CONTENT OF Ni, Cd AND Pb IN POTATOES CULTIVATED IN THE SOIL CONTAMINATED BY HEAVY METALS

MUSILOVA J.[1], VOLNOVA B.[1], HEGEDUSOVA A.[2], HARANGOZO L.[1] and ORSAK M.[3]

[1] Dept. of Chemistry, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture in Nitra, Slovak Republic, [2] Dept. of Vegetable Production, Faculty of Horticulture and Landscape Engineering, Slovak University of Agriculture in Nitra, Slovak Republic, [3] Dept. of Chemistry, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Czech Republic,
E-mail: janette.musilova@uniag.sk

ABSTRACT

Samples of 12 potato cultivars (mid-early: Arlet, Laura, Marabel, Megan, Red Anna, Smart, Spinela, Timea, Victoria, very early: Vivaldi, early: Svella, Malvina) were grown in three localities with a strong disturbed environment. Soil and plant samples were collected from the same sampling sites. In soil samples agrochemical characteristics as well as Ni, Cd and Pb mobile forms and total contents were determined. Content of P was determined spectrophotomertically, soil content of other nutrients as well as heavy metals (HMs) were determined by the method of AAS.

Contents of HMs in potato samples were determined using AAS method after previous mineralization using microwave digestion.

Determined total soil contents of heavy metals were in the range of 30.80-71.00 (Ni) 17.00-26.80 (Pb), resp. 0.94-1.56 (Cd) mg/kg FM. Limit values for Ni (40 mg/kg) were exceeded in 62 sampling sites (SS), while Cd limit (0.4 mg/kg) was exceeded in all SS. The determined total Pb content in soil was below the limit value (< 50 mg/kg). The contents of mobile Ni (Pb, Cd) forms were in intervals 0.019-0.475 (0.023-0.295, 0.004-0.055, respectively) mg/kg FM. Critical value given for Pb (0.1 mg/kg) was exceeded in 70 SS. Contents of mobile Ni and Cd forms were lower than critical values (Ni < 1.5 mg/kg, Cd < 0.1 mg/kg).

Only Pb content in potato tubers was higher than hygienic limit value (0.1 mg/kg FM) in 15 SS (interval was n.d.-0.2298 mg/kg FM).

Keywords: potato, disturbed environment, heavy metals

1. Introduction

Heavy metals contribute significantly to reduce of environmental quality. Heavy metals can originate from both natural and anthropogenic sources (Nagajyoti *et al.*, 2010). If occur naturally in the soil environment of the pedogenetic processes weathering of parent materials, their contents are at levels that are considered to be traces (<1000 mg/kg) (Wuana and Okieimen, 2011). Hazardous become heavy metals of anthropogenic origin.

There are different sources of heavy metals in the environment. Other than natural resources are agricultural sources (fertilizer use and sludge fertilization, metal-containing pesticides), industrial sources (petrochemicals), domestic effluents, atmospheric sources and other sources (disposal of high metal wastes in improperly protected landfills, leaded gasoline and leadbased paints, coal combustion residues) (Nagajyoti *et al.*, 2010; Wuana and Okieimen, 2011; Xu *et al*., 2013; Zhao *et al.*, 2014).

Heavy metals are very persistent in the environment; they are not bio- and thermo degradable, are highly toxic and bioaccumulative (Stasinos and Zabetakis, 2013; Liu *et al*., 2014).

Heavy metals represent a potential human health hazard if safe thresholds of exposure or absorption are exceeded. Dangerous are not only non-essential chemical elements (Cd, Pb, Hg etc.), which are toxic even at relatively low concentrations, but also biologically irreplaceable microelements (e.g. Cu, Zn, Mn, Co, Cr etc.) which are toxic, if a certain concentration level is exceeded (Tomas *et al*., 2000; Celik and Oehlenschlager, 2010; Zhu *et al*., 2011).

Cadmium (Cd) is a highly toxic metal with a natural occurrence in soil, but it is also spread in the environment due to human activities (Zhu *et al*., 2011) and can eventually enter the human body through the food chains (Chen *et al*., 2014). The primary route for Cd exposure in humans is through ingestion of foods (Pérez and Anderson, 2009). Cadmium is present in virtually all food, but the concentrations vary to a great extent, depending on the type of food and the Cd load in the food production environment (Hellström *et al*., 2007). The highest concentrations are present in seafood, mollusks and crus taceans, offal products and certain seeds. Among plant foods, the highest concentrations are generally present in cereals such as wheat (especially whole grain) and rice, leafy green vegetables and in potatoes and root vegetables (Engström *et al*., 2012; Ju *et al*., 2012).

Cadmium, which may accumulate in the human body has an adverse effect on human health and may cause proteinuria, can result in low bone mineral density, cause osteoporosis, and increase the risk of bone fracture. Cd also affects the female reproduction system and severely affects the feminine endocrine system. The chronic Cd dust or aerosols cause lung cancer, hypertension, and renal dysfunction (Peralta-Videa *et al*., 2009; Minh *et al*., 2012; Chen *et al.*, 2014; Zhang *et al*., 2014; Chen *et al*., 2015; Lin *et al*., 2015).

Lead (Pb) is a highly toxic element, is bioaccumulative and does not degrade in the environment nor easily metabolized. It is another wide spread toxic pollutant which has no known functions in biological systems. The main anthropogenic sources of Pb remain, such as mining, smelting, lead batteries, crystal and ceramic industry, undoubtedly contribute to the Pb-induced adverse effects in humans and the environment (Matovic *et al*., 2015). The excessive intake of Pb can damage the central nervous system, skeletal, circulatory, enzymatic, endocrine, and immune systems, kidneys and blood system in adults and delays in physical and mental development in children. It has been shown that Pb can disturb hemoglobin synthesis. After absorption, Pb enters blood and then accumulates in erythrocytes, is bound to proteins or complexed with low molecular weight sulfhydryl compounds (e.g., cysteine, homocysteine). Organic lead can be more toxic than inorganic lead because the body absorbs it more readily. Potential exposures to organic lead should be taken very seriously. (Peralta-Videa *et al*., 2009; Chen *et al*., 2014; Cherfi *et al*., 2014; Liu *et al*., 2014; Rahman, 2014; Chen *et al*., 2015; Matovic *et al*., 2015). Symptoms such as personality changes, irritability, persistent headache, abdominal colic, or treatment of neuropathy warrant parenteral chelation indicative of recent exposure to lead (Moriarity *et al*., 2014). Vyskocil *et al.* (2007) in Peralta-Videa *et al*. (2009) reported that in humans there is a correlation between Pb exposure and hearing losses.

