Carpathian Journal of Earth and Environmental Sciences, May 2013, Vol. 8, No. 2, p. 143 - 152

ASSESSMENT OF HEAVY METALS CONTENT AND POLLUTION LEVEL IN SOIL AND PLANTS IN BAIA MARE AREA, NW ROMANIA

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Abstract: In order to assess the soil pollution level by heavy metals and also the possibility of metals entrance in the food chain via plants, pollution load index (PLI), contamination factors (CF) and soil to plant transfer factors (TF) were calculated. Topsoil samples (1-10 cm) and plants growing on them were collected from four areas in Baia Mare city and surroundings: three polluted areas (Ferneziu, Săsar and Center) and one reference area. The following heavy metals: Cu, Zn, Pb, Cd, Ni, Cr, Co, Mn, Sn were analyzed in soil and plant samples by inductively coupled plasma atomic emission spectrometry. The highest TF were obtained for Cd (0.66-3.13) while the lowest values were calculated for Pb (0.004-0.02). The contamination level of the soil within the investigated areas was assessed according to PLI values. Ferneziu district, where the lead smelter is located, was found being the most polluted site for Cd, Pb, Cu, Zn and Sn. Cluster analysis was conducted in order to classify metals of different sources and origins. Cd, Pb, Sn, Zn and Cu occur as a result of anthropogenic activities while Co, Cr, Mn and Ni in soil can be naturally found in the soil composition

Keywords: contaminated soil, transfer factor, soil pollution, heavy metals, pollution load index

1. INTRODUCTION

The hazard represented by high metal concentrations in soils in the Baia Mare area of Northwest Romania, has been widely publicized and studied extensively since 1995 in several articles (Lăcătuşu et al., 1996; Ciobanu et al., 1999; Culicov et al., 2002; Damian et al., 2008; Levei et al., 2009; Damian et al., 2010) and in a book chapter too (Răuţă et al., 1995). Soil pollution is caused by the heavy metals bearing dust emissions and dispersion from the pollutant sources during over 100 years with a strong increase in the last 50 years.

The main soil pollution sources are: mine entrances (mine openings), ore processing factories, metallurgical factories (a lead smelter and a copper smelter), and tailing ponds. The lead smelter was closed in January 2012, after more than 150 years of production, and the copper smelter has been closed in 2008 after more than 80 years of production.

Currently, the mining and metallurgical industry has reduced the activity by closing or diminishing the production capacity and after the EU accession of Romania in 2007 January 1st, environmental protection measures were implemented and industrial emissions were considerably reduced. However, Baia Mare is facing the historical contamination of the soil with heavy metals (Lăcătuşu et al., 2002; Levei et al., 2009; Oprea et al., 2010, Mihali et al., 2012).

Baia Mare area exhibits a variety of soils that developed on diverse lithology such as volcanic and sedimentary rocks described in detail in the literature (Damian et al., 2008; Lăcătuşu et al., 2008). According to Damian et al., 2008, in the North part and north-eastern part of the city are represented by the regosol, eutricambosol, dystricambosol and andosols types, developed on volcanic deposits. In the South part of the investigated area the most common soils are: aluviosol, luvosol and stagnosol types.

Heavy metals are generally associated with other microelements, raising a major environmental and human health problem due to their high toxicity, low biodegradability and cumulative tendency.

Studies already carried out on the soil pollution with heavy metals in Baia Mare area have been found high concentrations of heavy metals that can be toxic for the vegetation (Schippers et al., 2000) and especially for the animals (Jelea, 2009) and human health (Lăcătuşu et al., 1995; Jelea & Jelea, 2007; Lăcătuşu et al., 2008; Levei et al., 2010).

Normal content levels for Co (12- 151 $mg \cdot kg^{-1}$), Mn (453-884$\cdot$mg kg^{-1}), Cr (12-31 $mg \cdot kg^{-1}$) and Ni (18-50 mg $\cdot kg^{-1}$) in urban soils in Baia Mare area were determined, but Cd (0.3-16.6 $mg \cdot kg^{-1}$), Cu (23-404 $mg \cdot kg^{-1}$), Pb (151-3261 $mg \cdot kg^{-1}$) and Zn (180-2695 $mg \cdot kg^{-1}$) reached strong and very strong polluting levels (Lăcătuşu et al., 2008).

The highest concentrations of heavy metals were found in the eastern part and around the industrial zones in Baia Mare. Concentrations up to 40375 $mg \cdot kg^{-1}$ for Pb and 6122 $mg \cdot kg^{-1}$ for Zn were determined close to the lead smelter and up to 5823 $mg \cdot kg^{-1}$ for Cu around the copper smelter (Damian et al., 2008; Damian et al., 2010). Cd contents in the investigated area (Petruşan et al., 2005) exceeded 10-24 times the intervention threshold value for sensitive use of the land, as set up by the Romanian legislation (Order no 756/1997).

