Assessment of Cu, Pb, Zn and Cd Availability to Vegetable Species Grown in the Vicinity of Tailing Deposits from Baia Mare Area

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In this study, the plant availability of Cu, Pb, Zn and Cd in plant soil-systems from the vicinity of tailing deposits in Baia Mare mining area was assessed. In order to evaluate the contamination level with heavy metals, aqua regia extractable metal contents from soil and tailings were determined. The DTPA extractable metals contents were correlated with those from carrots and cabbages. The results showed that significant percents of metals were extracted in DTPA and that soil and vegetables are highly polluted.

Keywords: heavy metals, DTPA, soil, vegetables, plant uptake.

In mining areas large quantity of mineral processing wastes are stored in tailing deposits characterized by high concentrations of metals that can be mobilized by weathering and leaching [1]. Soils from the vicinity of tailing deposits represent an increasing concern due to the excessive accumulation of metals, becoming toxic to both plants and animals by their entry into food chain [2]. The toxicity of metals depends not only on their total concentration but also on their mobility and availability to plants [3].

There are numerous studies about environmental pollution due to mining and ores processing [4 - 9]. Such studies were also carried out also in Romania [10 - 13]. Determination of total metal content is an important step in estimating the level of soil pollution and the potential risk in comparison with the quality standards but provides no information regarding their chemical nature or mobility. Different approaches have been used to describe the mobility of heavy metals in soils, but the most often used are selective extractions [14].

The objective of this study was to investigate the levels of Cu, Zn, Cd and Pb contamination in soils, tailings and vegetables in the vicinity of tailing deposits from Baia Mare mining area and to assess the availability of these metals to vegetables by computing the plant uptake factors.

Experimental Part

Site Description and Sampling

The studied villages (Recea and Tauti Magherausi) are located near three tailing deposits: one in preservation for 20 years and the other two still in use to collect the wastewaters from ore processing plants of Baia Mare area. The studied area is shown in figure 1.

In the autumn of 2007 a number of 30 soil, 30 cabbage leaves (*Brassica oleracea)*, 30 carrot taproots (*Daucus carota sativus*) samples were collected from private gardens of residents from the two villages. The studied vegetable species are commonly grown and consumed in the area and were collected just before shedding to assure maximum metal accumulation. Also 10 tailing samples were collected from the pond walls. The soil and tailing samples were collected from 0-20 cm depth, using a stainless steel shovel. All samples were stored in clean, labeled, polyethylene bags, closed tightly to avoid contamination during transportation to the laboratory.

Materials and methods

Soils and tailings

Soil and tailing samples were air dried to constant weight and sieved through the 2 mm sieve. The fraction < 2 mm was split in two parts. One part was stored in polyethylene bags for the determination of DTPA-extractable metal contents. The other part was ground to a fine powder in a tungsten-carbide swing mill for 3 min and sieved through 250 μm sieve, homogenized and stored in polyethylene bags until the *aqua regia* extraction.

The *aqua regia* extractable metals in soils and tailings were determined according to ISO 11466:1995. An amount of 1 g sample (<250 mm) was weighted, introduced into the reaction flask and maintained at room temperature for 16 h with 21 mL of 12 M HCl and 7 mL of 15.8 M HNO_3. The mixture was then heated under reflux conditions for 2 h. The solution was filtered and diluted to 100 mL with 0.5 M HNO_3. Heavy metal concentrations were determined by inductively coupled plasma atomic emission spectrometry

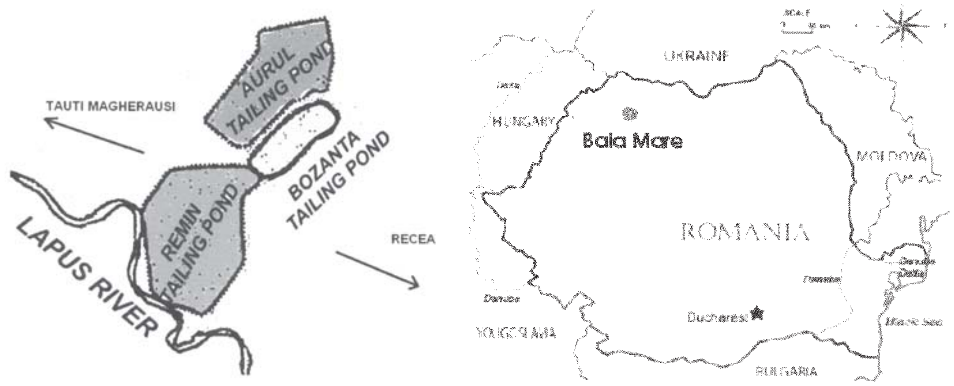

Fig. 1. Location of the study area

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(ICP-AES) using the scanning spectrometer SPECTROFLAME (Spectro Analytical Instruments, Kleve, Germany).