Nickel (Ni) is present in all soils, where it derives from either the parent material (lithosphere), anthropogenic deposition, or both (Yeganeh *et al*., 2013). Nickel is recognized as essential micronutrient for living organisms and is a component of the enzyme urease (Nagajyoti *et al*., 2010). While in small quantities nickel is necessary, its deficiency causes growth retardation, anemia and reduce the activity of certain enzymes (Das *et al*., 2008; Arvay *et al*., 2012); its toxicity at higher levels is more prominent (Zhu *et al*., 2011). Large quantities of nickel may cause various consequences on human bodies, such as inflammation, cancer, neurasthenia, system disorders, lower fertility, teratogenic, mutagenic, and heart disorders (Das *et al*., 2008; Qu *et al*., 2013). Absorbed nickel is distributed in the body by the blood. In human serum nickel binds predominantly to albumin, but also to l-histidine and alpha-2-macroglobulin (Sunderman, 1993). The main excretion route of absorbed nickel is via urine, independent of the route of exposure, small amounts of absorbed nickel are excreted in bile, sweat, hair, saliva, and mother's milk (Schaumlöffel, 2012). Higher concentration of nickel is exposed to people working in nickel production and processing industry. Their main route of exposure is inhalation, and to a lesser extent, in contact with skin (Schaumlöffel, 2012). Inhaled Ni compounds are carcinogenic to humans although there is a lack of evidence of a carcinogenic risk of Ni from oral exposure to human (Rahman, 2014).

The aim of this study was to assess the extent of accumulation of Cd, Pb and Ni in potato tubers cultivated in soils with a different degree of contamination by these metals as well as to compare the risk of potato consumption in investigated localities.

2. Material and methods

Potatoes for analyses were grown in three areas of region Middle Spis of Slovakia. Twelve potato cultivars with a different vegetation period were analysed: five cultivars (Arlet, Malvina, Megan, Spinela, Svella and Timea) from locality Matejovce, three cultivars (Laura, Marabel and Red Anna) from locality Odorín, and four cultivars (Laura, Smart, Victoria and Vivaldi) from locality Spissky Stvrtok.

Cultivars (maturity - shape of tubers - colour skin/colour flesh):

- Vivaldi: very early - oval - yellow/light yellow;
- Malvina, Svella: early - oval - yellow/yellow;
- Arlet, Marabel, Megan, Victoria: mid-early - oval - yellow/yellow;
- Laura: mid-early - oval - red/deep yellow;
- Red Anna: mid-early - short-oval - red/deep yellow;
- Smart: mid-early - short-oval - yellow/deep yellow;
- Spinela: mid-early - oval - red/deep yellow;
- Timea: mid-early - short-oval - yellow/yellow;

In all localities the standard technologies of potato cultivation were used.
Potatoes were harvested in their physiological maturity. Samples from each cultivar were collected in four repetitions in an amount of about 2 kg from each sample site. 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 Ni, Cd and Pb and in soil samples also agrochemical characteristics after previous preparing at the Department of Chemistry SUA in NItra were determined.

2.1. Soil samples

For determination of agrochemical characteristics as well as nutrient contents soil samples as *fine earth I* (average 2 mm particle size) and for Ni, Cd and Pb determination as *fine earth II* (average 0.125 mm particle size) were prepared.

Determinantion of agrochemical indicators, contents of nutrients and heavy metals:

- exchange soil reaction (pH/KCl), c (KCl) = 1 mol/dm^3, KCl: CentralChem, Slovakia; 691 pH Meter Metrohm, Swiss),
- content of oxidizable carbon (C_{OX}, %) volumetric method (H_2SO_4, $K_2Cr_2O_7$, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$: Merck, Germany) and content of humus (Hum, %) calculated from value of C_{OX} content,
- contents of nutrients (method by Mehlich III: P – spectrophotometrically, (λ = 666 nm, spectrophotometer *UV-VIS 1800*, Shimadzu); K, Ca, Mg – using AAS method; NH_4NO_3, NH_4F, EDTA, HNO_3, H_2SO_4, $(NH_4)_2MoO_4$, $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$, ascorbic acid: Merck, Germany),
- content of mobile forms of Ni, Cd and Pb was determined in soil extract by NH_4NO_3 (c = 1 mol/dm^3, NH_4NO_3: Merck, Germany);
- total content of Ni, Cd and Pb, including all metal forms with exception of silicate forms, determined in soil extract by *aqua regia* (HCl: CentralChem, Slovakia, HNO_3: Merck, Germany);

The contents of Ni, Cd and Pb in soil were determined using F-AAS method and GF-AAS method, resp. (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.

2.2 Plant samples

From undamaged tubers about 150 g potatoes were randomly selected, which after washing, peeling and chopping were homogenized and subsequently (after removal of about 30 g for the determination of dry matter) lyophilized.

Determination of heavy metals:

The contents of Ni, Cd and Pb were determined in potatoes in extracts of freeze-dried samples. Mineralization of the samples was performed by microwave digestion (MARS X-press, CEM USA). The contents of heavy metals were determined using AAS (atomic absorption spectrometry) method: Cd, Pb: GF-AAS and Ni F-AAS. The measured results were compared with multielemental standard for GF AAS (CertiPUR®, Merck, Germany) a subsequently expressed in mg/kg 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 and EC No. 1881/2006

2.3 Statistical analysis

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) was used.

