IOŚ-PIB OCHRONA ŚRODOWISKA I ZASOBÓW NATURALNYCH
ENVIRONMENTAL PROTECTION AND NATURAL RESOURCES 2013
VERSITA
VOL. 24, NO 2(56): 29–33
DOI 10.2478/oszn-2013-0013

Ľuboš Harangozo*, Mária Timoracká*, Július Árvay*, Alena Vollmannová*, Pavol Trebichalský*

Minority cereals cultivated under loaded model conditions

Rzadkie gatunki zbóż uprawiane w warunkach obciążenia metalami ciężkimi

* Ing. Ľuboš Harangozo PhD., Ing. Mária Timoracká PhD., Ing. Július Árvay PhD., prof. Ing. Alena Vollmannová, PhD., Ing. Pavol Trebichalský PhD., Dep. Of Chemistry, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture in Nitra, A. Hlinku 2, 949 76 Nitra, Slovak Republic, phone: +421736414378, e-mail: lubos.harangozo@uniag.sk

Keywords: *millet, oats, amaranth, heavy metals, cadmium, plants*
Słowa kluczowe: *proso, owies, szarłat, metale ciężkie, kadm, rośliny*

Abstract

The aim of this work is to evaluate the extent of risk for the transfer of heavy metals from contaminated soil to selected parts of crops. The goal is to be achieved under the model conditions of vegetation pot experiment. Soil taken from the area of Výčapy-Opatovce and three types of cereals – millet (*Panicum miliaceum*) cv. UNIQUM, oats (*Avena sativa*) cv. ATEGO and amaranth (*Amaranthus caudatus*) – were used. For each crop, four variants (A – control with basic ferilization, B, C, D) were made and cadmium in the form of a water-soluble salt of $Cd(NO_3)_2$ was applied in gradual specific doses with 5- (variant B), 10- (variant C), 15-fold (variant D) as the limit values by Law no. 220/2004 Z.z. to assess the state of soil contamination. Crops were harvested at 'full ripeness' and using the AAS method (VARIAN 240FS) the heavy metal content was determined by the wet mineralization of plant samples. The lowest cadmium content in the aboveground biomass was observed in millet in comparison to other plants, while the highest was recorded in amaranth. The highest increase in the cadmium content in the aboveground biomass in this crop (appr. 18-fold) was noticed in variant C. The lowest cadmium content was also observed in millet seeds. The highest content of Cd in the seeds was recorded in oats in all variants.

Streszczenie

Celem pracy jest ocena zakresu narażenia na przemieszczenie metali ciężkich z zanieczyszczonej gleby na wybrane części plonów. Ocenę przeprowadzono w doświadczeniu z uprawą roślin w pojemnikach w warunkach modelowych. Zastosowano próbki gleb z obszaru Výčapy-Opatovce oraz trzy typy zbóż: proso (*Panicum miliaceum*) cv. UNIQUM, owies (*Avena sativa*) cv. ATEGO oraz szarłat (*Amaranthus caudatus*). Dla każdego zboża wykonano cztery warianty eksperymentu (A – wariant kontrolny z normalnym nawożeniem, B, C, i D), w których do próbek gleb dodano kadm w postaci rozpuszczalnej soli $Cd(NO_3)_2$ w ilości stopniowo wzrastających dawek: 5 (wariant B), 10 (wariant C), i 15 (wariant D) – krotności wartości granicznej ustanowionej przez Ustawę nr 220/2004 Z.z. w celu oceny stopnia zanieczyszczenia gleby. Zboża uprawiano do całkowitej dojrzałości; zawartość metali ciężkich oceniono z zastosowaniem metody AAS (VARIAN 240FS) na próbkach roślin zmineralizowanych na mokro. Najniższą zawartość kadmu w biomasie naziemnej stwierdzono dla prosa. Najwyższą zawartość kadmu w biomasie naziemnej zanotowano dla szarłatu. Najwyższy wzrost zawartości kadmu w biomasie naziemnej w tym zbożu (około 18-krotny) stwierdzono w wariancie C. Najniższą zawartość kadmu zaobserwowano także w nasionach prosa. Najwyższą zawartość kadmu w nasionach stwierdzono dla owsa we wszystkich wariantach eksperymentu.

1. INTRODUCTION

The contaminants which are large in number also include heavy metals. Relatively wide use of heavy metals in various fields of human activities leads to their accumulation in soil, dust particles in the solid waste as well as waste water. Although the soil has relatively high ability to absorb or resist adverse environmental influences, it is prone to degradation (different types of erosion, contamination of hazardous trace elements, acidification, etc.). It takes exceedingly long time for remedying the influences of these degradation processes.

