J. Plant Develop.
17 (2010): 139-144

ASSESSMENT OF Pb, Cd, Cu AND Zn AVAILABILITY FOR PLANTS IN BAIA MARE MINING REGION

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Abstract. In order to evaluate the mobility of heavy metals in soil from Baia Mare mining region, the total, water and DTPA extractable metal contents were determined. The results showed that despite the high total metals contents and the high percentages of plant available metals only a low percent was water soluble, indicating a potential accumulation of metals in trophic chain and a potential risk for public health. Among the investigated metals, the plant available Pb and Cd species are the most severe contaminants. Significant correlations between total and DTPA extractable metals were found for Cu (r=0.510) and Pb (0.418), and also an affinity between total and water extractable metals were identified for Cu (0.366), Pb (0.502) and Zn (0.597).

Key words: Heavy metals availability, DTPA extraction, soil, mining

Introduction

Heavy metals represent a potential hazard to humans and environment. In industrial areas the heavy metal contents from anthropogenic sources are several times higher than those from natural ones [NRIAGU & PACYNA, 1988]. In addition, areas far from industrial centres also show increasing heavy metal concentrations due to long-range atmospheric transport [CEMEK & KIZILKAYA, 2006]. Mining and ore processing industry is one of the major sources of metals releasing into the environment [CASSELLA & al., 2007; BOUGHRIET & al., 2007; VANDERLINDEN & al., 2006; VANEK & al., 2005; CONESA & al., 2007; MACKLIN & al., 2003, LEVEI & al., 2009, MICLEAN & al., 2009].

Although the total metal concentration is commonly used in soil quality standards, it provides no information regarding the metals chemical nature or mobility [SILVEIRA & al., 2006; WALTER & al., 2006]. To assess the metals availability form soil to plant a great variety of single or sequential extraction schemes have been developed [FUENTES & al., 2004; PEREZ-SANTANA & al., 2007; ABOLLINO & al., 2006]. The DTPA (diethylenetriaminepentaacetic acid) extraction method was initially designed to predict micronutrient deficiencies in neutral to calcareous soils [LINDSAY & NORWELL, 1978], but it has been also employed for the estimation of metal availability for plants [MAIZ & al., 2000]. Water soluble metals represent the most ecotoxicologically relevant fraction in the environment, due to their high contamination potential of the food chain, surface water and groundwater [MEERS & al., 2006].

The objective of this study was to investigate the availability of Cu, Pb, Zn and Cd from soil to plants in Baia Mare mining region using selective extraction in water and DTPA.

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Material and methods

Site description and sampling

In the Baia Mare area, around an industrial complex involved in mining, metallurgical and chemical activities, the environment and particularly the soils are polluted due to the acid rains and heavy metal emissions [LACATUSU & al., 2001]. The region became of international concern after the cyanide spill accident in January 2000 that affected the ecosystem of Tisa and Danube rivers. Despite the fact that the large industrial plants have reduced their activities and some of them were closed, the area is still highly polluted [LEVEI & al., 2009].

A number of 50 surface soil samples were collected in the summer of 2009 from the Baia Mare town, using a stainless steel shovel. Samples were air dried to constant weight, sieved through the 2 mm sieve. The fraction < 2 mm was stored in polyethylene bags until the determination of total, water and DTPA-extractable metal contents.

Chemical analysis

The total metal concentrations in soils were determined after aqua regia digestion. An amount of 1 g soil sample was weighted, introduced into the reaction flask and heated under reflux conditions for 2 h with 21 ml of 12 M HCl and 7 ml of 15.8 M HNO_3. The solution was filtered and diluted to 100 ml with 0.5 M HNO_3. Total heavy metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using the scanning spectrometer SPECTROFLAME (Spectro Analytical Instruments, Kleve, Germany).