3. Results and discussion

3.1. Soil

The results of chemical analysis focused on agrochemical characteristics (values of exchangeable soil reaction, content of humus, oxidizable carbon and contents of available nutrients: P, K, Ca, Mg) are presented in Table 1.

Table 1: Basic agrochemical indicators and contents of nutrients (mg/kg)

Locality		pH/KCl	Humus (%)	C_{ox} (%)	P	K	Ca	Mg
Odorin	Min.	4.45	2.12	1.23	32.52	132.50	1032.00	102.00
	Max.	5.42	3.33	1.93	108.41	280.50	1880.00	188.00
	Average	5.15	2.65	1.54	79.22	188.96	1443.83	134.83
	STDEV	0.23	0.33	0.19	19.84	46.29	274.81	26.54
Matejovce	Min.	4.95	2.00	1.16	10.82	143.50	2008.00	124.00
	Max.	6.63	3.63	2.11	62.42	268.00	3408.00	292.00
	Average	5.64	2.65	1.54	35.59	186.23	2613.92	184.83
	STDEV	0.44	0.49	0.29	12.98	36.05	438.32	46.98
Spissky	Min.	4.69	2.36	1.37	15.66	111.50	1146.00	114.00
Stvrtok	Max.	6.61	3.57	2.07	98.69	256.50	3126.00	220.00
	Average	5.39	2.85	1.65	42.69	190.31	1764.75	167.50
	STDEV	0.60	0.31	0.18	21.84	44.53	573.13	29.47

The average soil P amount in all sampling sites was lower than satisfactory content for potato cultivation (100-125 mg P per kilogram of soil), contents of K and Mg were satisfactory (recommended values are 140-220 mg K/kg and 110-180 mg Mg/kg), average values of soil reaction were lower compared to recommended pH values (pH 5.5-6.5), although according to Vokal *et al*. (2003) there is no decrease of tubers yield at lower pH values about pH 4.8.

Optimal humus content for potato cultivation should be higher than 2%, this value was exceeded at all sampling sites. Based on these characteristics all three localities can be considered as suitable for potatoe cultivation with a requirement enhanced P content in soil. All investigated localities are a part of Spis region which was known by potato cultivation even in the past.

The Cd, Pb and Ni content determination served as hygienic criterion for assessment of soil suitability for potato cultivation. Heavy metal contents in soil (Table 2), determined using GF-AAS and Ni F-AAS methods were compared to limit values (for a soil extract by *aqua regia*) and critical values (for a soil extract by NH_4NO_3) according to legislation valid in the Slovak Republic (Act No. 220/2004).

Table 2: Contents of heavy metals in soil (mg/kg) determined in different soil extracts

Locality		*aqua regia*			NH_4NO_3		
		Cd	Pb	Ni	Cd	Pb	Ni
Odorin	Min.	0.94	17.00	30.80	0.026	0.080	0.140
	Max.	1.35	24.40	50.00	0.047	0.205	0.395
	Average	1.19	19.88	39.53	0.033	0.148	0.223
	STDEV	0.13	1.66	4.33	0.006	0.032	0.059
Matejovce	Min.	1.16	17.40	33.00	0.004	0.023	0.019
	Max.	1.56	25.40	71.00	0.055	0.295	0.380
	Average	1.34	21.84	52.59	0.045	0.227	0.228
	STDEV	0.12	1.69	9.01	0.012	0.035	0.066
Spissky	Min.	1.00	17.60	37.40	0.023	0.090	0.105
Stvrtok	Max.	1.44	26.80	51.20	0.047	0.210	0.475
	Average	1.21	20.44	45.95	0.034	0.149	0.241
	STDEV	0.12	2.17	3.37	0.007	0.030	0.072
Limit value		*0.4*	*70.0*	*50.0*			
Critical value					*0.1*	*0.1*	*1.5*

Determined total contents of heavy metals were in the range of 0.94-1.56 (Cd), 17.00-26.80 (Pb), resp. 30.80-71.00 (Ni) mg/kg.

Values for Cd limit (0.7 mg/kg) was exceeded in all sampling sites (SS), while the determined total Pb content in soil was below the limit value (< 70 mg/kg). The determined total Ni contents (> 50 mg/kg) in soil were exceeded in 14 SS (12 SS loc. Matejovce, 2 SS loc. Spissky Stvrtok). The total contents of heavy metals include all metal forms with exception of their residual fractions. Their high content determined in soil extract by aqua regia may be not reflected by high heavy metal content in the harvested crop. Bioavailability of heavy metals by plants can be affected by changes of soil properties. In general, the mobility of heavy metals is associated with the soil reaction, cation exchange capacity, soil organic content, soil texture and is increased with decrease of the soil pH value. Due the increased availability of heavy metals by plants, finally their input into human body via food chain could be increased (Vollmannova *et al*., 2002; Du Laing *et al*., 2007; Zeng *et al*., 2011; Gebrekidan *et al.*, 2013; Hudec *et al*., 2014; Yang *et al.*, 2014). Besides soil pH, organic matter content in soil is also one of the most important soil properties affecting heavy metal availability. Organic matter is a major contributor to the ability of soils for retaining heavy metals in an exchangeable form (McCauley *et al*., 2009, Zeng *et al*., 2011). Adsorption of heavy metals is also highly dependent on soil components that include silicate clays, organic matter, and iron, aluminium and manganese oxides (Bolan *et al*., 2003; Park *et al*., 2011).

The soil contents of Cd (Pb, Ni) are variable (e.g. northern Pakistan, southwestern China, Wallonia region of Belgium, northwest of Iran: Cd 0.08-4.5, Pb 17.0-672.0 and Ni 0.46-103.0 mg/kg soil) depending on agroclimatic conditionons (Khan *et al*., 2013; Yeganeh *et al*., 2013; Liénard *et al*., 2014; Li *et al*., 2015).