The transfer factors of heavy metals from soil to plants depend on the metal chemical character, on the plant species as well as on several soil characteristics such as pH, soil texture, clay content, organic matter, the presence and interference of other metals in soil, temperature, soil moisture and cation exchange capacity (Cui et al., 2004; Grytsyuk et al., 2006; Big et al., 2012).

The present study aimed to assess the actual state of surface soil pollution taking into account the sources of soil pollution and the most exposed areas: the Ferneziu district, the Săsar district and an area located in central part of the town (Center). The Ferneziu area has been impacted by the presence of the lead smelter that is located in close proximity to the residential zones. The Săsar district is located along the Săsar River and is exposed to the dominant East to West wind and the central area of the town of Baia Mare was influenced by the emissions from the copper smelter.

This paper aims to investigate the contents of heavy metals in soils and plants in Baia Mare area and to establish their transfer factors in several vegetables and plants as a "true" indicator of the soil pollution.

2. MATERIALS AND METHODS

2.1. Soil and plants sampling

Four study areas have been selected: Ferneziu district, Săsar district, the central zone of the municipality and surroundings (Center) as polluted areas and Dura district as reference area (Fig. 1).

According to the Romanian Soil Taxonomy (Florea & Munteanu, 2003; Damian et al., 2008) the main soil types from the studied areas are: eutricambosols and aluviosols in Ferneziu, aluviosols and luvosols in Săsar, luvosols in Center and aluviosols in Dura area.

A random soil sampling had been taken during July-August 2009 from the surface soil (0-10 cm depth) aimed to cover the entire surface of selected areas. Sampling was performed with a stainless steel shovel. A Global Positioning System instrument (GPS) was used to get the precise location of each sampling point.

The sampling locations included residential areas and public parks. They have been chosen in each studied zone by drawing an imaginary area of 1 m^2 on whose diagonal 3 samples of approximately 0.5 kg have been extracted from a depth between 0-10 cm, out of which through mixing and homogenization the representative sample had been obtained.

In Ferneziu area the sampling points were established primarily in private grounds or gardens used for growing vegetables located in the close proximity of residential buildings. People living in this district are growing vegetables for their own consumption. The soil is generally fertilized by application of barnyard manure.

The soil samples were crushed and dried at room temperature for 48 hours, then passed through a 2 mm sieve for the determination of soil characteristics like pH, sum of exchange bases, hydrolytic acidity, humus content and heavy metal content. In Ferneziu area, where the majority of samples were collected from vegetables garden, total nitrogen (N), mobile phosphorus and potassium were also analysed.

In the same time, there had been collected plants growing in the same locations from where the soil samples had been drawn. Especially samples of vegetables like onion (*Allium cepa*) and dill (*Anethum graveolens*) were collected in Ferneziu district while in Săsar district, in the Center area as in the reference Dura area, plants form spontaneous flora were collected: bentgrass (*Agrostis sp.*), clover (*Trifolium repens*) and nettle (*Urtica dioica*).

2.2. Determination of soil characteristics

The pH measurement of the aqueous suspension 1:5 (w/v) of the <2 mm fraction of the soil samples was performed using Consort 2000 pH-meter equipped with a combined pH electrode. Soil suspension was shaken for 2 hours until the pH measurement was taken. Humus content was determined using the Schollenberger method by oxidizing the organic matter from the soil with sulfochromic mixture (Schollenberger, 1945). The degree of bases saturation (V) was calculated using the relation:

$$V\% = \frac{SB}{SB + A_h} \cdot 100 \quad (1)$$

where *SB* represents the sum of exchange bases and A_h is the hydrolytic acidity.

The SB was performed according to Kappen method while the A_h was carried out by titration of the soil extract in sodium acetate solution 1 n with sodium hydroxide 0.05 n.

The total nitrogen content (N) was analysed by Kjeldahl method. Mobile forms of phosphorus and potassium were extracted in acetate-lactate ammonium solution at 3.7 pH followed by colorimetric analysis of phosphorus using Murphy method (Murphy & Riley, 1962) and flame spectrometric determination of potassium.

2.3. Heavy metals determination

Several heavy metals (Cu, Zn, Pb, Cd, Ni, Cr, Co, Mn, Sn) were assayed in the collected samples, both soil and plants samples, by inductively coupled plasma atomic emission spectrometry (ICP-AAS).

In order to perform the heavy metals content determination, a subsample of 100 g was obtained through the method of quarters from the sample of soil dried, crushed and passed through a 2 mm sieve. Then the soil subsample was ground to a fine powder in a Fritsch PM100 mill for 3 min and passed through a sieve of 150 µ. From this subsample, 2.5 g of soil were taken and subjected to mineralization with aqua regia according to ISO 11466: 1999. Blank extractions with quartz sand were carried out for each set of analyses.

