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Factors affecting heavy metals accumulation in potato tubers¹

Czynniki wpływające na akumulację metali ciężkich w bulwach ziemniaka

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Słowa kluczowe: metale ciężkie (Zn, Cu, Ni, Pb, Cd), kumulacja, ziemniaki, odmiana, uprawy

Abstract

Soil is one of the most important sources of plant foods' contamination by heavy metals which enter into human and animal organisms via the food chain. From the observed metals (Zn, Cu, Ni, Pb, Cd) the enhanced total contents of Cd and contents of mobile forms of Pb were determined. Especially mobile forms of Pb in soil (0.100–0.295 mg·kg⁻¹), higher than the critical value, represent a risk resulting in the high content of Pb in potatoes (0.244–0.855 mg·kg⁻¹ FM). The high significant correlations between soil and potatoes in values of Pb content and were between soil pH values and Pb content in potatoes were confirmed in two from three potato cultivars (P-value < 0.01). No correlation was confirmed between humus content in soil and Pb content in potatoes.

Streszczenie

Badano wpływ wybranych czynników agrochemicznych na akumulację metali ciężkich w bulwach ziemniaka. Gleby uprawne mogą być zanieczyszczone metalami ciężkimi. Pierwiastki, które występują w glebach w formach biodostępnych (mobilnych) mogą zostać włączone do obiegu biologicznego, mając tym samym negatywny wpływ na jakość plonów i zdrowie konsumentów/ człowieka. W badanych glebach oznaczono całkowitą zawartość: Zn, Cu, Ni, Pb, Cd oraz udział tych pierwiastków w formach mobilnych. Spośród badanych pierwiastków najbardziej mobilnym metalem był ołów, którego zakres zawartości w formach mobilnych wynosił: 0,100-0,295 mg·kg⁻¹, przekraczając dopuszczalne wartości dla tego pierwiastka. Zawartość ołowiu w ziemniakach wynosiła: 0.244–0.855 mg·kg⁻¹ FM. Analiza statystyczna wykazała istotną korelację pomiędzy zawartością pierwiastków w formach mobilnych i ich zawartością w ziemniakach oraz między odczynem badanych gleb, a całkowitą zawartością ołowiu w ziemniakach. Nie zaobserwowano istotnej statystycznie korelacji pomiędzy zawartością próchnicy w glebach a zawartością ołowiu w ziemniakach.

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1. INTRODUCTION

Problems of the impact of potentially toxic elements on the environment are high actual. Recently, this phenomenon is closely related to the elements which cause unwanted toxicity and contaminate the environment [Urminska 2013]. Heavy metals represent an important group of these contaminants. The term „heavy metals“ refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration [Nagajyoti et al. 2010]. Due to their potential toxicity, persistent and irreversible characteristic heavy metals such as Cd, Cr, As, Hg, Pb, Cu, Zn and Ni have been listed as priority control pollutants [Chen et al. 2015].

Heavy metals (HMs) are precipitated on the topsoil and can be transferred from soils to other ecosystem components, such as groundwater or crops, and can affect human health through the water supply and food chain. If heavy metals are shown to be carcinogens, the accumulation in vegetables and fruits may

increase the risk of cancer in individuals who consume these foods [Stasinis, Zabetakis 2013; Zhao et al. 2014; Lin et al. 2015]. Zinc (Zn) plays a part in the basic roles of cellular functions in all living organisms and is also involved in improving the human immune system. Zinc availability is highly dependent on pH. When the pH is above 6, the availability of Zn is usually very low. The availability of Zn in alkaline soils is reduced due to lower solubility of the soil Zn [Hafeez et al., 2013]. However, Zn accumulated in high amounts can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia [Fu, Wang 2011]. Copper (Cu) is a necessary trace element in most organisms, in which it performs functions such as aiding in the process of photosynthesis, and regulating iron and hemoglobin in the body [Gad 2014]. Ordinarily, the toxicity of copper is not of great concern, except in exposure to industrial dust and fumes. However, copper uptake through water and food must be carefully

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controlled by patients suffering from Wilson's disease [Verissimo et al. 2005]. Nickel (Ni) is an essential element, and performs a vital function in carbohydrate metabolism. Ni is an essential micronutrient at very low contents, but it can be toxic at high contents. Oral exposure to Ni compounds can lead to allergic contact dermatitis, eczema and respiratory problems [Yeganeh et al. 2013]. The accumulation of cadmium (Cd) in the human body can lead to kidney, bone and pulmonary damage [Liu et al. 2014; Zhang et al. 2014], may cause proteinuria, glucosuria and aminoaciduria [Minh et al. 2012]. Moreover, Cd exposure was associated with the chronic diseases, such as diabetes, diabetic nephropathy, hypertension and peripheral artery disease [Ju et al. 2012]. The accumulation of lead (Pb) can damage the central nervous system, kidneys and blood system [Liu et al. 2014]. It has been shown that Pb can disturb hemoglobin synthesis, a prolonged period of Pb exposure causes kidney problems or a high blood pressure in adults and delays a physical and mental development in children [Chen et al. 2014; Rahman et al. 2014].

