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ASSESSMENT OF THE SOIL CONTAMINATION EXTENT IN THE AREA OF ZEMPLÍN REGION (SLOVAKIA) AND THE CONSEQUENT HEALTH RISK FOR THE INHABITANTS

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ABSTRACT

In Slovakia, there are several regions with moderately disturbed environments. For example, in eastern Slovakia, it is the Zemplín region. The contents of risk elements were determined using AAS methods to evaluate the degree of soil contamination in five locations of Zemplín. Risk element indices were calculated based on Zn, Ni, Cd, and Pb concentrations.

Contamination factor (CF), Degree of contamination (C_{deg}), and Modified degree of contamination (mC_{deg}) were affected by a high concentration of Cd in its pseudototal form (CF 4.01–9.80, C_{deg} 8.42–17.1, mC_{deg} 2.11–4.28), which means a medium to high degree of contamination.

Other evaluated indexes were the Geoaccumulation index (I_{geo}), Ecological risk factor (E_r), Potential ecological risk index (PERI), and Pollution load index (PLI). In this case, the high concentration of Cd affected the increased values of the individual coefficients. According to I_{geo} (Cd), the soils of all locations are moderately to heavily contaminated. The highest values of PERI (323), and PLI (3.18), were determined in Belá n/Cirochou.

We assessed the consumption of potatoes grown in these locations based on the concentration of Zn, Ni, Cd, and Pb, as well as indices of risk elements in plants: Estimated daily intake (EDI), Target hazard quotient (THQ), and Hazard index (HI). Compared to the Tolerable daily intake (TDI), the EDI is higher only for Cd (Kamenná Poruba). THQ was lower than Toxical data and HI<1 for all risk elements and localities. Therefore, it is unlikely that the exposed population would experience obvious adverse health effects.

Keywords: contamination risk elements, soil, potato, health risk

INTRODUCTION

The quality of the environment is one of the decisive factors affecting human health. The main environmental determinants affecting health include air pollution, water pollution, and soil contamination.

The most frequently occurring contaminants in agricultural soils include risk elements – arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) **(Wuana, Okieimen, 2011; Zhao *et al.*, 2022)**. At almost all contamination levels, Cd, Pb, As, Hg, and Cr are high. If Cu, Zn, and Ni occur in higher concentrations, they harm plant health **(Rashid *et al.*, 2023)**.

The sources of risk elements in the soil ecosystem are (i) natural (geogenic) processes and (ii) anthropogenic processes. Natural processes supply risk elements through weathering and erosion of subsoil and mineralised deposits. Anthropogenic processes include industrial and mining activities, wastewater and agrochemicals in agriculture, and urban activities **(Ullah & Muhammad, 2020)**.

Risk element pollution is hidden, persistent, and irreversible **(Li *et al.*, 2014)**. The dangers of risk elements lie in their toxic effects on the environment, their ability to accumulate in soil, water, and living organisms, and their high persistence **(Islam *et al.*, 2015; Fazekašová *et al.*, 2021)**. Unlike most pollutants, risk elements are not biodegradable; they go through a global ecological cycle **(Mgbemena *et al.*, 2017)**, and their total concentration in soils persists long after their initial entry **(Wuana & Okieimen, 2011)**.

Soils are the main receiver of risk elements released into the environment by anthropogenic activities (emissions from industrial areas, mine tailings, disposal of high-metal waste, leaded gasoline and paints, applications of fertilisers, animal manure, sewage sludge, pesticides, wastewater irrigation, residues from coal combustion, leakage of petrochemical substances, etc.) **(Wuana, Okieimen, 2011)**.

Contamination of agricultural soil with risk elements is a worldwide problem. There are 5 million locations worldwide where the soil is contaminated with risk elements, or metalloids, while their concentrations are higher than the geo-baseline or regulatory levels **(Li *et al.*, 2019; Rashid *et al.*, 2023)**.

In Slovakia, regions with a moderate or strongly disturbed environment represent 50.2% of the total area. Agricultural landforms 48.5% of the total area of the Slovak Republic, of which at least one risk element contaminate at least 20,000 ha (approximately 80%). Soil pollution comes from natural and anthropogenic sources, especially industrial production, and mining **(Fazekašová *et al.*, 2021; Ministry of the Environment of the Slovak Republic, 2022)**. Geochemical anomalies occur mainly in volcanic and crystalline rocks, especially in mountainous locations. This process is reflected to a lesser extent in areas with agricultural land. The most widespread areas of geochemical anomalies occur in the Štiavnica Mountains, the Low Tatras, and the Slovak Ore Mountains **(Kobza, 2017)**. Among the most significant anthropogenic sources are emissions from mining and rock processing. As remnants of the past, old environmental burdens are a serious problem because mining activity has a centuries-old tradition in Slovakia and takes place in almost every mountainous region. Central Spiš is among the most burdened areas **(Musilová *et al.*, 2022)**. In modern history, the most significant human influence on soil contamination in Slovakia was after the Second World War, especially during the industrial period in the second half of the 20th century **(Kobza, 2017)**.

In the east of Slovakia (Zemplín region), there is an area called the "Triangle of Death" (the area between Vranov nad Topľou, Michalovce, and Humenné). In the past, a significant amount of hazardous waste was produced annually in this area. Companies such as Slovenské elektrárne a.s., Vojany, Chemko, a.s. Strážske, Bukóza Holding, a.s. Hencovce, and Slovnaft a.s., Bratislava, had the largest share in the production of hazardous waste **(Boltižiar *et al.*, 2018)**. The territory between Strážske, Vranov nad Topľou, and Humenné was identified as a probable environmental burden with a high priority in the State Programme for the Remediation of Environmental Burdens (2010 – 2015) **(Michaeli, Boltižiar, 2010)**.

Soils from individual locations provide a weakly acidic (Nižný Hrušov, pH = 5.93) to alkaline reaction (Belá nad Cirochou, pH = 7.72), with a small (Nižný Hrušov, 1.69) to good supply of humus (Belá nad Cirochou, 4.29). The content of K (Mg, P) was in the range 23 – 810 (216 – 926; 39 – 388). Except for the P content in the soil from Štefanovce (39 mg/kg), the content of the determined nutrients was high to very high. The predominant soil types are anthroposol (Belá nad Cirochou 82.04; 61.95 Brekov; 43.22 Nižný Hrušov, Štefanovce, Kamenná Poruba), fluvisol (23.24 Nižný Hrušov, Štefanovce, Kamenná Poruba; 19.16 Brekov), and stagnosol (25.02 Nižný Hrušov, Štefanovce, Kamenná Poruba).

Pollution of the environment by risk elements is becoming an increasing problem and causes great concern due to adverse effects on all its components: air, water, and soil. An important factor is the transfer of risk elements into plants and their subsequent entry into the food chain. Subsequently, risk elements can enter our bodies, bioaccumulate in physiological systems, and thus lead to biological and physiological complications **(Moukadiri *et al*., 2024)**.