Therefore, the contamination of soils with heavy metals ranks among the most important problems of soil protection and the environment.

Cadmium

Extensive studies about the environmental toxicity of cadmium in contaminated soils and waters were performed [Wu et al. 1992; Zhou 1995; Ghost, Kaviraj 2002; Evangelou et al. 2004]. A considerable part of the research has addressed the influences of cadmium on crops and other agricultural plants [Zhou, Gao 1994; Zhou, Gao 1994b; Cheng, Zhou 2002; Kukier, Chaney 2002; Selvi et al. 2003; Wang, Zhou 2005]. Fertilizers and their utilization on agricultural soil is considered to be the main source of Cd in soil [Tu et al. 2000]. Fertilizers are a major source of Zn, Cu and Cd [Nicholson et al. 2003; Rodriguez Martin et al. 2007; Ramos-Miras et al. 2011], as are liquid fertilizers as well as manure (or their derivatives, compost, sludge) or mineral fertilizers.

Cadmium not only accumulates in the root system, but is also easily transported and stored into all tissues of plants. Cd, in particular, compared to other heavy metals is accumulated in the grain [Zaujec 1999].

The distribution of cadmium in individual parts of plants has a clear progressive character: roots> stems> leaves> grains (seeds). The highest amount of cadmium from the soil receives root and greenhouse vegetables. The concentration of cadmium increases as follows: oat < wheat < fababean < pea < sunflower < corn < radish < tomato < carrot < lettuce [Kočík 1995].

Increased attention about the adverse effects of cadmium on human health began from the discovery of "Itai-Itai" disease in Japan in 1950, which was caused by the consumption of cadmium-contaminated rice [Wu et al. 1992; Zhou 1995; Ghosal, Kavirádž 2002; Evangelou et al. 2004].

Cadmium is classified among the most important environmental contaminants. Cadmium accumulates in human body and causes disorders of the cardiovascular system and central nervous system, kidney and liver damage, and further causes anemia and oncological diseases [Vollmannová 2006].

2. MATERIALS AND METHODS

The experiment was realized as pot trial in the vegetation cage of the Department of Chemistry of FBFS SUA in Nitra. In pot trial, the soil from the locality Výčapy-Opatovce near Nitra was used. In this experiment, three different species of pseudocereals were used: amaranthus (Amaranthus caudatus), oat (Avena sativa), cv. ATEGO, millet (Panicum miliaceum), cv. UNIQUM.

In the soil, the exchangeable reaction (pH/KCl), the contents of available nutrients (K, Mg, P) and mobile forms of Ca according to Mehlich II., content of humus by Tjurin method and content of N were determined. Pseudototal content of risk metals including all the forms besides residual metal fraction was assessed in the solution of *aqua regia* and content of mobile forms of selected heavy metals in soil extract of HNO_3 ($c = 2\ mol \cdot dm^{-3}$).

The vegetation pot experiment

Six kilograms of soil mixed with sand was weighed into plastic bowl-shaped pots (with average dimensions of 20 cm and height 25 cm) with foraminated bottom. Basic nutrients were added in the form of NPK fertilizer. The dose of the base fertilizer (NPK) – nitrogen in the form of urea, phosphorus in the form of superphosphate and potassium as the potassium salt – and the quantity of water-soluble cadmium salt required to simulate various metallic load soil was calculated. The experiment was based on four replications (variants).

Table 1. Variants of the experiment

Variants	Fertilization
A	NPK
B	NPK + 4,9 mg Cd
C	NPK + 9,1 mg Cd
D	NPK + 13,5 mg Cd

Four variants of this experiment were realized – A: control (without Cd addition), B: 5-fold $Cd \cdot kg^{-1}$ of soil, C: 10-fold $Cd \cdot kg^{-1}$ of soil, D: 15-fold $Cd \cdot kg^{-1}$ of soil of the indicative B value; this is the limit value for the analytical evidence of soil contamination (by law 531/1994 – 540 (Decision of the Ministry of Agriculture SR).

Pseudocereals were harvested at full ripeness. The content of risky elements in seeds was determined by wet mineralization of plant samples using atomic absorption spectrometry. The flame AAS (AAS Varian AA Spectr DUO 240 FS/240Z/UltrAA) was used for the determination of heavy metal contents in soil and plant materials.

