Research Article

Safety of Potato Consumption in Slovak Region Contaminated by Heavy Metals due to Previous Mining Activity

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Heavy metals are among the most serious environmental contaminants in mining districts. Soil, as one of the main components of the environment, is the place of heavy metal entry into plants and consequently into the food chain, too. Potatoes grown in the region of Middle Spis (Slovakia) may be a source of increased content of heavy metals and pose a health risk to the consumer. The contents of heavy metals (Cd, Pb, and Ni) in potato and soil samples were determined using the AAS method and compared with limit values set by the Slovak Republic and the European Union. The content of heavy metals was determined in 12 potato cultivars with different length of vegetation period (mid-early, very early, and early, resp.), which were grown in three localities with a highly disturbed environment. Total contents and mobile forms of heavy metals as well as physical and chemical properties were determined in soil samples which were collected from the same sampling sites. Only Pb content in potato tubers was higher than the hygienic limit value (0.1 mg kg\(^{-1}\) FM) in 15 sampling sites (interval was n.d.–0.2298 mg kg\(^{-1}\) FM). The contents of exchangeable forms (total content) of heavy metals in soil were ranged between the intervals: Cd 0.004–0.055 (0.94–156), Pb 0.023–0.295 (17.00–26.80), and Ni 0.019–0.475 (30.80–71.00) mg kg\(^{-1}\). At current average consumption levels of potatoes, tolerable weekly intake (TWI) or tolerable daily intake (TDI) for observed heavy metals was not exceeded.

1. Introduction

Heavy metals contribute significantly to a reduction in environmental quality. Heavy metals can originate from both natural and anthropogenic sources [1]. When occurring naturally in the soil environment as a consequence of the pedogenetic processes of weathering of parent materials, their contents are at levels that are considered to be trace (<1000 mg/kg) [2]. Hazardous levels of heavy metals are usually associated with anthropogenic sources.

There are different sources of heavy metals in the environment. Other than natural sources there are agricultural sources (fertilizer use, sewage sludge application, and metal-containing pesticides); industrial sources (petrochemicals); domestic effluents; atmospheric sources; and other sources (disposal of high metal waste in improperly protected landfill, leaded gasoline and lead-based paints, and coal combustion residues) [1–4]. Heavy metals are very persistent in the environment; they are not bio- and thermodegradable and are highly toxic and bioaccumulative [5, 6]. Heavy metals represent a potential human health hazard if safe thresholds of exposure or absorption are exceeded. Nonessential chemical elements (Cd, Pb, Hg, etc.) are toxic even at relatively low concentrations, but also biologically irreplaceable microelements (e.g. Cu, Zn, Mn, Co, Cr, etc.) would be toxic if a certain concentration level is exceeded [7–9].
The contamination of soil by cadmium is caused not only by industrial sources. One of important Cd sources could be also sewage sludge, which can be applied on soil as a fertilizer or as a treatment for improving soil structure [10]. 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 [11]. Nickel is present in natural soils at trace level concentration. However, its concentration is increasing in certain areas by human activities such as mining smelter emission, burning of coal and oil, sewage, phosphate fertilizers, and pesticides [1]. Accumulation of heavy metals such as lead and nickel in soil may impact soil properties, reduce soil biological activity, and hinder the effective supply of nutrients [12].

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 [9] and can eventually enter the human body through the food chain [13]. The primary route for Cd exposure in humans is through ingestion of foods [14]. Cadmium is present virtually in 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 [15]. The highest concentrations are present in seafood, molluscs and crustaceans, 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 potatoes and root vegetables [16, 17].

Cadmium, which may accumulate in the human body, has an adverse effect on human health and may cause proteinuria, result in low bone mineral density, cause osteoporosis, and increase the risk of bone fracture. Cd also affects the female reproductive system and severely affects the female endocrine system. Chronic Cd dust or aerosols cause lung cancer, hypertension, and renal dysfunction [13, 18–22].