Nickel (Ni) has many adverse effects on the human body, such as pulmonary embolism, pulmonary fibrosis, respiratory failure, asthma, cardiovascular disease, dizziness (after exposure to the gas), and increased chances of cancer. As a result of inhaling contaminated air, causes allergies, nose and lung cancer, and kidney and cardiovascular diseases. Ni can cause contact dermatitis, gastrointestinal disturbances (e.g., vomiting and diarrhoea), and neurological symptoms **(Briffa *et al*., 2020; Genchi *et al*., 2020; Augustsson *et al*., 2021; Mitra *et al*., 2022)**. Zinc (Zn) is an essential trace metal required for the growth of living beings, but its excessive intake can cause gastrointestinal problems with several symptoms, such as vomiting (with short-term high exposure), nausea, cramps, diarrhoea, and pain in the epigastrium. The toxic effects of zinc can be manifested by anaemia, reduction of high-density lipoprotein (HDL) cholesterol, pancreatic complications, fatigue, impaired immune function, copper deficiency, neutropenia, damage to the pancreas, and changes in blood lipid profile (with chronic exposure) **(Briffa *et al*., 2020; Augustsson *et al*., 2021; Hussain *et al*., 2022a)**. Cadmium (Cd) is primarily toxic to the kidneys, lungs, and bones. Its effects cause nephrotoxicity, infertility caused by reproductive system failure, changes in calcium metabolism leading to bone fractures, psychological disorders, gastrointestinal disorders, central nervous system complications, immune system deficiencies, DNA damage, Itai-Itai disease, and bone demineralisation. Cd severely affects PNS (peripheral nervous system) and CNS (central nervous system) functions with many clinical manifestations such as peripheral neuropathy, olfactory dysfunctions, neurological disorders, learning disabilities, and mental retardation, along with impaired motor function and behavioural changes in both adults and children. Cadmium can imitate the function and behaviour of essential metals. For example, like zinc, Cd binds to albumin in plasma. As a result, the homeostasis of calcium, zinc, and iron are dysregulated **(Briffa *et al*., 2020; Augustsson *et al*., 2021; Balali-Mood *et al*., 2021; Mitra *et al*., 2022)**. Exposure to lead (Pb) causes hypertension, kidney function disorders, brain injury, and peripheral nerve damage in humans and can cause neurological, respiratory, urinary, and cardiovascular disorders due to immunomodulating, oxidative, and inflammatory mechanisms. In women, it causes abortions, premature and low births, and stillborn children, in men - sperm damage. In children, there is a change in the development of the brain and central nervous system; there is a drop in educational results; a decrease in IQ; and an increase in antisocial behaviour. Acute exposure to Pb can cause renal dysfunction, hypertension, fatigue, arthritis, abdominal pain, insomnia, hallucinations, vertigo, and loss of appetite; chronic exposure can cause psychosis, mental retardation, allergies, birth defects, autism, neurodegenerative diseases, dyslexia, hyperactivity, weight loss, paralysis, brain and kidney damage, muscle weakness, and even death **(Briffa *et al*., 2020; Augustsson *et al*., 2021; Balali-Mood *et al*., 2021; Moukadiri *et al*., 2024)**.

IARC evaluated Ni compounds as carcinogenic to humans (Group 1), metallic nickel as possibly carcinogenic to humans (Group 2B) **(IARC, 2012a)**, inorganic Pb compounds are probably carcinogenic to humans (Group 2A), organic lead compounds are not classifiable as to their carcinogenicity to humans (Group 3) **(IARC,2006)**, and Cd and cadmium compounds are carcinogenic to humans (Group 1) **(IARC, 2012b)**.

Many studies have shown that excessive accumulation of risk elements in soil often threatens human health and food safety.

In the Slovak Republic, the degree of environmental quality of the territory is determined based on analyses of the environmental components (air, water, rocks, soil, biotopes) and waste management. Five environments are distinguished, from a high-quality environment to a heavily disturbed environment, from which stressed areas are defined: regions with an undisturbed, moderately disturbed, and severely disturbed environment **(Ministry of the Environment of the Slovak Republic, 2016)**. In 2020, 1815 locations were registered in IS EZ (Information System of Environmental Loads), of which 931 had a probable environmental load, 309 had an environmental load, and approximately 100 were classified as high-risk locations that pose a danger to human health and the environment **(Ministry of the Environment of the Slovak Republic, 2008)**.

Therefore, the aim of our study was: (i) assess the degree of soil contamination in the risk area of Slovakia using indicators of soil contamination by risk elements (Contamination factor (CF), Degree of contamination (C_{deg}), Modified degree of contamination (mC_{deg}), Geo-accumulation index (I_{geo}), Ecological risk factor (E_r), Potential ecological risk index (PERI), Pollution load index (PLI), and subsequently (ii) analyse the risks of possible contamination of home-grown potatoes based on the determination of Bioaccumulation factor (BAF), Estimated daily intake (EDI), Target hazard quotient (THQ), and Hazard index (HI).

MATERIAL AND METHODS

Sampling points

The sampling points were located in the districts of Humenné (Brekov), Vranov nad Topľou (Nižný Hrušov, Kamenná Poruba, Štefanovce), and Snina (Belá n/Cirochou) in the Middle Zemplín region (environment strongly to extremely disturbed) in eastern Slovakia (Figure 1). In the past, the Zemplín region was considered one of the most backward regions of Slovakia in terms of industrial development **(Hajduková, Sopirová, 2022)**. At the beginning of the fifties of the last century, an industrial boom took place. In 1948, the Hencovský wood industry was founded to process mainly beech wood using a chemical method (currently Bukóza Holding). In 1952, the national enterprise Chemko Strážske was established (in 1959, PCB production began; a total of 21,500 tons of PCB-containing products were produced; on January 1, 1984, production was finally stopped) **(Štibrányi, 2022)**. In 1959, the production of polyamide fibres was started in Chemlon Humenné.

The area between Vranov nad Topľou, Humenné, and Michalovce, which includes the three mentioned industrial plants, is referred to as the „Triangle of death“ (Figure 2) due to the devastated environment. This area is still ranked among those with the most significant environmental pollution (soil degradation, tailings ponds, landfills, and storage areas) even after the completion or significant limitation of their production **(Vaľuta, 2022)**.

Figure 1 Sample points: 1 – Brekov, 2 – Nižný Hrušov, 3 – Belá n/Cirochou, 4 – Kamenná Poruba, 5 – Štefanovce

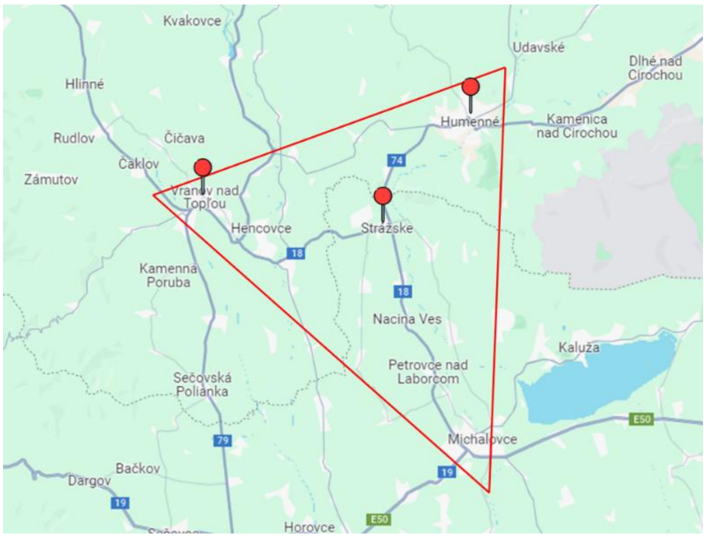

Figure 2 „Triangle of death“

Collection and preparation of samples

Soil samples and plant material samples (potatoes – *Solanum tuberosum* L.) come from small growers. They were taken from plots located in the locations of Brekov, Nižný Hrušov, Kamenná Poruba, Štefanovce, and Belá n/Cirochou. The plots were divided into smaller plots with an area of approximately 4 x 3 m, and on each of the four randomly selected small plots, 3 samples (soil, plant) were taken at a distance of 2.5 m. Samples from one small field formed one average sample. 4 average soil samples and 4 average plant material samples were obtained from one plot.