The contamination of soil by cadmium is caused not only by industrial sources, or sewage sludge, which is now aplicated into the soil as a fertilizer or a treatment for soil structure improving (Toth *et al*., 2006). The accumulation of Cd in the soil can be enhanced by the application of phosphate fertilizers, which are an important source of trace element enrichment in soils, but also of possible toxicity, especially of cadmium (Cd) (Corguinha *et al.*, 2012) Nickel is in natural soils at trace concentrations. However, concentration is increasing in certain areas by human activities such as mining works, emission of smelters, burning of coal and oil, sewage, phosphate fertilizers and pesticides (Nagajyoti *et al*., 2010). Accumulation of heavy metals, such as lead and nickel, in soils may impact soil properties, reduce soil biological activity and hinder the effective supply of nutrients (Cai *et al*., 2008).

Heavy metals in soils may be present in several forms with different levels of solubility: (1) dissolved (in soil solution), (2) exchangeable (in organic and inorganic components), (3) structural components of the lattices in soils and (4) insolubly precipitated with other soil components. Usually, only the first two forms are able to be absorbed and utilized by plants (Zeng *et al*., 2011). In our case mobile forms of heavy metals could be hazardous. The contents of mobile Cd (Pb, Ni) forms determined in soil extract by NH_4NO_3 were in intervals 0.004-0.055 (0.023-0.295, 0.019-0.475 mg/kg, respectively). Critical value given for Pb (0.1 mg/kg) was exceeded in 35 SS. Lead (Pb) is one of the ubiquitously distributed most abundant toxic elements in the soil. It exerts adverse effect on morphology, growth and photosynthetic processes of plants (Nagajyoti *et al*., 2010). Lead is the strongest bound by specific adsorption processes from all heavy metals, is immobilized in soil when it forms complexes with the organic matter (Alloway, 1990; Peralta-Videa *et al*., 2009). As a result of acid soil reaction (in some cases, strongly acid soil reaction, Table 1), its availability can be increased.Contents of mobile Ni and Cd forms were lower than critical values (Ni < 1.5 mg/kg, Cd < 0.1 mg/kg).

3.2. Plant

Increased levels of heavy metals in soil are reflected in increased metal concentration in potatoes only in limited extent (see Table 3).

Table 3: Contents of heavy metals in potato tubers (mg/kg FM)

Locality	Cultivar	Cd	Pb	Ni
Odorin	Laura	0.030±0.001[b]	0.074±0.062[a]	0.326±0.132[a]
	Marabel	0.024±0.002[a]	0.116±0.064[a]	0.249±0.091[b]
	Red Anna	0.031±0.001[c]	0.058±0.023[a]	0.112±0.027[b]
All cultivars	Min.	0.022	n.d.	0.078
	Max.	0.033	0.230	0.530
	Average	0.028	0.083	0.229
	STDEV	0.004	0.056	0.126
Matejovce	Arlet	0.014±0.002[d]	0.048±0.005[b]	0.108±0.019[a]
	Malvina	0.018±0.001[e]	0.088±0.046[c]	0.280±0.141[c]
	Megan	0.008±0.002[c]	0.060±0.025[bc]	0.175±0.092[ab]
	Spinela	0.021±0.001[f]	0.062±0.033[bc]	0.245±0.060[bc]
	Svella	0.002±0.002[b]	0.013±0.018[a]	0.238±0.012[bc]
	Timea	n.d.[a]	0.047±0.002[b]	0.191±0.094[abc]
All cultivars	Min.	0.000	n.d.	0.069
	Max.	0.022	0.155	0.464
	Average	0.011	0.053	0.206
	STDEV	0.008	0.033	0.096
Spissky Stvrtok	Laura	0.036±0.002[a]	0.103±0.036[c]	0.301±0.124[ab]
	Smart	0.041±0.002[b]	0.058±0.019[ab]	0.177±0.086[a]
	Victoria	0.057±0.005[d]	0.079±0.026[bd]	0.327±0.161[b]
	Vivaldi	0.047±0.002[c]	0.032±0.011[a]	0.168±0.027[a]
All cultivars	Min.	0.033	0.024	0.086
	Max.	0.065	0.163	0.589
	Average	0.045	0.068	0.243
	STDEV	0.009	0.036	0.127
EU No. 1881/2006 (FC SR)		*0.1 (0.1)*	*0.1 (0.1)*	- (0.5)

Notes: n.d. – not detected,
[a, b, c, d] – statistically significant differences between potato cultivars in the same locality, p-value < 0.05

Content of Cd determined in potato tubers was not in any investigated sample higher than 0.1 mg/kg FM. This value is given by Foodstuffs Codex of Slovak Republic as well as Commision Regulation (EC) No 1881/2006 as the maximal allowed amount of Cd in potatoes. The lowest Cd content (below the detection limit) was found in potatoes of cv. Timea (loc. Matejovce) and the highest one (average Cd content: 0.057±0.005 mg/kg FM) in cv. Victoria (loc. Spissky Stvrtok, max. Cd content: 0.065 mg/kg FM). The strong correlation between content of mobile Cd forms in soil and Cd content in potato tubers see Figure 1a-1c) was only in locality Spissky Stvrtok confirmed (R = 0.823, P-value = 7.881E-07).

