Journal of Microbiology, Biotechnology and Food Sciences

Tomáš et al. 2012 : 1 (February Special issue) 819-827

REGULAR ARTICLE

HEAVY METALS IN PRODUCTIVE PARTS OF AGRICULTURAL PLANTS

Ján Tomáš [1], Július Árvay[1], Tomáš Tóth[1,2]*

***Address**:* [1]Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovak Republic

[2]Institute of Chemistry, Center of excellence for white-green biotechnology, Slovak Academy of Sciences, Tr. A. Hlinku 2, 94976 Nitra, Slovak Republic

*Corresponding author: jan.tomas@uniag.sk

ABSTRACT

The contents of heavy metals in plants were not in relation to contents of heavy metals in soil. Increased content of heavy metals in soils was not in consistency with content in plants. Usually content of heavy metals in plants according to our results were lower than their content in soil. Only the over limit contents of copper and cadmium were assessed in grain of barley and oat. The results of heavy metals content showed that dominant part on content of elements in plants have their mobile forms what depends on pH, content of organic matter in soil and portion of clay parts.

Keywords: agricultural crops, soil type, heavy metals, AAS, highest acceptable amount

INTRODUCTION

In our century of advanced technologies and technical progress soil contamination by various pollutants is one of the most significant environmental problems, which is likely to become more serious and more widespread in the future. Soil is considered a critical environment as it accumulates pollutants produced by various anthropogenic activities - industry, agriculture, transportation, mining and processing of ores, etc. In the recent decades, soil pollution by heavy metals attracted considerable attention because they are non-degradable in comparison with organic pollutants or radionuclides, and in higher concentrations can become toxic. Metals exist in a number of different soluble and particulate forms, which influence their mobility and bioavailability **(Ge et al., 2005)**. High contents of heavy metals in soils would increase the potential uptake of these metals by plants. Therefore, a detailed risk assessment of heavy metal accumulation in agricultural lands is required for application of inorganic fertilizers, organic wastes and pesticides to soils in order to ensure the safe crop production **(Papafilippaki et al., 2007).** Characterizing the factors affecting bioavailability, leaching and toxicity of metals in soil is of substantial importance. Metals are significant natural components of all soils where their presence in the mineral fraction comprises a store of potentially-mobile metal species as important components of clays, minerals and iron and manganese oxides that, in turn, have a dramatic influence on soil geochemistry **(Gadd, 2008)**. Metals are also present in the organic fraction, frequently as bound forms, with some metal recycling occurring as a result of organic matter decomposition. The most important factors which affect their mobility are pH, sorbent nature, presence and concentration of organic and inorganic ligands, including humic and fulvic acids, root exudates and nutrients. There is always a background level of metals in soil originating from the parent rock; metals can be converted to mobile forms under certain conditions. Eco-toxicological studies oriented on metal speciation in soil showed that this is one of the key factors affecting uptake of metals by plants. Bioavailability of metals and their potential uptake is determined by the fraction of free metals present in the soil solution in relation to the total content of metals in the solid phase **(Moffett and Brand, 1996)**. More detailed analyses showed that chemical properties of metals in soil and their retention in the solid phase of soil is affected by pH, quantity of the metal, cation-exchange capacity, content of organic matter and mineralogy of soil. Soil pH was found to play the most important role in determining metal speciation, solubility from mineral surfaces, movement, and eventual bioavailability of metals, due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in the soil solution **(Zhao et al., 2010)**. Heavy metals could pose a risk not only for environment, but also for human population. Chronic lower level intakes of toxic elements have damaging effects on human beings and other animals **(Ikeda et al., 2000)**, since there is no efficient mechanism for their elimination, and the detrimental impact becomes apparent only after several years of exposure **(Bahemuka and Mubofu, 1999)**. Therefore, it is imperative to estimate the effect of soil properties on the availability and the uptake of heavy metals by plants to minimize the toxic effects and the translocation to food chains. In our study the contents of heavy metals in soil from various regions in Slovakia and the contents of heavy metals in agricultural crops from mentioned parts were assessed and compared with Slovak legislative norms from the standpoint of hygienic quality.

MATERIAL AND METHODS

For this study productive parts of plant material were collected in harvest ripeness. Sampling of plant material was carried out on the same sites, where the taking of soil samples was carried out (cadastre - Šurianky, Krompachy, Spišské Vlachy, Rudňany). Total content of monitored heavy metals (Cu, Mn, Zn, Cr, Cd, Co, Pb, Ni) after previous mineralization by dry way of flame AAS was assessed in plant samples.