The available metal contents of soils were extracted in DTPA (diethylenetriaminepentaacetic acid) according to ISO 14870:2001. An amount of 10 g of soil sample (<2 mm) was weighted into a 125 mL Erlenmeyer flask, then 20 mL of DTPA extracting solution was added and shaken for 2 h at room temperature using a magnetic stirrer. The solution was filtered and diluted to 100 mL with ultrapure water. DTPA-extractable contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) using the ELAN DRC II-Perkin Elmer, USA). The detection limits for metals determination in ICP-AES following the *aqua regia* extraction were Cu 0.35, Pb 2.2, Zn 0.5, Cd 0.25 mg/kg and in ICP-MS following the DTPA extraction were 0.005 mg/kg for Cu, 0.04 for Pb, 0.01 for Zn, 0.005 for Cd.

Vegetables

The collected vegetable samples were washed with tap water, then with distilled water to remove superficial dust, oven-dried at 80-90°C for 15-30 min and at 65°C for 12-24 h [15]. The dried samples were ground with a stainless steel mill to pass a 0.5 mm sieve. A portion of plant material (*ca.* 5 g) was accurately weighed into a reaction flask and digested with concentrated HNO_3 and $HClO_4$ (5:1 v/v). The metal contents were measured by the procedure described for DTPA-extractable metal analysis from soil. Blank extractions were carried out for each set of analyses. Analytical grade or suprapure quality reagents as well as ultrapure water obtained from a Milipore Direct Q 3 purifier system were used to prepare solutions.

Results and discussion

The DTPA extraction method was initially designed to predict micronutrient deficiencies in neutral to calcareous soils [16], but it has been also employed for the estimation of metal availability for plants [17]. Range, mean and standard error of mean for *aqua regia* and DTPA-extractable Cu, Pb, Zn and Cd contents in soils, tailings and vegetables are presented in table 1.

The obtained results showed that in soil, the *aqua regia* extractable Pb content ranged between 108-399 mg/kg, with an average value of 248 mg/kg. The concentration of

Table 1

RANGE, MEAN AND STANDARD ERROR OF MEAN FOR *AQUA REGIA* AND DTPA - EXTRACTABLE Cu, Pb, Zn AND Cd CONTENTS IN SOILS, TAILINGS AND VEGETABLES

	Pb	Cu	Zn	Cd
***Aqua regia*- extractable heavy metals in soil**				
Range	108-399	48.3-238	184-645	0.15-4.3
Mean	248	104	359	1.63
SEM	78.8	38.8	133	1.14
DTPA-extractable heavy metals in soil				
Range	7.61-98.4	10.6-52.1	10.3-101	0.01-1.85
Mean	46.7	26.5	40.6	0.47
SEM	23.0	10.2	22.0	0.48
Heavy metals in cabbages				
Range	0.07-2.57	0.34-16.1	3.41-30.2	0.05-1.99
Mean	0.77	3.78	9.03	0.61
SEM	0.55	3.41	5.64	0.58
Heavy metals in carrots				
Range	0.27-3.10	0.68-21.8	1.84-23.1	0.01-2.31
Mean	1.32	6.50	9.91	0.77
SEM	0.75	4.59	4.79	0.62
Heavy metals in tailings				
Range	200-4571	38.9-1435	199-6734	0.005-90.0
Mean	1885	453	1414	16.8
SEM	1550	403.2	2023	27.2

SEM = standard error of mean

Cu was between 48.3 and 238 mg/kg with an average of 104 mg/kg, Zn between 184 and 645 mg/kg, average 359 mg/kg and Cd concentration varied in the range of 0.15-4.3 mg/kg, with an average of 1.63 mg/kg.

Aqua regia extractable Pb contents exceeded the intervention level (100 mg/kg) in all soil samples, 43.3% of Cu, 56.6% of Zn and 10% of Cd samples contents exceeded alerts level (100 mg/kg, 300 mg/kg and 3 mg/kg, respectively) for sensitive soils, according to Romanian legislation (Ministerial Order 756/1997).

The average *aqua regia* extractable metal contents were, in all cases, lower than those found in soils collected from the vicinity of Pb and Ag processing smelter in the Pribram region in the Czech Republic [7]. The average values of Pb, Cu, Zn and Cd were also lower than that found by Burt in smelter contaminated soils from Deer Lodge Valley, Montana, USA [19].

A relatively high fraction of *aqua regia* extractable metal content was extracted in DTPA. Thus, an average of 18.5% of Pb, 11% of Zn, 26.2% of Cu and 30.9% of Cd, respectively were DTPA-extractable. These values were higher than those found in soils from a Spanish mining region [18]. The concentration limit of 20 mg/kg DTPA-extractable Pb advocated to avoid human risk [6] was exceeded in almost all samples.

The average *aqua regia* Cu concentration was lower to that found in soils from the vicinity of a deactivated mining site in the Amazon region of Brazil [20], whilst the average percent of DTPA-extractable Cu was much higher in our study (26.2% compared to 9.2%).

In tailing samples, the concentrations of studied metals varied widely. The average concentrations of Pb, Cu, Zn and Cd in tailings were 7.6, 4.4, 3.9 and 10.3 times higher than those in soils. The values for *p*H in tailing samples ranged between 3.52 and 6.21 showing an increased mobility of metals.