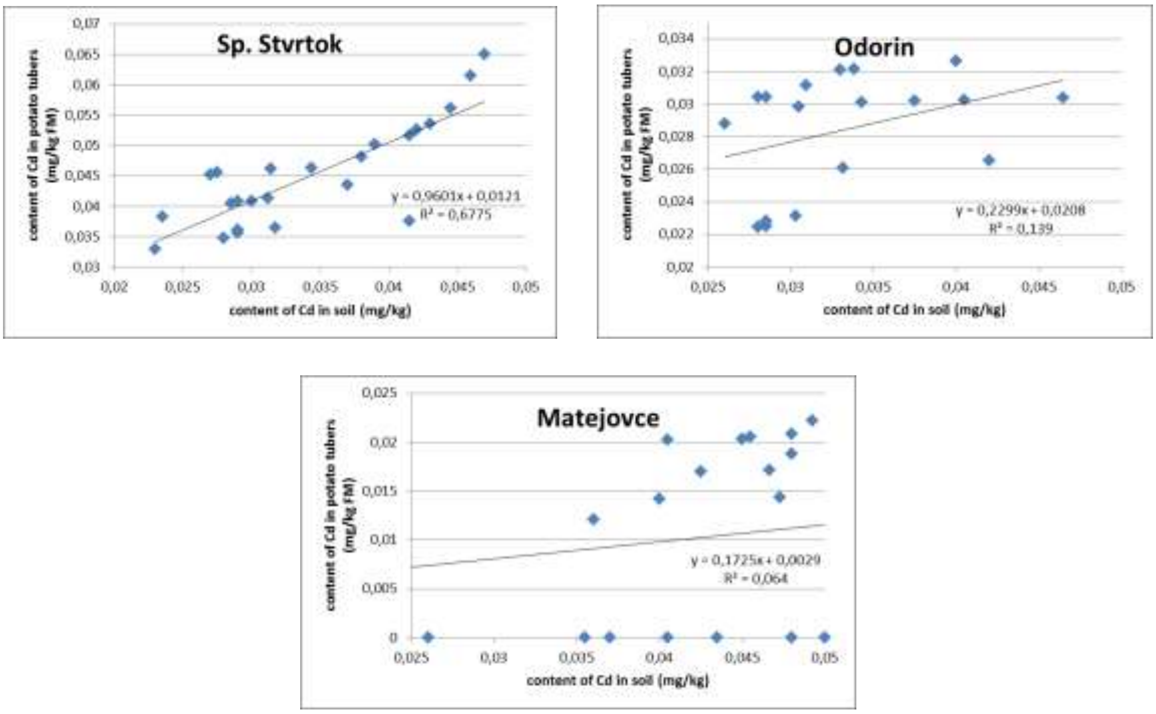
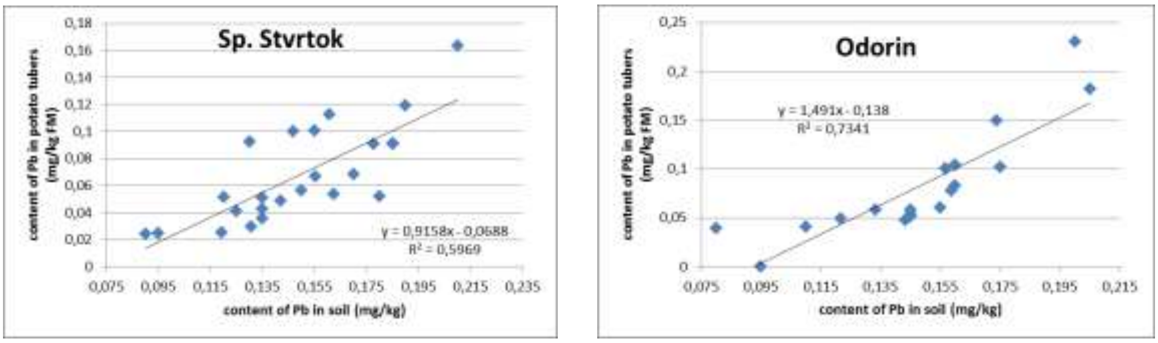


Figure 1: Content of Cd in potato tubers (mg/kg FM) in relationship to content of Cd in soil (mg/kg): a) loc. Spissky Stvrtok; b) locality Odorin; c) loc. Matejovce

Lead seems to be the most hazardous from the aspect of plant contamination from observed heavy metals. The high content of Pb mobile forms (the determined Pb content higher than limit value: 89.7% of all investigated soil samples) was reflected in enhanced Pb content in potato tubers. In 19.2% of potato samples the Pb content was higher than the maximum level for potatoes (0.1 mg Pb/kg FM). In samples from 3 sampling sites (2 SS cv. Svella, loc. Matejovce, 1 SS cv. Laura, loc. Odorin) the determined Pb content was below the detection limit, the highest average Pb content (0.117±0.064 mg Pb/kg FM) was in cv. Marabel, loc. Odorin (max. Pb content: 0.230 mg/kg FM). Middle strong correlation between content of Pb mobile forms in soil and Pb content in potato tubers was confirmed (from R = 0.344 (loc. Matejovce) to R = 0.857 (loc. Odorin), see Figure 2a-2c).



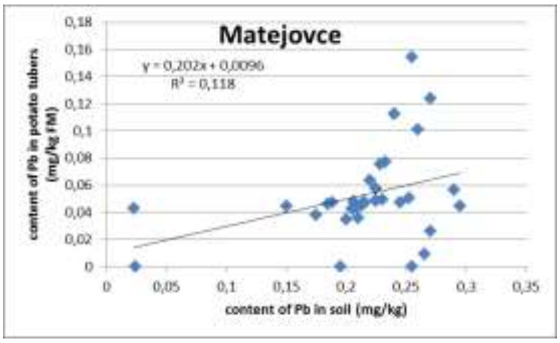


Figure 2: Content of Pb in potato tubers (mg/kg FM) in relationship to content of Pb in soil (mg/kg): a) loc. Spissky Stvrtok; b) locality Odorin; c) loc. Matejovce

For Ni content in foodstuffs there is not any limit value given by the legislation in EU. The determined Ni amount was compared to the limit value given FC SR (0.5 mg/kg FM). Only in 2 from all investigated potato samples the determined Ni content was higher than 0.5 mg/kg FM (0.530 (cv. Laura, loc. Odorin) and 0.589 (cv. Victoria, loc. Spissky Stvrtok) mg Ni/kg resp.). Despite of this fact the middle strong correlation between Ni content in soil and its content in potatoes was confirmed (from R = 0.531 (loc. Matejovce) to R = 0.729 (loc. Spissky Stvrtok), see Figure 3a-3c).