For statistical processing of the results, we used the statistical program STATISTICA Cz 6.0 (StatSoft, Inc., 2001), in which we tested the results on the level of descriptive statistical evaluation. To assess the relationship of risk metals in soil, seeds and biomass, we collected data subjected to regression analysis and correlation (Pearson, Spearmann, onesample and paired Student's t-test).

3. RESULTS AND DISCUSSION

The soil is characterized by a moderate supply of humus and extremely acid soil reaction. The used soil is characterized also by good content of potassium, low content of phosphorus as well as by a very high content of magnesium. The soil used in pot trial was relatively uncontaminated. Only the determined Cd content was on the level of limit value given for the soil extract by *aqua regia* (Table 2). The values of total risk element contents in soil extract by *aqua regia* were under the concentrations of the defined limit value with the exception of Cd; its total content had exceeded about 22.3% and the determined Co content was at the level of the limit value given for the soil extract by *aqua regia*. In Spain, the total average content of cadmium in the soil is $0.23\ mg \cdot kg^{-1}$ [Rodriguez Martin et al. 2005].

The lowest intake of cadmium into biomass was observed in millet in comparison to other crops under different loads of soil by cadmium. An increase in cadmium content in the biomass of millet with increasing doses of cadmium in the soil compared to the other two crops is insignificant ($2.7\ mg \cdot kg^{-1}$ Cd in D variant). The highest cadmium content in the biomass was recorded in amaranth. The highest increase of the cadmium content in the biomass of this crop (almost 18 fold) was observed in variant C ($17.9\ mg \cdot kg^{-1}$). The biomass of oats, the highest cadmium content was observed in variant D with the highest dose of deliberately added Cd in the soil (12-fold increase in comparison to the control variant). The cadmium content in the biomass of cereals produced in relatively uncontaminated soil varied in the range $0.47–1.28\ mg \cdot kg^{-1}$ [Tian Guo Rong et al. 2007]. The cadmium content in the biomass determines the following order of pseudocereals: amaranth > oats > millet.

While comparing the three crops, we evaluated the smallest amounts of cadmium in millet. Besides above-ground biomass, the lowest accumulation of Cd ($0.30–0.70\ mg \cdot kg^{-1}$) was also observed in seeds. As a result of the increasing doses of Cd added deliberately to the soil, the millet seeds showed insignificant increase in the cadmium content in all variants. At the highest doses of cadmium in the soil, its content in the seeds increased two-fold, which is insignificant in comparison to other crops. The highest content of Cd was recorded in oat seeds in all variants. In the seeds of oats, cadmium content increased in D variant 13-fold compared to the control variant A ($5.9\ mg \cdot kg^{-1}$). The cadmium content in seeds determines the following order of cadmium intake by pseudocereals: oats > amaranth > millet. [Melicháčová 2007] reported the average cadmium content in the seeds of amaranth grown in polluted soils containing cadmium at the level of the limit value from 0.62 to $0.88\ mg \cdot kg^{-1}$, and the cadmium content in millet seeds from 0.27 to $0.49\ mg \cdot kg^{-1}$. In polluted regions with cadmium content in the soil above $9\ mg \cdot kg^{-1}$, the seeds of amaranth measured the Cd values ranging $1.8–3.3\ mg \cdot kg^{-1}$ and in millet seeds $0.91–1.64\ mg \cdot kg^{-1}$.

Statistically highly significant correlation between the Cd content in biomass and seeds was recorded in sowing oats only in variant B ($p < 0.05$), while in the case of millet the statistically highly significant correlation was observed only in variant D. The results of amaranth showed no statistically significant correlation in all variants.

In all variants, we observed statistically significant differences between the high cadmium content in seeds and biomass of oat, millet and cadmium content in soil ($p < 0.05$). The difference between the content of cadmium in seeds and amaranth aboveground biomass and cadmium content in the soil in all variants was statistically highly significant, except for variant D, where the difference was not statistically significant.

4. CONCLUSION

The present results show that the deliberately added doses of cadmium in specific quantities into the soil are reflected in its content in the investigated crops, although in some crops the highest doses of cadmium have not expressed their increased content in the crop. We can conclude that the highest cadmium intake had oats, especially seeds. In the seeds of oats, a 13-fold increase of cadmium content in comparison to the control variant was observed.
Although in today's agriculture the biomass is not used as much as it was in the past, but still from the point of view of Cd cumulation its use as animal feed appears risky because it demonstrated significant cadmium intake especially by amaranth biomass.

