Long-term Effects on the Fractionation and Mobility of Heavy Metals in a Polluted Soil Treated with Bauxite Residues

PETRONELA-BIANCA PAVEL[1], **ELENA DIACU**[2*], **CONSTANTIN HORIA BARBU**[1]

[1] "Lucian Blaga" University of Sibiu, Faculty of Agricultural Sciences, Food Industry and Environmental Protection, 7-9 Ioan Ratiu Str., 550012, Sibiu, Romania

[2] University "Politehnica" of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Analytical Chemistry and Environmental Engineering, 1-7 Polizu Str., 011061, Bucharest, Romania

The main purpose of this study was to evaluate the efficiency of red mud (a bauxite residue) used as amendment to immobilize the metals present in a polluted soil and to assess the fractionation and mobility of the metals in soil after 6 years since red mud addition. In this context, the seven-step sequential extraction procedure (SEP) of Zeien and Brümmer was performed in order to investigate the mechanisms of metals in soil after the red mud addition. The analysis of heavy metals mobility (Zn, Cd and Pb) through sequential extraction showed a significant reduction of the metals concentrations in the mobile fraction (F1) and an increase of the metal concentration bounded to the less mobile fractions, the amorphous and crystalline Fe-oxides (F5 and F6). The red mud addition to soils caused a pH increase of the soil, up to 2 pH units (e.g. from 5 to 7) and had a pronounced effect in lowering the metal mobility in soil relative to the soil without the immobilizing amendment.

Keywords: red mud, heavy metals, immobilization, sequential extraction procedure

Soil pollution by toxic metals and metalloids is of major environmental concern as they harm human health and restrict multifunctional soil use and fertility [1]. Numerous strategies have been developed to remediate the affected soils or to prevent the movement of contaminants into non-polluted areas.

For the sustainable and cost – effective protection and restoration of soil ecosystems contaminated by heavy metals, their characterization is required, and soil treatment must be performed in conjunction with the treatment of leachate, wastewater and ground-water contaminated by various pollutants, including in situ and ex situ methods [2].

In-situ approach can immobilize toxic metals and minimize migration by addition of various low cost amendments. Considering the large extent of such areas and the communities demands, in-situ remediation is favoured in very many cases.

In-situ immobilization of metals is based on the addition of amendments that increase the proportion of metal burden within the soil solid phase, by precipitation or by increasing metals sorption, thus reducing their mobility and availability [3-5]. Therefore, the aim of immobilization is to reduce metals availability and activity, without their removal. Addition of amendments also reduces the exchangeable or phyto-available fractions of Pb and Mn, which are reflected in low plant tissue concentrations [6].

A large number of amendments have been proposed and tested for in-situ immobilization of heavy metals in degraded soils. The amendments include traditional agricultural materials, organic matter, and industrial by-products [7-14]. The use of various industrial materials, previously considered as "waste" for soil remediation represents a big step ahead in modern waste management, with huge economic and environmental benefits.

Among these "waste products" lays red mud (RM), a by-product of the alumina industry deriving from the digestion of crushed bauxite with caustic soda, which has shown some encouraging results as heavy metals sorbent, with great potential for their immobilization in soil and with subsequent capacity to reduce their uptake by plants [15, 16].

Because certain studies have demonstrated that a remobilization of metals may occur as a consequence of re-acidification of soils treated with alkaline amendments [6], red mud could be a suitable candidate for a more "sustainable" heavy metal immobilization [17-19].

Red mud is a heterogeneous material and its characteristics varies largely, even within the same landfill, depending on the sources of bauxite ores, alumina refining processes and the methods used for its disposal [19 - 21].

The main objective of this study was to assess the application effect of red mud on the distribution of Zn, Cd and Pb in various soil fractions and to evaluate the heavy metals mobility in soil after 6 years since its application to soil. The application of red mud to heavy metal contaminated soils was already described in our previous research [22].

Experimental part

Soil characteristics and sample preparation

Two mean soil samples (n=30) were collected from Copsa Mică, near the former smelter, SOMETRA S.A. The plots are characterized in table 1.

Soil samples used in the present study were collected from the field experiment, from both plots (table 1) on 0-20 cm depth, in two consecutive years, July 2012 and July 2013 (i.e. in the fifth and sixth year after red mud application).