Lead (Pb) is a highly toxic element, is bioaccumulative, and neither degrade in the environment nor is easily metabolized. It is another widespread toxic pollutant which has no known function in biological systems. The main anthropogenic sources of Pb that remain, such as mining, smelting, lead batteries, crystal, and ceramic industry, undoubtedly contribute to Pb-induced adverse effects in humans and the environment [23]. Excessive intake of Pb can damage the central nervous system, skeletal, circulatory, enzymatic, endocrine, and immune systems, and kidneys in adults and cause delays in physical and mental development in children. It has been shown that Pb can disturb haemoglobin synthesis. After absorption, Pb enters the blood and then accumulates in erythrocytes and is bound to proteins or complexed with low molecular weight sulphhydril 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 [6, 13, 18, 21, 23–25]. Symptoms such as personality changes, irritability, persistent headache, abdominal colic, or treatment of neuropathy warrant parenteral chelation indicative of recent exposure to lead [26]. Peralta-Videa et al. [18] reported that in humans there is a correlation between Pb exposure and hearing loss.

Nickel (Ni) is present in all soils, where it derives from either the parent material (lithosphere) or anthropogenic deposition or both [27]. Nickel is recognized as an essential micronutrient for living organisms and is a component of the enzyme urease [1]. While in small quantities nickel is necessary, deficiency causes growth retardation and anaemia and reduces the activity of certain enzymes [28, 29]. Its toxicity at higher levels is more prominent [9]. Large quantities of nickel may cause various consequences on human bodies, such as inflammation, cancer, neurasthenia, system disorders, lower fertility, and teratogenic, mutagenic, and heart disorders [28, 30]. 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 [31]. 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. People working in the nickel production and processing industry are exposed to a higher concentration of nickel. Their main route of exposure is inhalation and, to a lesser extent, contact with the skin [32]. Inhaled Ni compounds are carcinogenic to humans although there is a lack of evidence of a carcinogenic risk of Ni from oral exposure to humans [25].

Middle Spis is one of the at-risk regions of Slovakia with soils affected by acid pollutants as well as by heavy metals. Industrial enterprises in the localities Rudnany, Krompachy, and Spisska Nova Ves were the determining sources of environmental contamination for several decades. Despite a reduction in mining activities, the negative consequences of the metallurgical production in acid soils of this region still persist [33].

The aim of our study was to assess the quality of potatoes in terms of heavy metal content (Ni, Cd, and Pb) in their edible parts. Potatoes were grown in three localities of Middle Spis, one of the most loaded regions of Slovakia with a disturbed environment due to previous intense mining activity.

2. Material and Methods

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

**Cultivars (Maturity, Shape of Tubers, Colour Skin/Colour Flesh)**

(i) Vivaldi: very early, oval, yellow/light yellow
(ii) Malvina and Svella: early, oval, yellow/yellow
(iii) Arlet, Marabel, Megan, and Victoria: mid-early, oval, yellow/yellow
(iv) Laura: mid-early, oval, red/deep yellow
(v) Red Anna: mid-early, short-oval, red/deep yellow
(vi) Smart: mid-early, short-oval, yellow/deep yellow
(vii) Spinela: mid-early, oval, red/deep yellow
(viii) Timea: mid-early, short-oval, yellow/yellow

In all localities the standard technologies of potato cultivation were used.

In the autumn, 30 t/ha of farmyard manure was applied and ploughed into the soil. Immediately before planting, 335 kg of Patenkali (30% K₂O, 10% MgO, and 42.5% SO₄²⁻) was applied over the whole surface. During planting, 300 kg NPK (15:15:15) was applied directly under the planted tubers, and the potato tubers were treated with a preparation Maxim (0.1 L ha⁻¹) which protects tubers against Rhizoctonia solani. After planting, the area was sprayed against weeds. During vegetation, the potato crops were protected against late potato blight and some viral diseases. Vegetation of the plants was finished by mechanical crushing of leaves and subsequent application of the preparation Reglone. All preparations have been applied according to manufacturer’s recommendations. The tubers were harvested after the maturation of potato peels about 25 days after the application of Reglone.