On the other hand, due to the significant accumulation of Cd in amaranth plants and an excessive production of the biomass, amaranth is potentially useful as a fytoremediation crop for the rehabilitation of metallic polluted soils.

ACKNOWLEDGEMENT

This work was supported by the project VEGA 1/0724/12 "Specific points, diffusion and profiled mercury contamination of production areas in central Spiš, northern Gemer inputs and minimize the possibility of Hg in plant products."

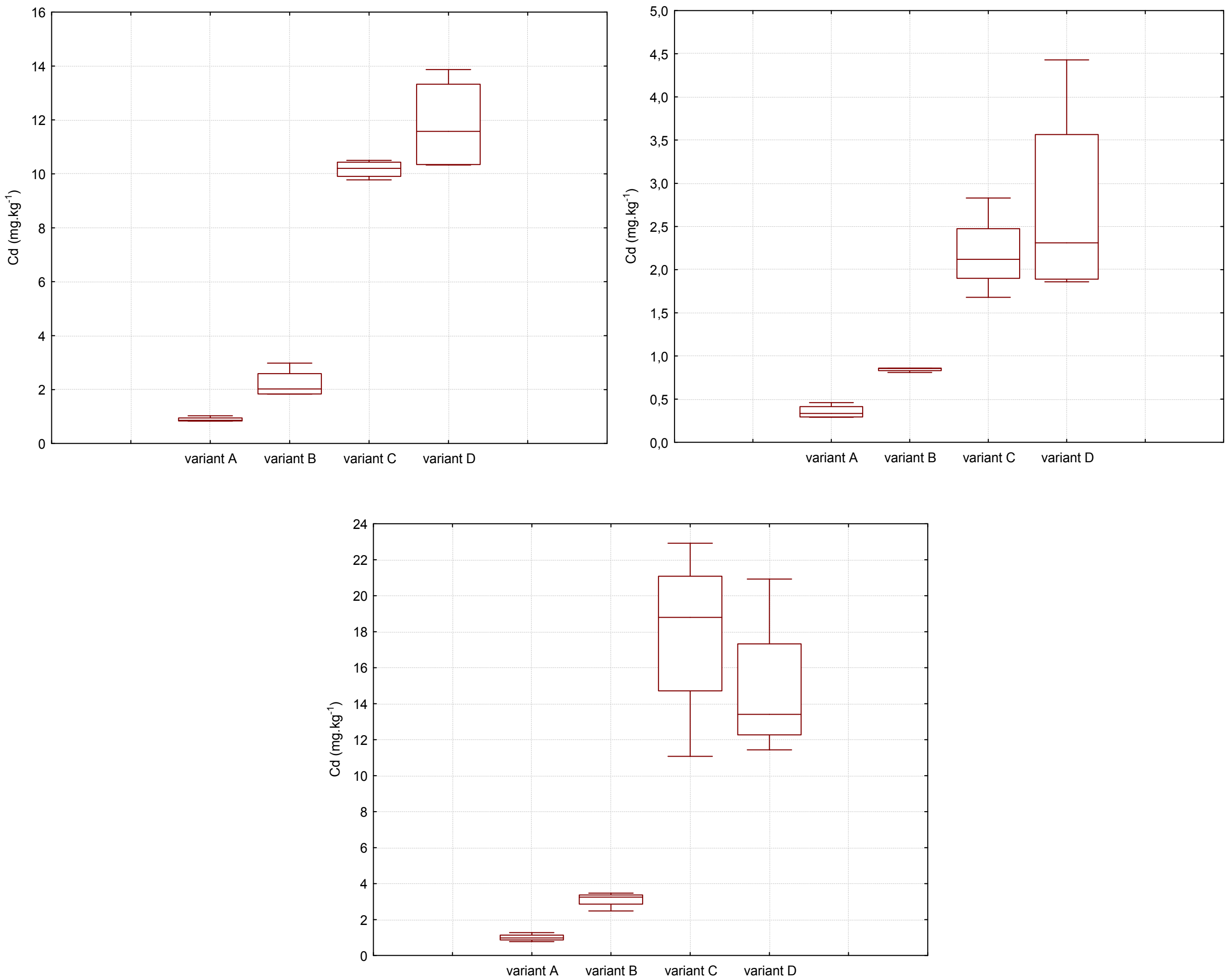

Figure 1. Comparison of cadmium taken in the observed variants in cereals (oats, millet, amaranth) in the aboveground biomass (mg•kg^{-1}).

(top left) Cadmium content in aboveground biomass of different oat variants in mg•kg^{-1}; (top right) Cadmium content in the aboveground biomass of millet variants in mg•kg^{-1}; (bottom) cadmium content in biomass of amaranth in different variants in mg•kg^{-1}.