Soil characteristics, total content of metal and metal fractionation were analysed using soil air-dried soil samples (to constant weight), homogenized and sieved through a 2-mm stainless sieve. Soil texture was analyzed using the sieve-pipette method. Soil *p*H was determined in a 1:5

---

*email: elena_diacu@yahoo.co.uk

Table 1
PLOTS CHARACTERIZATION

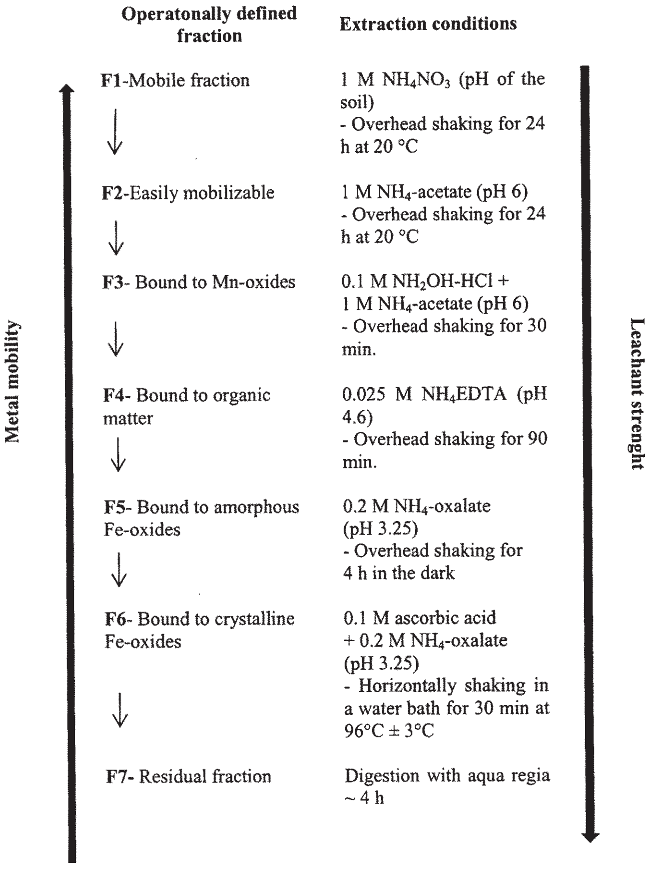
Plot notations	Soil treatments	GPS coordinates	Plot area (m^2)
P1-C	Untreated soil-control (C)	46°6'45.73"N 24°14'12.54"E	2248
P1-RM	1% red mud (RM) treated soil	46°06'41.42"N 24°14'14.12"E	2132

solution (deionized water). Organic carbon and humus content were analyzed according to Walkley-Black procedure, modified by Gogoaşă. Mobile forms of phosphorus and potassium were carried out by flame spectrometry, in calcium acetate lactate solution (CAL) at a ratio w/v 1:20 and buffered at *p*H 4.1. The total metal concentrations in soils were analyzed by FAAS method after digestion by *aqua regia*. For quality assurance, replicate samples, blanks and standardized reference materials were included in all analyses [23].

Soil sub-samples (2g fine-grained soil, with fraction < 2 mm) were used to investigate changes in the metal fractions (Cd, Zn and Pb) using the SEP of Zeien & Brummer (1989) [24]. This procedure is used for trace element fractionation in aerated soils with less than 5 % carbonate and is based on the use of a series of reagents to solubilize successively the different mineral fractions into operationally defined fractions [25]. Determined fractions and the extraction conditions are illustrated in figure 1.

The relative index of metal mobility was calculated as a mobility factor (MF%), according to the following equation [26]:

$$MF\% = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5 + F6 + F7} \cdot 100$$



Operatonally defined fraction	Extraction conditions
F1-Mobile fraction	1 M NH_4NO_3 (pH of the soil) - Overhead shaking for 24 h at 20 °C
F2-Easily mobilizable	1 M NH_4-acetate (pH 6) - Overhead shaking for 24 h at 20 °C
F3- Bound to Mn-oxides	0.1 M NH_2OH-HCl + 1 M NH_4-acetate (pH 6) - Overhead shaking for 30 min.
F4- Bound to organic matter	0.025 M NH_4EDTA (pH 4.6) - Overhead shaking for 90 min.
F5- Bound to amorphous Fe-oxides	0.2 M NH_4-oxalate (pH 3.25) - Overhead shaking for 4 h in the dark
F6- Bound to crystalline Fe-oxides	0.1 M ascorbic acid + 0.2 M NH_4-oxalate (pH 3.25) - Horizontally shaking in a water bath for 30 min at 96°C ± 3°C
F7- Residual fraction	Digestion with aqua regia ~ 4 h