Samples from each cultivar were collected in four repetitions at an amount of about 2 kg from each sample site. Soil samples were also taken at horizon 0–0.2 m, using a pedological probe (GeoSampler fy. Fisher).

2.1. Soil Samples. Soil samples were air dried and disaggregated. Two fractions, fine earth I (average 2 mm particle size) and fine earth II (average 0.125 mm particle size), were prepared for the determination for physical, chemical, and nutrient contents and for Ni, Cd, and Pb determination, respectively.

In soil samples the exchange soil reaction (pH/KCl) (i) and content of oxidizable carbon (C₇OX, %) using volumetric method (ii) were determined. The content of Soil Organic Matter (SOM, %) was calculated from value of C₇OX content.

Chemicals and Equipment

(i) KCl: CentralChem, Slovakia; 691 pH Meter Metrohm, Swiss; c (KCl) = 1 mol L⁻¹
(ii) H₂SO₄, K₂Cr₂O₇, and (NH₄)₂Fe(SO₄)₂·6H₂O: Merck, Germany

Content of nutrients was determined according to Mehlich III (iii), content of P using spectrophotometric method (iv), and content of K, Ca, and Mg (iv) using AAS method (v).

Chemicals and Equipment

(iii) NH₄NO₃, NH₄F, EDTA, HNO₃, H₂SO₄, (NH₄)₂MoO₄, C₆H₄K₂O₁₂Sb₂·3H₂O, and ascorbic acid: Merck, Germany
(iv) Spectrophotometer UV-VIS 1800, Shimadzu; λ = 666 nm
(v) VARIAN AASpectr DUO 240FS/240Z/UltrAA equipped with an air-acetylene flame, Varian Ltd., Mulgrave, Australia.

Content of two forms of dangerous metals Ni, Cd, and Pb was determined using AAS method. Content of exchangeable forms of Ni, Cd, and Pb was determined in soil extract by NH₄NO₃ (vi), total content of Ni, Cd, and Pb, including all metal forms with exception of silicate forms, in soil extract by aqua regia (vii).

Chemicals and Equipment

(vi) NH₄NO₃: Merck, Germany; c = 1 mol L⁻¹
(vii) HCl: CentralChem, Slovakia; HNO₃: Merck, Germany

Mineralization of the soil samples was performed by microwave digestion (MARS X-press, CEM USA) in a mixture of nitric acid and hydrochloric acid in a molar ratio of 1:3. Parameters used in the digestion process were heating to 150°C for 15 minutes, keeping it constant for 10 minutes, increasing to 160°C, again keeping it constant for 10 minutes, and cooling for 20 minutes. A blank sample was treated in the same way. The digested substances were subsequently filtered through a quantitative filter paper Filtrak 390 (Munktell, Germany) and filled with deionized water to a volume of 100 mL [34].

The contents of Ni, Cd, and Pb in soil were determined using F-AAS method and GF-AAS method, respectively. Concentrations of Ni, Cd, and Pb were assessed at wavelengths of 232.0, 228.8, and 217.0 nm, respectively. The respective limits of detection (LOD) for Cd, Pb, and Ni were 0.4, 0.05, and 1.0 mg kg⁻¹; and their respective limits of quantification (LOQ) were 1.2, 0.15, and 3.0 and mg kg⁻¹.

The contents of Ni, Cd, and Pb were compared with limit and critical values according to Act number 220/2004.

2.2. Plant Samples. Potato tubers were collected in full maturity from investigated localities. The weight of each average sample was 2 kg. After washing, peeling, and chopping approximately 150 g of sample was homogenized. About 30 g from homogenized sample was used for determination of dry matter and the rest of each sample was lyophilized and used for further analysis.

The contents of Ni, Cd, and Pb were determined in potatoes in extracts of freeze-dried samples. The samples were pulverized (i) and, afterwards, stored in precleaned polyethylene bottles until subsequent preanalytical operations.

