutants to arrive in food chain is represented by the plants grow on polluted soils with heavy metals (Ngole 2011). Generally, plants grown on contaminated soils are likely to absorb more trace elements and their concentrations in plant tissues are often positively correlated with the abundance of these elements in soil, and especially in soil solution (Lăcătușu et al., 1996 a, 2008, Yi et al., 2007). Even though many trace elements are essential for growth, they may have also toxic effects on plant metabolism at higher concentrations. Excessive heavy metal accumulation can hinder the growth of the different plants (Hung-Yu & Zueng-Sang, 2004).

Some metals are important as trace elements in plants; their solubility is pH dependent (Mohammed & Sulaiman, 2009).

The influence of mining activities from different parts of Romania on the heavy metals contents from vegetables was demonstrated by Lăcătușu et al., 1996b, 2004, 2008, Hărmănescu et al., 2011.

In present paper, we have studied the total form of heavy metals (Cu, Cd, Pb, Zn) in soils from Baia Mare area and the bioconcentration in the edible part of carrots.

2. MATERIAL AND METHODS

2.1. Studied Area

The soil and plants samples were taken at different distances from the main sources of pollution in Baia Mare area (Table 1). Samples of plants (carrots) were collected from private households in villages, presented in the map from figure 1, and are

representative for former mining areas.

2.2 Soil from studied area

Soil sampling was done in 21 locations from the Baia Mare area, especially around Romplumb metallurgical smelter, at two depths: 0-10 cm, 20-40 cm, from each location, in 2010 year. The two sampling depths correspond to A, E and B horizons.

The main soil types (Fig. 1) from the sampling area are: luvosols, eutricambosols, dystricambosols, aluviosols, lithosols, regosols, entiantrosols, stagnosols named by Romanian Soil Taxonomy (Florea & Munteanu, 2003). The physical and chemical properties of the studied soils were evaluated comparison with the pedological indicators (Florea et al., 1987).

Typical luvosol (Groși)

The soil reaction is medium acid-neutral in both horizons (pH 5.6 to 5.7). The degree of base saturation is 52% for higher horizon and 62% in depth. The cation exchange capacity is low. The humus content at the surface is poor and rich in depth and the nitrogen content is reduced.

Albic stagnic luvosol (Satu Nou de Jos, Recea, Mocira, Săsar, Tăuții Măgherăuși, Cicârlău, adjacent area of the Tăuții pond).

The soil texture is loamy and clayey in the upper horizons, clayey and loamy-sandy in the middle and lower horizons (Fig. 3). The reaction is extremely to slightly acid at the surface and becomes extremely acid-neutral in depth. After the base saturation, the soils falls into oligobazic-mezobazic group (13-45%) in the upper horizon and oligobazic to saturate in base in the lower horizon (23-100%). The humus content is insufficient to well assure at the surface and poor to sufficient in depth. The nitrogen supply is low.

Andic dystricambosol (Chiuzaiba)

The soil presents a sandy-loamy texture; it has a strongly-acidic to slightly acidic reaction (pH 5.1 to 6.2) and very strongly acid to neutral (pH 4.9 to 6.6) in depth. The degree of base saturation is oligobazic-oligomezobazic (25-36%) at the surface and oligomezobazic-eubazic (45-81%) in the depth of 20-40 cm, the humus supply is from medium to well assured and the total nitrogen content is small.

Andic lithosol (Mara, Cavnic)

This soil type is characterized by loamy-clayey texture and medium to acidic reaction at the surface (pH 5.5) and very strongly acid to medium acid in depth (pH 4.9 to 6). The degree of base saturation ranges from 19-42% at the surface