Fig. 1. Relationship between metal mobility in the different operationally-defined phases and leachant strenght of chemical reagents used for Zeien- Brümmer SEP [24]

Results and discussions

Some physico-chemical properties of soil samples are presented in table 2 and the total content of the Zn, Cd and Pb in the upper soil horizon are presented in table 4.

According to soil textural triangle method, the soil texture in both plots (P1-C and P1-RM) is sandy loam, with clay content ranging from 16.9 to 17.3% and a sand content below 74% (table 2). Soil reaction in the plot treated with red mud (P1-RM) is mostly neutral with *p*H ranging from 7.2 to 7.6 as compared to the control plot (P1-C) where the soil reaction is mostly acidic with *p*H (H_2O) ranging from 5.1 to 5.5. This increase in *p*H can be attributed to the red mud alkalinity (*p*H 11.6) shown in table 3.

According to soil textural triangle method, the soil texture in both plots (P1-C and P1-RM) is sandy loam, with clay content ranging from 16.9 % to 17.3% and a sand content below 74% (table 2). Soil reaction in the plot treated with red mud (P1-RM) is mostly neutral with *p*H ranging from 7.2 to 7.6 as compared to the control plot (P1-C) where the soil reaction is mostly acidic with *p*H (H_2O) ranging from 5.1 to 5.5. This increase in *p*H can be attributed to the red mud alkalinity (*p*H 11.6) shown in table 3.

As can be seen in table 4, the total contents of the investigated heavy metals are much higher than the limit values in soils according to the MAPPM Order No.756/1997 [27].

The immobilization effect of red mud addition (fig. 2) is clearly observed in the reduction of the Zn, Cd and Pb

Table 2
THE MAIN PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SOIL. THE RESULTS REPRESENT THE MEAN VALUES OF THREE INDEPENDENT DETERMINATIONS, REPORTED TO DRY WEIGHT

Parameter	Year	2012		2013	
	Unit.	P1-C	P1-RM	P1-C	P1-RM
pH (H_2O)	-	5.1	7.2	5.5	7.6
EC	µS/cm	169.9	218.3	95.0	249.0
Sand	%	72.5	73.1	71.5	73.2
Silt	%	10.6	9.6	11.3	9.8
Clay	%	16.9	17.3	17.2	17
Texture		Sandy loam			
Organic carbon	%	1.0	1.1	1.0	0.8
Humus (H)	%	1.7	1.9	1,7	1.4
P-CAL	mg kg^{-1}	33.2	37.0	31.2	40.5
K-CAL	mg kg^{-1}	143.0	207.4	139.2	198.7

EC=Electrical conductivity, CAL=calcium acetate lactate extraction

Table 3
THE BASIC PHYSICO-CHEMICAL CHARACTERISTICS OF RED MUD

Parameter	Unit	Red mud
pH	-	11.6
Humidity	%	5.0
Density	kg dm^{-3}	1.5
Total Pb	mg kg^{-1}	52.5
Total Cd	mg kg^{-1}	4.0
Total Zn	mg kg^{-1}	91.3
Total Cu	mg kg^{-1}	50.0
Total Mn	mg kg^{-1}	65.0

Table 4
TOTAL CONTENT OF HEAVY METALS IN THE UPPER SOIL HORIZON (0-20 cm). THE RESULTS REPRESENT THE MEAN VALUES OF THREE INDEPENDENT DETERMINATIONS, REPORTED TO DRY WEIGHT.