Soil samples were taken in the horizon 0 – 0.1 m into the pedological probe GeoSampler by Fisher (approximately 0.5 kg from one sampling point), and plant samples were also taken from one sampling point.

Sample processing

Soil samples were separated from organic impurities (leaves, needles, and roots), dried, and subsequently ground (using a VEB Thurm ZG 1 grinding machine). Ground samples were sifted through a sieve with a mesh diameter of 0.125 mm and stored in polyethene bags until analysis.

Immediately after harvesting, the potato samples were mechanically separated from organic and inorganic impurities, washed with distilled water, peeled, cut into slices, and dried to a constant weight at 45 °C. After drying, the samples were homogenised (IKA A10 basic, 30 sec., 25000 rpm). All samples were stored in polyethene bags until analysis.

Analyses

The contents of hazardous metals in both soil and plant samples were determined using the Flame AAS method (Zn, Ni) and the graphite Furnace AAS method (Cd, Pb) (VARIAN AASpectr DUO 240FS/240Z/UltrAA equipped with a D2 lamp background correction system, using an air -acetylene flame, Varian, Ltd., Mulgrave, VIC, AUS).
The contents of hazardous metals in the soil in their biologically accessible form were determined in soil extract by NH_4NO_3 (c = 1 mol/L, NH_4NO_3; Merck, Germany). The total contents of risk elements, including all metal forms except silicate forms, were determined after microwave digestion (70 min, MARS X-Press 5, CEM Corp., Matthews, NC, USA) in the soil extract by aqua regia (HCl:HNO3=1: 1; Merck, Germany).
The contents of hazardous metals in potatoes were determined after mineralization of plant samples using closed microwave digestion system (Mars X-Press 5) with HNO_3. Average samples of dried potatoes were used for analysis. Zn (Ni, Pb, and Cd) were determined at wavelength 213.9 (232.0, 217.0, and 228.8) nm, The limits of detection LOD were 0.3 (0.4, 1.0, and 0.05) mg/kg, and the limits of quantification LOQ were 0.9 (1.2, 3.0, and 0.15) mg/kg. Repeatability of determination during analysis: deviation max. 3%; gas flow rates: air 13.5 L/min, acetylene 2.0 L/min.
The measured results were compared with multi-elemental standards for GF-AAS (Merck, Germany).
The contents of risk elements determined in soil samples were compared with limit and critical values according to **Act No. 220/2004**. The contents of risk elements determined in plant samples were evaluated according to the maximum allowed amounts given to Commission Regulation (EC) (Cd – **CR (EU) 2021/1323,** Pb – **CR (EU) 2021/1317**), **Regulation SR 414/2003–100** (Ni). For Zn, there is currently no set max. level: therefore, the results were compared with the **Gazette MPSR, vol. XXXVI, 2004.**
Using Contamination indices (indices of risk elements in soils – CF, C_{deg}, mC_{deg}, I_{geo} E_r, PERI, PLI, and indices of trace elements in plants – BAF), and based on human health risk indicators (EDI, CDI, THQ, HI) the extent of soil contamination by Zn (Ni, Pb, and Cd), the risk of their impact on human health was assessed.

Indices of risk elements in soils

The soil contamination indices enable the normalisation of element concentrations in the soil to unitless „concentrations ", which facilitates comparisons among several elements.

1. The degree of soil contamination with a risk element is quantified by the Contamination factor (CF_i). The CF_i value is calculated as the ratio of the determined concentration of the given risk element in the soil (C_i) and its background concentration (level of geochemical background) B_i **(Antoniadis *et al.*, 2017; Jimoh *et al.*, 2020)**:

   $$CF_i = C_i/B_i \qquad \text{(eq. 1)}$$

   The background values of risk elements are Zn – 60.0, Ni – 26.0, Pb – 18.0, and Cd – 0.200 mg/kg **(Šefčík *et al.*, 2008)**.

2. Degree of contamination (C_{deg}) is expressed as the sum of contamination factors for all risk elements examined **(Mgbemena *et al.*, 2017)**:

   $$C_{deg} = \sum C_i/B_i = \sum CF_i \qquad \text{(eq. 2)}$$

3. Modified degree of contamination (mC_{deg}) is a global index of contamination, mC_{deg} is given by the ratio of the sum of the Contamination factor (CF_i) and the number of assessed risk elements n **(Custodio *et al.*, 2022; Hamid *et al.*, 2022)**:

   $$mC_{deg} = \sum CF_i/n \qquad \text{(eq. 3)}$$

   Modified degree of contamination integrates all toxic metals evaluated in the ecosystem.

4. Geoaccumulation index (I_{geo}) is used to assess risk element contamination by comparing their current concentrations with the original amount in the soil:

   $$I_{geo} = \log_2 (C_i / 1.5 \times B_i) \qquad \text{(eq. 4)}$$

   Constant 1.5 is used to correct possible variations in the background values of a particular metal in the environment **(Li *et al.*, 2014; Hussain *et al.*, 2022b)**. I_{geo} was developed by **Muller (1969)**.

5. Ecological risk factor (E_r) and Potential ecological risk index (PERI) are used to assess the toxicity of trace elements. Their calculation is based on the Toxicity index of each element (Tr). The standard value for Zn (Ni, Pb, and Cd) is 1 (5, 5, and 30) **(Hakanson, 1980)**:

   $$E_r = T_r \times CF_i \qquad \text{(eq. 5)}$$

   $$PERI = \sum T_r \times CF_i = \sum E_r \qquad \text{(eq. 6)}$$

   Potential ecological risk index (PERI) combines all toxicological effects of risk elements **(Saleem *et al.*, 2024)**.

6. The Pollution load index (PLI) determines the level of contamination load concerning all metals at different locations. It is the direct geometric mean of CF expressed as:

   $$PLI = (CF_1 \times CF_2 \times CF_3 \times ... CF_n)^{1/n} \qquad \text{(eq. 7)}$$

   whereas PLI ≤ 1 indicates that background amounts of contaminants are present, while PLI > 1 indicates that soil quality is deteriorating **(Hussain *et al.*, 2022b; Malav *et al.*, 2023)**.