Table 1 Cultivated crops on monitored sites

No. of Parcel Šurianky	2008	2009
1	Red clover	Red clover
2	Rapeseed	Winter wheat
3	Spring barley	Winter wheat
4	Spring barley	Maize
5	Spring barley	Maize
6	Rapeseed	Winter wheat
7	Wheat	Winter wheat
8	Wheat	Sunflower
9	Wheat	Sugar beet

Transfer coefficients that express relations between heavy metals contents in plant and heavy metals in soil extraction agents of different aggression, were calculated on evaluation of inputs of heavy metals into productive parts of plants. In our work there were strong acids (total contents of heavy metals), 2 M HNO_3 and 0.05 M EDTA.

RESULTS AND DISCUSSION

Results of assessment Pb, Cd, Co, Ni, Zn, Cu and Cr in productive parts of agricultural crops are reflection of soil contamination and afterwards content of risky substances in vegetation including agricultural crops. From the standpoint of risky metals content high requirements are posed especially on productive parts of plants that are used in human nutrition as plant products, raw-materials of food industry, forage crops, from which heavy metals could be transferred into different products. Monitoring of soil in SR has showed that more significant relation between total content of risky metals in soil and their content in plants had been manifested only by elevated values of heavy metals in soil, usually exceeding categories B and C of hygienic limits. In such cases also contents of mobile and mobilizable forms of some heavy metals in soil, especially Cd and Cu, are relatively high. With this objective the samples of agricultural crops cultivated in 1999 and in 2000 were analysed in soil HM in cadastre Šurianky. For eatables, including plant products, the highest acceptable amounts (NPM) of risky metals are defined by Official Publication of MZ SR no. 981/1996-100 and amounts of contaminants in foodstuffs are defined by Decision of MP SR and MZ SR no. 414/2003-100, and executive decree of law concerning foodstuffs no. 152/1995 Z.z. and its practices (Food Codex). NPM for feed and some heavy metals are given by Official Publication of MP SR 1055/1992 as following: Cr 3 $mg.kg^{-1}$; Pb 10 $mg.kg^{-1}$; Cd 1 $mg.kg^{-1}$, by other heavy metals the highest acceptable amounts were not defined. Contents of heavy metals in production parts of plants by which the samples were taken in harvest ripeness in cadastre Šurianky in 2008 are presented in Table 2 and in 2009 in Table 3.

Table 2 Contents of heavy metals in plant samples in $mg.kg^{-1}$(in grain, or rapeseeds; cadastre Šurianky) in year 2008

Site	Crop	Pb	Cd	Co	Ni	Zn	Cu	Cr
1	Red clover	1.60	0.16	1.35	2.13	26.90	14.63	3.63
2	Rape	0.95	0.07	0.40	1.00	33.23	5.98	1.40
3	Barley	0.28	0.03	0.15	0.27	18.00	22.55	1.05
4	Barley	0.52	0.04	0.15	0.67	15.75	6.27	1.47
5	Barley	0.98	0.04	0.13	0.30	29.83	7.38	1.33
6	Rape	0.27	0.13	0.23	0.70	32.20	5.00	1.43
7	Wheat	0.28	0.08	0.05	0.27	33.42	5.93	0.70
8	Wheat	0.38	0.10	0.28	0.43	15.60	6.53	0.80
9	Wheat	0.27	0.04	0.15	0.35	17.05	6.85	0.63

Table 3 Contents of heavy metals in plant samples in $mg.kg^{-1}$(in grain, seeds of sunflower; cadastre Šurianky) in year 2009

Site	Crop	Pb	Cd	Co	Ni	Zn	Cu	Cr
1	Clover	2.75	0.23	1.45	3.35	28.85	26.35	1.75
2	Wheat	0.43	0.11	0.17	0.27	18.00	4.40	0.37
3	Wheat	0.53	0.10	0.17	0.30	21.43	4.30	0.33
4	Maize for silage	0.85	0.12	0.20	0.45	22.10	9.60	1.35
5	Maize grain	0.13	0.11	0.20	0.30	18.40	4.23	0.40
6	Wheat	0.27	0.08	0.17	0.63	15.43	4.00	0.47

