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THE RELATIONSHIP OF HEAVY METAL CONTENTS IN SOILS TO THEIR CONTENT IN CHOSEN LEGUME SEEDS

ZALEŻNOŚĆ POMIĘDZY ZAWARTOŚCIĄ METALI CIĘŻKICH W GLEBIE I ICH ZAWARTOŚCIĄ W NASIONACH WYBRANYCH ROŚLIN STRĄCZKOWYCH

Key words: pea, bean, risky elements, soil.
Słowa kluczowe: groch, fasola, gleba.

Celem badań, których wyniki są prezentowane w niniejszym opracowaniu, jest określenie zawartości metali ciężkich (Cu, Fe, Mn, Cd, Pb, Ni, Co, Cr i Zn) w glebie oraz ich związek z wybranymi odmianami fasoli i grochu. Glebę (według rejestru PD Vinica), na której uprawiano zielony groszek i fasolę, charakteryzował odczyn obojętny do silnie kwaśnego, z typową zawartością kationów K, P i Mg. Całkowita zawartość badanych metali była większa niż wartość tła A, z wyjątkiem kadmu. Oznaczona zawartość metali w 2M kwasie azotowym nie przekroczyła wartości granicznej A_1. Kolejne badania obejmowały analizę gleb (według rejestru PD Horná Streda), na których uprawiano fasolę i groch. Wykazały one bardzo dużą zawartość magnezu w obu uprawianych roślinach oraz dużą zawartość potasu w grochu i bardzo dużą w fasoli.
Zawartość badanych metali była powyżej wartości tła A dla kadmu, miedzi i niklu, ale nie przekroczyła wartości granicznej określonej w aktach prawnych dotyczących zanieczyszczeń gleby.
Malejący szereg zawartości poszczególnych pierwiastków kształtował się następująco: Fe> Zn> Mn> Cu> Ni> Pb> Cr ≈ Co> Cd. Zawartość badanych metali z wyjątkiem kadmu, nie przekroczyła maksymalnej wartości dopuszczalnej w roślinach strączkowych, określonej w Kodeksie Żywnościowym.

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1. INTRODUCTION

Soil is a dynamic system which is influenced by various factors, whether natural or anthropic, causing the contamination. Changes that occur due to these factors in the soil cause bioaccessibility of metals and can enrich the soil with other elements that are biologically active, or contrary, degrade a land, and it becomes inappropriate for crop growth. Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem.

Living organisms require varying amounts of „heavy metals". Iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans. Excessive levels can be harmful to the organism. Other heavy metals such as mercury and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Certain elements that are normally toxic are, for certain organisms or under certain conditions, beneficial. Some of these elements are actually necessary for humans in trace amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth – nickel, cadmium, copper, chromium [Cimboláková, Nováková 2009]. Plants which exhibit hyper accumulation can be used to remove heavy metals from soils by concentrating them in their bio matter.

Legumes are rich and inexpensive source of proteins, carbohydrates, dietary fibres to millions of peoples. In addition to being an important source of protein, legumes are also reported to be a good source of minerals (K, P, Ca, Mg) and trace elements. Metals, such as iron, zinc and manganese are essential metals, since they play an important role in biological systems. Cu and Zn are essential micronutrients, they can be toxic when taken in excess. Lead and cadmium are non essential metals as they are toxic, even in trace [Gençcelep et al. 2009].

The monitoring of heavy metals content in legumes is very important because consumption of vegetable (e.g. green pea) is high. The aim of this research was to determine chosen heavy metals content of legume species - frozen vegetables (green pea) or dry grains.

2. MATERIALS AND METHODS

Material. In cooperation with PD Vinica, one of the most important producers of frozen vegetable on our market, samples of 5 fresh green peas' varieties were taken (Cezar, Joff, Fabundo, Primo, Favorit). Dry legumes (bean cv. Ema and pea Jadeit, Achát, Olivín, Xantos, Jantár, Svit) were purchased by fy Legusem Horná Streda.