Indices of trace elements in plants

Bioaccumulation factor (BAF) is used to calculate the transfer of metals from the soil to different plant parts, which is given by the ratio of the concentration of the risk element in the plant (mg/kg DW) and in the soil **(Hu *et al.*, 2017)**:

$$BAF = C_{i(plant)} / C_{i(soil)} \qquad \text{(eq. 8)}$$

Basic human health risk indicators

1. Estimated daily intake (EDI) of risk elements is determined based on their average concentration in each type of food sample and the daily intake in grams of the respective foods:

   $$EDI = C \times F_{IR} / BW \qquad \text{(eq. 9)}$$

   where C is given by the concentration of the element in the food (mg/kg FW), F_{IR} is the daily food intake (g/day), and BW is the reference body weight (70 kg) **(Antoine *et al.*, 2017)**.

2. The potential health risks of pollutants (non-carcinogenic risk assessment) are usually evaluated using the Target hazard quotient (THQ) **(Antoine *et al.*, 2017; Dee *et al.*, 2019; Nowakowski *et al.*, 2021)**. The THQ value is calculated from the equation:

   $$THQ = (EFR \times ED \times C \times FIR / RfD \times BW \times ATn) \times 10^{-3} \qquad \text{(eq. 10)}$$

   where EFR is the exposure frequency to the trace element (daily/year), ED is the duration of exposure (70 years), and RfD is the oral reference dose specific for every element (Zn – 0.3, Ni – 0.02, Pb – 0.0036, and Cd – 0.0005 mg/kg/day), ATn is the averaged exposure time for non-carcinogens (i.e., 70 years or 25,550 days), and 10^{-3} is the unit conversion factor.

3. Hazard index (HI) is the sum of individual target risk quotients **(Dee *et al.*, 2019)**:

   $$HI = \sum THQ \qquad \text{(eq. 11)}$$

   If HI > 1, there is a possibility of adverse non-carcinogenic health effects.

Statistical analyses

The obtained results were evaluated using descriptive statistical analysis (Microsoft Excel, Redmond, WA, USA) and analysis of variance (One-Way ANOVA multi-range tests, method: 95.0 percent LSD) using Statgraphics statistical software (Centurion XVI.I, USA).

RESULTS AND DISCUSSION

Soil

Contents of risk elements in soil

The contents of risk elements (Zn, Ni, Pb, Cd) from the monitored locations were determined in soil extracts by NH_4NO_3 and *aqua regia* (Table 1). In the case of extraction using NH_4NO_3, mobile (bioavailable) forms of risk elements are determined. They are prospectively of greatest importance for the assessment of the hygienic condition of soils (biotoxicity) **(Vollmannova *et al.*, 2016)**. Risk elements that are present in the soil solution as dissolved components or that are easily dissolved by root secretions are accessible to plants **(Chibuike, Obiora, 2014)**. During *aqua regia* mineralisation, most of the soil components are dissolved, and the elements are subsequently determined. These will probably all become bioavailable in the long term as well. Only components strongly bound in silicate minerals do not dissolve. The content of risk elements determined in *aqua regia* is also referred to as „pseudototal“**(Alloway, 2013)**.

Table 1 The contents of risk elements (Zn, Ni, Pb, Cd) in soil (mg/kg) from locality Brekov, Nižný Hrušov, Belá n/Cirochou, Kamenná Poruba and Štefanovce

		Bioavailable forms				Pseudototal forms			
locality		Zn	Ni	Pb	Cd	Zn	Ni	Pb	Cd
Brekov	Mean	0.290^{d}	0.290^{ab}	0.300^{ab}	0.104^{ab}	225^{a}	44.5^{b}	49.3^{a}	1.69^{bc}
	STDEV	0.044	0.034	0.045	0.016	26.5	5.69	7.62	0.113
	Min	0.240	0.249	0.248	0.085	194	37.4	40.3	1.55
	Max	0.342	0.325	0.354	0.120	252	50.3	56.6	1.79
Nižný Hrušov	Mean	0.150^{b}	0.310^{bc}	0.380^{c}	0.118^{b}	69.8^{a}	40.8^{ab}	30.2^{a}	0.802^{a}
	STDEV	0.019	0.047	0.058	0.018	8.92	6.28	4.55	0.124
	Min	0.126	0.267	0.308	0.101	58.6	33.0	25.0	0.656
	Max	0.170	0.360	0.448	0.137	78.9	48.1	35.6	0.920
Belá n/Cirochou	Mean	0.210^{c}	0.240^{a}	0.300^{ab}	0.108^{ab}	118^{b}	34.1^{a}	73.0^{c}	1.96^{c}
	STDEV	0.026	0.036	0.035	0.014	18.2	5.20	9.33	0.302
	Min	0.180	0.198	0.258	0.091	96.4	29.3	61.3	1.59
	Max	0.237	0.283	0.336	0.122	135	39.6	82.5	2.31
Kamenná Poruba	Mean	0.390^{e}	0.261^{ab}	0.250^{a}	0.095^{a}	79.5^{a}	46.2^{b}	35.5^{a}	1.43^{b}
	STDEV	0.059	0.040	0.032	0.015	12.1	6.96	4.17	0.175
	Min	0.335	0.213	0.210	0.077	68.4	38.2	30.5	1.23
	Max	0.452	0.299	0.283	0.112	92.2	54.5	39.8	1.61
Štefanovce	Mean	0.040^{a}	0.350^{c}	0.320^{bc}	0.097^{ab}	70.9^{a}	42.6^{ab}	35.5^{a}	1.02^{a}
	STDEV	0.0060	0.023	0.039	0.011	4.74	5.22	5.35	0.156
	Min	0.033	0.322	0.274	0.083	65.2	36.5	29.4	0.877
	Max	0.047	0.371	0.361	0.109	75.2	48.1	41.9	1.18
Limit value						150	50.0	70.0	0.700
Critical value		2.00	1.50	0.100	0.100				

Legend:$^{a-e}$ Statistically significant differences between localities, P value < 0.05