The plant available metal contents of soils were determined by extraction in water and DTPA. The DTPA extractable metal content was determined using a mixture of 0.005 mol L^{-1} DTPA, 0.01 mol L^{-1} $CaCl_2$, 0.1 mol L^{-1} triethanolamine (TEA) with pH adjusted to 7.3 with 1 mol L^{-1} HCl solution. An amount of 10 g of soil sample was weighted into a 125 mL flask, and shaken for 2 h at room temperature using a magnetic shaker with 20 mL of DTPA extracting solution. The extracts was filtered and diluted to 100 ml with ultrapure water. The water extractable metal content was determined in a 1:10 soil/water mixture. An amount of 5 g of soil sample was shaken with 50 ml water for 2 h at room temperature. The solution was filtered and diluted to 50 ml with ultrapure water. Water and DTPA-extractable metal contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) using the ELAN DRC II-Perkin Elmer, USA).

Soil pH was measured in a suspension of 1:5 soil/water ratio. The suspension was allowed to stand 1 h prior to pH measurement using a Jenway ion-meter.

Results and discussion

The statistic parameters of total, water and DTPA extractable Cu, Pb, Zn and Cd contents are presented in Tab. 1. Due to the fact that soils were sampled from the Baia Mare town the results were compared with the guidelines values for sensitive soil according to Romanian legislation [Ministerial Decree no. 756/1997].

The total contents of all metals were high, exceeding the alert values for sensitive soils (residential and agricultural use) for the most samples. In case of Pb and Zn the 1^{st} quartile is higher and in case of Cu and Cd is around the corresponding alert level for sensitive soil. For all samples the 3[rd] quartile was much higher than the action trigger value for all metals. The average total metal content exceeded the action trigger values for sensitive use according to Romanian legislation, 1.5 times in case of Cu and Cd, 3 times in case of Zn and 18 times in case of Pb.

Tab. 1. Descriptive statistics of total, water and DTPA extractable Cu, Pb, Zn and Cd in soil

	Cu			Pb		
	Total	**DTPA**	**Water**	**Total**	**DTPA**	**Water**
	(mg kg^{-1})					
Min	38.1	6.5	1.4	87.8	0.1	0.7
Max	1770	187	147	23300	753	16.2
Average	314	58	12.5	1790	153	3.3
Median	168	45.3	6.9	496	87	1.6
Skewness	2.68	1.63	5.39	4.66	2.99	2.32
Kurtosis	9.02	2.32	30.2	23.3	10.4	5.23
1 st quartile	109	25.6	5.5	404	70	1.2
3 rd quartile	367	70.0	11.0	1420	156	3.5
Alert value	100	-	-	50	-	-
Action trigger value	200	-	-	100	-	-
	Zn			**Cd**		
	Total	**DTPA**	**Water**	**Total**	**DTPA**	**Water**
	(mg kg^{-1})					
Min	109	16.3	0.66	1.9	0.28	0.01
Max	11500	351	355	29.9	9.4	2.2
Average	1828	96.9	26.7	7.9	2.3	0.56
Median	737	75.4	6.12	3.5	1.7	0.14
Skewness	2.43	1.94	4.26	1.59	2.30	1.68
Kurtosis	5.67	3.43	19.2	2.00	6.10	2.50
1 st quartile	436	39.6	1.8	3.1	1.2	0.1
3 rd quartile	1705	118	10.9	11.4	2.8	0.9
Alert value	300	-	-	3	-	-
Action trigger value	600	-	-	5	-	-

Total = concentration of metal extracted in aqua regia
DTPA = concentration of metal extracted in DTPA
Water = concentration of metal extracted in water

The total metal contents in soil were, in all cases, higher than those from the vicinity of Pb and Ag processing smelter in the Pribram region in the Czech Republic [VANEK & al., 2005]. The median values of total Pb, Zn and Cd were similar, whilst that of Cu was lower than those from Deer Lodge valley smelter area in Montana, USA [BURT & al., 2003]. The water soluble metal contents and the average percent of DTPA-extractable Cu were higher in our study, while the average total Cu concentration was similar to that found in heavily polluted soils from the vicinity of a deactivated mining site in the Amazon region of Brazil [CASSELLA & al., 2007]. The percentages of water extractable Pb and Zn in our soil samples were similar to those found in soils from a Spanish mining region, but the average percentage of the found DTPA extractable metals was much higher [CONESA & al., 2007].