The plant samples were thoroughly washed with tap water and distilled water in order to remove the dust, oven dried and ground until passing through a 100 µm sieve. A portion of 1.0 g plant sample was subjected to extraction with aqua regia and hydrogen peroxide following the method from ISO 11466:1999.

The determination of metals in soils and plants samples was done using the inductively coupled plasma atomic emission spectrometer with simultaneous detection Optima 5300 DV (Perkin Elmer), with axial and radial dual vision.

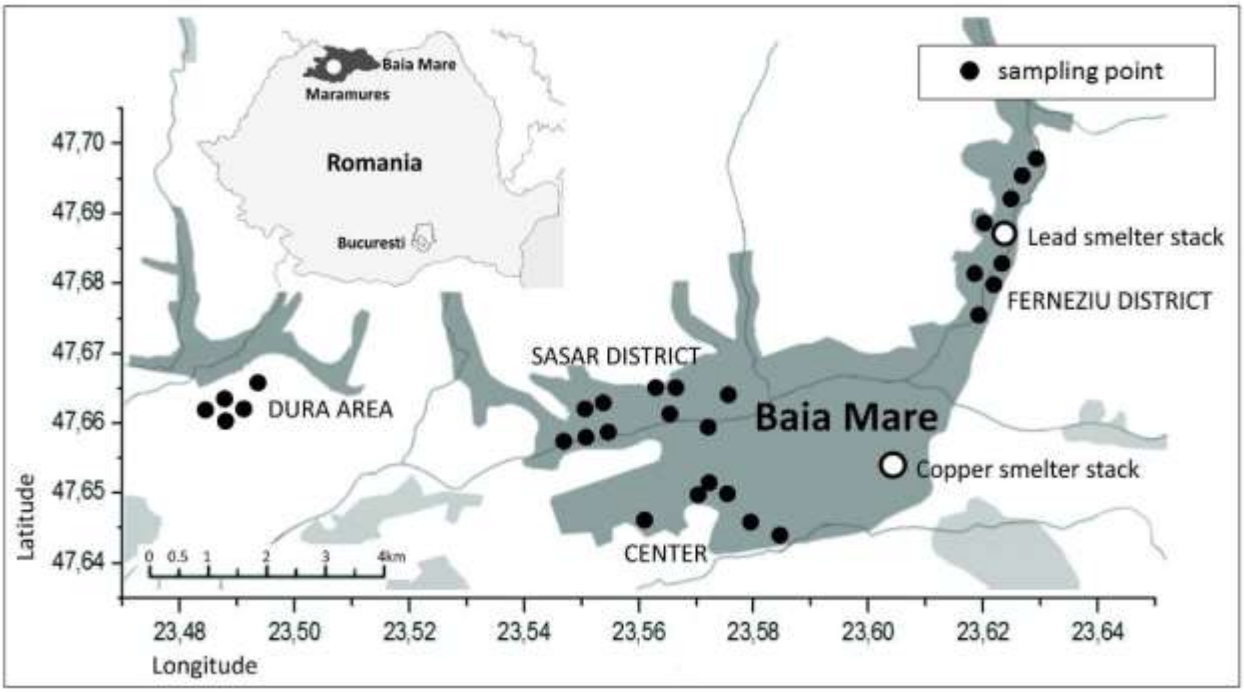

Figure 1. Locations of the investigated areas with the sampling points and the pollution sources in Baia Mare city

All the reagents used to the mineralization of the soil samples (65% HNO_3 and 32% HCl) were p.a. quality (Merck). External calibration were performed using multielemental stock solutions of 1000 $\mu g \cdot mL^{-1}$ from Merck. Dilutions were made with 2% (v/v) solution of nitric acid. The accuracy of the extraction procedures was estimated with a soil certified reference material (SRM 2709, San Joaquin Soil, NIST).

2.4. Pollution load index

In order to define and discuss the soil contamination level, the pollution load index (PLI) was calculated as the n^{th} root of the product of the n CF (Rashed, 2010):

$$PLI = (CF_1 \times CF_2 \times \ldots \times CF_n)^{1/n} \quad (2)$$

where *n* is the number of samples and *CF* is the contamination factor expressed as the ratio obtained by dividing the concentration of each metal in the soil by the background values (from reference area).

2.5. Transfer factors

Transfer factors are generally used in various correlation models for predicting the concentration of a given element in a given plant for a known level of soil contamination (Chojnacka et al., 2005). Soil to plant transfer of metals is one of the main ways of human exposure to soil contamination (Cui et al., 2004). The soil to plants transfer factors (TF) of heavy metals were discussed in numerous studies and research papers (Cui et al., 2004; Chojnacka et al., 2005; Intawongse & Dean, 2006; Kachenko & Singh, 2006; Grytsyuk et al., 2006; Kashif et al., 2009).