Table 2. Heavy metal content in soil extract by *aqua regia* in mg•kg^{-1}

	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
soil	25500	621,2	52,4	45,8	15,0	31,6	31,8	22,2	0,9
220/2004 Limit value	---	---	150	60	15	50	70	70	0,7

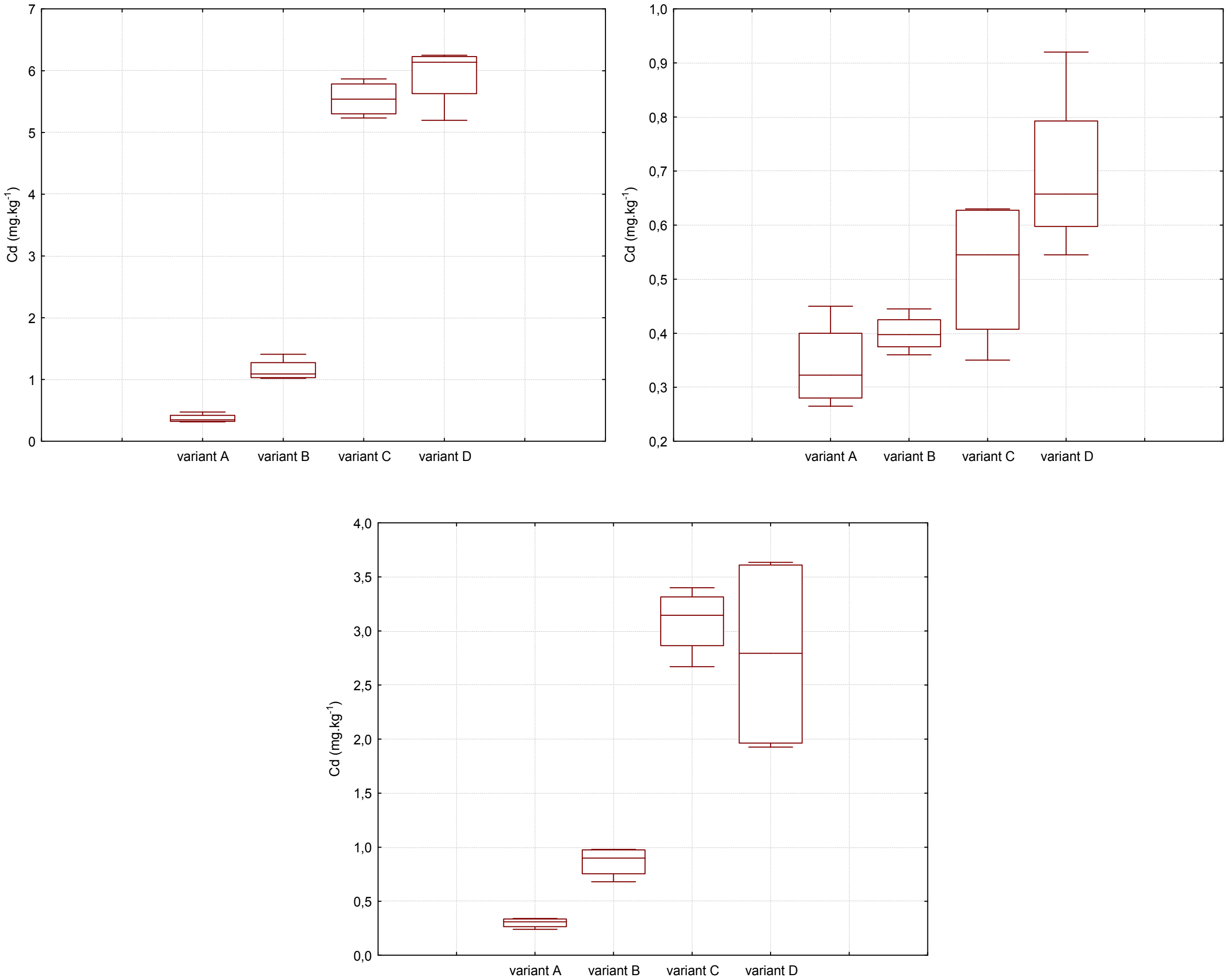

Figure 2. Comparison of cadmium taken in the observed variants in cereals (oats, millet, amaranth) in their seeds (mg•kg^{-1}).