Potatoes (*Solanum tuberosum*) belong to the most important crops in the world with a long tradition of the cultivation in the Slovakia. They also belong to the main components of the menu of Slovak population. Potatoes are the important source of many essential nutrients. However, it is important to be at the same time safe for the consumers, because the intake of vegetables contaminated by heavy metal may pose a risk to the human health [Ali, Al-Qahtani 2012].

The aim of this study was to compare the degree of Zn, Cu, Ni, Pb and Cd accumulation in tubers of three potato varieties grown in soils with a different content of risky metals, humus and values of the soil reaction.

2. MATERIAL AND METHODS

2.1. Sample collection

To study the factors influencing the different level of accumulation of heavy metals in potato tubers, we compared three cultivars of potatoes that have been grown in eight locations in Slovakia with different degrees of soil burden by heavy metals: cv. Agria (loc. Dolne Obdokovce-Celadice; Dolne Obdokovce-Babindol; Vrbova n. Vahom-Pod horou), cv. Impala (loc. Nitra; Radosina; Vrbova n. Vahom-Kamenicna) and cv. Desiree (loc. Imel; Vrbova n. Vahom-Majer).

Potatoes were harvested in their physiological maturity. Samples from each cultivar were collected in four (8, 12) repetitions (depending on the extent of area) in an amount of about 2 kg from each sample site (SS). Immediately with the plant material also soil samples in horizon 0–0.2 m were collected (into pedological probe GeoSampler fy. Fisher). In all samples contents of Zn, Cu, Ni, Cd and Pb and in soil samples also agrochemical characteristics after previous sample preparing at the Department of Chemistry SUA in Nitra were determined.

2.2. Analysis

Soil samples – For the determination of agrochemical characteristics as well as nutrient contents the soil samples as

a fine earth I (average 2 mm particle size) and for Zn, Cu, Ni, Cd and Pb determination as a fine earth II (average 0.125 mm particle size) were prepared.

Determination of agrochemical indicators: exchange soil reaction (pH/KCl), $c(KCl) = 1 \text{ mol} \cdot \text{dm}^{-3}$ (691 pH Meter Metrohm, Swiss), content of oxidisable carbon (C_{ox} , %) – volumetric method and content of humus (Hum, %) calculated from the value of C_{ox} content.

Determination of nutrient contents was realised using Mehlich III method: P – spectrophotometrically ($\lambda = 666 \text{ nm}$, spectrophotometer UV-VIS 1800, Shimadzu); K, Ca, Mg – using F-AAS method.

Determination of the heavy metal contents:

- total contents of Zn, Cu, Ni, Cd and Pb, including all metal forms with the exception of silicate forms were determined in soil extracts by *aqua regia*;
- mobile forms of HMs were determined in soil extracts by NH_4NO_3 ($c = 1 \text{ mol} \cdot \text{dm}^{-3}$).

The contents of Zn, Cu, Ni in soil were determined using F-AAS method and Cd, Pb using GF-AAS method, respectively (VARIAN AASpectr DUO 240FS/240Z/UltrAA equipped with a D2 lamp background correction system, using an air-acetylene flame, Varian, Ltd., Mulgrave, Australia) and compared with limit and critical values according to Act No. 220/2004 and proposals of threshold values for investigated metals in soils [OJEC, 1986].

Potato samples – from undamaged tubers about 150 g potatoes was randomly selected and, after washing, peeling and chopping homogenised and subsequently (after removal of about 30 g of sample for the determination of dry matter amount) lyophilised.

The contents of Zn, Cu, Ni, Cd and Pb were determined in potatoes in extracts of freeze-dried samples. Mineralisation of the samples was performed by microwave digestion (MARS X-press, CEM USA) [Arvay et al. 2014]. The contents of HMs were determined using F-AAS (Zn, Cu, Ni) and GF-AAS (Cd, Pb) method, respectively. The measured results were compared with a multielemental standard for GF-AAS subsequently expressed as $\text{mg} \cdot \text{kg}^{-1}$ of fresh matter (FM).

