IOŚ-PIB OCHRONA ŚRODOWISKA I ZASOBÓW NATURALNYCH
ENVIRONMENTAL PROTECTION AND NATURAL RESOURCES 2013

VERSITA VOL. 24, NO 2(56): 25–28
DOI 10.2478/oszn-2013-0011

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Does consumption of potatoes cultivated in soils contaminated by heavy metals pose any risk to human health?

Czy istnieje ryzyko związane ze spożyciem ziemniaków uprawianych w glebach zanieczyszczonych metalami ciężkimi?

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Keywords: *heavy metals, potatoes, cultivar, accumulation*
Słowa kluczowe: *metale ciężkie, ziemniaki, kultywar, akumulacja*

Abstract
Soil is one of the most important environmental backgrounds, as it provides water and nutrients for plant production. It is the starting point for the entry of heavy metals into plants and then into the food chain. Of risk elements studied (Zn, Ni, Cd, Pb), we found increased Cd and Pb content in the soil extract by *aqua regia* and NH_4NO_3, respectively. More than twofold content of Pb mobile forms (0.218 mg•kg^{-1}) resulted in enhanced Pb content in tubers of all three potato cultivars: cv. Volumia 0.404, cv. Cicero 0.580 and cv. Mozart 0.638 mg•kg^{-1} FM. In all investigated cultivars, highly statistically significant differences in content of Pb between studied potato cultivars (P-value<0.01) were confirmed.

Streszczenie
Gleba należy do najważniejszych elementów środowiska, dostarczając wodę i składniki odżywcze do uprawy roślin. Stanowi początkowy etap wprowadzania metali ciężkich do roślin a następnie do łańcucha pokarmowego. Spośród badanych pierwiastków stanowiących zagrożenie (Zn, Ni, Cd, Pb), stwierdzono podwyższone zawartości Cd i Pb w roztworze glebowym po zastosowaniu odpowiednio wody królewskiej i NH_4NO_3. Ponad 2-krotne stężenie mobilnych form Pb (0.218 mg•kg^{-1}) spowodowało podwyższoną zawartość Pb w bulwach wszystkich trzech kultywarów ziemniaka: cv. Volumia 0.404, cv. Cicero 0.580 i cv. Mozart 0.638 mg•kg^{-1} FM. We wszystkich badanych kultywarach potwierdzono istotne statystycznie różnice w zawartości Pb (P<0.01).

1. INTRODUCTION

Heavy metals are elements having atomic weights between 63.5 and 200.6, whose density exceeds 5 g•cm^{-3}. Human industrial activities greatly enhance metal distribution in the global environment by discharge to soil, water and air. These metals accumulate in plants, animals and soil, and pose significant hazard to human health [Ogunbileje et al. 2013]. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms, and many heavy metal ions are known to be toxic. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases even death. **Cadmium** can be easily transported within plants in the form of metallo-organic complexes. The mechanisms of uptake, translocation and deposition depend upon the bio-availability of soil, pH, temperature, redox potential and concentration of other elements. Cd can easily penetrate the root system of xylem through the apoplastic and/or symplastic pathway and reach tissues of aerial parts of the plants [Epstein, Bloom 2005; Irfan et al. 2013]. Exposure to cadmium may cause kidney damage, renal disorder; cadmium is human carcinogen, Cd exposes human health to severe risks. **Zinc** is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, Zn accumulated in high amounts in plants and especially in roots can be phytotoxic [Tomáš et al. 2007] and too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia [Fu, Wang 2011]. **Nickel** is an essential element for plants and some animals. When nickel is present in high concentrations in soil, it is toxic for plants. High Ni levels are also known to have toxic effects on human health. Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis. Nickel is also known as a respiratory tract carcinogen that is deposited in the lungs [Fu, Wang 2011; Ogunbileje et al. 2013]. **Lead** is an environmental contaminant that occurs naturally and, to a greater extent, from anthropogenic activities. Food is the major source of exposure to Pb and a possible risk for the population can be caused by the bioaccumulation of Pb in edible vegetables because it may be taken up by edible plants from the soil via the root system, by direct foliar uptake and translocation within the plant and by surface deposition of particulate matter. The bioavailability of Pb in soil to plants is limited because of the strong adsorption to soil; the bioavailability increases when pH and the organic matter content of the soil are reduced [Beccaloni et al. 2013]. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage [Barakat 2011].

Potato is the fourth most important crop in the world and is considered an important staple food in developing countries, where areas for potato cultivation have an increasing trend and potatoes are used mainly for consumption in the diet of the population.