7	Wheat	0.23	0.08	0.10	0.30	18.83	3.60	0.43
8	Sunflower	0.93	0.35	0.27	5.83	77.06	26.07	0.43
9	Sugar beet	0.80	0.06	0.27	0.57	11.60	9.93	1.13

According to Food Codex (Appendix 2 of third chapter, second part) chemical elements as contaminants can translocate into foodstuffs from soil and atmosphere, in some cases also from technological equipment, various damaged materials, pipes, etc. Soil is the starting place of risky heavy metals into plant products and through feeds into animal products. The evaluation of contaminating heavy metals is a serious problem while the highest acceptable amounts for plant products are designed for particular forage crops and some heavy metals and NPM are further designed only for products, especially cereals. Therefore, other plants products are evaluated according to NPM for foodstuffs. As it results from the evaluation of content of risky elements in grain of cereals with NPM in eatables (Official Publication of MZ SR no.981/1996-100- Food Codex SR), it will be necessary to pay attention to content of Pb in flour and in products from flour. (An enhancement of the limit 0.5 mg $Pb.kg^{-1}$ in grain of wheat grown in HM parcel no.3 cadastre Šurianky). When using the grown crops on the production of cereal products where the maximal value of Pb is defined 0.7 $mg.kg^{-1}$, all of them will fulfil the criteria of hygienic safety from the standpoint of Pb content in both monitored years. In grown oil-seed plants (in 2008 - rape seed, in 2000 - sunflower) the legislatively determined NPM of Pb is 1.0 $mg.kg^{-1}$. Contents of Pb in oil-seeds did not exceed 0.7 mg $Pb.kg^{-1}$, while NPM for Pb in the oil-seed plants in HM in cadastre Šurianky were relatively approximated. Content of Pb in forage crops was significantly lower than NPM. Contents of Pb in monitored commodities in 2000 were significantly lower than in 1999. The explanations could be seen mainly in extreme climatic situation in 2000, extremely dry and hot vegetation period, extremely moisture deficit that caused not only 50 - 60 % for reducing of plant production, but also disrupted uptake of plant nutrients, including reducing of uptake of heavy metals by plants. Contents of Cd in grain of cereals grown as wheat grain in HM from cadastre Šurianky (parcel no.7 in 1999 and parcels 2, 3, 6 and 7 in 2009) from the point of view of Cd content, these exceeded defined NPM. It will be necessary to pay increased attention to this heavy metal in mentioned parcels. NPM for oil-seed plants it is defined as 0.5 mg $Cd.kg^{-1}$. In seeds of rape the content of Cd was 0.038 $mg.kg^{-1}$, what presents 7.6 % NPM and by sunflower the content of Cd was 0.085 $mg.kg^{-1}$ that is also significantly under value NPM. In sunflower grown in HM the content of Cd was assessed 0.35 mg $Cd.kg^{-1}$. Despite the fact that the content of Cd in soil is in all monitored sites over value A and A_1, its input into plants is significant only in grain of cereals. The highest acceptable amount of Cd in forage crops 1.0 $mg.kg^{-1}$ in clover, alfalfa, maize used for silage was not exceeded. With regard to absence NPM for Co in foodstuffs (Food Codex) its content was not legislatively evaluated. It could only be presumed, that with regard to total content of Co in soil that is not exceeding limit value A, as well as low content of actual mobilizable (0.42 - 9.56 % from total content) and mobile, for plants directly available form Co (0.12 - 0.82 %), there is not assumption of such increased content in plants that will not fulfil requirements for safe foodstuffs. NPM for Ni in cereal products is 3.0 mg $Ni.kg^{-1}$, and for other foodstuffs 2 mg $Ni.kg^{-1}$. Cereals grown in HM had in 2008, also in 2009 content of Ni significantly under particular limits. For the evaluation of Zn content in foodstuffs the valid NPM value is 50 $mg.kg^{-1}$. Content of Zn in monitored crops was not elevated in any case. In 1999 its content was in range from 15.60 to 34.42 $mg.kg^{-1}$, i.e. on the level significantly lower than NPM. Its content was 33.20 and 33.23 $mg.kg^{-1}$ in rape-seed and by grown sunflower its content was 77.06 $mg.kg^{-1}$. While the norm does not define NPM for the content of Zn in oil-seed plants, it was not possible to evaluate its content from the standpoint of valid legislative. With regard to low total content of Zn in soil, as well as minor abundance of mobile and mobilizable forms in key sites, there is not an assumption for exceeding of NPM for Zn. Decision of MZ SR defined the highest acceptable amount for copper as value 10.0 $mg.kg^{-1}$ for cereal products. Legislative limit for Cu was elevated in 2008 in grain of barley grown in HM (parcel 3, cadastre Šurianky).

