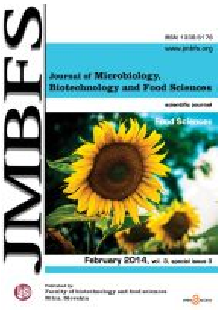

JMBFS

Journal of Microbiology, Biotechnology and Food Sciences

International peer-reviewed scientific online journal

Published by Faculty of Biotechnology and Food Sciences

THE HEAVY METALS CONNTENT IN VEGETABLES FROM MIDDLE SPIŠ AREA

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ARTICLE INFO

Received 19. 10. 2013
Revised 19. 11. 2013
Accepted 9. 1. 2014
Published 1. 2. 2014

Regular article

OPEN ACCESS

ABSTRACT

In the middle area of Spiš, it is significantly burden by heavy metals what is documented by radical content of Hg in soil from Rudňany 58.583645 mg.kg $^{-1}$. On the content of heavy metals in vegetables grown in this soil it has the same effect. 61.5% samples exceeded the limit value of heavy metals. The most dangerous vegetables were *Lactuca sativa* L. The limit value was exceed in all determine heavy metals - Hg, Cd, Pb and Cu in this vegetables. In the case of Hg, the limit value exceed 93.86 times. For relatively safety is growing of *Pisum sativum* L., where there was no exceed any limits values. The root vegetables are dangerous, where the sample of *Raphanus sativus* L. exceed 6.71978 times the limit values for Pb although the content of lead in the soil was under hygienic limits. Transfer of heavy metals into consume parts of vegetables was no limited by high content of humus into soil. Transfer of heavy metals into consume parts of vegetables was no limited by weakly alkaline soil reaction. These factors are considered for factors limited mobility and input heavy metals into plants. We determined heavy metals by AAS method on a *Varian 240* FS and method AMA 254.

Keywords: mercury, cadmium, lead, cooper, soil

INTRODUCTION

The area of middle Spiš is significantly burden by heavy metal in content of soils (**Hronec et al. 2008**). In addition to air pollution, there are other sources of pollution. They came from the extraction of minerals, their modification and processing. From the iron manufactory in Rudňany were emitted into air 120 tons of mercury. These data prepared by measuring groups of Research Institute of Mineral (now Research Institute of Geotechnics SAS) in Košice. These amounts have been challenged by State Inspection of SR. Based on the balance of atmospheric emission of mercury they calculated, that in the environment received 40 tons Hg per year. It means the highest source of mercury pollution in Europe (**Závodský, 1991**). In this area, the specific sources of pollution endogenous geochemical anomalies, especially in the area of Rudňany, Poráč, Gelnice, Slovinky and Krompachy (**Čurlík a Šefčík, 1999**). In these days, the highest producer of air pollution is town Krompachy, where kovohuty Krompachy and iron foundry Slovak energy manufactory (SEZ) produce 90% of total emissions (Hronec et al. 2008). This loaded area (Rudniansko-Gelnická) has 52 000 residents living in the area of 357 km ^{2}. This area has a rural character, with significant incidence of private occupation of farmland. Soil contaminated with metals is a primary route of toxic element exposure to humans. Toxic metals can enter the human body by consumption of contaminated food crops, water or inhalation of dust.and cause damage to the organism, its toxic efects. (**Mahmoode *et al.* 2013**)Vegetables are the important life-supporting materials for human beings and animals because vegetables contain essential components as proteins, vitamin, iron, calcium and other nutrients **Yang *et al.* 2011**). At the same time, however, the possibility of accumulation of risk elements vegetables grown on contaminated soil (**Luo *et al.* 2010**).Heavymetals released from industrial production penetrate the soils where vegetables and crops are grown by contaminating irrigation water and through direct deposition by air. Plants can take up these metals from soil by their roots, transport them upwards to their shoots, and finally accumulate them inside their tissues, s, although there are large variations among different plant species in terms of metal accumulation ability (**Luo *et al.* 2010).** Most dangerous elements in terms of their content in the soil to a possible accumulation of plants in this area appear Hg, Cd, Pb, and Cu. Toxic effect of Hg and its compounds is largely the reaction of Hg ion with SH-groups of biomolecules with subsequent changes in the permeability of cell membranes and damage cellular enzymes. Mercury has the ability to accumulate in the human body. Leads to toxic manifestations of brain damage and peripheral nerves. (**Zahir *et al.*, 2005**). All compounds of cadmium are toxic. Cd has a high acute toxicity tests and certified short current (short-term) inhalation of high levels may result in the human body resulting in lung damage. It is highly toxic, causing inhibition of sulfhydryl enzymes in particular. Binds in the liver, but also affects the metabolism of carbohydrates and inhibits insulin secretion (**Godt *et al.*, 2006**). Depending on the amount of exposure, lead can adversely affect the nervous system, kidneys, the immune system, reproductive and developmental systems and the cardiovascular system. Its toxic effects vary from subtle changes in neurocognitive function in low-level exposures to a potentially fatal encephalopathy in acute lead poisoning (**Gillis *et al.*, 2012**). Copper is one of the essential elements for humans, but many copper compounds are potentially toxic. Excessive intake of copper is manifested neurological disorders (**Shaligram, Campbel, 2013**). This study was conducted to assess the heavy metal concentration in soils, resulted uptake by the vegetables and eminent transfer to the food chain which assist in evaluating the related health hazards linked with it.