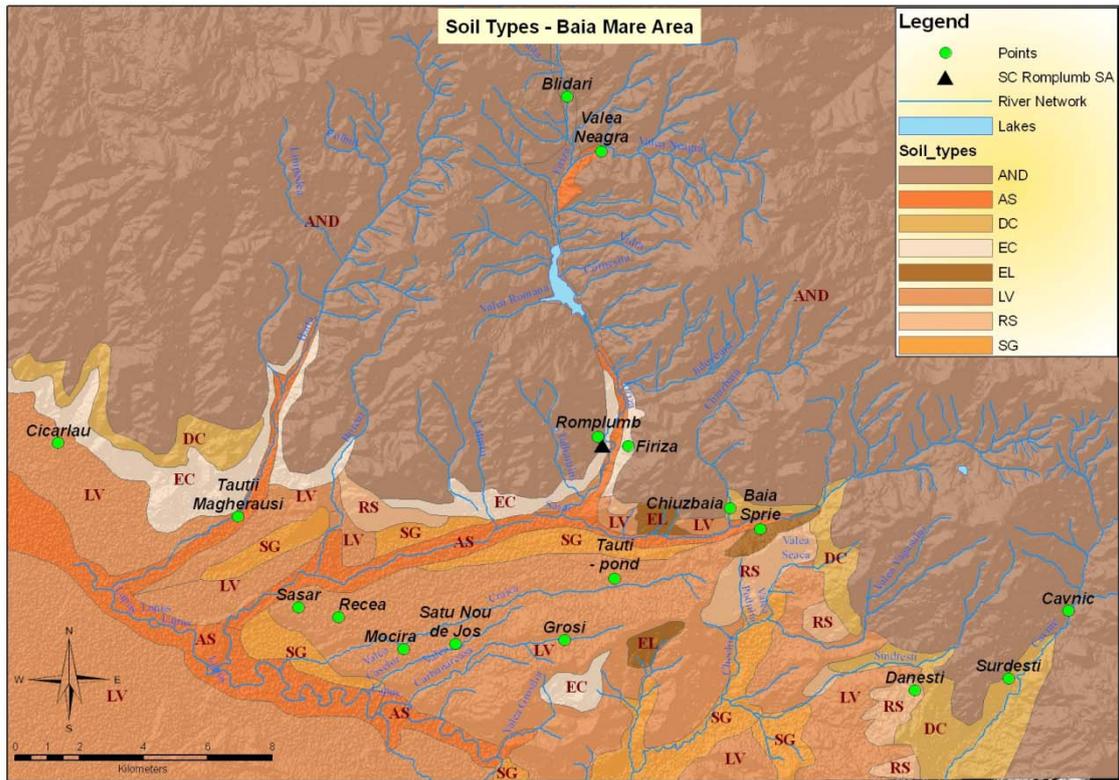


Figure 1. - Soil Map of the Baia Mare area Legend: AND andosol, AS aluviosol, DC dystricambosol, EC eutricambosol, EL preluvosol, RS regosol, LV luvosol, SG stagnosol

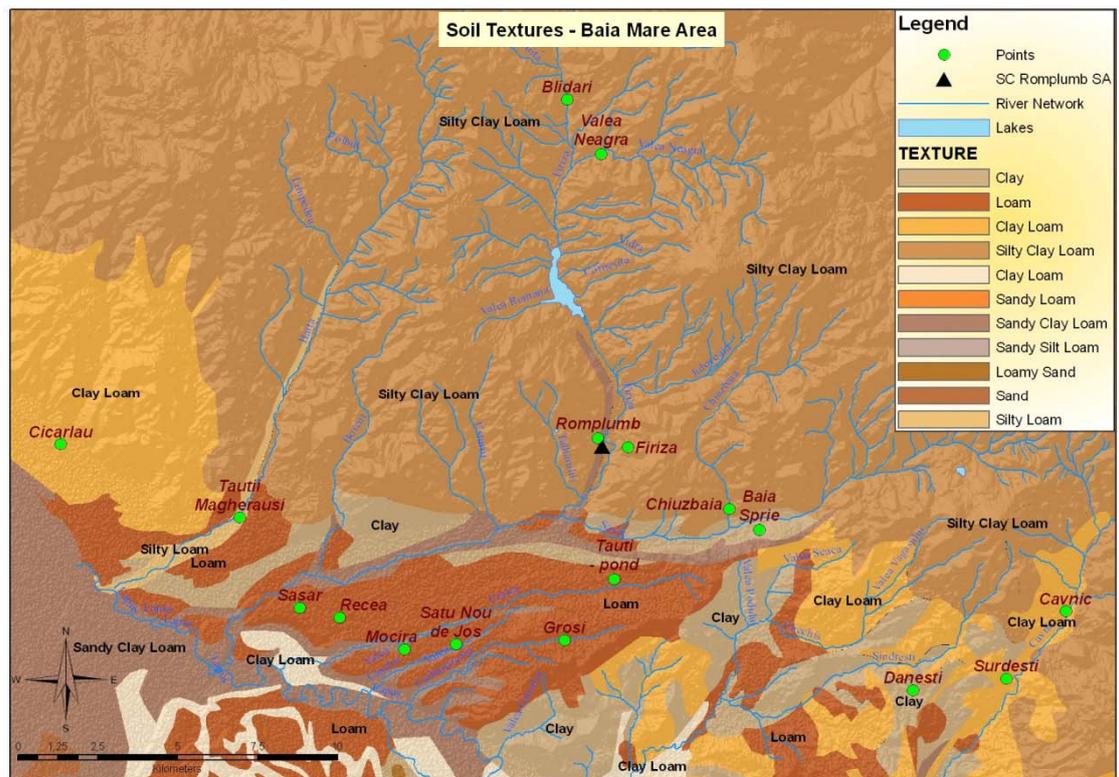


Figure 2. - Soil Texture of Baia Mare area

(oligobasic to oligomezobasic) and between 19-62% in depth. The humus supply is sufficient to good (3.31 to 4.26%) and the total nitrogen content is small.

Dystric regosol (Dănești, Șurdești)

The soil reaction is strongly to medium acid (pH range 5.4 to 5.5). The degree of base saturation is oligobasic to oligomezobasic (21-45%) at the surface and oligobasic in depth (20-28%). In terms of humus content, the soils are well insured at the 0-10 cm depth being comprised between 5.14 to 6.53% and 1.55 to 4.21% at 20-40 cm depth.

Prundic aluviosol (Firiza 1, Firiza 2)

This soil presents a very acid reaction to neutral at the surface (pH 3.2 to 6.8) and extremely to slightly acid (pH 3.2 to 6.3) in depth. According to the degree of base saturation, the soil falls from oligobasic (21%) at the surface to mezobasic (52-58%) in depth. Soils are very poor in humus in depth and well assured at the surface.

Coluvic aluviosol (Valea Neagră)

This soil is strongly acid within the profile and oligobasic to mezobasic (31-58%) according to the base saturation degree (31.5%). The humus supply is low in depth (2.97%) and good at the surface (7.29%).

Dystric andosol (Blidari)

The soil is well supplied with humus at both depths (6.40 at 0-10 cm depth and 4.48 at 20-40 cm depth), very oligobasic (2.96 to 2.98%) depending on the degree base saturation and in terms of soil reaction it is acid to strongly acid.

Eutricambosol (Romplumb 1)

It features with a very strong acid reaction at the surface (pH 4.9) to strongly acid in depth (pH 5.1). Soil type according to the degree of base saturation is oligomezobasic (31-51%) and the supply with humus is good and falls to intermediate horizons.

In the figure 2 it is showed the textural class's map of the main studied soil types. The loamy, clayey and silty-clayey loam soils are predominant in the sampling area.