Content of Cu in grown oil-seed plants was not evaluated, while Official Publication of MZ SR NPM for Cu in oil-seed plants is not legislatively defined. Assessed contents of Cr in tested plant products exceeded NPM that is defined as 0.5 $mg.kg^{-1}$. In HM NPM for Cr in grain of barley was exceeded in 1999 (parcel 3, 4 and 5), in grain of wheat (parcel 7, 8 and 9). Content of Cr in cereal grain in 2000 was under defined limit. NPM of mentioned Cr in oil-seed plants is not defined. **Hronec, Tóth, Holobradý (1992)** and others reported that the dynamics of metals in system soil - plants is affected not only by distribution of metals in soil, but also intensity and specificity of physiological processes in plant have important role that varies among plant species. Contents of heavy metals in plant material not always exerted direct proportionality with content of heavy metals in soil. As we have already emphasised, an uptake of heavy metals by plants depends on soil traits (soil reaction, content and quality humus, physical soil traits, contents of nutrients in soil), from agricultural engineering, climatic conditions (especially from composition and amount of rainfalls) and from grown plant on the other hand. It is known, that some plants are against some heavy metals more tolerant, others are highly sensitive. Physiological state of plant is determined by selectivity of heavy metals intake, while specificity of plant species is significant from standpoint of taking of particular heavy metal from soil and its distribution into individual plant organs. Negative manifestation of heavy metals in plant could include many physiological and biochemical changes, which by yield depression reduce the nutritive, sensory as well as hygienic value of grown products.

CONCLUSION

Contents of heavy metals in plant material not always exerted direct proportionality with content of heavy metals in soil. Enhanced contents of heavy metals in soil did not determined enhanced content of elements in plants. As it results from our gained data the dominant portion of element content in plant are formed by mobile and mobilizable forms, while their availability and mobility has been in relation to soil reaction, content of organic matter in soil, as well as portion of clay particles. Under conditions of tested crops the influence of weakly alkali soil reaction on mobility, and thus the bioavailability of monitored elements in soil was manifested. With regard to low content of available forms of Cu in soil, assessed low content of Cu in plant and low values of transfer coefficients are natural, that NPM for copper content in eatables (10 $mg.kg^{-1}$) were not exceeded and plant products are suitable for production of safe foodstuffs. The cause of low accumulation of Cu in plants, in spite of its high total content in soil, is high value of soil reaction.

Low transfer of Pb into plants also resulted from low percentual composition of mobile forms from total content (in average 28.83 % by 0.05 M EDTA and 0.72 % by 0.01 $CaCl_2$) in 2008 and in 2009 it was in average 21.44 % by 0.05 M EDTA and 1.36 % by 0.01 M $CaCl_2$. Gained results confirmed the fact that lead ranks among the least mobile heavy metals in soil and its uptake by plant is low **(Beneš, Pabianová,1987; Makovníková, 1998; Zaujec, 1999)**.

Solubility of Zn increases directly proportional with aggression of extraction reagent, while in plants, the values reflects natural content in plants and its significance as biologically important microelement. Most of plants have Zn content in range 25 - 100 $mg.kg^{-1}$. Significant inhibition of its uptake is caused by the presence of Cu^{2+}, Mg^{2+} **(Fecenko, Ložek, 2000)**.

Beneš (1994) reported that most plants well tolerate elevated values of Cd in soil. Higher uptake of Cd from soil the plants eliminate by uptake of Ca^{2+} a Mg^{2+}, or by retention of abundant ions in roots or within borders of metabolic important organs, reducing of activity of abundant ions and their transfer into physiologically inert forms.

Over limit contents of copper and cadmium were assessed in grain of barley and oat **(Appendix no.2 of third chapter of second part in Food Codex SR no. 981/1996-100)**. However, the assessed amounts of heavy metals in biomass are in consistency with NPM in forage crops **(Appendix of Decision no.117/1987)**. Significant variability of gained results was influenced also by methodical procedure, when all analysed plants were taken directly from parcels, in which content of heavy metals in individual extraction reagents were assessed. Contamination of plants from atmosphere under mentioned conditions could not be eliminated. Thus some authors, **Hecl (2000), Hegedüsová (2001)** evaluated uptakes of heavy metals into plants and transfer coefficients under conditions of vegetation pot trials. In spite of results gained in terrain, the results on the same soil and the same crop under conditions of vegetation trials showed relatively higher rates of correlation.