Metal (total content)	Unit	Limit values MAPPM Order No.756/1997	July 2012		July 2013	
			P1-C	P1-RM	P1-C	P1-RM
Zn	mg kg^{-1}	**100**	882.4±9.3	749.8±11.4	784.7±11	689.1±8.9
Cd	mg kg^{-1}	**1**	13.2±0.3	11.5±0.6	12.8±0.2	10.5±1.4
Pb	mg kg^{-1}	**20**	608.2±13.6	532.1±9.6	587.3±7.3	543±5.6

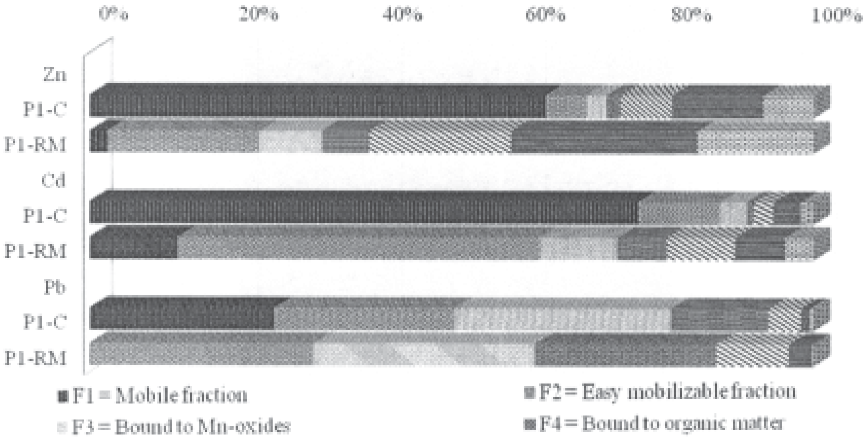


Fig. 2. Zn, Cd and Pb distribution in different geochemical fractions in soil samples (0-20 cm depth) collected in july 2012

Table 5
THE CONTENT OF Zn, Cd AND Pb EXTRACTED IN THE 7 GEOCHEMICAL FRACTIONS PROPOSED BY ZEIEN-BRÜMMER (mg kg^{-1}), THE SUM (Σ) OF THESE FRACTIONS (mg kg^{-1}) AND THE MOBILITY FACTOR (MF%)

Metal	Plot	F1	F2	F3	F4	F5	F6	F7	$\Sigma F_{i,\, i=1-7}$	MF %
Zn (mg kg^{-1})	P1-C	556.8	49.4	24.7	16.8	63.5	109.4	61.8	882.4	68.7
	P1-RM	18.7	156.0	64.5	49.5	148.5	192.7	120.0	749.8	23.3
Cd (mg kg^{-1})	P1-C	10.1	1.4	0.5	0.1	0.3	0.5	0.2	13.2	87.5
	P1-RM	1.4	5.7	1.3	0.7	1.0	0.8	0.5	11.5	62.5
Pb (mg kg^{-1})	P1-C	154.5	152.1	182.5	81.5	27.4	7.3	3.0	608.2	50.4
	P1-RM	1.1	161.8	164.4	133.0	53.7	17.0	1.1	532.1	30.6

concentrations found in the mobile fraction (F1) of the treated soil (P1-RM) compared to the control (untreated) soil (P1-C). This reduction is also reflected in the relative distribution of these elements among the all seven operationally defined chemical fractions shown in table 5.

The addition of red mud amendment has significantly reduced the Zn amount in the mobile fraction (F1), with up to 60.3%, i.e. from 556.8 mg kg-1 Zn found in the untreated soil (P1-C) to 18.7 mg kg-1 Zn found in the treated soil (P1-RM). Due to the redistribution of the mobile fraction the other Zn fractions increased, especially in F2 - easily mobilizable fraction (up to 15.2%), F6 - bound to crystalline Fe-oxides (up to 13.3%) and F5 - bound to amorphous Fe-oxides (up to 12.6%), follow by F7 - residual fraction (up to 9 %), F3 - bound to Mn-oxides (up to 5.8%) and F4 - bound to the organic matter (up to 4.7%).

In the case of Cd, the red mud addition had a bigger impact in reducing the F1 – mobile fraction (up to 64%), from 10.1 mg kg^{-1} Cd found in the control soil (P1-C) to 1.4 mg kg^{-1} Cd found in the treated soil (P1-RM). The total content of Cd reduced from the mobile fraction was found redistributed among the other fractions, especially in F2 (up to 39%), followed by F3 (up to 7.3%), F5 (up to 5.3%), F4 (up to 5.2%), F6 (up to 3.3%) and F7 (up to 2.6 %).