Site selection was made to provide new data on the evolution of pollution in Baia Mare area associated with the heavy metal accumulation in soils. It was also emphasized the pollution intensity in relation to the distance towards the main sources of pollution (metallurgical smelters, ponds, slag dumps). Soil profiles were located around the main smelters with extension in the suburban area (Firiza area) up to the villages surrounding Baia Mare area, (Fig. 1).

The soil pH was determined in aqueous solution in 25 ml distilled water: 10 g soil. Determination of total cation exchange capacity (CEC) (Mathieu & Pielain, 2003) was done by

calculating the total values of basic exchange cation content (SB) and the exchange capacity for hydrogen (SH).

Determination of base saturation (V), (Mathieu & Pielain, 2003) was done by calculation, reporting the amount of exchange bases (SB) in cation exchange capacity (CEC):

$$V\% = (SB/CEC) \cdot 100$$

Determination of total nitrogen (Mathieu & Pielain, 2003) was performed using the elemental analyzer Vario MICRO. Determination of humus was done indirectly by determining the organic carbon content, using the formula: (MO %) = 1.724 × C by the Walkley-Black (1934) method, modified by Gogoasă (1959).

The soil samples were dried and mineralized by mixing with acids, nitric acid and the mixture of hydrochloric acid-nitric in open and hot environment (150°C). The heavy metals were analyzed using the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.3 Plants samples

To understand the uptake of heavy metals by plants grown on different soil types, it has been taken vegetable samples (carrots), in the 2010 year. The fresh vegetable samples were put in clean plastic bags and transported to the laboratory for sample treatment as soon as possible.

The plants were washed, dried, crushed subjected to total digestion in closed medium using HNO₃ 65%, H₂O₂, HCl and then submitted to the heavy metal analysis using the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The heavy metal analyses in soil and in plants were completed within the laboratories of the Ecole Nationale Supérieure des Mines Saint-Etienne, Centre SPIN.

3. RESULTS AND DISCUSSIONS

3.1. Heavy metals in soil

The main properties, pH, humus content which influence the biodisponibility and the heavy metals absorption by the plants, are presented in table 1.

The pH indicates a variation between 3.2 and 6.8 as extreme values, but with a reduced frequency. The most common pH value is between 4.4 and 5.9. Samples with extremely acid values of pH correspond to the highest concentration of heavy metals analyzed. The weak acid – neutral pH soil may be caused by a possible amendment of soils with limestone.

Table 1. The physical and chemical properties and the heavy metals content of the soils around Romplumb smelter

Soil type	Sample location	Distance from source	Horizon depth	Organic matter	N total	CEC	V	pH	Cu	Cd	Pb	Zn
		(km)	(cm)	(%)	(%)	me/100g	(%)		mg.kg ⁻¹			
0	1	2	3	4	5	6	7	8	9	10	11	12
	Tăuți pond	6	0-10	6.26	0.52	7.08	31	5.4	112.39	2.00	250.64	146.74
			20-40	1.6	0.04	6.36	51	4.8	17.52	1.30	102.27	61.70
	Satu Nou de Jos	7	0-10	5.05	0.23	11	20	5.4	70.05	1.52	221.55	89.04
			20-40	3.49	0.12	8.09	37	5.1	27.84	1.06	160.39	59.88
	Recea	9	0-10	6.95	0.27	12.74	18	5.2	59.19	1.70	273.13	122.19
			20-40	2.67	0.03	9.49	30	5.3	24.04	1.95	142.10	64.06
Stagnic luvisol	Mocira	9	0-10	10.19	0.54	15.49	13	4.7	310.82	3.60	767.91	142.02
			20-40	1.38	0.02	1.21	23	4.4	9.13	1.20	105.20	113.23
	Săsar 1	9	0-10	2.69	0.12	12.17	20	5.9	33.29	2.00	163.28	103.64
			20-40	2.38	0.9	9.99	33	6	29.68	1.90	154.47	97.79
	Săsar 2	9	0-10	4.28	0.17	12.36	21	6.1	50.91	2.80	231.30	163.71
			20-40	2.45	0.05	10.7	45	6.1	37.62	2.90	210.11	144.37
	Tăuții Măgherauși	9	0-10	5.07	0.17	12.47	29	5.7	185.56	12.60	804.09	1110.20
			20-40	2.36	0.03	14.82	31	5.9	236.31	5.10	846.21	1251.10
	Cicârlău	18	0-10	10.1	0.5	12.51	31	5.9	85.99	1.60	212.86	138.25
			20-40	2.32	0.06	9.71	65	6.5	15.93	1.20	114.83	63.03
Typic luvisol	Groși	7	0-10	5.05	0.2	3.96	52	5.6	147.44	6.40	283.46	433.97
			20-40	1.48	0.01	5.33	62	5.7	29.58	2.80	117.48	155.09
Preluvisol	Baia Sprie	9	0-10	4.03	0.14	8.19	45	5.9	2109.00	6.40	1054.50	2352.70
			20-40	1.59	0.02	7.72	100	6.2	1441.60	8.10	1659.30	3576.70
Dystricambosol andic	Chiuzbaia	14	0-10	3.22	0.9	12.38	36	6.2	74.23	3.80	444.55	664.68
			20-40	1.97	0.02	9.25	81	6.6	77.23	4.10	731.99	1629.70
Eutricambosol	Romplumb 1	0.02	0-10	6.26	0.25	7.08	31	4.9	298.20	1.60	595.12	171.25
			20-40	1.6	0.04	6.36	51	5.1	377.98	1.90	532.53	196.74

(continued Table 1)