Closed system of microwave digestion (ii) without using hydrogen peroxide was used for the mineralization of homogenized potato samples (1.000 g in a mixture of 5 mL HNO₃ and 5 mL deionized water (iii)). Digestion process steps comprised heating to 160°C for 15 minutes and keeping it constant for 10 minutes. The same way was used for blank sample preparation. After filtration (Filtrak 390; Munktell, Germany) of digested substances deionized water was added to a volume of 50 mL [34, 35]. 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 the multielemental standard for GF-AAS (iv) and subsequently expressed in mg kg⁻¹ of...
Table 1: Basic agrochemical indicators and contents of nutrients.

<table>
<thead>
<tr>
<th>Locality</th>
<th>pH/KCl (Min.)</th>
<th>Humus (%)</th>
<th>N (mg/kg)</th>
<th>P (mg/kg)</th>
<th>K (mg/kg)</th>
<th>Ca (mg/kg)</th>
<th>Mg (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odorin</td>
<td>4.45</td>
<td>2.12</td>
<td>1400.0</td>
<td>32.52</td>
<td>132.50</td>
<td>1032.00</td>
<td>102.00</td>
</tr>
<tr>
<td></td>
<td>5.42</td>
<td>3.33</td>
<td>2625.0</td>
<td>108.41</td>
<td>280.50</td>
<td>1880.00</td>
<td>188.00</td>
</tr>
<tr>
<td></td>
<td>5.15</td>
<td>2.65</td>
<td>1954.2</td>
<td>79.22</td>
<td>188.96</td>
<td>1443.83</td>
<td>134.83</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.33</td>
<td>386.5</td>
<td>19.84</td>
<td>46.29</td>
<td>274.81</td>
<td>26.54</td>
</tr>
<tr>
<td>Matejovce</td>
<td>4.95</td>
<td>2.00</td>
<td>2450.0</td>
<td>10.82</td>
<td>143.50</td>
<td>2008.00</td>
<td>124.00</td>
</tr>
<tr>
<td></td>
<td>6.63</td>
<td>3.63</td>
<td>4900.0</td>
<td>62.42</td>
<td>268.00</td>
<td>3408.00</td>
<td>292.00</td>
</tr>
<tr>
<td></td>
<td>5.64</td>
<td>2.65</td>
<td>3441.7</td>
<td>35.59</td>
<td>186.23</td>
<td>2613.92</td>
<td>184.83</td>
</tr>
<tr>
<td></td>
<td>0.44</td>
<td>0.49</td>
<td>728.6</td>
<td>12.98</td>
<td>36.05</td>
<td>438.32</td>
<td>46.98</td>
</tr>
<tr>
<td>Spissky Stvrtok</td>
<td>4.69</td>
<td>2.36</td>
<td>1400.0</td>
<td>15.66</td>
<td>111.50</td>
<td>1146.00</td>
<td>114.00</td>
</tr>
<tr>
<td></td>
<td>6.61</td>
<td>3.57</td>
<td>3150.0</td>
<td>98.69</td>
<td>256.50</td>
<td>3126.00</td>
<td>220.00</td>
</tr>
<tr>
<td></td>
<td>5.39</td>
<td>2.85</td>
<td>2395.3</td>
<td>42.69</td>
<td>190.31</td>
<td>1764.75</td>
<td>167.50</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.31</td>
<td>556.0</td>
<td>21.84</td>
<td>44.53</td>
<td>573.13</td>
<td>29.47</td>
</tr>
</tbody>
</table>

The water content of the samples was determined by the moisture analyser (v).

Chemicals and Equipment

(i) Grindomix 200 GD (Retsch, Germany)
(ii) Mars X-Press 5 (CEM Corp., USA)
(iii) HNO₃: Suprapur, Merck, Germany; deionized water: 0.054 mS cm⁻¹ from Simplicity185 (Millipore, UK)
(iv) CertiPUR*: Merck, Germany
(v) DLB 160-3A: Kern, Germany

Contents of heavy metals determined in plant samples were evaluated according to maximum allowed amounts given by the Foodstuffs Codex of the Slovak Republic and EC number 1881/2006.