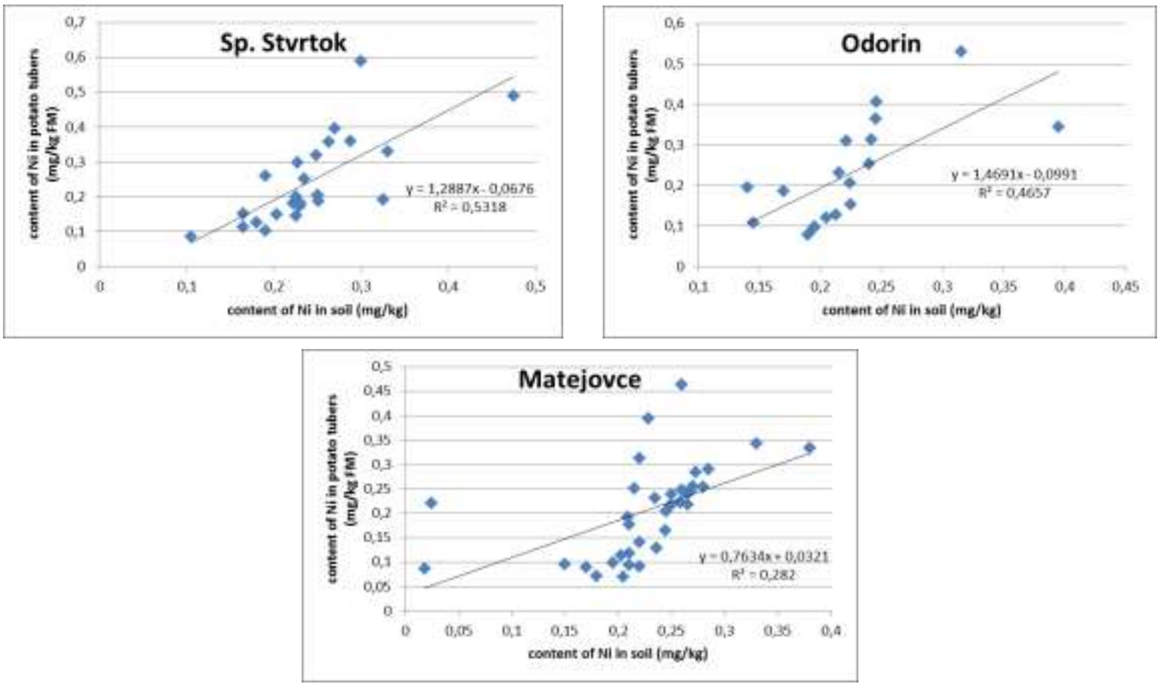


Figure 3: Content of Ni in potato tubers (mg/kg FM) in relationship to content of Ni in soil (mg/kg): a) loc. Spissky Stvrtok; b) loc. Odorin; c) loc. Matejovce

Heavy metal accumulation may also differ greatly within cultivars of an individual species when grown on the same soil (Tang *et al.*, 2012). This fact is confirmed also by our results (see Table 3).

The obtained results of determined heavy metal contents in potatoes in this study are in correlation to results obtained in previous research. The Cd (Pb, Ni) content in Slovakian potato cultivars were in intervals 0.028-0.357 (n.d.-0.638 and 0.194-0.220 mg/kg FM, respectively) (Musilova *et al.*, 2011; 2013). Similar results were published also by other authors. Average values (mg/kg FM) of Cd (n.d.-3870), Pb (0.005-4.65) and Ni (n.d.-2.50) contents were determined in potatoes conventionally and organically farmed in Egypt, in potatoes from Algeria, Australia, Bolivia, Brazil, China, Pakistan, Saudi Arabia, Ethiopia, Iran (Miller *et al*., 2004; Mansour *et al*., 2009; Yang *et al*., 2011; Ali and Al-Qahtani 2012; Corguinha *et al*., 2012; Gebrekidan *et al*., 2013; Khan *et al*., 2013; Yeghaneh *et al*., 2013; Cherfi *et al*., 2014; Rahman *et al*., 2014).

4. Conclusions

The soil samples from all 3 investigated localities the determined total Cd content was at least 100% higher than the limit value, but the maximum contents of mobile forms were significantly lower than the critical value. Similarly, the increased total content of Ni (max. 42%) was not reflected in increased content of mobile forms. The contents of Cd and Ni in potatoes cultivated in observed localities are lower than allowed hygiene standards. On the other hand the total Pb contents in soil were below the limit value, but the determined contents of mobile Pb forms exceeded the limit value in 16 SS by at least 100%. Enhanced soil Pb contents were reflected in Pb accumulation in potatoes. The Pb content exceeded the limit value in almost 20% of analyzed samples. The high content of mobile forms of Pb, but also the high Cd total content may be reflected in their increased mobility and the ability to be accumulated in cultivated crops at change of soil conditions.