We compared the contents of monitored risk elements in their mobile forms with the critical values established for the risk elements in **Act No. 220/2004**. In the case of Zn and Ni, all determined contents were lower than their critical values. It can also be stated that there are statistically insignificant differences in the content of Ni and Cd between the individual locations. There are statistically significant differences in the case of Zn, where its highest content was in the soil from Kamenná Poruba (0.390 mg/kg). Cadmium and lead appear to be risky from the point of view of the content in its mobile form. Cd contents exceed the limit value (0.100 kg/kg) by 8 to 18% (locations Brekov, Belá n/Cirochou, Nižný Hrušov). The lowest concentration of Pb (0.210 mg/kg – Kamenná Poruba) exceeds the critical value (0.100 mg/kg) more than twice, and the highest determined concentration of mobile forms of Pb in the soil (0.405 mg/kg – Nižný Hrušov) more than four times. Even though soils show a high affinity for retaining Pb, which significantly reduces its mobility compared to most other trace elements **(Elbana *et al.*, 2022)**, the presence of such high concentrations of Pb in the soil can lead to a decrease in soil productivity and fertility. It can also pose a risk to the cultivation of hygienically safe crops and their entry into the food chain. High concentrations of Pb in the soil are also in their pseudo-total forms (location Belá n/Cirochou). Exceeding limit values for Cd (0.700 mg/kg) **(Act No. 220/2004)** were determined in soils from all monitored locations (from 0.802 mg/kg Nižný Hrušov to 0.96 mg/kg Belá n/Cirochou). Cadmium has high bioavailability in soil and higher mobility in plants compared to other risk elements. It is very easily transported by the roots to the shoots. This migration is enhanced by acidic pH. Although it is a pseudototal form of Cd, its availability can be increased by lowering the pH of the soil. In general, metal solubility is higher at lower pH, and this increased solubility increases plant availability **(Hamid *et al.*, 2022).** pH has a significant effect on Cd sorption, while soil texture has a weak effect on Cd sorption (sorption on sandy loam is slightly greater than on loamy sand) **(Smolders, Mertens, 2013).** Other factors influencing the entry of risk elements into plants include organic matter content, cation exchange capacity, rhizosphere chemistry, and microbial activity **(Rashid *et al.*, 2023).** Contamination of soil, including agricultural soil, caused by high levels of risk elements is a worldwide problem. High concentrations were determined in China (Zn: 5.2 – 227.0, Ni: 15.5 – 44.2, Pb: 17.1 – 104.3, Cd: 0.52 – 2.7 mg/kg; **Hu *et al.*, 2017**), India (Ni: 99.15 – 148.6, Cd: 110.3 – 156.2, Pb: 102.35 – 276.9 mg/kg; **Upadhyay *et al*., 2024**), Africa (Zn: 15.21 – 99.21, Ni: 2.52 – 43.18, Pb: 3.37 – 16.81 mg/kg; **Mussa *et al.* , 2020**), Poland (Zn: 1062.98 ± 124.22, Pb: 781.91 ± 54.16, Cd: 12.32 ± 1.62 mg/kg; **Diatta *et al*., 2008**), Czech Republic (Zn: 60.91 – 393.08, Pb: 11.09 – 174.24, Cd: 0.05 – 1.18 mg/kg; **Doležalová Weissmannová *et al*., 2019**), in Slovakia (Zn: 35.71 – 362, Ni: 13.27 – 63.0, Pb: 10.0 – 49.5, Cd: 0.74 – 9.59 mg/kg; **Musilova *et al*., 2016, 2022; Vollmannova *et al*., 2021; Lidiková *et al*., 2021**).

Table 2 Contamination factor (CF), Degree of contamination (C_{deg}), Modified degree of contamination (mC_{deg}) for soils from the localities of Brekov, Nižný Hrušov, Belá n/Cirochou, Kamenná Poruba and Štefanovce

locality		CF (Zn)	CF (Ni)	CF (Pb)	CF (Cd)	C_{deg}	mC_{deg}
Brekov	Mean	3.76	1.71	2.74	8.45	16.7	4.16
	STDEV	0.441	0.22	0.42	0.565	1.64	0.411
	Min	3.23	1.44	2.24	7.77	14.7	3.67
	Max	4.21	1.93	3.14	8.96	18.2	4.56
Nižný Hrušov	Mean	1.16	1.57	1.68	4.01	8.42	2.11
	STDEV	0.149	0.24	0.25	0.619	1.25	0.312
	Min	0.977	1.27	1.39	3.28	6.92	1.73
	Max	1.31	1.85	1.98	4.60	9.75	2.44
Belá n/Cirochou	Mean	1.96	1.31	4.06	9.80	17.1	4.28
	STDEV	0.303	0.20	0.52	1.51	2.50	0.624
	Min	1.61	1.13	3.41	7.94	14.1	3.52
	Max	2.25	1.52	4.58	11.6	19.9	4.98
Kamenná Poruba	Mean	1.33	1.78	1.97	7.15	12.2	3.06
	STDEV	0.202	0.27	0.23	0.88	1.57	0.392
	Min	1.14	1.47	1.70	6.13	10.4	2.61
	Max	1.54	2.10	2.21	8.07	13.9	3.48
Štefanovce	Mean	1.18	1.64	1.97	5.10	9.89	2.47
	STDEV	0.079	0.20	0.30	0.778	1.34	0.335
	Min	1.09	1.40	1.63	4.39	8.51	2.13
	Max	1.25	1.85	2.33	5.92	11.3	2.84
B_i		60.0	26.0	18.0	0.200		

Indices of risk elements in soils

All indices of soil contamination are based on the same concept: they measure the ratio of the concentration of an element in the soil to the reference concentration of the same element in uncontaminated soil (background values) **(Linkeš *et al.*, 1997)**. These background reference levels are characteristic only of the studied area; they are specific to the given location **(Antoniadis *et al.*, 2017)**. To express the degree of pollution (soil, sediments), several pollution indices are used (the pollution indices), which can provide information on 1) individual levels of pollution from each of the analysed risk elements; 2) the extent of total pollution; 3) sources of risk elements; 4) potential environmental risk; 5) areas with the highest potential risk of accumulation of risk elements; and 6) the ability of the horizon surface to accumulate risk elements **(Kowalska *et al.*, 2018)**.

Indices CF, C_{deg}, and mC_{deg} expressing soil contamination with risk elements due to anthropogenic influence in the monitored locations are shown in Table 2.

The degree of contamination is expressed in four categories based on the value of the Contamination factor (CF): $CF < 1$ – low degree, $1 \leq CF < 3$ – moderate degree, $3 \leq CF < 6$ – considerable degree, and $CF \geq 6$ – very high degree **(Antoniadis *et al.*, 2017; Jimoh *et al.*, 2020; Custodio *et al.*, 2022)**, or $CF < 1$ – low pollution, $1 \leq CF < 3$ – medium pollution, $3 \leq CF < 6$ – high pollution, and $CF \geq 6$ – extremely polluted **(Hamid *et al.*, 2022)**. CF values are calculated according to Equation 1. None of the soils were categorised as uncontaminated or having a low degree of contamination. The locations of Brekov, Nižný Hrušov, Belá n/Cirochou, Kamenná Poruba, and Štefanovce showed a moderate degree of contamination with zinc, nickel, and lead. The location of Brekov and Belá n/Cirochou was an exception, where CF (Zn) was in the range of 3 – 6 (considerable degree). There was also a considerable degree of contamination ($3 \leq CF (Cd) < 6$) in the localities of Nižný Hrušov and Štefanovce. In other localities, CF (Cd) ranged from a minimum of 6.13 (Kamenná Poruba) to a maximum of 9.80 (Belá n/Cirochou), which means a very high degree of contamination (Table 2).

The influence of all risk elements (in our study, Zn, Ni, Pb, and Cd), which is given by the sum of CF for determined elements, represents the Degree of contamination (C_{deg}). The mean total contamination degree (C_{deg}) of Zn, Ni, Pb, and Cd was from 8.42 (Nižný Hrušov) to 17.1 (Belá n/Cirochou) (Table 2). According to the C_{deg} value, the contamination degree of the environment can be classified as low contamination ($C_{deg} < 5$), moderate contamination ($5 \leq C_{deg} < 10$), considerable contamination ($10 \leq C_{deg} < 20$), and very high contamination ($C_{deg} \geq 20$) **(Luo *et al.*, 2007)**. It can be concluded that the soils in Nižný Hrušov and Štefanovce are moderately contaminated (mean C_{deg} is 8.42 and 9.89). Considerable contamination in the locations of Brekov, Belá n/Cirochou, and Kamenná Poruba (C_{deg} from 10.4 to 13.9) is mainly influenced by high Cd contents (Table 1) and high CF values (Table 2). If the classification of soils according to **Hamid *et al.* (2022)** (low pollution ($C_{deg} < 7$), medium pollution ($7 \leq C_{deg} < 14$), high pollution ($14 \leq C_{deg} < 28$), and extremely polluted ($C_{deg} \geq 28$), we evaluate the soil from the locality Kamenná Poruba as medium polluted.