0	1	2	3	4	5	6	7	8	9	10	11	12
	Mara	38	0-10	4.92	0.21	10.6	31	5.5	41.40	1.90	122.29	146.93
			20-40	2.64	0.15	8.75	62	5.5	15.49	1.70	83.05	68.42
	Cavnic	30	0-10	6.4	0.26	9.01	42	5.5	45.18	3.30	294.08	164.09
			20-40	4.48	0.17	8.13	81	6	31.57	3.00	225.77	142.80
Andosol dystric	Blidari	12	0-10	8.76	0.37	11.76	25	5.1	660.57	11.10	2386.00	6019.00
			20-40	5.57	0.22	9.41	45	4.9	191.35	5.00	700.43	2170.70
Regosol dystric	Dănești	17	0-10	6.53	0.28	16.78	21	5.4	938.07	6.60	5607.10	8886.60
			20-40	4.21	0.09	16.12	28	6	1510.10	7.30	8039.90	11445.00
	Șurdești	15	0-10	5.14	0.2	18.18	26	5.5	62.88	2.60	270.86	408.92
			20-40	1.55	0.03	16.72	45	6	18.67	1.50	155.01	155.01
Aluviosol prundic	Firiza 1	9	0-10	0.16	0.09	18.81	20	3.2	2592.60	7.24	4493.20	6521.20
			20-40	0.12	0.07	11.13	52	3.2	1475.10	7.97	3117.80	3102.80
	Firiza 2	9	0-10	4.55	0.11	20.56	21	6.8	341.08	18.08	3530.40	349.30
			20-40	7.43	0.019	11.99	58	6.3	237.84	27.48	171.04	387.22
Aluviosol coluvic	Valea Neagră	17	0-10	7.29	0.39	9.76	31	4.9	40.04	3.20	323.42	164.32
			20-40	2.97	0.12	8.54	58	5.1	11.36	2.70	118.37	89.65
Entiantrosol urbic	Romplumb 2	0.025	0-10	6.95	0.27	12.74	18	5.3	63.16	5.74	1257.90	177.48
			20-40	2.67	0.03	9.49	30	5.2	70.31	8.47	1004.80	207.43

The analyzed soil pH range a little bit at the two sampling depths, with a slight upward trend at the depth of 20-40 cm. Exception to this rule is achieved in the case of stagnic luvosols (Tăuți pond (Table 1) where the pH value is lower at this depth. In this area also the heavy metal concentrations is bigger in depth caused by the tailings dam as source (Lăcătușu et al., 2002a and 2002b, Lăcătușu et al., 2007, Bukar et al., 2012). From the distribution pollution maps of the heavy metals content in soils, the affected areas from Baia Mare are the ones near by the metallurgical smelter factories (Lăcătușu et al., 1996a, Damian et al., 2008, 2010).

Generally, the highest concentrations of heavy metals were determined in urban areas under the influence of metallurgical smelter and in the rural area supposed under the influence of the tailing ponds Tăuții Măgherauși and Șurdești.

Low pH values determine the mobility of heavy metals in soil which is confirmed by their higher content in carrots. The higher pH affects negatively the mobility of heavy metals in soil, which are more resistant to leaching, (Szabo & Czeller, 2009).

A part of concentrations of heavy metals, in total form exceed MAL (maximum allowable limit) after the Order no. 756/1997. The highest concentrations were obtained for Pb, Zn, Cd, at both sampling depths (Table 1).

Lead generally decreases from the sampling depth of 0-10cm to the sampling depth of 20-40 cm, which highlights its immobilization at the organic horizon and the association with acid values of soil reaction.

For zinc, the values indicate an excessive pollution (Table 1). Zinc concentrations are higher at the sampling depth of 20-40 cm, compared to the surface, suggesting a higher mobility of this metal. Alert threshold exceeding for Zn ranges between 1.4 -12 times and in exceptional mode for some samples between 20-38 times.

The cadmium concentrations present values that exceed the alert threshold and tend to increase with depth in relation to moderately acid or neutral values of pH.

Copper presents concentrations that exceed the alert threshold in the first sampling depth (0-10 cm), having decreasing trend in the second sampling depth. The alert threshold is exceeded by 1 to 26 times.

The exceeding of the alert threshold is different, depending on the sample position towards the pollution sources. The largest excess of the intervention threshold are in evidence near the metallurgical plants and the tailing ponds.

3.2 Heavy metal in carrots

The results of analytical determinations for the content of heavy metals in the edible parts of carrots collected from Baia Mare area are presented in table. 2.

Table 2. - Heavy metals content in carrots roots

Locality	Cu	Cd	Pb	Zn
	(mg.kg ⁻¹)			
Romplumb	24.83	4.22	15.35	41.04
Firiza	6.51	5.23	5.01	55.91
Blidari	17.87	1.64	1.86	40.45
Valea Neagră	47.49	2.66	5.54	87.84
Chiuzbaia	5.79	0.27	2.52	20.98
Baia Sprie	8.65	1.47	9.08	62.27
Dănești	9.01	1.42	2.56	42.10
Șurdești	8.45	0.72	3.32	66.13
Cavnic	7.96	2.77	7.79	92.12
Groși	8.20	1.71	2.87	35.21
Satu Nou de Jos	6.10	0.76	2.87	37.15
Mocira	5.98	1.69	2.65	27.62
Recea	7.11	0.44	0.76	23.82
Săsar	7.72	1.50	1.11	43.70
Tăuții Măgherauși	65.97	0.48	10.18	125.87
Cicârlău	99.86	0.86	5.86	97.17
Mara	5.92	0.65	0.49	26.08
NC*	5-10	1.00	10-15	20-50
MAL**		0.10	0.50	50.00

*after Fritz et al., 1977; **after Tyree & Ewers, 1991

NC-normal concentration, MAL- maximum allowable limit

Copper presents high content in carrot roots. Thus the Cicârlău carrots have the highest values of Cu (100 mg.kg⁻¹), followed by carrots values from Tăuții Măgherauși (66 mg.kg⁻¹) and Valea Neagră (47.5 mg.kg⁻¹). Exceeding up to 2.5 and 1.8 times the normal concentration of Cu (5-10 mg.kg⁻¹) in carrots samples appears in the Romplumb and Blidari areas.