The formula for TF's calculation is the same whatever is the intended purpose of the research works as was indicated by Cui et al., 2004:

$$TF = \frac{\text{Concentration of heavy metals in plants}\,(mg \cdot kg^{-1})}{\text{Concentration of heavy metals in soils}\,(mg \cdot kg^{-1})} \quad (3)$$

2.6. Cluster analysis

The cluster analysis was carried out by using the Statgraphics program, based on Ward's method in which the similarity criterion is the squared Euclidean distance. Euclidean distance provides a measure of the similarities between samples. The distance coefficients express the degree of similarity as distance in multidimensional space and thus, as the distance value decreases, the similarity increases (Melegy & El-Agami, 2004).

3. RESULTS AND DISCUSSIONS

3.1. Soil characteristics

Table 1 presents some of the soil characteristics: pH, humus content, sum of the bases (SB) and the degree of base saturation (V) in the studied areas. Ferneziu district is a suburban area with agriculture practice, especially for vegetables grown in households. Therefore, further agrochemical characteristics of soil were also analysed and presented in table 2.

In the Ferneziu area the pH reaction of the soil samples that were collected especially from the garden is medium acid-neutral (5.7-7.5). The degree of base saturation corresponds to oligomezobazic to bazic while the humus supply was medium to high.

Other studies found the pH reaction of the soil in Ferneziu area collected just in the area of lead smelter, acidic for eutricambosol type (3.77-4.40) and slight acid-to neutral for aluviosol type (Damian et al., 2008). In our study the soil sampling was done in agricultural areas where the soil characteristics are influenced by anthropic inputs represented by the natural fertilizers (barnyard manure).

Table 1. Soil characteristics in the studied areas

	pH	SB *(meq/100 g)*	Humus *(%)*	V *(%)*
Ferneziu (8)[a]	6.8 (5.7-7.5)[b]	22.7 (11-37.9)	4.40 (3.48-6.40)	84.9 (61.7-92.5)
Săsar (10)	6.02 (4.5-7.2)	21.97 (1.33-39.68)	7.27 (3.84-10.05)	71.02 (22.97-97.25)
Center (6)	6.63 (6.3-7.1)	23.43 (11.63-37.93)	3.00 (1.39-3.79)	91.62 (84.46-96.51)
Dura (5)	5.84 (5.6-6)	22.08 (17.24-32.67)	3.76 (3.32-4.19)	90.41 (87.84-92.63)

(a) Number of samples; (b) Average (min-max)

Table 2. Agrochemical characteristics of the soils samples in Ferneziu (8) [a]

	N total *(%)*	P mobile *($mg \cdot kg^{-1}$)*	K mobile *($mg \cdot kg^{-1}$)*
Average	0.23	745.62	515
Minim	0.11	121	166
Maxim	0.37	1200	1062

(a) Number of samples

In the Săsar area the pH was more acidic than in Ferneziu area with an average value of 6.02. The type of soil in Săsar district were aluviosols and eutricambosols. The degree of base saturation (V) varied in a large range from oligobazic to bazic (22.97-97.25%). The humus supply was medium to high.

In the Center area the soil reaction was slight acidic to neutral with an average value of 6.63 and submezobazic according to the degree of base saturation. The humus supply was low to medium (1.39-3.79%) with an average value of 3%.

In Dura area the soil presents an acidic reaction (average value of 5.84). According to the degree of base saturation the soil was submezobazic. The soil is moderately assured with humus (average value of 3.76%).

As is shown in table 2, the soil in Ferneziu area is highly supplied with phosphorus considering the mobile phosphorus content in soil while the mobile potassium content in soil reveals a medium to high supply level of this macroelement. Nitrogen content of soil is medium. The microelements contents in soil are due to natural content and anthropogenic inputs (as consequence of the fertilization of the soils in the vegetable gardens).

Although the macroelements N, P and K in soil do not influence directly the uptake of the heavy metals (microelements) from soil to plants but they influence the radicular and the foliar systems of plants. As the radicular and foliar systems are better developed, as the soil volume explored by roots is higher increasing the transfer of microelements from soil to plants.

3.2. Metals concentrations in soil and plants

The metals concentrations in soil and plants samples determined on dry weight (DW) basis in the investigated areas (F-Ferneziu district, S-Săsar district, C-Center) are listed in table 3. Background levels in soil and plants refer to values analyzed in the reference area (Dura area). The average content in plants of each studied heavy metal was compared with the content of the same metal in the plants collected from the reference area. In the case of Cd, Pb, Cu and Zn, the comparison was done also with the MAL (maximum allowable level) according to Romanian legislation (Order no 975/1998).