The total degree of contamination at a certain location can be estimated using the Modified degree of contamination (mC_{deg} or mC_d). Based on mC_{deg}, environmental pollution can be classified into seven grades: 1) uncontaminated to very low contamination grade ($mC_{deg} \leq 1.5$), 2) low contamination grade ($1. 5 < mC_{deg} \leq 2$), 3) moderate contamination grade ($2 < mC_{deg} \leq 4$), 4) high contamination grade ($4 < mC_{deg} \leq 8$), 5) very high contamination grade ($8 < mC_{deg} \leq 16$), 6) extremely high contamination grade ($16 < mC_{deg} \leq 32$), and 7) ultra-high contamination grade ($mC_{deg} > 32$) **(Devanesan *et al.*, 2017; Custodio *et al.*, 2022; Hamid *et al.*, 2022)**. The values of mC_{deg} for individual locations, calculated according to eq. 3, are presented in Table 2. Based on mC_{deg}, it is not possible to classify soils as uncontaminated or soils with a low degree of contamination in any location. Soils from the Brekov locality ($mC_{deg} = 4.16$) and the Belá n/Cirochou locality showed a high contamination grade ($mC_{deg} = 4.28$).

The assessment of environmental contamination allows the comparison of differences between current and pre-industrial Geoaccumulation index (I_{geo}) concentrations. It was originally used with river bottom sediments. It can also be used to assess soil contamination **(Li *et al.*, 2014).**

To quantify the potential risk to the environment and human health from soil contamination with risk elements, the Potential ecological risk index (PERI) is used, which represents risk element toxicity and environmental response **(Mussa *et al.*, 2020).** PERI is calculated from the sum of the Ecological risk factors (E_r) for each assessed toxic metal **(Costudio et al., 2022)**. **Devanesan *et al.* (2017)** define E_r as the monomial potential ecological risk factor. The Pollution load index is used to identify the accumulation levels of risk element contamination in soils. PLI provides a simple and comparative means of quality assessment. These indices provide a simple and comparative means of assessing soil quality in the studied location **(Doležalová Weissmannová *et al.*, 2019)**.

The I_{geo} (eq. 4), E_r (eq. 5), (eq. 6) and PLI (eq. 7) values for risk elements in the soil from the monitored localities are presented in Table 3.

Table 3 Geoaccumulation index (I_{geo}), Ecological risk factor (E_r), Potential ecological risk index (PERI) and Pollution load index (PLI) for soil from Brekov, Nižný Hrušov, Belá n/Cirochou, Kamenná Poruba and Štefanovce

		I_{geo}				E_r				PERI	PLI
locality		Zn	Ni	Pb	Cd	Zn	Ni	Pb	Cd		
Brekov	Mean	1.32	0.856	0.856	2.49	3.76	8.56	13.7	254	280	1.87
	STDEV	0.172	0.228	0.228	0.097	0.441	1.09	2.12	16.9	20.6	0.272
	Min	1.11	0.579	0.579	2.37	3.23	7.19	11.2	233	255	1.54
	Max	1.49	1.07	1.07	2.58	4.21	9.67	15.7	269	298	2.17
Nižný Hrušov	Mean	-0.376	0.149	0.149	1.41	1.16	7.85	8.39	120	138	1.87
	STDEV	0.189	0.219	0.219	0.228	0.149	1.21	1.26	18.6	21.1	0.272
	Min	-0.618	-0.112	-0.112	1.13	0.98	6.36	6.94	98	113	1.54
	Max	-0.190	0.400	0.400	1.62	1.31	9.26	9.90	138	158	2.17
Belá n/ Cirochou	Mean	0.376	1.43	1.43	2.69	1.96	6.56	20.3	294	323	3.18
	STDEV	0.228	0.189	0.189	0.226	0.303	1.00	2.59	45.2	49.0	0.460
	Min	0.100	1.18	1.18	2.40	1.61	5.64	17.0	238	262	2.65
	Max	0.588	1.61	1.61	2.95	2.25	7.61	22.9	347	380	3.67
Kamenná Poruba	Mean	-0.191	0.387	0.387	2.24	1.33	8.88	9.86	214	234	2.40
	STDEV	0.221	0.172	0.172	0.179	0.202	1.34	1.16	26.3	28.9	0.322
	Min	-0.397	0.177	0.177	2.03	1.14	7.35	8.48	184	201	2.04
	Max	0.035	0.558	0.558	2.43	1.54	10.5	11.0	242	265	2.75
Štefanovce	Mean	-0.347	0.382	0.382	1.75	1.18	8.19	9.86	153	172	2.10
	STDEV	0.097	0.219	0.219	0.221	0.079	1.00	1.49	23.3	25.8	0.255
	Min	-0.464	0.121	0.121	1.55	1.09	7.02	8.16	132	148	1.82
	Max	-0.260	0.634	0.634	1.98	1.25	9.24	11.6	177	200	2.38
T_r						1	5	5	30		

According to Geoaccumulation index (I_{geo}), soils can be classified by seven levels of contamination: 1) not polluted (uncontaminated) – level 0: $I_{geo} \leq 0$; 2) not polluted to moderately polluted (uncontaminated / moderately contaminated) – level 1: $0 < I_{geo} \leq 1$; 3) moderately polluted (moderately contaminated) – level 2: $1 < I_{geo} \leq 2$; 4) moderately to heavily polluted (moderately / strongly contaminated) – level 3: $2 < I_{geo} \leq 3$, 5) heavily polluted (strongly contaminated) – level 4: $3 < I_{geo} \leq 4$; 6) heavily to extremely polluted (strongly / extremely contaminated) – level 5: $4 < I_{geo} \leq 5$; and 7) and extremely polluted (extremely contaminated) – level 6: $I_{geo} > 5$, whereby the highest class 6 reflects a 100-fold enrichment above the background values **(Li *et al.*, 2014; Jimoh *et al.*, 2020; Abowaly *et al.*, 2021; Custodio *et al.*, 2022; Hussain *et al.*, 2022b)**.

The I_{geo} values indicate uncontaminated soils with Zn in the locations Nižný Hrušov, Kamenná Poruba, and Štefanovce. Moderately to heavily contaminated soils with cadmium are in Brekov, Belá n/Cirochou, and Kamenná Poruba. In the other localities, the soils range from not polluted to moderately polluted with Zn, Ni, Pb, and Cd. Strong or extremely severe soil contamination was not confirmed in any location.

For example, **Li *et al.* (2014)** report average I_{geo} values of the examined mining areas in China from -1.09 to 3.05 for Zn, from -0.59 to 2.12 for Ni, from 0.12 to 8.53 for Cd, and from -0.49 to 5.74 for Pb. I_{geo} is also influenced by different soil layers. **Abowaly *et al.* (2021)** determined in three different depths (0–30, 30–60, and 60–100 cm) the average values of I_{geo} (Ni) of 3.82, 3.87, and 3.66.