Contents of heavy metals determined in plant samples were evaluated according to maximal allowed amounts given by Foodstuffs Codex of Slovak Republic [FC SR] and EC No. 1881/2006.

Chemicals: KCl, HCl: CentralChem, Slovakia; H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, NH_4NO_3 , NH_4F , EDTA, HNO_3 , $(\text{NH}_4)_2\text{MoO}_4$, $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$, ascorbic acid, multielemental standard for GF-AAS: Merck, Germany.

2.3. Statistical methods

Results were statistically evaluated by the analysis of variance (ANOVA – multiple range tests, method: 95.0 percent LSD) using statistical software STATGRAPHICS (Centurion XVI.I, USA) and the regression and correlation analysis (Microsoft Excel) were used.

Table 1. The content of macroelements (mg·kg⁻¹), humus (%), oxidisable carbon (C_{ox}, %) and exchange soil reaction (pH/KCl) in soil

Loc.	P	K	Ca	Mg	pH/KCl	humus	C _{ox}
1	233.9	329.8	3287.0	330.0	6.40	2.42	1.41
2	188.3	302.3	2842.0	369.0	6.31	2.70	1.57
3	571.8	207.1	5903.9	314.6	7.24	1.57	0.91
4	513.2	163.0	5806.8	325.6	7.16	1.42	0.82
5	432.4	156.2	5591.1	310.5	7.13	1.42	0.82
6	191.1	325.0	6480.7	606.4	7.19	1.76	1.02
7	142.6	232.8	6375.7	287.4	7.46	1.36	0.79
8	79.8	221.5	4952.0	230.0	7.86	1.45	0.84

Notes: 1 – Dolne Obdokovce-Celadice, 2 – Dolne Obdokovce-Babindol, 3 – Vrbova n. Vahom-Pod horou, 4 – Vrbova n. Vahom-Kamenicna, 5 – Vrbova n. Vahom-Majer, 6 – Nitra, 7 – Radosina, 8 – Imel

3. RESULTS AND DISCUSSION

Soil

Agrochemical properties of soil were evaluated according to the Code of Good Agricultural Practise in Slovak Republic [Bielek 1996]. Soils in observed localities have a high content of P, a middle till a high content of K and a high till a very high content of Mg. For the potato cultivation soils with a weak acid soil reaction (pH 5.5 až 6.5) and humus content higher than 2% are suitable [Vokál et al. 2003]. Only soil from localities 1 and 2 meets these conditions (Table 1).

In collected soil samples contents of risky heavy metals (HMs) – total contents of Zn, Cu, Ni, Pb, Cd and contents of their mobile forms were determined. In 3 localities (1, 2, 8) Cd contents were at all exactly defined sampling sites (SS) and in localities 6 and 7 at 4 SS higher than the threshold value. In locality 6 at the same SS also the enhanced Zn content compared with the threshold value n was determined. More dangerous are mobile forms of HMs, when their contents exceed the critical value. The critical value given for Pb was exceeded at all SS in localities 1, 2, 4, 7 and 8, and in localities 3, 5 and 6 at 1, 2 and 8 SS, respectively. Contents of mobile Zn, Cu, Ni and Cd were lower in comparison to their critical values (Table 2).

Total contents and contents of mobile Zn, Cu, Ni, Pb and Cd forms in investigated soil samples were significantly lower in comparison to determined HMs contents in soils of other countries in Europe or Asia. The total content of Zn (Cu, Ni, Pb and Cd) was in intervals 0.2–8222 (0.24–752; 0.26–103; 13–3286 and n.d.–82.6) mg·kg⁻¹ and contents of mobile forms of Zn (Cu, Pb and Cd) were in intervals 7.9–1705 (1.49–82.5; 10.4–1561 and 0.37–39.2) mg·kg⁻¹ resp. [Madejón et al. 2011; Khan et al. 2013; Yeganeh et al. 2013; Liénard et al. 2014; Li et al., 2015].

Potato

At present the limit values in foods according to EU No. 1881/2006 are given only for lead, cadmium, mercury and tin (FC SR: Cd, Pb, Hg). For potatoes only Pb and Cd limit values 0.1 mg·kg⁻¹ FM are given. The determined Pb content in all our potatoes samples

was higher than the limit value, in one case (loc. 1, 1 SS) even more than 10-fold. The enhanced Cd content was determined in potato samples from 4 SS in locality 2 (Table 3).