Table 3. Metals concentrations in soil and plants samples (cultivated plants: onion, dill and plants from spontaneous flora: bentgras, clover and nettle)[a]

		Cd	Pb	Cu	Zn	Co	Cr	Ni	Mn	Sn
Vegetable (mg·kg^{-1} DW)	F (12)[b]	1.51 (0.02-4.81)[c]	38.82 (1.04-255.0)	8.17 (0.35-33.6)	96.45 (30.1-199.0)	0.12 (0.03-0.46)	0.98 (0.15-2.85)	0.92 (0.21-3.22)	60.48 (0.2-260.0)	0.07 (0.02-0.15)
	S (10)	0.67 (0.02-2.58)	2.49 (0.05-11.65)	11.3 (4.9-16.7)	119.28 (19.5-273.0)	0.24 (0.03-1.54)	3.65 (0.08-10.2)	1.75 (0.28-3.02)	71.49 (6.5-202.0)	0.52 (0.06-2.24)
	C (6)	0.11 (0.02-0.21)	1.86 (0.02-5.1)	3.68 (1.05-6.6)	26.88 (2.3-57.1)	0.14 (0.09-0.19)	1.74 (0.5-6.05)	1.15 (0.61-1.85)	17.31 (1.65-29.5)	0.17 (0.03-0.48)
Background level in plants (mg·kg^{-1} DW)		0.16 (0.08-0.24)	1.71 (1.48-2.12)	3.46 (0.45-9.45)	19.7 (13.6-25.1)	0.27 (0.19-0.32)	8.78 (5.95-10.3)	3.49 (3.16-4.09)	203.7 (92.8-389.0)	0.21 (0.09-0.47)
MAL[d] plants (mg·kg^{-1})		0.5	3	50	50	-	-	-	-	-
Soil (mg·kg^{-1} DW)	F (8)	26.0 (0.15-113.0)	4407.5 (115.0-19195)	640.6 (6.5-1730)	1080.3 (100.0-3791)	13.1 (0.2-23.5)	24.8 (0.2-50.5)	13.6 (0.2-29.3)	967.2 (4.25-2124)	5.9 (1.3-21.4)
	S (10)	2.9 (0.6-12.1)	724.5 (257.0-1647)	554.4 (104.0-2968)	574.8 (256.0-1598)	4.3 (0.65-21.1)	14.9 (7.5-25.1)	5.9 (0.35-21.5)	809.0 (453.0-1370)	1.9 (0.6-3.3)
	C (6)	0.5 (0.1-1.2)	264.9 (14.3-152.0)	165.3 (16.6-250.0)	266.0 (58.0-426.0)	3.6 (1.7-6.5)	27.8 (8.1-38.6)	9.0 (7.1-13.0)	484.0 (240.0-876.0)	0.5 (0.2-0.8)
MAL[d] plants (mg·kg^{-1} DW)		0.5	3	50	50	-	-	-	-	-
Background level in soil (mg·kg^{-1} DW)		0.08 (0.05-0.15)	76.7 (65.6-90.2)	83.4 (39.4-139.0)	100.3 (86.5-129.0)	5.3 (3.5-7.8)	27.0 (24.6-31.4)	10.3 (8.7-14.2)	656.5 (608.0-699.0)	0.2 (0.2)
ATV[e] soil (mg·kg^{-1} DW)		3	50	100	300	30	100	75	1500	35

(a) In the Ferneziu area plant species collected were: onion, dill and bentgras while in Săsar, Center and reference area were collected bentgras, clover and nettle (b) Investigated area (number of samples); (c) Average (min-max); (d) Maximum allowable level in dehydrated vegetables and fruits (food), mg·kg^{-1} DW (Order no 975/1998); (e) Alert threshold value in residential soils, mg·kg^{-1} DW (Order no 756/1997).

The plants content of other studied heavy metals (Co, Cr, Ni, Mn and Sn) were compared only with the background values because no MAL's was set up in Romanian legislation (Order no. 975/1998).

Based on the ratio of the average metal content in plant in the investigated area related to the average metal plant content of the background, two groups of heavy metals can be drawn, as shown in table 3: (i) Cd, Pb, Cu and Zn, with contents higher than the background values in Ferneziu district (9.4, 22.7, 2.4 and 4.9 times higher) and Săsar district (4.1, 1.5, 3.3 and 6.1 times higher) while in Center, their contents are similar to the background values; (ii) Co, Cr, Ni, Mn and Sn, with contents in plants lower or equal to the background values.

Compared to the MAL in plants, Cd, Pb and Zn contents are much higher than MAL in Ferneziu district (3.0, 12.9 and 1.9 times higher) and Cd and Zn also in Sasar district (1.3, 2.4 times higher) and under the MAL in Center, while Cu contents in plant are under the MAL in all the investigated areas.