REFERENCES

1. Act No. 220/2004 (2004) On the Protection and Use of Agricultural Land. National Council of Slovak Republic, Bratislava. URL: http://www.lecol.sk/images/stories/lecol/220_2004.pdf (accessed 17/03/2015).
2. Alloway B.J. (1990) Heavy metal in soil. Blackie and son Ltd., Glasgow, 1-339.
3. Ali M.H.H. and Al-Qahtani K.M. (2012) Assessment of some heavy metals in vegetables, cereals and fruits in Saudi Arabian markets, Egyptian Journal of Aquatic Research, **38**, 31-37.
4. Arvay J., Bajcan D. and Tomas J. (2012) The quality of environmental components in the Stiavnica river alluvium. SUA in Nitra. 221 p. [in Slovak]
5. Bolan N.S., Adriano D.C., Duraisamy P. and Mani A. (2003) Immobilization and phytoavailability of cadmium in variable charge soils. III. Effect of biosolid compost addition, Plant Soil, **256**, 231-241.
6. Cai L.M., Ma J., Zhou Y.Z., Huang L.C., Dou L., Zhang C.B. and Fu S.M. (2008) Multivariate Geostatistics and GIS-based Approach to Study the Spatial Distribution and Sources of Heavy Metals in Agricultural Soil in the Pearl River Delta, China. Environmental Science, **29**, 3496-3502 (in Chinese).
7. Çelik U. and Oehlenschläger J. (2007) High contents of cadmium, zinc and copper in popular fishery product sold in Turkish supermarkets, Food Control, **18**, 258-261.
8. Chen X., Wang K., Wang Z., Gan C., He P., Liang Y., Jin T. and Zhu G. (2014) Effects of lead and cadmium co-exposure on bone mineral density in a Chinese population, Bone, **63**, 76-80.
9. Chen H., Teng Y., Lu S., Wang Y. and Wang J. (2015) Contamination features and health risk of soil heavy metals in China, Sci Total Environ, **512-513**, 143-153.
10. Cherfi A., Abdoun S. and Gaci O. (2014) Food survey: Levels and potential health risks of chromium, lead, zinc and copper content in fruits and vegetables consumed in Algeria, Food Chem Toxicol, **70**, 48-53.
11. Corguinha A.P.B., Gonçalves V.C., de Souza G.Amaral, de Lima W.E.A., Penido E.S., Pinto C.A.B.P., Francisco E.A.B. and Guilherme L.R.G. (2012) Cadmium in potato and soybeans: Do phosphate fertilization and soil management systems play a role? J Food Compos Anal, **27**, 32-37.
12. Das K.K., Das S.N. and Dhundasi S.A. (2008) Nickel, its adverse health effects and oxidative stress, Indian J Med Res, **128**, 117-131.
13. Du Laing G., Vanthuyne D.R.J., Vandecasteele B., Tack F.M.G. and Verloo, M.G. (2007) Influence of hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil, Environ Pollut, **147**, 615-625.
14. EC No. 1881/2006. Commision Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. URL: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:364:0005:0024:EN:PDF (accessed 24/02/2015)
15. Engström A., Michaëlsson K., Vahter M., Julin B., Wolk A. and Åkesson A. (2012) Associations between dietary cadmium exposure and bone mineral density and risk of osteoporosis and fractures among women, Bone, **50**, 1372-1378.

16. FC SR. Foodstuffs Codex of Slovak Republic, URL: http://www.potravinarstvo.com/pksr/2cast_pksr/10_hlava_kontaminanty_v_potravinach/2004_608%20%203.pdf (accessed 17/03/2015)
17. Gebrekidan A., Weldegebriel Y., Hadera A. and Van der Bruggen B. (2013) Toxicological assessment of heavy metals accumulated in vegetables and fruits grown in Ginfel river near Sheba Tannery, Tigray, Northern Ethiopia, Ecotox Environ Safe, **95**, 171-178.
18. Hellström L., Persson B., Brudin L., Petersson Grawé K., Öborn I. and Järup L. (2007) Cadmium exposure pathways in a population living near a battery plant, Sci Total Environ, **373**, 447-455.
19. Hudec M., Jenisova Z. and Braniša J. (2014) Spectroscopic characteristics of humic substances in relation to lead and cadmium levels in contaminated soils from western carpathians, Carpath J Earth Env, **9**, 47-54.
20. Ju Y.R., Chen W.Y. and Liao C.M. (2012) Assessing human exposure risk to cadmium through inhalation and seafood consumption, J Hazard Mater, **227-228**, 353-361.
21. Khan K., Lu Y., Khan H., Ishtiaq M., Khan S., Waqas M., Wei L. and Wang T. (2013) Heavy metals in agricultural soils and crops and their health risks in Swat District, northern Pakistan, Food Chem Toxicol, **58**, 449-458.
22. Li P., Lin Ch. Cheng H., Duan X. and Lei K. (2015) Contamination and health risks of soil heavy metals around, a lead/zinc smelter in southwestern China, Ecotox Environ Safe, **113**, 391-399.
23. Liénard A., Brostaux Y. and Colinet G. (2014) Soil contamination near a former Zn–Pb ore-treatment plant: Evaluation of deterministic factors and spatial structures at the landscape scale, J Geochem Explor, **147**, 107-116.
24. Lin L.Q., Cong L., Yun W.H., Yang J., Ming H., Wan Z.B., Kai Ch. and Lei H. (2015) Association of soil cadmium contaminationwith ceramic industry: A case study in a Chinese town, Sci Total Environ, **514**, 26-32.
25. Liu G., Yu Y., Hou J., Xue W., Liu X., Liu Y., Wang W., Alsaedi A., Hayat T. and Liu Z. (2014) An ecological risk assessment of heavy metal pollution of theagricultural ecosystem near a lead-acid battery factory, Ecol Indic, **47**, 210–218.
26. Mansour S.A., Belal M.H., Abou-Arab A.A.K., Ashour H.M. and Gad M.F. (2009) Evaluation of some pollutant levels in conventionally and organically farmed potato tubers and their risks to human health, Food Chem Toxicol, **47**, 615-625.
27. Matovic V., Buha A., Đukić-Ćosić D., Bulat Z. (2015) Insight into the oxidative stress induced by lead and/or cadmium in blood, liver and kidneys, Food Chem Toxicol, **78**, 130-140.
28. McCauley A., Jones C. and Jacobsen J. (2009) Soil pH and Organic Matter. URL: http://landresources.montana.edu/nm/documents/NM8.pdf (accessed 13/03/2015)
29. Miller J.R., Hudson-Edwards K.A., Lechler P.J., Preston D. and Macklin M.G. (2004) Heavy metal contamination of water, soil and produce within riverine communities of the Río Pilcomayo basin, Bolivia, Sci Total Environt, **320**, 189-209.
30. Minh N.D., Hough R.L., Thuy L.T., Nyberg Y., Mai L.B., Vinh N.C., Khaim N.M. and Öborn I. (2012) Assessing dietary exposure to cadmium in a metal recycling community in Vietnam: Age and gender aspects, Sci Total Environt, **416**, 164-171.
31. Moriarity R.S., Harris J.T. and Cox, R.D. (2014) Lead toxicity as an etiology for abdominal pain in the emergency department, J Emerg Med, **46**, e35-e38.
32. Musilova J., Jonasova D. and Polakova Z. (2011) Variety as one of the factors affecting the accumulation of risk elements of potato tubers, Environmental protection and natural resources, **48**, 131-142.
33. Musilova J., Hrabovska D., Volnova B. and Polakova Z. (2013) Does consumption of potatoes cultivated in soils contaminated by heavy metals poses any risk to human health? Environmental protection and natural resources, **24**, 25-28.
34. Nagajyoti P.C., Lee K.D. and Sreekanth T.V.M. (2010) Heavy metals, occurrence and toxicity for plants: a review, Environ Chem Lett, **8**, 199-216.
35. Peralta-Videa J.R., Lopez M.L., Narayan M., Saupe G. and Gardea-Torresdey J. (2009) The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain, The International Journal of Biochemistry & Cell Biology, **41**, 1665-1677.
36. Pérez A.L. and Anderson K.A. (2009) DGT estimates cadmium accumulation in wheat and potato from phosphate fertilizer applications, Sci Total Environ, **407**, 5096-5103.
37. Qu M., Li W. and Zhang Ch. (2013) Assessing the risk costs in delineating soil nickel contamination using sequential Gaussian simulation and transfer functions, Ecol Inform, **13**, 99-105.
38. Rahman M.A., Rahman M.M., Reichman S.M., Lim R.P. and Naidu R. (2014) Heavy metals in Australian grown and imported rice and vegetables on sale in Australia: Health hazard, Ecotox Environ Safe, **100**, 53-60.