The content of DTPA-extractable Pb, Cu and Cd from soil exceeded the alert level in 83%, 9% and 17% of samples, respectively. The concentration limits of 20 mg kg^{-1} and

70 mg kg^{-1} DTPA-extractable Pb and Zn respectively, advocated to avoid human risk [WINTER SYDNOR & REDENTE, 2002] were exceeded in 94% and 54% of samples in case of Pb and Zn respectively. In case of Pb the 1^{st} quartile of the DTPA-extractable content exceeded the alert value and the 3^{rd} quartile the action trigger value for sensitive soils. A relatively high fraction of the total metal content was extracted in DTPA. Thus, an average of 22% of the total Pb content was DTPA-extractable and only 0.5% was water-extractable. The corresponding percentages for the other metals were: 11% and 2.3% for Zn, 24% and 4.4% for Cu and 43% and 4.1% for Cd, respectively.

The water soluble content of Cu, Pb and Zn was small compared to the total metal content and that of Cd was below the detection limit (1.4 mg kg^{-1}) of the method in the majority of samples. The average percentages of DTPA and water soluble metals are presented in Fig. 1.

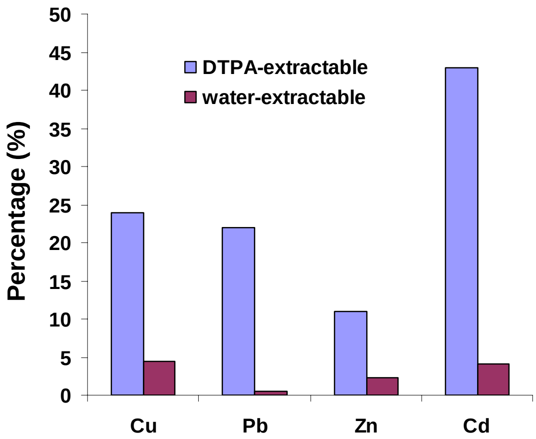

Fig. 1. The average percentage of DTPA and water extractable Cu, Pb, Zn and Cd

Significant correlations between total and DTPA extractable metals were found only for Cu and Pb suggesting that the percent of available metal depends on the nature and mobility of metals species exhausted by polluters. Significant correlations were found between total and water extractable metal content for Cu, Pb and Zn (Tab. 2).

Tab. 2. Correlation coefficients between total-DTPA extractable contents and total-water extractable contents of metals

	Total Cu	Total Pb	Total Zn	Total Cd
DTPA-extr.	0,510**	0,418*	0,258^{ns}	0,260^{ns}
Water-extr.	0.366*	0.502**	0.597**	0.131^{ns}
ns-not significant;* correlation significant at p<0.05; ** correlation significant at p<0.01				

The pH values in soil ranged between 3.0-8.23, with average value 6.74, but no statistically significant relationship between pH and available metal content was found. Strong negative correlations were found between water-extractable Cu (r = -0.393), Zn (r =

-0.532), Cd (r = -0.744) and pH. The lack of pH influence on DTPA extractable metal contents is probably due to high buffering capacity of DTPA solution.

Conclusions

The results showed that metal concentrations of polluted soils varied widely, in most cases exceeding the corresponding alert levels, indicating a severe situation, needing urgent measurements of pollution stopping and applying soil decontamination solutions, especially they cannot be degraded or destroyed. The high percentages of DTPA - extractable metals indicate an anthropogenic pollution, and a potential metal accumulation in vegetables, posing a potential risk for public health.

Acknowledgements

The financial support provided by the Romanian Ministry of Education and Research, PNCDI II Project RESOLMET no. 32161/2008 is greatly appreciated.

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