The heavy metals in soil in the investigated areas in Baia Mare city, as shown in table 3 can be classified in three groups (after the ratio between the average content of metal in the considered area and the average content of the background): (i) Pb, Cu and Zn, whom contents are much higher than the background values and alert threshold value (ATV) in all the investigated areas, with special remark to Ferneziu district (57.5, 7.7 and 10.8 times higher than the background values and 88.2, 6.4 and 3.6 times higher than ATV) excepting the Zn contents in Center that are at the same level that ATV; (ii) Cd and Sn, for which the soil contents are much higher than the background values in Ferneziu district (260.0, 29.5 times higher) and Săsar district (29.0, 9.5 times higher) and at the same level in Center, but they do not exceed the ATV, excepting Cd contents in Ferneziu district (8.7 times higher); (iii) Co, Cr, Ni and Mn with contents in soil generally at the same level that in reference area but much lower than ATV.

Hence, it can be assumed that metals as Cd, Pb, Cu, Zn and Sn are coming from anthropogenic activities (mining and non-ferrous metallurgy) and Co, Cr, Mn and Ni are rather related to their natural occurrence in soil. The most polluted area is Ferneziu district, just around the lead smelter, followed by Săsar district, located in the north side of the city contaminated by air pollution with the dust emitted from the lead smelter and Center at the lowest pollution level, even if it is located close to the copper smelter

3.3. Contamination factors and soil contamination level

In order to define and discuss the soil contamination level, the pollution load index (PLI) was calculated. The background values are the average metal concentrations in Dura area.

The contamination level of the soil within the investigated areas was assessed according to PLI values as shown in table 4 while the PLI values calculated for the whole urban area in Baia Mare city are plotted in figure 2.

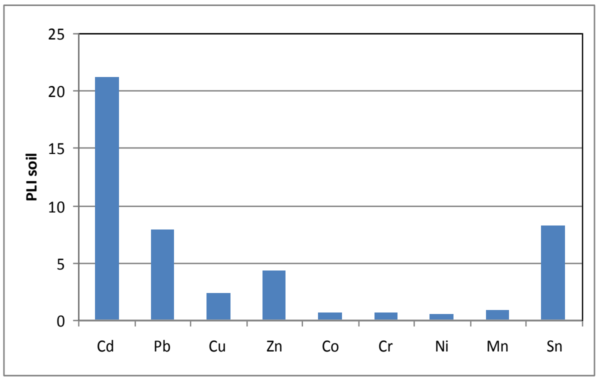

Figure 2. Pollution load index (PLI) for soil from Baia Mare urban area

The highest contamination level in soil was found again for Cd, Pb, Cu, Zn and Sn. As presented before, soil pollution in Baia Mare area is discussed in several papers for years, but no mentions were found for Sn pollution. It was unexpected also for us to find such high contents of this metal in soils sampled from the investigated areas. It is known that Sn shows chemical similarity to Pb, and hence it may occur in the processed ores along with Pb and Cd.

The following cluster analysis will focus on the source of trace metals in soil. The highest contamination level for Cu occurs in Săsar district. This residential area is close to the copper metallurgical smelter being for long time impacted with particulate matters emitted from the dispersion stack and preferentially transported by the dominant East to West wind.

Table 4. Contamination level of the soil in the investigated areas (PLI's)

Area	Cd	Pb	Cu	Zn	Co	Cr	Ni	Mn	Sn
Ferneziu district	56.05	21.06	1.95	6.04	0.69	0.36	0.47	0.48	20.93
Săsar district	24.61	7.57	3.61	4.82	0.46	0.52	0.35	1.16	8.12
Center	4.52	2.31	1.48	2.28	0.65	0.91	0.85	0.67	2.42

No contamination in soil was found for Co, Cr, Ni and Mn, as expected. Cu and Zn produce moderate contamination in soil, they mainly comes from the dust emitted from the copper metallurgical smelter, but Zn was also emitted from the lead smelter, and as it can be seen, it has higher contamination level than Cu.

The individual results related to the contamination level of the soil with metals in the investigated polluted areas matches very well with the global PLI for the whole urban area in Baia Mare city.

Again, the highest contamination level according to PLI's is shown for Cd, Pb and Sn (21.19, 7.91 and 8.22), moderate contamination level for Zn and Cu (4.31 and 2.35) and no contamination for Co, Cr, Ni and Mn (0.57, 0.53, 0.48 and 0.76).

3.4. Transfer factors

The soil to plants transfer factors (TF) for metals were calculated and discussed in order to assess the "true" pollution level of the soil as related to their possible entrance in the food chain. Soil to plant transfer of metals is the major way of human exposure to soil contamination (Cui et al., 2004).

TF values are affected by several factors as: metal chemistry, type of soil, soil characteristics and also the plant species. TF (on dry weight basis) were calculated for all the sampling points and all the plants sampled from the soil in each polluted area for the investigated trace metals and are listed in table 5.

The contamination factors (CF) are presented also in table 5. Based on the CF values, PLI's indexes were calculated and discussed in section 3.3. The TF values must be discussed by taking into account the soil content of the heavy metal or the CF. High TF values accompanied by high CF levels represent a potential hazard for the health of consumer as well as for grazing (Rashed, 2010).