Then the pH was determined, the nutrients contents and the risk elements contents in soil from the same sites, from which the legume samples were taken with the aim to find out the relations between soil traits in grain. Soil samples were taken by pedologic tool in the depths 0–10 cm (A horizon).

Methods. Major mineral elements (K, Ca, Mg) and trace elements (Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, Cd) – in soil and matter – were determined using a Varian AA240FS atomic absorption spectrometer equipped with a D2 lamp background correction system, using an air – acetylene flame.

Soil reaction was determined as pH/ KCl, nutrients contents were determined by Mehlich II. procedure and by AAS method the total and releasable (in the solution of 2 M HNO_3) content of risk elements was determined. The sample of legume grains to the same place were collected the soil sample after their drying, regulation and decomposition by HNO_3 on the microwave digestion. The legume samples was incinerated in a Nabertherm muffle furnace MARS X Press Microwave Oven at 200°C and dissolved ash was diluted to a certain volume with water. The mixture was heated in a digestion block according to the following sequence: 20–175°C/15 min, 175°C /15 min, 175–80°C/20 min. Minerals and trace elements concentrations were determined on a dry weight basis as $mg \cdot kg^{-1}$.

The results were evaluated according to the Decision of Ministry of Agriculture in Slovak republic about highest acceptable limits of toxic compounds in soil No. 531/1994 – 540 and Food Codex SR.

3. RESULTS AND DISCUSSION

Vinica cadastre. Soils from four plots from which samples of green peas were collected, were moderately humus-containing with neutral to extremely acid soil reaction. It was characterized by moderate to good potassium content, medium to high phosphorus content and good to high magnesium content. Nutrient content determined in soil samples ranged from 1575 to 1750 $mg \cdot kg^{-1}$ N, 66,4–103,8 $mg \cdot kg^{-1}$ P, 173–250 $mg \cdot kg^{-1}$ K, 1225–2644,5 $mg \cdot kg^{-1}$ Ca, 199–289 $mg \cdot kg^{-1}$ Mg.

Table 1. Nutrients contents (Mehlich II) in $mg \cdot kg^{-1}$ and soil reaction in soils PD Vinica
Tabela 1. Zawartość nutrientów w $mg \cdot kg^{-1}$ i charakterystyka gleb w rejonie PD Vinica

Area / variety	Ca	Mg	K	P	N	pH_{KCl}	% Humus
1A / Cesar	2644.5	209.5	221.5	101.8	1750.0	6.60	2.26
2A / Primo	1841.5	241.5	173.0	66.4	1575.0	5.52	2.52
3A / Favorit	2016.0	289.0	223.0	103.8	1575.0	5.70	2.35
4A / Fabundo, Joff	1225.0	199.0	250.0	86.6	1575.0	4.50	2.64

The values of total risk elements contents (Tab. 2) were under the concentrations defined under A limit value with the exception of Cd (a background value A is 0,8 mg·kg^{-1}), because its total contents were enhanced on all 4 plots. In soil samples the releasable risk elements contents were also determined in the solution of HNO_3 (c = 2 mol·dm^{-3}). All of determined values were lower than reference value A_1 (a background value A_1 for Cd is 0,3 mg·kg^{-1}) (Tab. 3).

Table 2. Total risk elements contents in soils PD Vinica in mg·kg^{-1}

Tabela 2. Całkowita zawartość metali ciężkich w glebach rejonu PD Vinica w mg·kg^{-1}

Area / variety	Zn	Cu	Cr	Cd	Pb	Ni	Co
1A / Cesar	77.6	26.0	40.8	1.24	30.0	34.4	13.6
2A / Primo	73.2	32.4	49.6	1.00	33.6	34.4	18.4
3A / Favorit	75.6	29.6	35.6	0.92	28.4	34.8	15.6
4A / Fabundo, Joff	63.2	24.0	42.8	1.12	28.8	31.6	14.8

Table 3. Risk elements content in mg·kg^{-1} in nitric acid extract (c = 2 mol·dm^{-3}) in the soils from PD Vinica