2.3. Statistical Analysis. Results were statistically evaluated by Analysis of Variance (ANOVA, Multiple Range Tests, Method: 95.0 percent LSD) using statistical software Statgraphics (Centurion XVI.I, USA) and a 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.

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⁻¹ and 110–180 mg Mg kg⁻¹), and average values of soil reaction were lower compared to recommended pH values (pH 5.5–6.5), although according to Vokal et al. [36] there is no decrease of tuber yield at lower pH values around pH 4.8.

Optimal Soil Organic Matter (SOM) 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 suitable for potato cultivation with a requirement of P enrichment through fertilization. All surveyed localities are a part of the Spis region which was known for potato cultivation in the past.

The determination of Cd, Pb, and Ni content 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 NH₄NO₃) according to legislation valid in the Slovak Republic (Act number 220/2004).

Determined total contents of heavy metals were in the range of 0.94–1.56 (Cd), 17.00–26.80 (Pb), and 30.80–71.00 (Ni) mg kg⁻¹, respectively.

Values for the Cd limit (0.7 mg kg⁻¹) were exceeded in all sampling sites (SS), while the determined total Pb content in soil was below the limit value (<70 mg kg⁻¹). The determined total Ni content (>50 mg kg⁻¹) in soil was exceeded in 14 SS (12 SS locality Matejovce, 2 SS locality Spissky Stvrtok).

The total contents of heavy metals include all metal forms with the exception of their residual fractions. Their high content determined in a 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 in soil properties. In general, the mobility of heavy metals is associated with soil reaction, cation exchange capacity, soil organic content, and soil texture and is increased with decrease in soil pH value. Due to the increased availability of heavy metals by plants, their input into the human body via the food chain could ultimately be increased [37–42]. 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 to retain heavy metals in an exchangeable form [38, 43]. Adsorption of heavy metals is also highly dependent on soil components that include silicate clays, organic matter, iron, aluminium, and manganese oxides [44, 45].

The soil contents of Cd, Pb, and Ni are variable (e.g., northern Pakistan, southwestern China, Wallonia region of Belgium, and northwest of Iran: Cd 0.08–4.5, Pb 17.0–672.0, and Ni 0.46–103.0 mg kg\(^{-1}\) soil) depending on agroclimatic conditions [27, 46–48]. Heavy metals in soils may be present in several forms with different levels of solubility: (1) being dissolved (in soil solution); (2) exchangeable organic and inorganic components; (3) structural components of the lattices in soils; and (4) being insolubly precipitated with other soil components. Usually, only the first two forms are able to be absorbed and utilized by plants [38]. In our case, mobile forms of heavy metals could be hazardous. The contents of exchangeable Cd, Pb, and Ni forms determined in soil extract by NH\(_4\)NO\(_3\) were in intervals 0.004–0.055 (0.023–0.295, 0.019–0.475 mg kg\(^{-1}\), resp.). Critical value given for Pb (0.1 mg kg\(^{-1}\)) was exceeded in 35 SS. Lead (Pb) is one of the most ubiquitously distributed abundant toxic elements in the soil. It exerts an adverse effect on the morphology, growth, and photosynthetic processes of plants [1]. Lead has the strongest chemical bond by specific adsorption processes of the all heavy metals and is immobilized in soil when it forms complexes with organic matter [18, 49]. As a result of acid soil reaction (in some cases, strong 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\(^{-1}\), Cd < 0.1 mg kg\(^{-1}\)). No correlation between total contents of metals and their exchangeable forms could be explained by the fact that the part of Cd and Ni is irreversibly bound on Fe and Mn oxides as well as clay minerals. Nickel is partly bound also with silicates [50].