TF values ranged between 0.00009 for Pb and 16.466 for Cd. The highest TF was obtained for Cd in all areas, including the reference area (1.47-1.78). In fact, Cd is already known for its mobility from soil to plants (Kachenko & Singh, 2006; Kirkham, 2006). TF's are even higher than 1, which means vegetables are accumulating Cd and should be recommended to not use them as food especially when the plants are grown in soil with high contamination factors. Thus, TF value of 3.13 for Cd in Ferneziu and CF value of 347.1 represent a concern for the health of the consumers.

Low and very low values of TF for Pb (0.004-0.02) were calculated, that is somewhat unexpected for us, because the CF's for Pb in soil are very high. It can be concluded that in Baia Mare city, where soil is highly contaminated (as defined by the Romanian legislation or compared to the background values in the reference area), Pb is not transferred from soil to plants as dramatically as it was expected. However, Pb contents in plant in Ferneziu area exceed the MAL, but referred to its huge content in soil, its TF is much lower than for other metals. TF for Sn, Zn and Cu are lower than for Cd, but slightly higher than for Pb.

Table 5. Soil to plant transfer factors (TF) for metals

Metals		Ferneziu district	Săsar district	Center	Reference area (Dura)
Cd	TF*	3.13 (5E-04-16.47)	0.48 (0.01-1.31)	0.66 (0.03-3.0)	1.68 (1.47-1.78)
	CF**	347.1 (2.0-1506.7)	38.1 (7.33-161.3)	6.56 (0.67-15.3)	
Pb	TF	0.01 (2E-04-0.02)	0.004 (1,4E-05-0.01)	0.02 (9E-05-0.1)	0.02 (0.018-0.03)
	CF	57.45 (1.5-250.2)	9.44 (3.35-21.5)	3.45 (0.19-6.67)	
Cu	TF	0.09 (0.001-0.51)	0.05 (0.003-0.09)	0.08 (0.005-0.37)	0.07 (0.003-0.24)
	CF	7.69 (0.08-20.8)	6.65 (1.25-15.9)	1.98 (0.2-3.0)	
Zn	TF	0.24 (0.03-0.91)	0.25 (0.07-0.58)	0.17 (0.01-0.66)	0.2 (0.15-0.25)
	CF	10.77 (1.0-37.8)	5.73 (2.55-15.9)	2.65 (0.58-4.25)	
Co	TF	0.08 (0.001-0.27)	0.15 (0.001-0.68)	0.04 (0.03-0.06)	0.05 (0.04-0.07)
	CF	2.48 (0.04-4.45)	0.82 (0.12-4.0)	0.77 (0.32-1.43)	
Cr	TF	0.18 (0.004-0.95)	0.3 (0.004-0.75)	0.15 (0.02-0.75)	0.33 (0.22-0.41)
	CF	0.92 (0.01-1.87)	0.55 (0.28-0.93)	1.03 (0.3-1.43)	
Ni	TF	1.25 (0.01-9.4)	0.84 (0.03-3.17)	0.14 (0.05-0.25)	0.36 (0.24-0.47)
	CF	1.32 (0.02-2.85)	0.57 (0.03-2.09)	0.88 (0.69-1.27)	
Mn	TF	0.31 (1E-04-1.87)	0.11 (0.01-0.45)	0.04 (0.003-0.07)	0.32 (0.13-0.64)
	CF	1.47 (0.01-3.24)	1.23 (0.6-3.25)	0.74 (0.37-1.33)	
Sn	TF	0.02 (0.004-0.11)	0.27 (0.02-0.83)	0.56 (0.05-2.4)	1.06 (0.44-2.35)
	CF	29.66 (6.68-107.1)	9.35 (3.0-16.25)	2.63 (1.0-3.75)	

* Transfer factor: average (min-max); ** Contamination factor for soil: average (min-max)

Table 6. The matrix of correlations for the transfer factors of selected microelements and soil characteristics

	log(TF Cu)	log(TF Cd)	log(TF Pb)	log(TF Sn)	log(TF Zn)	pH	V	Humus
[(a)]log(TF Cu)	1							
log (TF Cd)	0.672*	1						
log (TF Pb)	0.515*	0.601*	1					
log(TF Sn)	-0.124	0.170	0.243	1				
log (TF Zn)	0.657*	0.683*	0.661*	-0.174	1			
pH	0.142	0.065	0.008	-0.122	-0.148	1		
V	0.063	0.042	0.011	0.228	-0.206	0.616*	1	
Humus	-0.104	-0.189	-0.406*	-0.584*	0.046	-0.096	-0.331	1

a - TF were transformed as log (TF) in order to obtain normal variables;* Marked correlations are significant at $P < 0.05$ at the 95% confidence level

Similar results for Cd, Pb, Cu and Zn were obtained in other researches (Cui et al., 2004; Intawongse & Dean, 2006; Kachenko & Singh, 2006; Grytsyuk et al., 2006). TF for Co, Cr and Mn are low (<0.4). Special mention has to be done for Ni where TF in Ferneziu is higher than 1, but its contents in soil and plants are small. Similar conclusions were mentioned also by Chen et al., (2009). Average TF for each metal calculated for all the sampling locations in Baia Mare city decrease following the sequence: Cd >Ni >Sn >Cr ≅Zn ≅Mn >Co ≅Cu >Pb. Similar results were obtained in several researches (Chojnacka et al., 2005; Intawongse & Dean, 2006; Kachenko & Singh, 2006).