MATERIAL AND METHODS

Sampling Samples

Collection of plant and soil samples was carried out by 08 July 2013 in the village Rudňany, which were taken from the first soil sample locations and 3 vegetables species (*Lactica sativa,* L., *Allium cepa,* L., *Pisum sativum,* L.) GPS coordinates N 48 ° 52.986 E 20 ° 40.560. The second site is also a soil sample and 4 vegetables species (*Allium cepa,* L., *Pisum sativum,* L.,*Daucus carota,* L.,*Raphanus sativus,* L.,). GPS coordinates N 48°52,696 E 20°39,815. The third soil sample locations, and 3 types of vegetables (B*eta vulgaris var conditiva, Allium cepa,* L.,*Daucus carota,* L.) GPS coordinates N 48°52,679 E 20°39,703.

And 10 July 2013 in the village Odorín where we sampled the soil and 3 vegetables species (*Allium cepa*, L., *Brassica oleracea conv. Gongylodes*, L., *Daucus carota*, L.). GPS coordinates N 48° 56'5,247 E 20° 38' 25,3428.

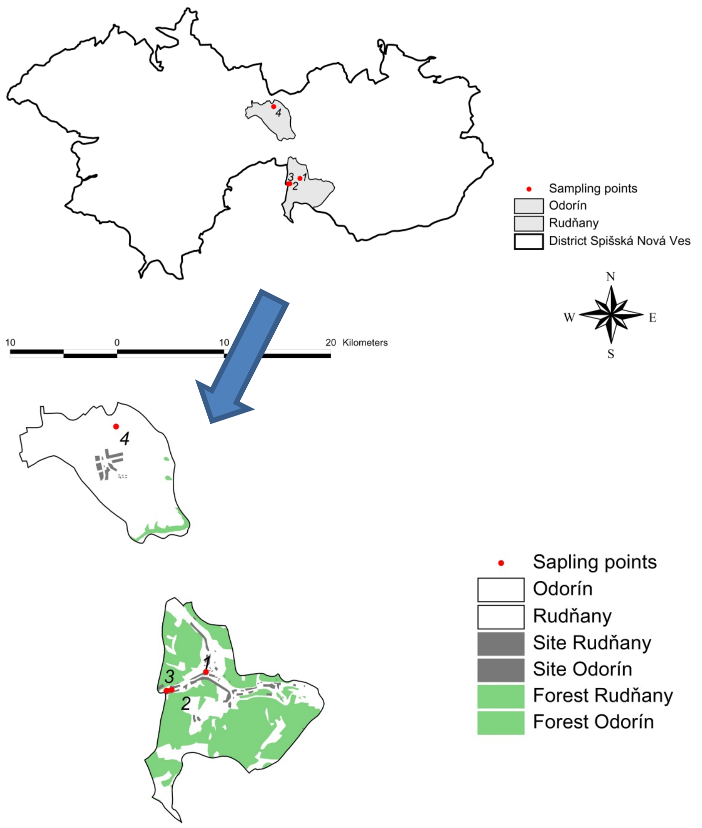

Figure 1

Processing of soil samples

The soil samples were dried on filter paper, removed from the plant material and soil milled at the mill. We were sieved through the sieve with a mesh size of 0.125 mm.

Processing of plant samples

Individual pieces of vegetables were divided according to the type and the point of consumption, purified the soil and temporarily kept in the cold to perform the analysis on the content of heavy metals.

Performed analyzes

Determination of organic carbon and humus in the soil according to Turin and the modifications by Nikitin

Soil organic carbon is oxidized with oxygen in chromo-sulfuric mixture. The amount of oxygen consumed in the oxidation is determined by the difference consumed and unconsumed chromo-sulfuric mixture. Humus content was found by calculation according to the following of relations:

$$C_{ox} = \frac{(a-b)\times 0{,}03\times 1{,}17\times f_{mohr}}{n} [\%]$$

(a - b) = difference between sample and blank test
f_{mohr} = accurate substance concentration of Mohr salt
n = sample weight in g
humus content = c_{ox} x 1, 724 [%]
c_{ox} = percentage of oxidizable carbon
1, 724 = conversion factor to humus content in the soil sample.

Determination of exchange reactions in soil KCl (pH/KCl)