(top left) Cadmium content in the seeds of oat variants in mg•kg^{-1}; (top right) cadmium content in the seeds of millet variants in mg•kg^{-1}; (bottom) the cadmium content of amaranth seeds in variants in mg•kg^{-1}.

REFERENCES

CHENG Y., ZHOU Q. X. 2002. Ecological toxicity of reactive X-3B red dye and cadmium acting on wheat (Triticum aestivum). J. Environ. Sci. 14: 136–140.

EVANGELOU M. W. H., DAGHAN H., SCHAEFFER A. 2004. The influence of humic acids on the phytoextraction of cadmium from soil. Chemosphere 57: 207–213.

GHOSAL T. K., KAVIRAJ A. 2002. Combined effects of cadmium and composted manure to aquatic organisms. Chemosphere 46: 1099–1105.

GUOA T. R., ZHANG G. P., ZHANG Y. H. 2007. Physiological changes in barley plants under combined toxicity of aluminum, copper and cadmium. Colloids and Surfaces B: Biointerfaces 57, 2: 182–188.

KOČÍK K., DUCSAY L. 1995. Aktívny biomonitoring rizikových prvkov v systéme pôda – rastlina. In : Cudzorodé látky v poľnohospodárstve. Nitra, SPU: 29-31.

KOZÁK J., JEHLIČKA J. 1992. Retence vybraných kovú púdami. Pedol. Melior. 28, 1: 3–11.

KUKIER U., CHANEY R. L. 2002. Growing rice grain with controlled cadmium concentrations. J. Plant Nutr., 25: 1793–1820.

MELICHÁČOVÁ S. 2007. Využitie netradičných rastlinných druhov na výrobu funkčných potravín, Nitra, SPU NITRA, dizertačná práca: 81–95.

NICHOLSON F., SMITH S., ALLOWAY B., CARLTON-SMITH C., CHAMBERS B. 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. Science of the Total Environment. 311: 205–219.

RAMOS-MIRAS J., ROCA-PEREZ L., GUZMÁN-PALOMINO M., BOLUDA R., GIL C. 2011. Background levels and baseline values of available heavy metals in Mediterranean greenhouse soils (Spain). Journal of Geochemical Exploration 110: 186–192.

RODRÍGUES MARTÍN J.A., LÓPEZ ARIAS M., GRAU CORBÍ J.M., 2005. Metales pesados, materia orgánica y otros parámetros de los suelos agrícolas y de pastos de España, Marm-Inia, Madrid.

RODRÍGUES MARTÍN J.A., VÁZQUEZ DE LA CUEVA A., GRAU CORBÍ J.M., LÓPEZ ARIAS M. 2007. Factors controlling the spatial variability of copper in topsoils of the Northeastern Region of the Iberian Peninsula, Spain. Water, Air and Soil Pollution 186: 311–321.

SELVI M., GÜL A., YILMAZ M. 2003. Investigation of acute toxicity of cadmium chloride ($CdCl_2 \cdot H_2O$) metal salt and behavioral changes it causes on water frog (Rana ridibunda Pallas, 1771). Chemosphere 52: 259–263.

TU C., ZHENG C., CHEN H., 2000, Effect of applying chemical fertilizers on forms of lead and cadmium in red soil. Chemosphere 41: 133–138.

VOLLMANNOVÁ A., TÓTH T., LAHUČKÝ L., STANOVIČ R. 2006. Využitie láskavca na znižovanie pôdnych obsahov kadmia. In: Environmentálne inžinierstvo (zb. príspevkov z 3. vedeckej konferencie s medzinárodnou účasťou., ISBN 80-8073-607-3 Košice: TU:136.

WANG M. E., ZHOU Q. X. 2005. Single and joint toxicity of chlorimuron-ethyl, cadmium and copper acting on wheat, Ecotoxicol. Environ. Saf. 60: 169–175.

WU Y. Y., TIAN J. L., ZHOU Q. X. 1992. Study on the proposed environmental guidelines for Cd, Hg, Pb, and As in soil of China. J. Environ. Sci. 4: 66–73.

ZAUJEC A. 1999. Cudzorodé látky a hygiena pôd. ISBN 80-7137-567-5. Nitra, SPU: 39–62

ZHOU Q. X, GAO Z. M. 1994a. Compound contamination and secondary ecological effects of Cd and As in soil–alfalfa ecosystems. J. Environ. Sci. 6: 330–336.

ZHOU Q. X., GAO Z. M. 1994b. Interaction between Cd and Zn in seeds of crops and its mechanisms. Agro-Environ. Prot. 13: 148–151.