Pb, Cu, Zn and Cd concentrations in vegetables sampled varied similarly with those in soil. Pb levels ranged from 0.07 to 2.57 mg/kg dry weight in cabbages and from 0.27 to 3.10 mg/kg in carrots, with mean values of 0.77 and 1.32 mg/kg, respectively. Cu concentrations were between 0.34 and 16.1 mg/kg in cabbages and between 0.68 and 21.8 in carrots with an average of 3.78 and 6.50 mg/kg, respectively. For Zn, the concentration ranges were 3.41-30.2 mg/kg for cabbages and 1.84-23.1 mg/kg for carrots. Cd concentrations varied between 0.05 and 1.99 mg/kg in cabbages and between 0.01 and 2.31 mg/kg in carrots, with mean values of 0.61 and 0.77 mg/kg, respectively.

The metals concentrations in vegetables were compared to maximum levels of lead (0.30 mg/kg in cabbage and 0.10 mg/kg in carrot) and cadmium (0.20 mg/kg in cabbage and 0.10 mg/kg in carrots) according to European Commission Regulation (EC) No 1881/2006. In all carrot samples Pb concentrations are above maximum levels and Cd concentrations exceeded maximum level in 90% of carrots. In cabbage samples Pb concentrations are above maximum level in 73.3% of samples and Cd exceeded maximum level in 70%.

Interrelationships among the aqua regia and DTPA-extractable heavy metals in soil*s*

Correlation matrices for heavy metals in the soils and vegetables to determine the interrelationships between metals are presented in tables 2-5. A*qua regia* extractable Pb was positively correlated with Pb extractable in DTPA and with Pb in both vegetables, similar correlations were found for Cu, Zn and Cd; Pb extractable in DTPA with Pb in both vegetables, Zn extractable in DTPA with Zn in cabbages; Pb in cabbages with Pb in carrots and similar correlations for Zn and Cd.

These findings suggest interaction between Pb, Cu, Cd and Zn in both vegetables and soil is important, in relation to the known geochemical association between the studied metals. The soil metal concentrations appear to influence the uptake of Pb, Cu, Cd, Zn in vegetables [21].

The correlation analysis of *aqua regia*-extractable metals in tailings (10 samples) revealed a significant correlation (r=0.937, at p<0.01) between Cu and Zn, indicating similar sources of contamination.

The relationship between contaminant concentrations in soil and edible plant material is highly specific to the plant species. The relationship between contaminant concentration in vegetables and the concentration in soil is described using Plant Uptake Factor (PUF), which is defined as follows:

PUF = Concentration in plant (mg/kg) / Concentration in soil (mg/kg)

Table 2
CORRELATION MATRIX FOR PB IN SOIL AND VEGETABLES

	PbT	PbE	PbCabbage	PbCarrot
PbT	1.00	0.825*	0.804*	0.813*
PbE		1.00	0.699*	0.579*
PbCabbage			1.00	0.761*
PbCarrot				1.00

T denotes *aqua regia*-extractable metal; E denotes DTPA-extractable heavy metals;

* significant at p=0.01 levels, n=30.

Table 3
CORRELATION MATRIX FOR CU IN SOIL AND VEGETABLES

	CuT	CuE	CuCabbage	CuCarrot
CuT	1.00	0.778*	0.579*	0.599*
CuE		1.00	0.401	0.475
CuCabbage			1.00	0.527
CuCarrot				1.00

Table 4
CORRELATION MATRIX FOR ZN IN SOIL AND VEGETABLES

	ZnT	ZnE	ZnCabbage	ZnCarrot
ZnT	1.00	0.862*	0.736*	0.575*
ZnE		1.00	0.757*	0.540
ZnCabbage			1.00	0.798*
ZnCarrot				1.00

Table 5
CORRELATION MATRIX FOR CD IN SOIL AND VEGETABLES

	CdT	CdE	CdCabbage	CdCarrot
CdT	1.00	0.583*	0.857*	0.798*
CdE		1.00	0.420	0.510
CdCabbage			1.00	0.782*
CdCarrot				1.00

The PUF values quantify the relative differences in bioavailability of metals to plants and identify the efficiency of a plant species to accumulate a given metal. The PUFs for Cu and Pb (0.01-0.1), and Cd and Zn (1-10) were used for comparison [22]. These factors were based on the root uptake of metals and surface absorption of atmospheric metal deposits [21].

The obtained values for PUF are shown in table 6. No sample exceeded the PUF values[22].

Table 6
THE AVERAGE PUFs VALUES FOR THE VEGETABLES

Element	Cabbages	Carrots
Pb	0.0029	0.0051
Cd	0.3797	0.5729
Zn	0.0246	0.0284
Cu	0.0355	0.0616

The DTPA-extracted Pb have a positive correlation (r=0.51) with the metal uptake factor in cabbages. No other significant correlation were found between DTPA-extractable metal and its uptake factor.

Conclusions

The results showed that metal concentrations of polluted soils varied widely, in most cases exceeding the corresponding alert levels. The high percentages of DTPA-extractable metals indicate an anthropogenic pollution. The risk is especially high for Cd and Pb, more toxic elements. Due to the high heavy metal content in the studied area the metal accumulation in vegetables grown in the vicinity of industrial sites represents a potential risk for public health.

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