39. Schaumlöffel D. (2012) Nickel species: Analysis and toxic effects, J Traca Elem Med Bio, **26,** 1-6.
40. Stasinos S. and Zabetakis I. (2013) The uptake of nickel and chromium from irrigation water by potatoes, carrots and onions, Ecotox Environ Safe, **91**, 122-128.
41. Sunderman F.W. Jr. (1993) Biological monitoring of nickel in humans, Scand J Work Environ Health, **19**, 34-38.
42. Tang Y.T., Deng T.H.B., Wu Q.H., Wang S.Z., Qiu R.L., Wei Z.B., Guo X.F., Wu Q.T., Lei M., Chen T.B., Echevarria G., Sterckeman T., Simonnot M.O. and Morel J.L. (2012) Designing Cropping Systems for Metal-Contaminated Sites: A Review, Pedosphere, **22**, 470-488.
43. Tomas J., Toth T. and Lazor, P. (2000) The state of soil hygiene in regions lowlands SR in terms of heavy metals in different extractant, Acta fytotechnica et zootechnica, **3**, 16-20. [in Slovak]
44. Toth T., Tomas J., Lazor P., Bajcan D., Lahucky L. (2006) The impact of bio-sludge obtained by continuous co-fermentation of animal waste to the state of soil health and quality of of grown crops, Chemické listy, **100**, 718-719. [in Slovak]
45. Vokal B., Čepl J, Hausvater E, Rasocha V. (2003) Grown potatoes. Grada Publishing. 1-112. [in Czech]
46. Vollmannová A., Lahučký L., Tomáš J., Hegedűsová A. and Jomová K. (2002) The arrangement of extremely acid soil reaction in relationship to Cd, Pb, Cr and Ni intake by the plants. Ekologia Bratislava, **21**, 442-448.
47. Wuana R.A. and Okieimen F.E. (2011) HeavyMetals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation, ISRN Ecology, **2011**, 1-20.
48. Xu D., Chen Z., Sun K., Yan D., Kang M. and Zhao Y. (2013) Effect of cadmium on the physiological parameters and the subcellular cadmium localization in the potato (Solanum tuberosum L.). Ecotox Environ Safe, **97**, 147-153.
49. Yang Q.W., Xu Y., Liu S.J., He J.F. and Long F.Y. (2011) Concentration and potential health risk of heavy metals in market vegetables in Chongqing, China, Ecotox Environ Safe, **74**, 1664-1669.
50. Yang L., Huang B., Hu W., Chen Y., Mao M. and Yao L. (2014) The impact of greenhouse vegetable farming duration and soil types on phytoavailability of heavy metals and their health risk in eastern China. Chemosphere, **103**, 121-130.
51. Yeganeh M., Afyuni M., Khoshgoftarmanesh A.H., Khodakarami L., Amini M., Soffyanian A.R., and Schulin R. (2013) Mapping of human health risks arising from soil nickel and mercury contamination, J Hazard Mater, **244-245**, 225-239.
52. Zeng F., Ali S., Zhang H., Ouyang Y., Qiu B., Wu F. and Zhang G. (2011) The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants, Environ Pollut, **159**, 84-91.
53. Zhang W.L., Du Y., Zhai M.M. and Shang Q. (2014) Cadmium exposure and its health effects: A 19-year follow-up study of a polluted area in China. Sci Total Environt, **470-471**, 224-228.
54. Zhao Q., Wang Y., Cao Y., Chen A., Ren M., Ge Y., Yu Z., Wan S., Hu A., Bo Q., Ruan L, Chen H., Qin S., Chen W., Hu Ch., Tao F., Xu D., Xu J., Wen L. and Li L. Potential health risks of heavy metals in cultivated topsoil and grain, including correlationswith human primary liver, lung and gastric cancer, in Anhui province, Eastern China, Sci Total Environ, **470-471**, 340-347.
55. Zhu F., Fan W., Wang X., Qu L. and Yao S. (2011) Health risk assessment of eight heavy metals in nine varieties of edible vegetable oils consumed in China, Food Chem Toxicol, **49**, 3081-3085.