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

Content of Cd determined in potato tubers was not higher than 0.1 mg kg\(^{-1}\) FM. This value is given by the Foodstuffs Codex of the Slovak Republic as well as Commision Regulation (EC) number 1881/2006 as the maximum allowed amount of Cd in potatoes. The lowest Cd content (below the detection limit) was found in the potatoes of cultivar Timea (locality Matejovce) and the highest one (average Cd content: 0.057±0.005 mg kg\(^{-1}\) FM) in cultivar Victoria (locality Spissky Stvrtok, max. Cd content: 0.065 mg kg\(^{-1}\) FM). A strong correlation between content of exchangeable Cd forms in soil and Cd content in potato tubers was confirmed in the locality of Spissky Stvrtok (\(R = 0.823, P\) value = 7.881E – 07 (Figure 1(a))). In localities Odorin (Figure 1(b)) and Matejovce (Figure 1(c)) only weak correlation between exchangeable Cd forms in soil and Cd content in potato tubers was confirmed.

Of the observed heavy metals, lead seems to be the most hazardous one from the aspect of plant contamination. 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\(^{-1}\) FM). In samples from 3 sampling sites (2 SS cultivar Svella, locality Matejovce, and 1 SS cultivar Laura, locality Odorin) the determined Pb content was below the detection limit; the

### Table 2: Contents of heavy metals in soil determined in different soil extracts.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Cd (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Ni (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Odorin</strong></td>
<td>Min. 0.94</td>
<td>17.00</td>
<td>30.80</td>
<td>0.026</td>
<td>0.080</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>Max. 1.35</td>
<td>24.40</td>
<td>50.00</td>
<td>0.047</td>
<td>0.205</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>Average 1.19</td>
<td>19.88</td>
<td>39.53</td>
<td>0.033</td>
<td>0.148</td>
<td>0.223</td>
</tr>
<tr>
<td></td>
<td>STDEV 0.13</td>
<td>1.66</td>
<td>4.33</td>
<td>0.006</td>
<td>0.032</td>
<td>0.059</td>
</tr>
<tr>
<td><strong>Matejovce</strong></td>
<td>Min. 1.16</td>
<td>17.40</td>
<td>33.00</td>
<td>0.004</td>
<td>0.023</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>Max. 1.56</td>
<td>25.40</td>
<td>71.00</td>
<td>0.055</td>
<td>0.295</td>
<td>0.380</td>
</tr>
<tr>
<td></td>
<td>Average 1.34</td>
<td>21.84</td>
<td>52.59</td>
<td>0.045</td>
<td>0.227</td>
<td>0.228</td>
</tr>
<tr>
<td></td>
<td>STDEV 0.12</td>
<td>1.69</td>
<td>9.01</td>
<td>0.012</td>
<td>0.035</td>
<td>0.066</td>
</tr>
<tr>
<td><strong>Spissky Stvrtok</strong></td>
<td>Min. 1.00</td>
<td>17.60</td>
<td>37.40</td>
<td>0.023</td>
<td>0.090</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td>Max. 1.44</td>
<td>26.80</td>
<td>51.20</td>
<td>0.047</td>
<td>0.210</td>
<td>0.475</td>
</tr>
<tr>
<td></td>
<td>Average 1.21</td>
<td>20.44</td>
<td>45.95</td>
<td>0.034</td>
<td>0.149</td>
<td>0.247</td>
</tr>
<tr>
<td></td>
<td>STDEV 0.12</td>
<td>2.17</td>
<td>3.37</td>
<td>0.007</td>
<td>0.030</td>
<td>0.072</td>
</tr>
</tbody>
</table>