In developed countries, a decrease of cultivation area is recorded due to the decline of the potato starch and alcohol production. Consumption of fresh potatoes and derived products is more or less stable stabilizovaná [Heldák et al. 2008]. Potato is not only a good source of vitamin C and vitamin B6 but also a good source of minerals including mainly potassium, and also magnesium, phosphorus, manganese, zinc and iron to a lesser extent [Legay et al. 2012]. Potato plants can be exposed to various types of environmental agents, either accidentally, by compounds present in polluted air, soil or water, or deliberately, as in the case of agricultural pesticides and plant growth regulators [Gonçalves et al. 2009]. The aim of the work was to compare the degree of Zn, Ni, Cd and Pb accumulation in tubers of three potato cultivars with different vegetation periods cultivated in soils with enhanced contents of observed risk metals.

2. MATERIAL AND METHODS

2.1 Locality

Site characteristics – Danubian Lowland in southwestern Slovakia with an area of about 10,000 km^2 is one of our most productive areas used for agricultural purposes. Predominant soil types are Eutric Fluvisols, Mollic Fluvisols and Eutric Regosols.

Continuous high Cd mainly in the western part of southern Slovakia is a result of high doses of phosphate fertilizers application, especially until 1989 [Tomáš et al. 2007].

Locality Stará zem from which soil and plant samples were collected is the cadastral territory of Imel village, between Nitra and Žitava rivers. The locality is characterized by planar relief, such as the whole territory of the Danube Lowland.

Soil characteristics – The soil type was calcareous Haplic Chernozem with a middle till good P and K contents and a high Mg content, with a strong alkaline soil reaction and a small humus supply [Bielek 1996].

2.2 Samples collection and preparation

Soil samples were taken in soil horizon 0–0.2 m according to the exact method using the pedological probe GeoSampler fy. Fisher. Sampling was carried out as single from three sampling sites in each variety. After their air-drying and grinding with soil grinding machine *VEB Thurm ZG 1* on fine earth I (average 2 mm particle size), soil samples were sieved through sieves with an average size 0.125 mm (fine earth II). Fine earth I was used on an assessment of soil reaction, contents of nutrients and contents of mobile forms of Zn, Ni, Cd and Pb. Fine earth II was used on an assessment of pseudototal contents of Zn, Ni, Cd and Pb. Contents of bioavailable nutrients and humus as well as the values of soil reaction are presented in Table 1; contents of heavy metals are listed in Table 2.

Plant samples were taken from the same sampling sites as the soil samples. Three potato cultivars with different vegetation period were investigated. Very early (VE) cv. Volumia, early (E) cv. Cicero and middle early (ME) cv. Mozart had vegetation periods 132, 146 and 152 days respectively. Sample of a fresh matter was prepared by homogenizing all potato tubers taken from one sampling site. Contents of Zn, Ni, Pb and Cd in potato tubers were assessed in four repetitions after mineralization of the sample by wet way method.

2.3 Chemicals

Conventional chemicals: ammonium nitrate (pro analysi ACS; Merck Germany), fuming hydrochloric acid (37%, pro analysis; Merck Germany), nitric acid (65%, pro analysis; Merck Germany).

2.3 Analysis

Assessment of soil reaction, content of nutrients and risky metals in soil samples

Changeable soil reaction pH/KCl, content of nutrients and contents of heavy metals were assessed in taken soil samples. Contents of nutrients (P, K, Ca, Mg) were determined by the method of Mehlich II, pseudototal contents of risky metals in extract of *aqua regia* and the contents of mobile forms of risky metals in soil extract with NH_4NO_3 (c = 1 mol•dm^{-3}) (Law No. 220/2004). Analytical method of the determination of contents of macroelements and risky elements was flame atomic spectrometry (AAS Varian AA Spectr DUO 240FS/240Z/UltrAA).

Assessment of heavy metals content in edible parts of potato tubers

Potatoes were harvested in full ripeness. Fresh tubers were used for analyses of heavy metals contents (2nd day after sampling). Mineralization of samples was carried out by microwave digestion in the microwave MARS X-press (CEM USA). Contents of heavy metals were assessed in a filtrate of mineralizate and after filling with distilled water till mark in 50 cm^3 by AAS method; content of Zn was assessed at wavelength 213.9 nm (detection limit 0.0006 µg•cm^{-3}), of Ni at 232.0 nm (detection limit 0.008 µg•cm^{-3}), Pb at 217.0 nm (detection limit 0.020 µg•cm^{-3}), Cd at 228.8 nm (detection limit 0.001 µg•cm^{-3}). The contents of heavy metals were assessed after homogenization of samples and after mineralization by wet way method of AAS.