A recent study concerning the bioavailability of heavy metals (Cd, Cu, Pb, Zn) in soil-plants system around the city of Baia Mare (Big et al., 2012) where the carrot roots were investigated, reported also Cd having the highest mobility while a low mobility was found for Pb. High values of transfer factors for Cd and Zn were reported (Lăcătuşu et al., 2012) in particular soil-plants systems with plants grown in the mud pond with sludge from municipal wastewater having high trace metal content and high moisture content.

The correlation coefficients for the transfer factors of heavy metals with the highest PLI's indexes (Cd, Pb, Zn, Sn, Cu) and also the correlation coefficients between the considered TF's and the main soil characteristics were calculated using Stagraphics program (table 6).

Positive correlations were found between the pairs of TF for Cu, Zn, Cd and Pb indicating synergetic uptake of these elements by plants. Negative correlations were found between humus content of soil and TF for Sn and Pb indicating a reduce uptake of these metals when the plants are grown in rich in humus soil.

3.5. Cluster analysis

To further explore the correlation between the studied metals in soil, cluster analysis was performed. The cluster analysis for the studied heavy metals for Baia Mare city is shown by the dendrogram in figure 3.

The general shape of the dendrogram suggests two groups of metals: (i) group 1 - Cd, Pb, Sn, Zn and (ii) group 2 - Co, Ni, Mn, Cr, Cu, that appear to be rather different as their linkage distance is 60. Since group 1 contains metals that tend to come from anthropogenic activities, it results that metal's source plays an important role in grouping the metals when the Ward's method is used.

Metals included in the first cluster are very similar (distance<5) and seems to originate from the dust emitted from the lead smelter running in Baia Mare city from more than 150 years. Metals in the second cluster can be divided also into two subgroups, the first one: Co, Ni, Mn, Cr shows moderate similarity (distance <20) and are related rather to the natural occurrence in the soil.

A special remark has to be done to Cu that represents the second subgroup and joints the first one at 10 points distance. Cu was mainly emitted by the copper smelter located near Center area and appears to be very different from metals in the first group that comes from the lead smelter.

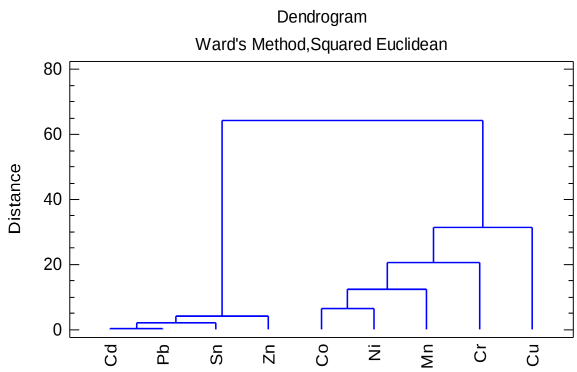

Figure 3. Dendrogram for heavy metals contents in soil in Baia Mare area

4. CONCLUSIONS

The soil and plants pollution level with trace metals was studied in Baia Mare area using contamination factors, pollution load index and cluster analysis. Ferneziu district, where the lead smelter is located, was found as the most polluted site, for Cd, Pb, Cu, Zn and Sn followed by Săsar district. The third investigated area (Center) undergoes moderate to strong pollution. This reveals that emission of the dust from the metallurgical smelters is the main way of introducing metals into the environment.

The traceability of metals in plants was studied using the soil to plant transfer factors.

The high mobility of Cd and the low mobility of Pb were highlighted, even in Ferneziu area, where the soil pollution is extremely strong. It is assumed that the vegetables grown in this area pose a potential health risk on the consumers, due to their high contents of Cd.

The differences between metals shown by the cluster analysis were explained by their different origin. Cd, Pb, Sn, Zn and Cu occur as a result of anthropogenic activities with smelters being the likely contributor. On the other hand, Co, Cr, Mn and Ni in soil can be naturally found in the soil composition.

ACKNOWLEDGEMENTS

The present researches were supported by the Romanian Ministry of Education and Research, within the PNCDI II Program (Project CISPPA no. 52157/2008). We grateful thank for the financial support.

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Received at: 18. 06. 2012
Revised at: 12. 04. 2013
Accepted for publication at: 16. 04. 2013
Published online at: 22. 04. 2013