**Limit value** 0.4 | 70.0 | 50.0

**Critical value** 0.1 | 0.1 | 1.5
Table 3: Contents of heavy metals in potato tubers.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Cultivar</th>
<th>Cd (mg/kg FM)</th>
<th>Pb (mg/kg FM)</th>
<th>Ni (mg/kg FM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odorin</td>
<td>Laura</td>
<td>0.030 ± 0.001&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.074 ± 0.062&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.326 ± 0.132&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Marabel</td>
<td>0.024 ± 0.002&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.116 ± 0.064&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.249 ± 0.091&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Red Anna</td>
<td>0.031 ± 0.001&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.058 ± 0.023&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.112 ± 0.027&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>All cultivars</td>
<td>Min.</td>
<td>0.022</td>
<td>n.d.</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>0.033</td>
<td>0.230</td>
<td>0.530</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.028</td>
<td>0.083</td>
<td>0.229</td>
</tr>
<tr>
<td></td>
<td>STDEV</td>
<td>0.004</td>
<td>0.056</td>
<td>0.126</td>
</tr>
<tr>
<td>Matejovce</td>
<td>Arlet</td>
<td>0.014 ± 0.002&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.048 ± 0.005&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.108 ± 0.019&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Malvina</td>
<td>0.018 ± 0.001&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.088 ± 0.046&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.280 ± 0.141&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Megan</td>
<td>0.008 ± 0.002&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.060 ± 0.025&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>0.175 ± 0.092&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Spinela</td>
<td>0.021 ± 0.001&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.062 ± 0.033&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>0.245 ± 0.060&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Svela</td>
<td>0.002 ± 0.002&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.013 ± 0.018&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.238 ± 0.012&lt;sup&gt;bc&lt;/sup&gt;</td>
</tr>
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<td></td>
<td>Timea</td>
<td>n.d.&lt;sup&gt;*&lt;/sup&gt;</td>
<td>0.047 ± 0.002&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.191 ± 0.094&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>All cultivars</td>
<td>Min.</td>
<td>0.000</td>
<td>n.d.</td>
<td>0.069</td>
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<tr>
<td></td>
<td>Max.</td>
<td>0.022</td>
<td>0.155</td>
<td>0.464</td>
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<tr>
<td></td>
<td>Average</td>
<td>0.011</td>
<td>0.053</td>
<td>0.206</td>
</tr>
<tr>
<td></td>
<td>STDEV</td>
<td>0.008</td>
<td>0.033</td>
<td>0.096</td>
</tr>
<tr>
<td>Spissky Stvrtok</td>
<td>Laura</td>
<td>0.036 ± 0.002&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.103 ± 0.036&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.301 ± 0.124&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Smart</td>
<td>0.041 ± 0.002&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.058 ± 0.019&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.177 ± 0.086&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Victoria</td>
<td>0.057 ± 0.005&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.079 ± 0.026&lt;sup&gt;bd&lt;/sup&gt;</td>
<td>0.327 ± 0.161&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Vivaldi</td>
<td>0.047 ± 0.002&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.032 ± 0.011&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.168 ± 0.027&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>All cultivars</td>
<td>Min.</td>
<td>0.033</td>
<td>0.024</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>0.065</td>
<td>0.163</td>
<td>0.589</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.045</td>
<td>0.068</td>
<td>0.243</td>
</tr>
<tr>
<td></td>
<td>STDEV</td>
<td>0.009</td>
<td>0.036</td>
<td>0.127</td>
</tr>
</tbody>
</table>

EC No. 1881/2006 (FC SR) 0.1 (0.1) 0.1 (0.1) — (0.5)

Notes: n.d.: not detected, a, b, c, and d: statistically significant differences between potato cultivars in the same locality, and P value < 0.05.

Figure 1: Content of Cd in potato tubers in relationship to content of cadmium (exchangeable forms) in soil: (a) locality Spissky Stvrtok; (b) locality Odorin; (c) locality Matejovce.
highest average Pb content ($0.117 \pm 0.064 \text{ mg Pb kg}^{-1} \text{ FM}$) was in cultivar Marabel, locality Odorin (max. Pb content: $0.230 \text{ mg kg}^{-1} \text{ FM}$). Medium-to-strong correlation between content of Pb mobile forms in soil and Pb content in potato tubers was confirmed (from $R = 0.344$ (locality Matejovce) to $R = 0.857$ (locality Odorin), Figures 2(a)–2(c)).