Twenty grams of soil samples were taken. Subsequently 50 ml of KCl (c =1 M) was added. The suspension was allowed 10 minutes to shake by shaker Heidolphpromax 1020 at a frequency of 180 oscilation per minute. After shaking and settled solution we were filtered suspension through filter paper *FILTRAK* 390. After filtering the suspension, the pH of the filtrate was measured on the pH meter Metrohm 691, we calibration aparat to two buffers at pH 4 and 7. The resulting values were subtracted from pH meter display with two decimal places.

Extraction of soil HNO3 + HCl (aqua regia)

In terms of the current legislation (Law no. 220/2004 Coll on the conservation and use of agricultural land). We proceeded in accordance with the applicable methodology, and heavy metal content were determined on a *Varian 240 FS*.

Determination of total mercury content

To determine the content of total mercury in samples of vegetables and soil, we used the same device. AMA 254 (Advanced Mercury Analyser) is special purpose atomic absorption spectrophotometer for the determination of mercury. It is designed for direct determination of mercury in solid and liquid samples without the need for chemical pretreatment of the sample (mineralization etc.). Using the technique of generating a vapor of metallic mercury with subsequent interception and enrichment on a gold amalgamator achieves a high sensitivity setting and independence the result of determining the sample matrix. All mercury concentrations were expressed in mg kg^{-1} dry matter.

RESULTS AND DISCUSSION

Table 1 results in soil from sample points

sample point	pH H_2O	pH KCl	% Cox	% humus	VGS 84
1	7.77	7.00	2.9601	5.103212	N 48° 52.986 E 20° 40.560
2	7.65	5.97	3.0654	5.28475	N 48°52.696 E 20°39.815
3	8.04	7.25	3.5919	6.192436	N 48°52.679 E 20°39.703
4	7.37	6.50	2.5389	4.377064	N 48°56'5.247 E 20°38'25.3428

All four soil samples were sandy-loam,loam. Acidity-alkalinity of the soil was evaluated as follows: soil samples from sampling point 1, 2 and 4 were slightly alkaline soil sample from the sampling point 3 was moderately alkaline enlarged scale by USDA. In terms of content of humus samples were evaluated as follows: a sample soil from the sampling point 4 was strongly humic-rich humus. Soil samples from sampling points 1, 2 and 3 were very strongly humic with high humus content.