The results (E_r) indicate a low risk for Zn, Ni, and Pb. The exception is Cd, which showed considerable ecological risk in the Nižný Hrušov and Štefanovce localities and high risk in the other three localities. The significant influence of Cd on the Ecological risk factor is reported in the study by **Saleem *et al.* (2024)**. The average values of E_r increased in all localities in the order Zn < Ni < Pb < Cd. E_r (Cd) is 68 to 161 times higher than E_r (Zn) (localities Brekov and Kamenná Poruba). High values of E_r (Cd) are also related to high values of PERI, which were calculated as the sum of E_r for Zn, Ni, Pb, and Cd. The lowest value of the Potential ecological risk index (138), which represents low risk, was calculated for the location Nižný Hrušov. On the contrary, for the localities Belá n/Cirochou, PERI = 323, which means considerable risk. In the other three locations, the PERI was from 148 to 298, which represents a moderate ecological risk.

PERI is classified as low potential ecological risk (PERI ≤ 95), moderate potential ecological risk (95 < PERI ≤ 190), significant potential ecological risk (190 < PERI ≤ 380), and very high potential ecological risk (PERI > 380) **(Custodio *et al.*, 2022)**. Similar to C_{deg} and I_{geo}, in the case of E_r and PERI, different authors give different descriptions of individual degrees of soil contamination. The differences are not only in the word characteristics (Table 4) but also in the value intervals for the same degree of contamination (**Custodio *et al.*, 2022** vs. other authors listed in Table 4).

Table 4 Description of Ecological risk factor (E_r) and Potential ecological risk index (PERI) in soil **(Guo *et al.*, 2010[1]; Hamid *et al.*, 2022[2]; Saleem *et al.*, 2024[3])**

Scope of potential E_r	Ecological risk level of single-factor pollution	Scope of PERI	General level of potential ecological risk
$E_r < 40$	low[1] / low risk[2,3]	PERI < 150	low-grade[1] / low risk[2,3]
$40 \leq E_r < 80$	moderate[1] / medium risk[2] / moderate risk[3]	150 ≤ PERI < 300	moderate[1] / medium risk[2] / moderate risk[3]
$80 \leq E_r < 160$	higher[1] / significant risk[2] / considerable risk[3]	300 ≤PERI <600	severe[1] / significant risk[2] / considerable risk[3]
$160 \leq E_r < 320$	high[1] / high risk[2,3]	600 ≤ PERI	serious[1] / very high risk[2,3]
$320 \leq E_r$	serious[1] / very high risk[2,3]		

The last index we used to assess ecological risk was the Pollution load index (PLI). PLI values range from zero (uncontaminated) to 10 (highly contaminated) **(Hamid *et al.*, 2022)**. If PLI = 0 means the state of perfection of the evaluated ecosystem, PLI = 1 means the presence of only basic levels of contaminants, and PLI > 1 indicates the progressive deterioration of the state of the soil in terms of contamination with dangerous elements **(Islam *et al.*, 2015; Custodio *et al.*, 2022)**. Based on the mentioned criteria, PLI > 1 means soil contamination with risk elements in all locations (PLI ranged from 1.87 (Brekov, Nižný Hrušov) to 3.18 (Belá n/Cirochou, Table 3)).

Plant

Contents of risk elements in plants

Potatoes were grown on the monitored plots in the locations of Brekov, Nižný Hrušov, Belá n/Cirochou, Kamenná Poruba, and Štefanovce. Samples for analysis were taken from the same sampling points as soil samples. Likewise, samples of plant material were analysed for the content of the risk elements Zn, Ni, Pb, and Cd. The determined contents (in mg/kg DW) were converted to fresh weight (FW) for the purposes of comparison with the maximum content values (according to the given legislation). The results are presented in Table 5.

Table 5 The contents of risk elements (Zn, Ni, Pb, Cd) in potatoes (mg/kg DW) and Bioaccumulation factor (BAF) for potatoes and soils from the localities Brekov, Nižný Hrušov, Belá n/Cirochou, Kamenná Poruba and Štefanovce

		potatoes				BAF			
locality		Zn	Ni	Pb	Cd	Zn	Ni	Pb	Cd
Brekov	Mean (DW)	BDL^{a}	0.500^{b}	0.200^{a}	BDL^{a}	NC	0.0112	0.0041	NC
	STDEV		0.0763	0.0256					
	Mean (FW)	BDL	0.261	0.104	BDL				
	STDEV		0.0398	0.0134					
Nižný Hrušov	Mean (DW)	10.0^{b}	0.200^{a}	0.700^{c}	BDL^{a}	0.1433	0.0049	0.0232	NC
	STDEV	1.28	0.0235	0.108					
	Mean (FW)	3.54	0.071	0.248	BDL				
	STDEV	0.45	0.0083	0.0382					
Belá n/ Cirochou	Mean (DW)	9.42^{b}	1.00^{d}	0.600^{c}	0.360^{bc}	0.0799	0.0296	0.0082	0.1843
	STDEV	1.45	0.0668	0.0915	0.0460				
	Mean (FW)	3.54	0.376	0.226	0.135				
	STDEV	0.547	0.0251	0.0344	0.0173				
Kamenná Poruba	Mean (DW)	12.7^{c}	0.300^{a}	0.144^{b}	0.380^{c}	0.1597	0.0065	0.0112	0.2660
	STDEV	1.94	0.0462	0.0216	0.0446				
	Mean (FW)	5.75	0.136	0.181	0.172				
	STDEV	0.878	0.0209	0.0273	0.0202				
Štefanovce	Mean (DW)	8.90^{b}	0.702^{c}	0.200^{a}	0.320^{b}	0.1255	0.0164	0.0056	0.3141
	STDEV	0.595	0.108	0.0245	0.0482				
	Mean (FW)	4.00	0.315	0.090	0.144				
	STDEV	0.267	0.0487	0.0110	0.0216				
ML (for FW)		10.00[1]	0.500[2]	0.100[3]	0.100[4]				

Legend:$^{a-d}$ Statistically significant differences between cadastres, P value < 0.05; BDL – below detection limit; DW – dry weight, FW – fresh weight, NC – not calculated, ML – maximum levels (mg/kg FW) according to: [1]**Decree No. 2/1994;** [2]**Regulation SR 414/2003–100;** [3]**CR (EU) 2021/1317.** [4]**CR (EU) 2021/1323**