For Ni content in foodstuffs there is not any limit value given by legislation in the EU. The determined Ni amount was compared to the limit value given FC SR (0.5 mg kg$^{-1}$ FM). Only in 2 from all the investigated potato samples was the determined Ni content higher than 0.5 mg kg$^{-1}$ FM (0.530 (cultivar Laura, locality Odorin) and 0.589 (cultivar Victoria, locality Spissky Stvrtok) mg Ni kg$^{-1}$ resp.). Despite this fact, a medium-strong correlation between Ni content in soil and its content in potatoes was confirmed (from $R = 0.531$ (locality Matejovce) to $R = 0.729$ (locality Spissky Stvrtok), Figures 3(a)–3(c)).

Based on the statement on tolerable weekly intake for Cd and Pb and tolerable daily intake for Ni and considering the relatively low potato consumption in Slovakia (47 kg per person/year) potatoes as the traditional food in this region are safe [51].

Potatoes (Solanum tuberosum) are one of the most important crops in the world (potato production in 2013: 376.453 mil. tons (http://potatopro.com/)). Their cultivation in Slovakia has a long tradition; despite this fact, the potato consumption during the last twenty years gradually decreases. While in 1993 potato consumption was 89.0 kg/person/year, in 2014 it was reduced by 48% (47.0 kg/person/year) [51]. At current consumption, the weekly intake of Cd (Pb, Ni) due to the consumption of potatoes is with the highest content of these heavy metals (Cd 0.065, Pb and Ni 0.230 and 0.589 mg kg$^{-1}$ FM, Table 3) lower compared to values of TWI for Cd and Pb and TDI for Ni given by EFSA (Tables 3 and 4).

Neither due to the consumption of potatoes in the amount of 84.9 kg, which is the maximum allowed interval of rational potato consumption (76.3–84.9 kg per person/year), nor due to the recommended dose of potatoes (80.6 kg per person/year) was the TWI or TDI for observed heavy metals exceeded (Table 4).

Heavy metal accumulation may also differ greatly within cultivars of an individual species when grown on the same soil [56]. This fact is also confirmed by our results (Table 3).

Results in this study correlate with results obtained in previous research. The Cd, Pb, and Ni contents in Slovakian potato cultivars were in the intervals 0.028–0.357, n.d.–0.638, and 0.194–0.220 mg kg$^{-1}$ FM, respectively [57, 58]. Similar results were published also by other authors. Average values (mg kg$^{-1}$ FM) of Cd (n.d.–3870), Pb (0.005–4.65), and Ni

![Figure 2: Content of Pb in potato tubers in relationship to content of lead (exchangeable forms) in soil: (a) locality Spissky Stvrtok; (b) locality Odorin; (c) locality Matejovce.](image-url)
4. Conclusions

In soil samples from all 3 investigated localities, the determined total Cd content was at least by 100% higher than the limit value. On the other hand the maximum content of exchangeable forms was 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 by 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 analysed samples. The high content of mobile forms of Pb and also the high Cd total content may be reflected in their increased mobility and their ability to be accumulated in cultivated crops during change of soil conditions.

Additional Points

Practical Applications. Increased content of heavy metals in soil represents a potential risk of contamination for agricultural production. Therefore, not only the yield of tubers but...
also their quality including safety to human health is important for producers and consumers of potatoes. Increased levels of heavy metals in soil are reflected in increased metal concentration in potatoes only to a limited extent (determined Pb content higher than limit value: 89.7% of soil samples, 19.2% of potato samples). Our results confirmed correlations between Ni, Cd, and Pb contents in soil and potatoes. This fact indicates the risk of potato contamination by heavy metals when their soil contents, especially contents of mobile metals forms, are high. Based on the statement on TWI for Cd and Pb and TDI for Ni and considering the relatively low potato consumption in Slovakia, potatoes are safe.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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