Table 2 results of heavy metals content in soil from HNO_3 + HCl extraction (aqua regia)

sample points	Hg(AMA 254) mg.kg^{-1}	Cd mg.kg^{-1}	Pb mg.kg^{-1}	Cu mg.kg^{-1}
1	58.583645	2.38	70.9	201.3
2	19.882359	1.48	32.3	27.2
3	14.83145	2.12	35.1	75.9
4	1.038726	1.88	39.2	39.3
Min	1.038726	1.48	32.3	27.2
Max	58.583645	2.38	70.9	201.3
Median	17.3569045	2	37.15	57.6
STDV	24.6547751	0.382405	17.9089	79.65427

The contents of heavy metals in soil were evaluated according to the Annex. 2 of the law. 220/2004 Z. z. Type of soil samples from the point of delivery 1 was sandy-loam, loam and mercury content exceeded 117,16 times. The content of cadmium was exceeded 3.4 times. When the lead content limit has been exceeded by 0.9 mg.kg -1. The copper content exceeded 3,355 times. Type of soil samples from the point of delivery 2 was sandy-loam, loam. Mercury content was 39.76 times exceeded it. The cadmium content exceeded 2.11 times. The lead content did not exceed the limit value of 70 mg. kg -1. The copper content did not exceed the limit value of 60 mg. 1.soil kg-kind samples from the point of delivery 3 was sandy-aluminum oxide. Mercury content exceeded 29.6629 times. The content of cadmium was exceeded 3 times. The lead content did not exceed the limit value. The copper content exceeded 1.29 times. Type of soil samples from the point of delivery 4 was sandy-loam, loam. Mercury content was exceeded 2 times. The cadmium content exceeded 2.68 times. The content of lead and copper were below the limit values. The results showed that all the studied soil were heavily burdened with heavy metal.

Table 3 heavy metals content in vegetable (fresh mass)

sample point		Hg	Cd	Pb	Cu	
1	1	4.69319	0.248930	3.385443	14.03963	*Lactuca sativa* L.
	2	0.035835	0.083963	2.052430	7.183506	*Allium cepa* L.
	3	0.009366	0.008749	0.087489	5.424322	*Pisum sativum* L.
2	4	0.022672	0.000000	0.093432	4.017565	*Allium cepa* L.
	5	0.007837	0.019820	0.099098	4.459419	*Pisum sativum* L.
	6	0.058203	0.046856	0.093712	4.029613	*Daucus carota* L.
	7	0.406264	0.163195	0.671978	2.879908	*Raphanus sativus* L.
3	8	0.051668	0.014585	0.145847	4.812951	*Beta vulgaris v. conditiva* L.
	9	0.004868	0.029394	0.097982	4.115226	*Allium cepa* L.
	10	0.033513	0.028289	0.094295	4.243281	*Daucus carota* L.
4	11	0.013271	0.038691	0.154763	2.708349	*Allium cepa* L.
	12	0.002657	0.147289	1.196723	3.590168	*Brassica oleracea c. Gongylodes* L.
	13	0.009872	0.100417	0.617951	3.707709	*Daucus carota* L.