Based on the presented results lead can be considered to be the most risky metal in potatoes. Similar Pb contents in potatoes (even 23.76 mg·kg⁻¹ DM) are presented also by Cherfi et al. [2014]. Contents of other hazardous elements (in mg·kg⁻¹ FM) in potato samples are reported in intervals 2.2–7.6 (Zn), 0.5–5.898 (Cu), n.d.–28.0 (Ni), 0.02–4.752 (Pb) and n.d.–0.069 (Cd) [Burlingame et al. 2009; Mansour et al. 2009; Madejón et al. 2011; Corguinha et al. 2012; Yeganeh et al. 2013; Cherfi et al. 2014].

The extent of accumulation of HMs in potatoes, that is, their transfer into the plant is affected by many factors, such as soil content of HMs, and especially the content of their mobile forms. Generally, the metal mobility in soil is connected with the soil properties (soil reaction, cation exchangeable capacity, soil organic content, soil texture) and is increased with the decreased value of soil pH. Consequently, the transfer of nutrients from the soil into the plant is inhibited and on other hand the bioavailability of heavy metals is increased which represents a danger for the human health [Zeng et al. 2011; Gebrekidan et al. 2013; Yang et al. 2014]. Accumulation of heavy metals, such as Pb and Ni, in soils may impact soil properties [Qu et al. 2013], the Cd concentration in potatoes and carrots has been shown susceptible to changes in soil pH during Swedish field conditions [Hellström et al. 2007].

The influence of various factors on the HMs accumulation was evaluated using the regression and correlation analysis (Table 4). Our results confirmed the most significant influence of soil HMs content on the HMs content in potato tubers, but also the cultivar influence on the extent of HMs accumulation in potato tubers was observed. Statistically significant correlation between HMs content in soil and potato tubers in cultivars Agria and Desiree was confirmed.

Fan et al. [2009] found no significant differences in the Cd concentrations in potatoes grown in different areas of Quebec, Canada. However, wheat, corn, soybean, peanuts and lettuce grown in different areas of the United States of America have different Cd concentrations. This variation may be related to the variability of cultivars as well as climate, soil and fertilisation practices [Corguinha et al. 2012]. Heavy metal toxicity in plants

Table 2. The content of heavy metals (mg·kg⁻¹) in soil determined in *aqua regia* and NH₄NO₃

Loc.		Zn	Cu	Ni	Pb	Cd
(SS)						
1	<i>aqua regia</i>	56.00±3.27	16.80±1.15	28.40±2.05	22.90±1.30	1.130±0.134
(8)	NH ₄ NO ₃	0.073±0.005	0.075±0.007	0.178±0.017	0.295±0.032	0.064±0.004
2	<i>aqua regia</i>	65.10±4.42	18.10±1.15	32.00±1.806	24.70±1.69	1.380±0.081
(8)	NH ₄ NO ₃	0.068±0.005	0.073±0.009	0.170±0.010	0.278±0.021	0.061±0.004
3	<i>aqua regia</i>	113.80±6.94	52.00±3.17	27.80±1.694	8.00±0.49	0.290±0.018
(4)	NH ₄ NO ₃	0.430±0.026	0.330±0.020	0.020±0.001	0.020±0.001	0.030±0.002
4	<i>aqua regia</i>	100.20±6.11	48.30±2.94	27.10±1.652	9.40±0.57	0.260±0.016
(4)	NH ₄ NO ₃	0.300±0.018	0.160±0.010	0.100±0.006	0.230±0.014	0.010±0.001
5	<i>aqua regia</i>	93.50±5.70	41.90±2.55	30.70±1.871	8.60±0.52	0.230±0.014
(4)	NH ₄ NO ₃	0.460±0.028	0.210±0.013	0.010±0.001	0.100±0.006	0.060±0.004
6	<i>aqua regia</i>	146.23±45.35	35.47±6.10	38.87±2.913	18.00±3.97	0.687±0.148
(12)	NH ₄ NO ₃	0.760±0.070	0.220±0.083	0.040±0.017	0.137±0.081	0.057±0.022
7	<i>aqua regia</i>	72.60±4.57	18.20±1.05	40.85±2.408	9.25±1.47	0.645±0.212
(8)	NH ₄ NO ₃	0.455±0.026	0.130±0.007	0.060±0.011	0.135±0.009	0.065±0.006
8	<i>aqua regia</i>	41.80±2.55	27.40±1.67	19.80±1.207	20.20±1.231	2.720±0.166
(4)	NH ₄ NO ₃	0.050±0.003	0.140±0.009	0.190±0.012	0.210±0.013	0.050±0.003
Threshold value*		150	60	50	70	0.7
Critical value**		2.0	1.0	1.5	0.1	0.1
determined content lower than threshold/critical value			threshold/critical value exceeded at some SS		threshold/critical value exceeded at all SS	