Cadmium, in contrast to other toxic metals, as Pb and Zn, has a high mobility in the soil. Cd is accumulated in the edible parts of plants (Adriano, 2001). The highest value of Cd is presented in the carrots samples from Firiza locality, on a prundic aluviosol characterized with a strong acid reaction of soil. All values of Cd concentrations exceed normal concentrations in vegetables (1mg.kg⁻¹) (Table 2).

Lead exceeds normal concentration in carrots samples from Romplumb (15.4 mg.kg⁻¹) and Tăuții Măgherauși areas (10.2 mg.kg⁻¹). The soil from Romplumb area is a eutricambosol characterized by

a strong acid pH (4.9). For all the other analyzed carrot samples, lead values fall within the normal concentration. For the samples Recea, Mara, Săsar Groși, Mocira, Blidari, Dănești, Șurdești, Satu Nou de Jos, the values are even below the maximum allowable limit (10-15 mg.kg⁻¹). These results are in contrast with those obtained by Lăcătușu and Lăcătușu, (2008), which reported a Pb content, which exceeds 11 times the maximum allowable limit in the carrot roots cultivated in Baia Mare area.

The highest value of zinc is found in carrots from Tăuții Măgherauși (126 mg.kg⁻¹) and exceeds 2.5 times the maximum allowable limit (50 mg.kg⁻¹). MAL overruns occur in the carrots samples from Cicârlău (97 mg.kg⁻¹), Cavnic (92 mg.kg⁻¹), Valea Neagră (87.8 mg.kg⁻¹), Șurdești (66 mg.kg⁻¹), Firiza (55.6 mg.kg⁻¹). The lowest value, falling within the normal concentrations (20-50 mg.kg⁻¹), is of the 23.8 mg.kg⁻¹ and appears in the Recea carrots, grown on a stagnic luvosol, characterized by a moderately acidic pH (5.2).

Higher concentrations in carrots were obtained for Cu and Zn which are associated with the high mobility of these metals. Different concentrations of the four metals in carrot root in the analysed samples suggests that this vegetable can grow on soils polluted with heavy metals (Singh et al., 2012) and could represent a potential health risk (Li et al., 2006, Kachenko & Singh 2006).

3.3 Pearson correlation and the transfer factor

To determine the influence of heavy metals from soils (total forms) on vegetables (carrots roots), simple correlations were performed using the Statistical Package for the Social Sciences (SPSS) 17 statistical package, yielding Pearson correlation

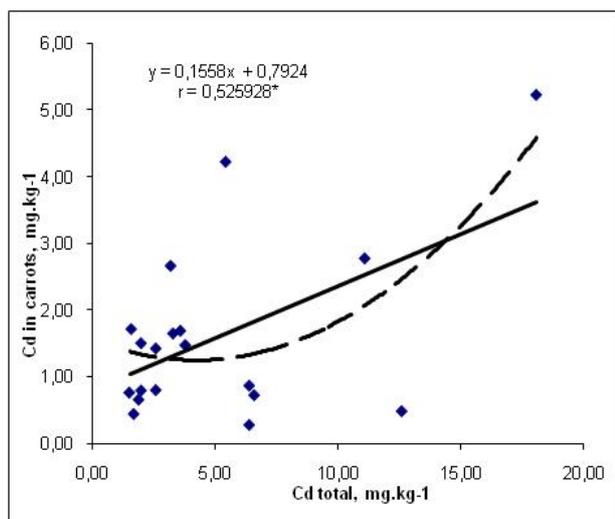
coefficient values which were compared with the limit values. Carrots were chosen because they are very often used in human nutrition. The total heavy metal content is corresponding to each type of soil from which plant samples were taken.

Between heavy metal content determined in carrots and total content of heavy metals in soil were determined directly proportional relationships (Table 3). A correlation coefficient has values towards to 1 for total Cd element (0.53 at 0-10 cm, Fig. 3a and 0.46 at 20 -40 cm, Fig. 3b), followed by total Zn (0.27 at 0-10 cm). The other elements, Cu, Pb, and Zn at 20-40 cm does not present a distinctly correlation on the soil-plant relation.

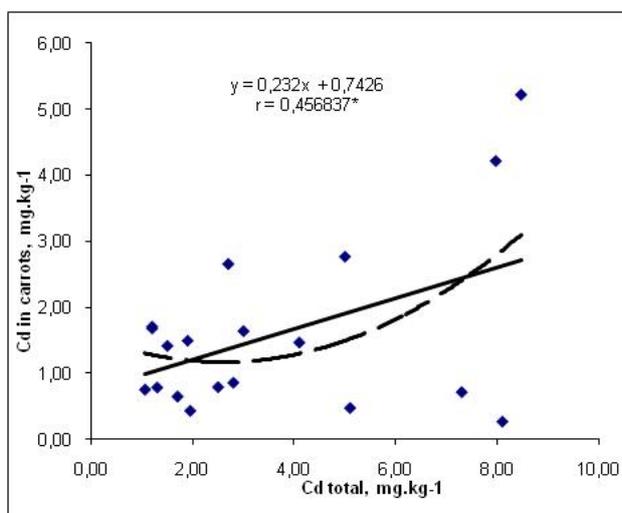
Table 3. - Pearson correlation coefficients of heavy metals from soil and carrots