In sample No. 1 (*Lactuca sativa,* L.) elevated levels of heavy metals were detected in the case of mercury 93.86 times more than the legislation indicates, rescript Dietary Code. 18558/2006-SL 2006. The cadmium content in this sample was 1,244 times higher than the limit for wheatgrass rescript by the Ministry of Agriculture and Ministry of Health no. 608/3/2004 - 100 The lead content exceeded 11.28 times as indicated by Commission Regulation (EC) no. 1881/2006 2006 for lead content in leafy vegetables. The copper content exceeded 1,403 times as indicated by the Dietary Code restcript of Ministry of Agriculture and the Ministry of Health no. 608/3/2004-100 of 15 March 2004. These values are higher than those found by **Zheng *et al.* (2007)**. In sample No. 2 (*Allium cepa* L.) has been exceeded cadmium 1.67926 times as indicated by Commission Regulation (EC) no. 1881/2006 2006 for vegetables. The lead content exceeded 20.52 times the limit value for vegetables. In the sample No. 6 (*Daucus carota* L.) has been exceeded 1,164 times the mercury content than the income limit under the Food Code no. 18558/2006-SL 2006. Similar results were also recorded by **Miklavčič *et al.* (2013)**. In the sample no. 7 (*Raphanus sativus* L.), we found exceeded 8,125 times the mercury content, the content of cadmium was exceeded 1, 63195 times as indicated by Commission Regulation (EC) no. 1881/2006 2006 for root vegetables. The lead content exceeded 6.71978 times. These values are higher than those found by **Ali (2012)** In the sample No. 8 (*Beta vulgaris. conditiva* L.) limit has been exceeded in the case of mercury 1,03336 times and the lead content of 1,45847 times more than the income limit under the Ministry of Agriculture and Ministry of Health no. 608/3/2004 - 100 for vegetables. In the sample No. 11 (*Allium cepa* L.) exceeded the lead content of 1,54763 times the limit yield under the Ministry of Agriculture and Ministry of Health no. 608/3/2004 - 100 for vegetables. In the sample No. 12 (*Brassica oleracea c. Gongylodes* L.) has been exceeded cadmium 1,47289 times the limit rescript under the Ministry of Agriculture and Ministry of Health no. 608/3/2004 - 100 for root vegetables. The lead content exceeded 11.96 times. Similar results were found by **Mahmood (2013)**. In the sample No. 13 (*Daucus carota* L) was exceeded cadmium 1,00417 times the limit rescript under the Ministry of Agriculture and Ministry of Health no. 608/3/2004 - 100 for root vegetables. The lead content exceeded 6,179 times. These values are higher than stated by **Tiwarii *et al.* (2011)**. Particularly at risk are growing phenomena of *Lactuca sativa L.* on the contaminated soils, as well as several species of root vegetables.

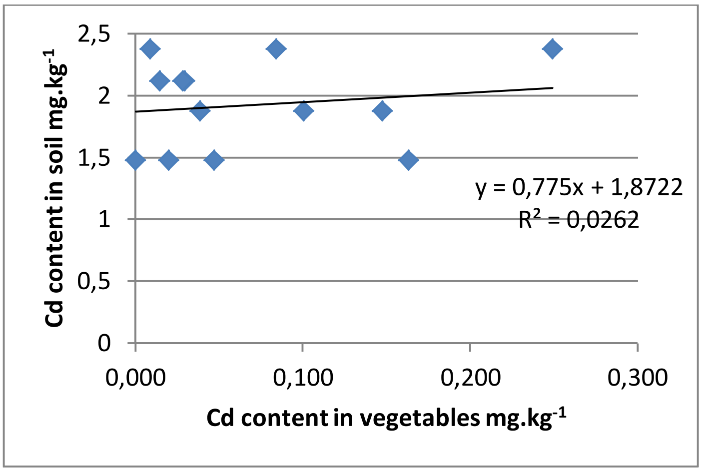

Figure 2 dependence of Cd content in vegetables

We found a slight dependence of Cd content in vegetables from the Cd content in the soil.

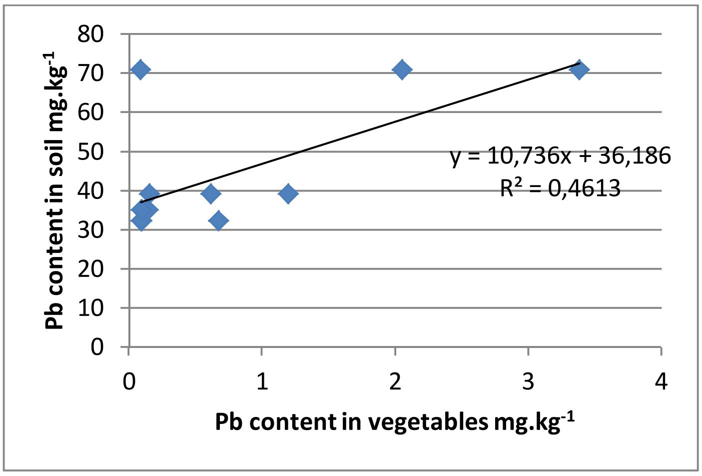

Figure 3 Pb content in Vegetables

Confirmed the dependence of Pb content in vegetables from the Pb content in the soil.