Tabela 3. Zawartość metali ciężkich w glebach rejonu PD Vinica w mg·kg^{-1}, oznaczona wobec 2M kwasu azotowego

Area / variety	Zn	Cu	Cr	Cd	Pb	Ni	Co
1A / Cesar	13.5	8.3	2.9	0.19	9.5	4.5	3.2
2A / Primo	10.6	7.9	4.0	0.19	11.6	4.1	3.9
3A / Favorit	12.0	8.2	2.4	0.16	9.8	4.0	3.1
4A / Fabundo, Joff	8.5	6.1	1.8	0.17	8.9	3.9	2.3

The heavy metals contents in soil did not exceeded the limit values specified by law 531/1994 – 540 (Decision of the Ministry of Agriculture SR). However, from the point of view of risky metal intake by plants, is important content of accessible, respectively potentially mobilizable forms of heavy metal. And from this perspective soil can be described as relatively uncontaminated. Any of the determination of heavy metals content in the soil below the threshold does not guarantee that the plants growing on this soil will always contain their tolerable amounts. It is therefore crucial in terms of hygiene, whether the heavy metals accumulate in parts of plant used for consumption [Zrůst 2003].

Table 4. Heavy metals content in mg·kg^{-1} in legume from PD Vinica
Tabela 4. Zawartość metali ciężkich w roślinach strączkowych w mg·kg^{-1}, hodowanych w rejonie PD Vinica

Crop	Variety	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
Green pea	Cezar	91.84	15.97	43.40	10.24	0.69	2.60	0.86	0.17	1.04
	Fabundo	75.85	12.00	42.90	7.65	0.40	2.60	0.45	0.45	0.08
	Favorit	69.35	15.30	35.35	7.55	0.30	3.05	0.30	0.70	0.13
	Jof	67.10	10.60	42.60	7.60	0.15	2.00	0.35	0.65	0.10
	Primo	62.20	10.75	38.80	8.80	0.20	2.35	0.30	0.90	0.12
Yellow bean	Ema	60.50	17.40	29.90	5.75	0.35	3.20	0.55	1.00	0.14

Food Codex of Slovak Republic has set a limit for the maximum levels of chosen risk elements in legumes; for cadmium, lead, chromium, copper and nickel are maximum values 0.1; 1.0; 4.0; 15.0; 6.0 mg·kg^{-1}, respectively. Limits for contaminants in Slovak food commodities are harmonized with EU limits [Cimboláková, Nováková 2009]. The risky elements contents, with the exception of Cd, did not exceed limit for the maximum levels of chosen risk elements in studied legume.

Horná Streda cadastre. Soils from sites from which bean and peas were collected, were medium to high humus with extremely acid soil reaction. Exchangeable pH value in the Horná Streda soils were 5.24 (bean) and 5.41 (pea), that means the sites with acidic soils. This was characterized by good (pea) to high (bean) potassium content and very high magnesium content. Nutrient content determined in soil samples ranged from 2012 to 2100 mg·kg^{-1} N; 61.8–63 mg·kg^{-1} P; 294–318 mg·kg^{-1} K; 2725.5–2981.5 mg·kg^{-1} Ca; 593–612 mg·kg^{-1} Mg.

Table 5. Nutrients contents (Mehlich II) and soil reaction in soils PD Horná Streda
Tabela 5. Zawartość nutrientów w mg·kg^{-1} i charakterystyka gleb w rejonie PD Horná Streda

Locality	Crop	Ca	Mg	K	P	N	pH KCl	% Humus
Horná Streda	kidney bean	2981.5	593.0	318.0	61.8	2100.0	5.24	3.21
Horná Streda	pea	2725.5	612.0	294.0	63.0	2012.5	5.41	2.92

A background value A for the total risk element content in soil were exceeded for Cd (limit exceeded to 46.6%); Cu (limit exceeded to 4.76%); and Ni (limit exceeded to 31.6%), but in neither case it reached the indicative limit values B established by legislative for soil contamination. The law 531/1994 – 540 has set a limit for the maximum levels of total content for chosen risk elements in soils; for cadmium, copper and nickel are maximum values 0.8; 36.0; 35.0 mg·kg^{-1}, respectively.