Metal specie	Form of heavy metal	Depth/heavy metals values of coefficients	
		0-10 cm	20-40 cm
Cu	Total	0.07	0.06
Cd	Total	0.53*	0.46*
Pb	Total	0.05	0.2
Zn	Total	0.27	0.06

Order correlation values for the mobile forms of heavy metals in soil is: Cd> Zn> Pb> Cu. Correlation coefficient values less than 1 indicates a weak correlation between heavy metal values in soil and carrots, which indicates that heavy metals comes from other sources than soil, e.g. atmospheric deposition, as the case of Pb (0.2, respectively 0.05) and Cu (0.07, respectively 0.06).



a



b

Figure 3. (a and b) – The relationship between the Cd content in carrots and the total Cd content in soil (0-10 cm), (20-40 cm)

The transfer factor (TF) can be used to estimate the potential of a plant for phytoremediation. The ability of a plant to accumulate metals from soil can be estimated using the transfer factor (TF). The transfer factor is defined as the ratio of metal concentrations in the roots compared to those in the soil (Kabata-Pendias, 1992).

$$\text{Transfer factor} = \frac{\text{total concentration heavy metals in plant} \left(\frac{\text{mg}}{\text{kg}} \right)}{\text{total concentration heavy metals in soil} \left(\frac{\text{mg}}{\text{kg}} \right)}$$

The species that showed high values of TF (>1) can be considered as hyperaccumulators, (Sun et al., 2008). The capacity of these plants to tolerate and accumulate heavy metals may be useful for phytoremediation (Lorestani et al., 2008).

Lăcătușu et al., 2012, obtained for the transfer and bioaccumulation factors values higher than 1 especially for cadmium in case of the different species of plants grown on sludge.

Plants can immobilize heavy metals through absorption and accumulation in roots, and also by adsorption onto roots or precipitation in the rhizosphere. This process reduces the mobility, leaching of metals into groundwater, and also reduces the bioavailability of metals to get into the food chain.

Kloke et al., (1984) developed a classification of plant species (Table 4) depending on the relative accumulation of heavy metals, as follows:

Table 4- Relative degree of accumulation of heavy metals (after Kloke, 1984)

high	medim	low	very low
salad	beet	corn	beans
spinach	celery	cauliflower	peas
endive	cabbage	broccoli	melon
carrot	potato	celery	tomato

The transfer factors from soil to plant of Cd, Cu, Pb and Zn for carrots samples are given in Table 5. The transfer factor of heavy metals from soil to plants can be used to assess the effect on human health of polluted soil, (Cui et al., 2004). The bioaccessible heavy metal concentrations are useful for selecting remedial measures, (Poggio et al., 2009).

Transfer factor values for the analyzed carrot vary with the soil type that has been grown on. The transfer factor for Cu varies from 0 (Chiuzbaia locality) to 1.19 (Valea Neagră locality). Values for Cd are slightly higher than those of Cu in carrots ranging from 0.04 (Tăuții Măgherauși village, Chiuzbaia) to 1.07 (Groși village). For Pb, the transfer factor is lower; in most places is 0, the

highest value being of 0.04 in Poiana Izvoarelor village. As for Pb, the transfer factor for Zn is low and in the range of 0.01 (Chiuzbaia, Șurdești villages) to 0.42 in Săsar village.

Table 5. - Transfer factor of heavy metals from soil to vegetables (carrots)

Sample	Cd	Cu	Pb	Zn
Romplumb	0.78	0.44	0.03	0.15
Firiza	0.29	0.02	0.00	0.16
Blidari	0.50	0.40	0.01	0.25
Valea Neagră	0.83	1.19	0.02	0.26
Chiuzbaia	0.04	0.00	0.00	0.01
Baia Sprie	0.39	0.12	0.02	0.09
Dănești	0.55	0.14	0.01	0.27
Șurdești	0.11	0.01	0.00	0.01
Cavnic	0.25	0.01	0.00	0.02
Groși	1.07	0.10	0.01	0.25
Satu Nou de Jos	0.50	0.09	0.01	0.42
Mocira	0.47	0.02	0.00	0.19
Recea	0.26	0.12	0.00	0.19
Săsar	0.75	0.23	0.01	0.42
Tăuții Măgherauși	0.04	0.89	0.01	0.11
Cicârlău	0.13	0.68	0.02	0.22
Mara	0.34	0.14	0.00	0.18

The values order, for the analyzed carrots, was: Cd>Cu>Zn> Pb. Only Cd and Cu present values higher than 1 (in Groși and Valea Neagră villages). In the other locations the transfer factor was under 1 which means that all studied metals has a poor translocation in plants and demonstrates that the carrots show an exclusionary behavior towards these metals.

Concentration of heavy metals in carrot root is lower than in the soil, in all analyzed samples. The obtained dates and the calculation of the transfer factor (Table 5) demonstrate this.

4. CONCLUSIONS

In the studied area, the pollution with the four heavy metals analyzed: Pb, Zn, Cu, Cd, is specified at the surface horizons of the Baia Mare urban area and for the localities nearby. The maximum values for Zn are up to 11445 mg.kg⁻¹, for Pb are up to 5607 mg.kg⁻¹, for Cd up to 18 mg.kg⁻¹ and for Cu up to 2593 mg.kg⁻¹.

The second sampling depth (20-40 cm) presents situations in which the heavy metals concentrations are

higher than at the surface especially in the localities from the eastern part of the investigated area. These values are: 3577 mg.kg⁻¹ for Zn, 1659 mg.kg⁻¹ for Pb and 8.10 mg.kg⁻¹ for Cd in Baia Sprie area and 11445 mg.kg⁻¹ for Zn, 8040 mg.kg⁻¹ for Pb, 6.6 mg.kg⁻¹ for Cd and 939 mg.kg⁻¹ for Cu in Dănești area.