The positive effect of the RM application in reducing the heavy metals mobility in soil can be also observed due to the decrease of the Pb mobile fraction - F1 (tabel 5), compared with the untreated soil. The Pb content reduced from the mobile fraction was redistributed mainly in F4 - bound to the organic matter (up to 11.6%), but also in F5 - bound to amorphous Fe-oxides (up to 5.6%) and F2 - easily mobilizable fraction (up to 5.4%).

The red mud addition increased soil *p*H and consistently reduced the Pb, Cd and Zn concentrations in the mobile fraction (F1), relative to the soil without the immobilizing amendment (fig. 2). These positive effects of the RM application in reducing the heavy metals mobility in soil was also observed in the decreasing of the mobility factor (MF %) calculated for all three metals of concern. The most important reduction of the mobility factor was observed for Zn (from 68.7% to 23.3%), followed by Cd (from 87.5% to 62.5%) and Pb (from 50.4 % to 30.6%).

Conclusions

The results presented in this study emphasize that SEP according to Zeien and Brümmer method can contribute to the better understanding of the heavy metals retention phenomena in soil by supplying information on the solid – phase partitioning of the heavy metals. The sequential extraction results suggest that the potential availability of the studied heavy metals in the soil is extremely high, especially for Cd.

Our results show that in the control soil (P1-C) large proportions of Cd (87.5%), Zn (68.7%) and Pb (50.4%) were associated with the mobile and easily mobilizable fractions, indicating that these metals are extremely mobile and thus potentially bioavailable. These results suggest that the potential availability of the studied heavy metals is extremely high in the untreated soil compared with the red mud treated soil. As indicated by the mobility factor (MF %) the apparent mobility and potential bioavailability of heavy metals in the studied soils followed the order: Cd > Zn >Pb.

The research findings obtained from this study showed that the red mud application on the strongly contaminated soils from Copsa Mică increased the soil *p*H (~ 2 units) and changed the heavy metals distribution in all seven operationally defined chemical fractions. The most significant change was observed in the reduction of the mobile fractions of Zn, Cd and Pb and in the increase of the metal concentration bounded to the amorphous and crystalline Fe oxides (F5 and F6) of the treated soil (P1-RM) compared to the untreated soil (P1-C).

The results from this study clearly revealed that red mud application has a long-term effect in reducing the mobility of Zn, Cd and Pb and the potential biodisponibility of these heavy metals, this significant impact being observed even after 6 years since its application to soil.