2.4 Statistical methods

Two-factor analysis of variance (ANOVA) was used for statistical evaluation of results and program Statgraphics (multifactorial analysis of variance, LSD-test contrasts, $P<0.01$) was used to process gained data.

3. RESULTS AND DISCUSSION

Soil

The determined values were evaluated according to limit values stipulated by Law No. 220/2004. The determined soil contents of Zn and Ni were below the limit values stipulated by Law No. 220/2004, while Cd content determined in the soil extract by *aqua regia* was 4.85-fold and Pb content determined in the soil extract by NH_4NO_3 was 2.18-fold higher than limit values (Table 2). Toxic metals, especially Zn, Pb and Cd get into the soil in large quantities due to dust deposition from industrial processes, exhaust gases, contaminated wastewater and fertilizers. Ions of these metals are easily taken up by roots because the selectivity of transport proteins is probably insufficient to distinguish them from those elements that are essential for plant life [Zrůst 2003].

The content of **Zn** is the highest one in the potato tubers cv. Volumia (3.456 mg•kg^{-1} FM), content of **Ni** assessed in potato tubers after their mineralization by dry way method is the highest one in

Table 1. The content of macroelements (mg • kg^{-1}), humus (%), active soil reaction (pH/H_2O) and exchange soil reaction (pH/H_2O) in soil

cultivar	P	K	Ca	Mg	humus	pH/H_2O	pH/KCl
Volumia	58.19	207.50	12854.00	230.00	1.63	8.94	7.96
Cicero	104.37	239.00	5622.00	240.00	1.33	8.95	7.89
Mozart	71.52	185.17	8130.00	278.00	1.94	8.79	7.81

Table 2. Content of heavy metals (mg•kg^{-1}) in soil determined in different extraction reagents

	Zn	Ni	Cd	Pb
	Aqua regia			
	34.64 ± 2.46	19.76 ± 1.05	**1.94 ± 0.49**	18.40 ± 1.56
Limit value	*100.0*	*40.0*	*0.4*	*70.0*
	NH_4NO_3 (c = 1 mol•dm^{-3})			
	0.060 ± 0.011	0.169 ± 0.022	0.058 ± 0.021	**0.218 ± 0.023**
Critical value	*2.0*	*1.5*	*0.1*	*0.1*

the potato tubers cv. Mozart (0.220 mg•kg^{-1} FM, Table 3). None of the contents of Zn and Ni was higher than the legislative limits. The maximal allowed amounts defined by legislation are for Zn 10.0 and for Ni 0.5 mg•kg^{-1} FM (Table 3).

The high Cd content in the soil extract by *aqua regia* (Table 2) does not inevitably result in the high Cd content in agricultural plant (Table 3). Visioli, Marmiroli [2013] describe plant species, so-called hyperaccumulators, able to tolerate phytotoxic levels of heavy metals without any visible symptoms of toxicity. Despite the fact that potatoes do not belong to the hyperaccumulators, they have a higher tolerance to heavy metals. Otabong et al. [2001] present the ability of potatoes to accumulate twofold more Cd in comparison to wheat and 2.6-fold more than in barley. According to Egyűdová and Šturdík [2004], potatoes together with cereals and leafy vegetable are the main sources of Cd in the human diet.

Lead seems to be the most risky metal from the aspect of mobile forms quotient in the investigated locality (Table 3). Despite the fact that potatoes are less sensitive to enhanced Pb soil content than Cd content [Hlušek et al. 1996], the enhanced Pb content in potato tubers of investigated cultivars were determined due, probably, to synergism with Cd [Hronec et al. 2002].

In potatoes, from various regions of Egypt, the followed Pb, Cd and Zn contents were determined: 0.01 ± 0.05, 0.02 ± 0.01 and 7.16 ± 0.06 mg•kg^{-1} DM, respectively [Radwan, Salama 2006]. Authors compared their own results with previously published results from other parts of the world – Pb: Pakistan 0.16, USA 0.009; Cd: Pakistan 0.08, Greece 0.0223, USA 0.031, and Zn: Pakistan ND, Nigeria 3.00, USA 2.10, East Asia 0.30, Sweden 3.0 mg•kg^{-1}.