The highest heavy metals concentrations in carrot roots were obtained in the areas with the soils excessive affected by the heavy metals pollution. The values for Cu, Cd, Pb and Zn concentrations for the 20 samples analyzed carrots vary between 5.8-196 mg.kg⁻¹ Cu, 0.3-5.2 mg.kg⁻¹ Cd, 0.5-15 mg.kg⁻¹ Pb, respectively 21-126 mg.kg⁻¹ Zn (on dry weight basis).

In the Pb case were obtained lower concentrations in carrot roots compared with the Pb concentration in soil. This is evident also by the low value of the correlation factor.

An order of correlation values between total forms of heavy metals in soil is: Cd>Zn>Cu>Pb. For Cd and Cu, the transfer factor shows values higher than 1, which means that these heavy metals can be uptake by the carrot roots. The transfer factor order values for the analyzed carrots were: Cd>Cu>Zn>Pb.

In these conditions the carrots grown on the soils from Baia Mare area, which are often used in the human alimentation, presents a higher risk for the population health.

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REFERENCES

Adriano, D.C., 2001. *Trace Elements in the Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals*, Springer, New York, Berlin, Heidelberg, Tokyo, 866p.

Bukar Lawan I., Hati Stephen S. Dimari Goni A. & Tijjani Muhammad, 2012. *Study of Vertical Migration of Heavy Metals in Dumpsites Soil*, ARPN Journal of Science and Technology, Vol 2, No. 2. p. 50-55.

Cui Yu-Jing, Zhu Yong-Guan, Zhai Ri-Hong, Chen Deng-Yun, Huang Yi-Zhong, Qiu Yi & Liang Jian-Zhong, 2004. *Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China*, Environment International 30, p. 785–791.

Damian F., Damian Gh., Lăcătușu R., Macovei Gh., Iepure Gh., Năprădean I., Chira R., Kollar L., Rață L. & Zaharia D. C., 2008. *Soils from the Baia Mare zone and the heavy metals pollution*, Carpathian Journal of Earth and Environmental Sciences, Vol. 3, No. 1, p. 85 -98.

Damian Gh., Damian F., Năsui D., Pop C. & Pricop C., 2010. *The soil quality from the southern-eastern part of Baia Mare zone affected by metallurgical industry*, Carpathian Journal of Earth and Environmental Sciences, Vol. 5, No. 1, p. 139-147.

Dube A., Zbytniewski R., Kowalkowski T., Cukrowska E. & Buszewski B., 2001. *Adsorption and Migration of Heavy Metals in Soil* Polish Journal of Environmental Studies Vol. 10, No. 1, p. 1-10.

Florea N., Bălăceanu V., Răuță C. & Canarache A., 1987, *Metodologia elaborării studiilor pedologice, Partea a III-a- Indicatorii pedologici*, Redacția de propagandă tehnică agricolă, București (in Romanian).

Florea N. & Munteanu I., 2003. *Sistemul Român de Taxonomie a Solurilor (SRTS)*, Editura Estfalia, Bucuresti, 182 p (in Romanian).

Fritz, I., Smith F. & Lacroix M., 1977. *Secretion of plasminogen activator by Sertoli cell enriched cultures*, Molecular and Cellular Endocrinology, Volume 9, Issue 2, December, p. 227–236.

Gogoasă T., 1959. *Dosage titration of soil humus*, Dări de Seamă Comitetul Geologic 42:251-271 (in Romanian).

Härmănescu M., Alda L., Bordean D., Gogoasă I. & Gergen I., 2011. *Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study: Banat County, Romania* Chemistry Central Journal,5:6http://journal.chemistrycentral.com/content/5/1/64.

Hung-Yu Lai & Zueng-Sang Chen, 2004. *Effects of EDTA on solubility of cadmium, zinc, and lead and their uptake by rainbow pink and vetiver grass*, Journal Article: Chemosphere, 55(3) p. 421-30.

Jung Myung Chae, 2008. *Heavy Metal Concentrations in Soils and Factors Affecting Metal Uptake by Plants in the Vicinity of a Korean Cu-W Mine*, Sensors, 8, p. 2413-2423.

Kabata-Pendias A. & Pendias H., 1992. *Trace elements in soils and plants*. 2nd edition CRC Press, Boca Raton., FL. 365 p.

Kachenko Anthony George & Singh Balwant, 2006. *Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia*, Water, Air, and Soil Pollution 169, p. 101–123.

Kalbitz K. & Wennrich R., 1998. *Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter*, The Science of the Total Environment 209, p. 27-39.