Table 6. Total risk elements contents in soils PD Horná Streda in mg·kg^{-1}
Tabela 6. Całkowita zawartość metali ciężkich w glebach rejonu PD Horná Streda w mg·kg^{-1}

Locality	Crop	Zn	Cu	Cr	Cd	Pb	Ni	Co
Horná Streda	kidney bean	83.2	39.6	44.4	1.28	30.0	51.6	17.6
Horná Streda	pea	90.0	36.0	48.8	1.72	29.2	50.8	17.6

The contents of potentially mobilizable heavy metals in nitric acid extract (a background A_1) did not exceed a limit and fluctuated above allowable concentration only in case of nickel (limit is 10 mg·kg^{-1}). Nickel may accumulate to toxic levels in soils due to anthropogenic activities.

Table 7. Risk elements content in mg·kg^{-1} in nitric acid extract (c = 2 mol·dm^{-3}) in Horná Streda
Tabela 7. Zawartość metali ciężkich w glebach rejonu PD Horná Strefa w mg·kg^{-1}, oznaczona wobec 2M kwasu azotowego

Lokality	Crop	Zn	Cu	Cr	Cd	Pb	Ni	Co
Horná Streda	kidney bean	14.0	14.3	2.3	0.35	12.6	11.6	3.5
Horná Streda	pea	13.7	16.1	2.4	0.34	13.7	10.6	3.4

The risky elements contents, again with the exception of Cd, did not exceed limit for the maximum levels of chosen risk elements in studied legume seeds from this locality. Nickel content in seeds was also determined bellow limit value (6.0 mg·kg^{-1}).

Table 8. Heavy metals content in mg·kg^{-1} in legume from Horná Streda
Tabela 8. Zawartość metali ciężkich w roślinach strączkowych w mg·kg^{-1}, hodowanych w rejonie PD Horná Streda

Crop	Variety	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
Pea	Jadeit	56.30	10.05	41.00	6.90	0.20	2.85	0.30	0.55	0.13
	Achat	50.85	10.40	39.90	8.35	0.25	2.45	0.25	0.65	0.10
	Olivín	52.85	9.75	37.60	8.50	0.30	2.60	0.25	0.55	0.15
	Jantar	54.75	9.55	35.85	6.90	0.20	2.55	0.25	0.30	0.14
	Svit	56.75	9.30	43.15	8.65	0.20	2.45	0.30	0.50	0.13
	Xantos	47.10	10.65	35.85	6.75	0.20	2.35	0.30	0.30	0.09
Kidney bean	Ema	70.15	15.35	29.50	7.50	0.65	3.15	0.50	0.60	0.13

Legumes seeds. The order of the elements levels in all tested legumes seeds was determined as following: Fe> Zn> Mn> Cu> Ni> Pb> Cr ≈ Co> Cd. The risky elements contents, with the exception of Cd, did not exceed a limit for the maximum levels of chosen risk elements in legumes (Food Codex SR). The levels of essential elements in legume species were higher than those of toxic elements. The concentrations obtained by us were similar to the concentration published by some researches [Augustin et al. 1981; Oomah et al. 2008; Campos-Vega et al. 2010].

The most abundant element was found to be iron (ranging from 47.10 to 91·84 mg·kg^{-1}), while at least variable elements were nickel, cobalt and cadmium contents. Legumes are known as zinc accumulators [Gençcelep et al. 2009] and zinc concentrations of our tested legume ranged from 29.50 to 43.40 mg·kg^{-1}. The minimum zinc levels were found in bean with comparable values for yellow and dry bean of the same variety from different localities. In the case of pea samples, zinc content depends on variety. Copper concentrations, accumulated in legume species, were 5.75–10.24 mg·kg^{-1}, which does not pose a health risk.