References

1. ADRIANO, D.C., Trace elements in the terrestrial environment. 2nd Edition. New York: Springer, Verlag, 2001.
2.ABOULROOS, S.A., HELAL, M.I.D., KAMEL, M.M., (2006), Remediation of Pb and Cd polluted soils using in situ immobilization and phytoextraction techniques, Soil and Sediment Contamination, 15, 2006, p.199-215
3.OSTE, L.A., LEXMOND, T.M., RIEMSDIJK, W.H.V., Metal immobilization in soils using synthetic zeolites. Journal of Environmental Quality 31, 2002, p. 813-821.
4. BASTA, N.T., SLOAN, J.J., Bioavailability of heavy metals in strongly acidic soils trated with exceptional quality biosolids, J. Eviron. Qual., 28, 1999, p. 633-638.
5. HALÁSZ, J., MÉHN, D., GUNGL, A., KIRICSI I., Destruction of halogenated organic compounds by catalytic oxidation over red mud originated catalysts, în Proceedings of the 5th Intern. Symp. Exhib. Environ. Cont. in Central and Eastern Europe, Praga, Cehia, 2000.
6. PADMAVATHIAMMA, P.K., LI L.Y, Bioresource Technology 101, 2010, p. 5667–5676.
7. BECK D., DGT as an assessment tool for the impact of soil amendments on the bioavailability of cadmium and zinc, MasterThesis - Institut für Bodenforschung (IBF), BOKU-Universität für Bodenkultur, 2012.
8. LOMBI, E., ZHAO, F.J., ZHANG, G., SUN, B., FITZ, W., ZHANG, H., MCGRATH, S. P., In situ fixation of metals in soils using bauxite residue: chemical assessment, Env. Pollut., 112, 2002a, p. 435-443.
9. LOMBI, E., ZHAO, F.J., WIESHAMMER, G., ZHANG G., MCGRATH, S.P., In situ fixation of metals in soils using bauxite residue: biological effects, Env. Pollut., 118, 2002b, p. 445-452.
10. FRIESL, W., LOMBI, E., HORAK, O., WENZEL, W.W., Immobilization of heavy metals in soils using inorganic amendments in a greenhouse study, J. Plant Nutr. Soil Sci., 166, 2003, p. 191-196.
11. MELAMED, R., CAO, X., CHEN, M., MA, L.Q., Field assessment of lead immobilization in a contaminated soil after phosphate application. The Science of the Total Environment 305, 2003, p. 117-127.
12. WALKER, W., HARREMOES, P., ROTMANS, J., VAN DER SLUIJS, J., VAN ASSELT, M., JANSSEN, P., KRAYER VON KRAUSS, M. De□ning uncertainty: A conceptual basis for uncertainty management in model-based decision support, Integrated Assessment 4(1), 2003, p. 5–18.
13. BROWN, S., CHANEY, R., HALLFRISCH, J., RYAN, J.A., BERTI, W.R., In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc, and cadmium J. Of Environ. Qual., vol. 33, 2004, p. 522-531.
14. FARFEL, M.R., ORLOVA, A.O., CHANEY, R.L., LEES, P.S.J., ROHDE, C., ASHLEY, P.J., Biosolids compost amendment for reducing soil lead hazards: a pilot study of Orgro amendment and grass seeding in urban yards. Science of the Total Environment 340, 2005, p. 81-95.
15. GUPTA, S. K., ATEN, C., Comparison and evaluation of extraction media and their suitability in a simple model topredict the biological relevance of heavy metal concentrations in contaminated soil. Int. J. Anal Chemist., 1993, 51, p. 25-46.
16. SANTONA, L., CASTALDI, P., MELIS, C., Evaluation of the interaction mechanisms between red muds and heavy metals. Journal of Hazardous Materials (in press), 2006
17. CASTALDI, P., SANTONA, L., MELIS, P., Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth. Chemosphere 60(3): 2005, p. 365-371.
18. GARAU, G., CASTALDI, P., SANTONA, L., DEIANA, P., MELIS, P., Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil. Geoderma 142, 2007, p. 47-57.
19. LIU, W.C., YANG, J.K., XIAO, B., Review on treatment and utilization of bauxite residues in China. Int. J. Miner. Process. 93, 2009, p. 220–231.
20. GRÄFE, M., POWER, G., KLAUBER, C., Bauxite residue issues: III. Alkalinity and associated chemistry. Hydrometallurgy, 108, 2011, p. 60–79.
21.MENCH, M., VANGRONSVELD, J., LEPP, N., BLEEKER, P., RUTTENS, A., GEEBELEN, W., Phytostabilisation of Metal-Contaminated Sites in Jean-Louis Morel, Guillaume Echevarria, Nadezhda Goncharova (Editors) Phytoremediation of Metal-Contaminated Soils, Springer Verlag. NATO Science Series, 2006, 68, p.109-190.
22. PAVEL, P.B., PUSCHENREITER, M., WENZEL, W.W., DIACU, E., BARBU, C.H., Aided phytostabilization using Miscanthus sinensis × giganteus onheavy metal-contaminated soils, Science of the Total Environment, 479–480, 2014, p. 125–131.
23. PAVEL, P.B., DIACU, E., BARBU, C.H., Rev. Chim. (Bucharest), **64**, no. 1, 2013, p. 22
24. ZEIEN, H., BRÜMMER, G.W., Chemische Extraktionen zur Bestimmung der Bindungsformen von Schwermetallen in Böden, Mitteilng. Dtsch. Bodenkundl. Gesellsch. 59, 1989, p. 505-510.
25. WENZEL, W.W., KIRCHBAUMER, N., PROHASKA, T., STINGEDER, G., LOMBI, E., ADRIANO, D.C., As fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta 436, 2001, p. 309–323.
26. NARWAL, R.P., SINGH, B. R., SELBU, B., Association of cadmium, zinc, copper. and nickel with components in naturally heavy metal rich soils studied by parallel and sequential extraction. Commun. Soil Sci. Plant Anal., 30, 1999, p. 1209 – 1230.
27. ***Romanian Ordinance Ministry No. 756/1997 official Gazette of Romania, I Part, No. 303, 1997

Manuscript received: 26.09.2013