Kloke A., Sauerbeck D.R. & Vetter H., 1984. *The*

- contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chains. In: Changing metal cycles and human health. Springer, Berlin, Heidelberg, New York, Tokyo: p. 113–141.
- Kobza J.**, 2005. *Soil and plant pollution by potentially toxic elements in Slovakia*, Plant, Soil and Environment 51, (6), p. 243–248.
- Kugonič Nives & Grčman Helena**, 1999. *The Accumulation of Cadmium, Lead and Zinc by different Vegetables from Zasavje (Slovenia) Phytion (Austria) Special issue: "Plant Physiology"* Vol. 39 Fasc. 3 p. 161-165.
- Lăcătușu R., Breabăn I., Cârstea St., Lungu M. & Bretan A.**, 2007. *Abundance of heavy metals in urban soils as concerns genesis and polluting impact*, Lucr. Științ. USAMV Iași, vol 50, seria Agronomie, p. 141-149.
- Lăcătușu R., Cârstea S. & Lungu M.**, 2004. *Soil quality- guiding factor of food quality*, Journal of Environ. and Ecology, 5, 4, p. 736-746.
- Lăcătușu R., Cârstea S., Lungu Mihaela, Kovacsovics Beatrice & Lazăr, Rodica** 2002a. *Soil pollution with cyanides and heavy metals in the Baia Mare area. Ecological reconstruction*, Soil Science, vol. XXXVI, 1, p. 77-87.
- Lăcătușu R., Kovacsovics Beatrice, Bretan A. & Lungu Mihaela**, 2002b. *Heavy metals in the soil after the ecological accident in the Baia Mare area*, Proc. of the 5-th Inter. Symp. On Metal Elements in Environment, Medicine and Biology, Timișoara, November 4-6, p. 227-234.
- Lăcătușu R. & Lăcătușu A. R.**, 2008. *Vegetable and fruits quality within heavy metals polluted areas in Romania*, Carpathian Journal of Earth and Environmental Sciences, Vol. 3, No. 2, p. 115-129.
- Lăcătușu R., Lăcătușu A. R., Stanciu-Burileanu M., Lazăr D. R., Lungu M., Rizea N. & Catrina V.**, 2012. *Phytoremediation of a sludge deposit proceeded from a city wastewater treatment plant*, Carpathian Journal of Earth and Environmental Sciences, Vol. 7, No. 1, p. 71-80.
- Lăcătușu R., Răuță C., Avram N., Cârstea S., Lungu M., Medrea N., Kovacsovics B. & Serdaru M.**, 1996a. *Heavy metals flow in a soil-plant-animal system within the Baia Mare Area (Romania)*, Trans. of the 16-th Symp. "Mengen-und Spurenelemente", Jena, Germany, p. 338-345.
- Lăcătușu R., Răuță C., Cârstea S. & Ghelase I.**, 1996b. *Soil-Plant-Man relationships in heavy metal polluted areas in Romania*, Applied Geochemistry, vol.11, p. 105-107.
- Li J. T., J.W. Qiu J. W., X.W. Wang X.W., Zhong Y., Lan C.Y., W.S. & Shu W.S.** 2006. *Cadmium contamination in orchard soils and fruit trees and its potential health risk in Guangzhou, China*, Environmental Pollution 143, p. 159-165.
- Lorestani B., Cheraghi M., & Yousefi N.** 2011. *Accumulation of Pb, Fe, Mn, Cu and Zn in plants and choice of hyperaccumulator plant in the industrial town of Vian Iran*, Arch. Biol. Sci., Belgrade, 63 (3), p. 739-745.
- Mathieu C. & Pieltain F.**, 2003. *Analyse chimique de sol: méthodes choisies*, Paris, Tec & Doc, 388 p.
- Mohammed M.I. & Sulaiman M.A.**, 2009. *Analysis of some metals in some brands of tea sold in Kano, Nigeria*, Bayero Journal of Pure and Applied Sciences, 2(2) p. 34 – 39.
- Ngole V. M.**, 2011. *Using soil heavy metal enrichment and mobility factors to determine potential uptake by vegetables* Plant, Soil and Environment, 57, (1) p. 75–80.
- Oluwatosin G. A., Adeyolanu O.D., Dauda T.O., & Akinbola G. E.**, 2008. *Levels and geochemical fractions of Cd, Pb and Zn in valley bottom soils of some urban cities in southwestern Nigeria*, African Journal of Biotechnology Vol. 7 (19), p. 3455-3465.
- Order no. 756/1997.** for the approval of the regulation regarding environmental pollution assessment, emitted by: Water, Forests and Environmental Protection Minister, published in: the Official Monitor no. 303 bis from Nov. 6.
- Poggio Laura, Vrščaj Borut, Schulin Rainer, Hepperle Erwin & Marsan Franco Ajmone**, 2009. *Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy)* Environmental Pollution 157, p. 680–689.
- Puschenreiter M. & Horak O.**, 2000. *Influence of different soil parameters on the transfer factor soil to plant of Cd, Cu and Zn for wheat and rye*, Die Bodenkultur 51(1), p. 3-10.
- Singh S., Zacharias M., Kalpana S. & Mishra S.**, 2012. *Heavy metals accumulation and distribution pattern in different vegetable crops*, Journal of Environmental Chemistry and Ecotoxicology Vol. 4 (4), p. 75-81.
- Sun Yuebing, Zhou Qixing & Diao Chunyan** 2008. *Effects of cadmium and arsenic on growth and metal accumulation of Cd-hyperaccumulator Solanum nigrum L.* Bioresource Technology 99, p. 1103–1110.
- Szabó György & Czeller Krisztina**, 2009. *Examination of the heavy metal uptake of carrot (Daucus Carota) in different soil types*, AGD Landscape and Environment 3 (2), p. 56-70.
- Tyree, M.T. & F.W. Ewers**, 1991. *The hydraulic architecture of trees and other woody plants*. New Phytologist, Tansley Review No. 34, 119, p. 345-360.
- Walkley, A. & I. A. Black.** 1934. *An Examination of Degtjareff Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration Method*. Soil Science 37:29-37.
- Yi Li, Hong Yetang, Wang DuoJun & Zhu Yongxuan**, 2007. *Determination of free heavy metal ion concentrations in soils around a cadmium rich zinc deposit* Geochemical Journal, Vol. 41, p. 235-240.
- Yuan-peng Wang, Ji-yan Shi, Qi Lin, Xin-cai Chen & Ying-xu Chen**, 2007. *Heavy metal availability and*

*impact on activity of soil microorganisms along a
Cu/Zn contamination gradient, Journal of*

Environmental Sciences 19, p. 848–853.

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