Copper can be found in many enzymes, some of which are essential for Fe metabolism and there are probable direct correlation between the dietary Zn and Cu ratio and the incidence of cardiovascular disease [Campos-Vega et al. 2010]. Manganese was found to be relatively high, its content in samples were between 9.30 and 17.40 mg·kg^{-1}. The highest manganese concentrations were found in cv. Ema (yellow and white dry together). Bean samples also contained higher amounts of lead, chromium, nickel. The nickel and cobalt levels in legume samples were found to be in the range of 2.00–3.20 mg·kg^{-1} and 0.15–0.69 mg·kg^{-1}, respectively. Nickel values were found to be very similar between species of legume. Chromium content ranged from 0.25 mg·kg^{-1} (dry pea) to 0.86 (green pea) mg·kg^{-1}.

The toxic risk elements contents were between 0.17 (Cezar) – 1.00 (Ema) mg·kg^{-1} for Pb and 0.08 (Fabundo) – 1.04 mg·kg^{-1} (Cezar) for Cd. Most of the trace elements present in bean and pea, their content is generally below the limit values or few higher (Cd), as the maximum level allowed in Food Codex valid in Slovak Republic. The exception is cv. Cezar (green pea), which grew in the soil with the highest content of cadmium. Generally, this cultivar has been an accumulator of chosen monitored elements.

4. CONCLUSION

Target of this investigation was to evaluate the level of heavy metal contamination of monitored two areas of Slovakia (Vinica – southern Slovakia, Horná Streda – western Slovakia) and to determine the relationship of heavy metal contents in soils to their content in grown legume seeds.

According to results obtained in this study these grains are allowed for food industry. However, given the low value of soil reaction (acid soils) and perspective can be reflected in the deterioration of crops and then in increased penetration of various pollutants into the food chain, it is appropriate to recommend optimization of soil acidity by liming to prevent mobilization of heavy metals and decreasing of toxic element contents is an advantage.

The results obtained by our research confirm the fact that there is a considerable need to devote closer attention to the hygienic control of legume quality as well as eatables quality control generally.

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REFERENCES

AUGUSTIN J., BECK C.B., KALBFLEISH G., KAGEL L.C., MATTHEWS R.H. 1981. Variation in the vitamin and mineral content of raw and cooked commercial Phaseolus vulgaris classes. Journal of Food Science, vol. 46:1701–1706.

CAMPOS-VEGA R., LOARCA-PIÑA G., DAVE OOMAH B. 2010. Minor components of pulses and their potencial impact on human health. Food Research International, vol. 43: 461–482.

CIMBOLÁKOVÁ I., NOVÁKOVÁ J. 2009. Heavy metals – the important element of the food chain. Potravinárstvo, vol. 3, No. 3:14–16.

GENÇCELEP H., UZUN Y., TUNÇTŰRK Y., DEMIREL K. 2009. Determination of mineral content of wild-grown edible mushrooms. Food Chemistry, vol. 133:1033–1036.

OOMAH B.D., BLANCHARD C., BALASUBRAMANIAN P. 2008. Phytic acid, phytase, minerals, and antioxidant activity in Canadian dry bean (*Phaseolus vulgaris* L.) cultivars. Journal of Agricultural and Food Chemistry, vol. 56:11 312–11 319.

Decision of the Ministry of Agriculture SR No. 531/1994-540 o najvyšších prípustných hodnotách rizikových látok v pôde. MP SR: Vestník MP SR, roč. XXVI, čiastka I., rozhodnutie 3, číslo 531/1994.

Výnos Ministerstva Pôdohospodárstva Slovenskej republiky a Ministerstva Zdravotníctva Slovenskej republiky z 15. marca 2004 No. 608/3/2004 – 100, ktorým sa vydáva hlava Potravinového Kódexu Slovenskej republiky upravujúca kontaminanty v potravinách. 2004 Food Codex.

ZRŮST J. 2003. Riziko pěstování brambor v půdách kontaminovaných těžkými kovy. Vědecký výbor fytosanitární a životního prostředí. Praha: 36.