Notes: 1 – Dolne Obdokovce-Celadice, 2 – Dolne Obdokovce-Babindol, 3 – Vrbova n. Vahom-Pod horou, 4 – Vrbova n. Vahom-Kamenicna, 5 – Vrbova n. Vahom-Majer, 6 – Nitra, 7 – Radosina, 8 – Imel *soil extract by *aqua regia*; **soil extract by NH₄NO₃

Table 3. The content of heavy metals (mg·kg⁻¹ FM) in potato tubers

Loc.	cultivar	Zn	Cu	Ni	Pb	Cd
1	Agria	2.575±0.679	1.301±0.436	0.222±0.051	0.855±0.147	0.062±0.014
2	Agria	3.226±0.679	1.805±0.0199	0.395±0.052	0.790±0.059	0.100±0.015
3	Agria	5.504±0.289	2.026±0.106	0.526±0.028	0.250±0.013	0.033±0.002
4	Impala	3.348±0.049	1.759±0.026	0.440±0.006	0.244±0.004	0.042±0.001
5	Desiree	3.579±0.011	0.566±0.002	0.438±0.001	0.309±0.001	0.057±0.000
6	Impala	3.923±0.052	0.982±0.267	0.605±0.092	0.254±0.032	0.061±0.011
7	Impala	2.129±0.800	0.578±0.097	0.529±0.071	0.265±0.064	0.050±0.001
8	Desiree	2.459±0.129	1.132±0.059	0.244±0.013	0.563±0.030	0.047±0.002
Limit value*		no limits	no limits	no limits	0.1	0.1
Limit value**		no limits	no limits	no limits	0.1	0.1
determined content lower than limit value			limit value exceeded at some SS		limit value exceeded at all SS	

Notes: 1 – Dolne Obdokovce-Celadice, 2 – Dolne Obdokovce-Babindol, 3 – Vrbova n. Vahom-Pod horou, 4 – Vrbova n. Vahom-Kamenicna, 5 – Vrbova n. Vahom-Majer, 6 – Nitra, 7 – Radosina, 8 – Imel * EU No. 1881/2006; ** FC SR

Table 4. Relationship between heavy metal content in soil and its content in potato tuber (HMs/HMp), soil reaction and heavy metal content in potato tuber (pH/HMp) and between humus content in soil and heavy metal content in potato tuber (hum/HMp)

Cultivar		Zn	Cu	Ni	Pb	Cd
Agria	HMs/HMp	8.02E-08**	0.026	1.44E-03**	1.60E-13**	7.89E-04**
	pH/HMp	0.094	0.174	0.714	0.728	0.285
	hum/HMp	0.865	0.017	0.220	0.012	3.68E-10**
Impala	HMs/HMp	1.17E-03**	0.089	0.420	0.166	2.01E-04**
	pH/HMp	0.983	0.716	0.015	9.20E-05**	0.139
	hum/HMp	1.01E-06**	0.249	4.94E-05**	0.249	4.38E-06**
Desiree	HMs/HMp	3.56E-06**	4.93E-04**	4.21E-06**	2.27E-07**	1.37E-03*
	pH/HMp	0.117	0.038	0.092	3.58E-02*	0.213
	hum/HMp	0.816	0.513	0.744	0.499	0.979

Notes:

* – significant differences (P-value < 0.05)

** – high significant differences (P-value < 0.01) a negative correlation

varies with plant species, specific metal, concentration, chemical form and soil composition and pH, as many heavy metals are considered to be essential for plant growth [Nagajyoti et al. 2010].

4. CONCLUSION

Content of mobile forms of heavy metals in the soil was the most important factor affecting their accumulation in potatoes. Especially increased levels of lead in soil resulted in its

accumulation in potato tubers (statistically significant correlation between Pb content in soil and potato tubers in cultivars Agria and Desiree was confirmed), while in samples of all potato cultivars the determined Pb content was higher than the limit value for this element. The influence of soil reaction on the extent of HMs accumulation in potato tubers was confirmed only in 13.3% of collected samples as well as the significant correlation between HMs content in potato tubers and organic matter content in the soil was confirmed in 26.6% of collected samples.

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