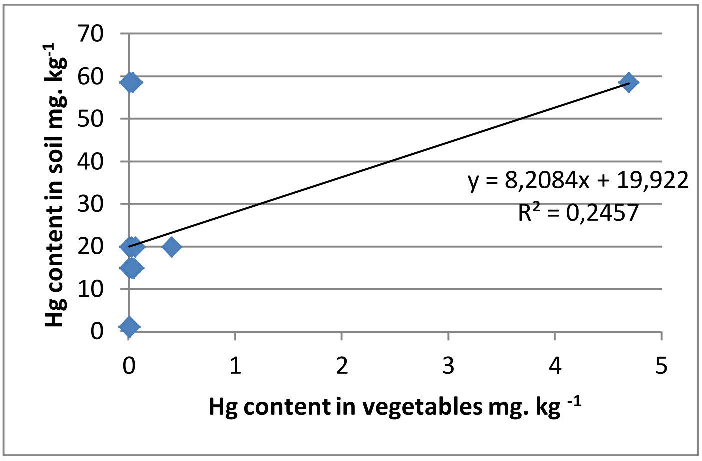

Figure 4 dependence of Hg content in vegetables

We found a strong dependence of the Hg content in vegetables by Hg content in the soil.

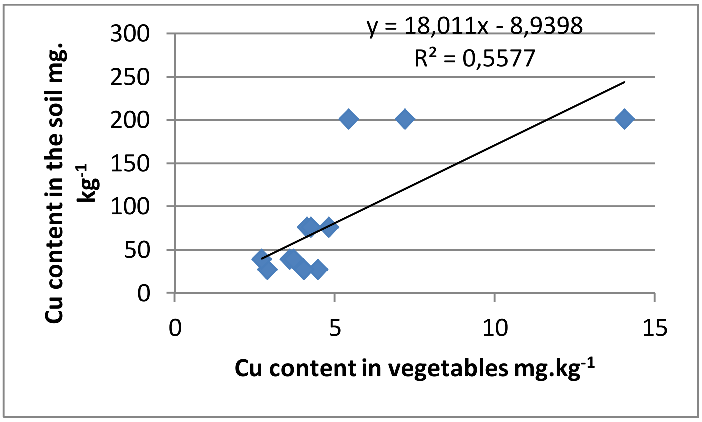

Figure 5 dependence of Cu content in vegetables

We found a strong dependence of the Cu content in vegetables of the Cu in the soil.

CONCLUSION

We found that growing vegetables on soil contaminated by heavy metals is high risk. In terms of number exceeded health limits can be argued that heavy metals accumulate in parts of vegetable consumption from the area of interest in order Pb > Cd > Hg > Cu . However, there are significant interspecies differences , for the most risky type of vegetable can be called Lactuca sativa L. where it was found the most extreme hygienic limit exceeded in all samples 93.86 times the limit value for mercury content in vegetables . Also, root vegetables significantly accumulates heavy metals. The difference observed in Pisum sativum L. where limit is not exceeded in value despite the heavily contaminated soil in which to grow. Landowners from which we sampled was recommended to them consists in not cultivating vegetables Javascript significant risk of transfer of toxic heavy metals in their diet . The potential agronomic interventions to improve the condition of land is the most practical phenomena replacement of topsoil.

Acknowledgments: We would especially like to thank the citizens of municipalities and Rudňany Odorín, which allowed us to sampling their land. SUA also colleagues from which we sampled as well department of Chemistry workers who worked in the processing of samples.
The research was funded by VEGA 1/0630/13 and 1/0124/12 Vega.

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