Acknowledgments: This contribution is the result of the project implementation: VEGA no. 1/2428/05. This contribution is the result of the project implementation: Centre of excellence forwhite-green biotechnology, ITMS 26220120054, supported by the Research & Development Operational Programme funded by the ERDF.

REFERENCES

BAHEMUKA, T.E. - MUBOFU, E.B. Heavy metals in edible green vegetables grown along the sites of the Sinza and Msimbazi rivers in Dar es Salaam, Tanzania. In *Food Chem.,* vol.66, 1999, 63-66 p.

BENEŠ, S. - PABIANOVÁ, J. 1987. Přirozené obsahy, distribuce a klasifikace prvku v půdach. Natural contents, distribution and classification of element in soils. VŠZ. VN MON Praha, 1987, 205 p.

BENEŠ, S. 1994. Obsahy a bilance prvků ve sférach životního prostředí. I., II. část. Praha MZ ČR, 1994. Contents and balance of elements in spheres of environment, I., II. part, Prague MZ CR, 125 p.

FECENKO, J. - LOŽEK, O. 2000. Výživa a hnojenie poľných plodín. Nutrition and fertilizing of agricultural crops, SUA Nitra, 452 p. ISBN 80-7137-777-5

GADD, G.M. 2009. Heavy metal pollutants: environmental and biotechnological aspects. In *Encyclopedia of Microbiology.* Ed: M. Schaechter, Elsevier, Oxford. 321-334 p.

GE, Y. - MACDONALD, D. - SAUVOÉ, S. - HENDERSHOT, W. 2005. Modeling of Cd and Pb speciation in soil solutions by WinHumic V and NICA-Donnan model. In *Environ. Model. Softw.* vol. 20, 2005, 353-359 p.

HECL, J. 2000. Vplyv rozdielnych dávok Cd a Pb na jeho distribúciu v jarnom jačmeni. In *Cudzorodé látky v životnom prostredí*. Influence of various doses of Cd and Pb on its distribution in spring barley. In *Foreign matters in environment,* SUA Nitra, p. 66 - 69. ISBN 80-7137-745-7

HEGEDÜSOVÁ, A. 2001. Ťažké kovy v pôdach južného Slovenska a hygienická nezávadnosť pestovaných druhov zeleniny. In *Doktorandská dizertačná práca*. Heavy metals in soils of southern Slovakia and hygienic safety of grown vegetable species. In *Doctoral thesis,* SUA Nitra, 165 p.

HRONEC, O. - TÓTH, J. - HOLOBRADÝ, K. 1992. Exhaláty vo vzťahu k pôdam a rastlinám východného Slovenska. Air pollutants in relation to soil and plants of eastern Slovakia, Príroda Bratislava 1992. 194 p. ISBN 80-07-00546-3

IKEDA, M. – ZHANG, Z. W. – SHIMBO, S. – WATANABE, T. – NAKATSUKA, H. – MOON, C.S., et al. Urban population exposure to lead and cadmium in east and south-east Asia. In *Sci Total Environ,* vol. 249, 2000, 373- 84 p.

MOFFETT, J. W. - L. E. BRAND. 1996. The production of strong, extracellular Cu chelators by marine Cyanobacteria in response to Cu stress, In *Limnnology and Oceanography*, vol. 41, 1996, 288-293 p.

PAPAFILIPPAKI A. - GASPARATOS D. - HAIDOUTI C. - STAVROULAKIS G. 2007. Total and bioavailable forms of Cu, Zn, Pb and Cr in agricultural soils. A study from the hydrological basin of Keritis, Chania, Greece. In *Global Nest J.*, vol. 9, 2007, 201-206 p.

ZAUJEC. A. 1999. Cudzorodé látky a hygiena pôd. Foreign matters and soil hygiene, SUA Nitra. VES Nitra

ZHAO, K.L. - LIU, X.M. – XU, J.M. - SELIM, H.M. 2010. Heavy metal contaminations in a soil-rice system: identification of spatial dependence in relation to soil properties of paddy fields. In *Journal of Hazardous Materials*, vol. 181, 2010, 778-787 p.