Mansour et al. [2009] determined heavy metal contents in 12 different potato samples from different local markets and locations in Giza Governorate, Egypt. These represented 6 kg from conventionally-farmed potatoes and 6 kg from organically-farmed potatoes. The mean concentration levels of Zn (Ni, Pb and Cd) throughout the whole year ranged between the following values: 1.044–3.603 (ND–0.045, 0.08–0.624 and ND–0.168) mg•kg^{-1} FM in potato tuber samples from conventional farming, and 0.637–3.971 (0.013–0.069, 0.037–0.514 and ND–0.652) mg•kg^{-1} FM in potato tuber samples from organic farming.

Heavy metal accumulation may also differ greatly within cultivars of an individual species when grown on the same soil [Tang et al. 2012], as can be confirmed also by our results (Table 3).

In all investigated cultivars, highly statistically significant differences in content of Pb between studied potato cultivars (P-value<0.01) (Table 4, 5) were confirmed.

On the other hand, Hellström et al. [2007] found not a statistically significant association between Cd concentrations in soil and Cd values in potatoes: Cd in soil: 0.30–6.29 (0.14–0.52) mg•kg^{-1} dry weight – after extraction in boiling 2 M HNO_3, Cd in potatoes: 0.02–0.08 (0.00–0.04) mg•kg^{-1} fresh weight.

The degree of Cd accumulation in potato tubers can be affected by various factors: potato cultivar, plant organ, essential element, growth medium and period. Based on these results, excessive Cd^{2+} accumulation may affect the uptake and distribution of certain nutrients in the potato cultivars, and consequently may be responsible for mineral disturbances and depression of plantlet growth [Gonçalves et al., 2009].

4. CONCLUSION

The soil samples from the locality Stará zem do not contain enhanced Zn and Ni amounts. The determined contents of pseudototal and mobile Zn and Ni forms were below the limit values stipulated by Law No. 220/2004. Although the pseudototal Cd content determined in the soil extract by *aqua regia* exceeded 4.85 fold the limit value, the content of mobile Cd forms was only 48% of the critical limit value given by the legislation. From the aspect of Zn, Ni and Cd content, the potato cultivation in the investigated locality is safe. Pb seems to be the most risk metal from the observed elements. More than twofold content of Pb mobile forms (0.218 mg•kg^{-1}) determined in the soil extract by NH_4NO_3 resulted in enhanced Pb content in tubers of all three potato cultivars. The average Pb content in observed potato cultivars were in the interval 0.404–0.638 mg•kg^{-1} FM, which is an increase of more than fourfold the limit value.

From the aspect of the producers, the selection of plant types as well as plant cultivars suitable for growing in soils with enhanced heavy metal contents are important factors. On the basis of the results obtained, it can be concluded that cultivar Mozart with the longest vegetation period was the most sensitive to the presence of increased levels of lead and cadmium in the soil, whereas very early cultivar Volumia seems to be the most suitable for growing in the investigated locality.

Table 3. Content of heavy metals (mg•kg^{-1}) in potato tubers

	Zn		Ni		Cd		Pb	
Cultivar	FM	DM	FM	DM	FM	DM	FM	DM
Volumia	3.456	16.559	0.205	0.980	0.039	0.225	**0.404**	2.352
Cicero	1.831	11.212	0.194	1.185	0.028	0.173	**0.580**	3.555
Mozart	2.775	12.772	0.220	1.163	0.059	0.271	**0.638**	2.942
**Limit value:*	*10.0**		*0.5**		*0.1**		*0.1**	

FM – fresh mater; DM – dry mater; * Foodstuffs Codex of Slovak Republic

Table 4. Analysis of Variance for Pb by cultivar

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
Between groups	8.678	2	4.339	147.91	0.0000
Within groups	0.968	33	0.029		
Total (Corr.)	9.646	35			

Table 5. Multiple Range Tests for Pb by cultivars (Method: 95,0 percent LSD)

Cultivar	*Count*	*Mean*	*HGroups*
Volumia	12	2.35192	X
Mozart	12	2.94417	X
Cicero	12	3.5545	X

HG – Homogeneous Groups

Contrast	*Sig.*	*Difference*	*± Limits*
Cicero – Mozart	*	0.610333	0.14226
Cicero – Volumia	*	1.20258	0.14226
Mozart – Volumia	*	0.59225	0.14226

* denotes a statistically significant difference.

ACKNOWLEDGEMENT

This work was supported by grant VEGA 1/0456/12 and APVV SK-CZ-0102-11.

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