In terms of Zn and Ni content, potatoes are hygienically safe. The contents of these risk elements are lower than their maximum limits. In potatoes from the Brekov location, the Zn content was below the detection limit. These results correspond to low Zn and Ni contents in the soils of the monitored locations. On the other hand, the contents of Pb and Cd are higher than their maximum limits (0.1 mg/kg FW for both Pb and Cd). Lead concentrations were higher than 0.1 mg/kg FW in samples from all locations, except Štefanovce. The content of Pb was up to 2.48 times higher than its maximum limit in potatoes from Nižný Hrušov. We also determined higher Cd contents in samples from locations Belá n/Cirochou, Kamenná Poruba, and Štefanovce. Cd concentrations in potatoes were 35 to 72% higher than the established maximum limits for Cd. There are statistically insignificant differences (P value > 0.05) in the content of Zn (Nižný Hrušov, Belá n/Cirochou, and Štefanovce), Pb (Štefanovce, Brekov, Nižný Hrušov, and Belá n/Cirochou), and Cd (Brekov and Nižný Hrušov, Štefanovce, and Belá n/Cirochou, or Belá n/Cirochou and Kamenná Poruba) (Table 5). Increased contents of Pb and Cd in potatoes are related to their higher contents in soils in bioavailable or pseudototal forms (Table 1). However, the mentioned authors state that the variety has a considerable influence on the content of risk elements **(Öztürk *et al.*, 2011; Musilová *et al.*, 2013; Raletsena *et al.*, 2023)**. Several authors confirmed the connection of higher contents of risk elements in plants with their high concentration in the soil: **Shi *et al.* (2022)** (average concentrations of Zn, Pb, and Ni in the soils were 175, 59.3, and 50.8 mg/kg, average concentrations of Zn, Pb, and Ni in potatoes were 2.73 ± 1.02, 0.027 ± 0.018, 0.055 ± 0.032 mg/kg FW), **Orellana *et al.* (2020)** (concentrations of Zn, Cd, and Pb in the soils were 44.17 – 118.49, 0.143 – 0.567, and 4.67 – 59.59 mg/kg, average concentrations of Zn, Cd, and Pb in potatoes were 18.25, 0.042, and 0.414 mg/kg DW), **AE Abdelrazek (2017)** (in soils grown with potatoes were mean values of Zn 55.6, Ni 32.9, Cd 2.2, and Pb 10.4 mg/kg, in potato tuber were mean values of Zn 22, Ni 13.5, Cd 0.9, and Pb 4.2 mg/kg DW), **Musilova *et al.* (2022)** (mean values of Zn, Ni, Cd, and Pb concentrations in soils were 90.2 – 394, 25.4 – 65.9, 2.41 – 4.33, and 39.0 – 53.3 mg/kg, mean values of Zn, Ni, Cd, and Pb concentrations in potato tuber were 12.5 – 25.2, BDL – 0.552, BDL, and 1.07 – 3.48 mg/kg DW).

Indices of trace elements in plants

Increased contents of risk elements in soils can lead to their transfer to plants and, subsequently, their accumulation in different parts of plants. The ratio of the concentration of the risk element in the plant and in the soil is used to quantify the degree or extent of risk element accumulation in the ecosystem. This can be expressed as Bioconcentration factor (BCF), Bioaccumulation coefficient (BAC) **(Ali *et al.*, 2019),** Transfer factor (TF) **(Ribeiro *et al.*, 2018),** Plant bioaccumulation (PB) **(Ullah, Muhammad, 2020),** Soil-Plant Transfer

Coefficients **(Kacholi, Sahu, 2018),** Biological Concentration Factor (BAC = risk element in shoot/risk element in soil), Translocation Factor (TF = risk element in shoot/risk element in root), and Biological Concentration Factor (BCF = risk element in root/risk element in soil) **(Enya *et al.*, 2019)**. Bioaccumulation factor (BAF) is an important indicator of environmental contamination with risk elements and the subsequent danger of their entry into the food chain **(Bhatti *et al.*, 2016; Hu *et al.*, 2017)**.

The BAF values, calculated from the ratio of the concentration of the risk element in the plant and in the soil (eq. 8), are shown in Table 5. The results show that potatoes accumulate Pb and Ni to a lesser extent (BAF (Pb) = 0.0041–0.0112, BAF (Ni) = 0.0049–0.0296); higher cumulation was in the case of Zn (BAF = 0.0079–0.1597). The highest BAF values were for Cd (0.1843–0.3141). Although the soils of the Brekov and Nižný Hrušov localities showed higher concentrations of Zn resp. Cd. The contents of these risk elements in the potatoes studied localities were below the detection limit. The BAF of crops collected from different regions of China showed a similar order of Pb < Cu < Zn ≤ Cd **(He *et al.*, 2021)**. Also, **Hu *et al.* (2017)** report the total BAF for all crops in the order Cd (0.249) > Zn (0.133) > As (0.076) > Cu (0.064) > Ni (0.018) > Hg (0.011) > Cr (0.010) > Pb (0.001). Cd was most readily taken up by crops, while Pb was identified as having the lowest crop accumulation.

A BAF greater than 1 indicates poor retention of metals in the soil or a high absorption capacity of the plant. In the opposite case (strong retention of metals in the soil or low absorption capacity of the plant), the BAF is less than 1 **(Aina *et al.*, 2024)**. This means that potatoes have a good tolerance for the monitored risk elements.

Basic indicators of human health risk

To assess the health risk resulting from the consumption of food (in our case, potatoes) containing risk elements, we used the parameters EDI, THQ, and HI. The results obtained based on individual calculations (according to equations 9, 10, and 11) are presented in Table 6.

Table 6 Estimated daily intake (EDI), Target hazard quotient (THQ) and Hazard index (HI)

		EDI				THQ				HI
locality		Zn	Ni	Pb	Cd	Zn	Ni	Pb	Cd	
Brekov	Mean	NC	0.555	0.222	NC	NC	0.0278	0.0617	NC	0.611
	STDEV		0.0847	0.0284			0.0042	0.0079		0.0920
	Min		0.477	0.187			0.0239	0.0518		0.505
	Max		0.644	0.251			0.0322	0.0697		0.721
Nižný Hrušov	Mean	7.53	0.151	0.527	NC	0.0251	0.0075	0.146	NC	0.179
	STDEV	0.962	0.0177	0.0811		0.0032	0.0009	0.0225		0.0265
	Min	6.32	0.130	0.427		0.0211	0.0065	0.119		0.146
	Max	8.51	0.169	0.622		0.0284	0.0084	0.173		0.210
Belá n/ Cirochou	Mean	7.53	0.799	0.480	0.288	0.0251	0.0400	0.133	0.575	0.774
	STDEV	1.16	0.0534	0.0731	0.0368	0.0039	0.0027	0.0203	0.0735	0.0994
	Min	6.16	0.735	0.412	0.242	0.0205	0.0368	0.115	0.483	0.655
	Max	8.64	0.847	0.556	0.325	0.0288	0.0424	0.154	0.650	0.876
Kamenná Poruba	Mean	12.2	0.289	0.385	0.366	0.0408	0.0144	0.107	0.732	0.894
	STDEV	1.9	0.0444	0.0580	0.0430	0.0062	0.0022	0.0161	0.0860	0.110
	Min	10.5	0.234	0.318	0.315	0.0351	0.0117	0.0885	0.629	0.764
	Max	14.2	0.341	0.454	0.410	0.0473	0.0170	0.126	0.819	1.01
Štefanovce	Mean	8.49	0.670	0.191	0.305	0.0283	0.0335	0.0530	0.611	0.726
	STDEV	0.568	0.103	0.0234	0.0460	0.0019	0.0052	0.0065	0.0920	0.105
	Min	7.82	0.548	0.164	0.253	0.0261	0.0274	0.0454	0.505	0.604
	Max	9.00	0.768	0.215	0.360	0.0300	0.0384	0.0598	0.721	0.849
TDI		371^1	2.8^2	3.57^3	0.357^1					
TD						0.3	0.02	0.0036	0.0005	

Legend: TDI – Tolerable daily intake according to: ^{1}**EFSA (2019);** ^{2}**EFSA (2015);** ^{3}**EFSA (2010)**
TD – Toxical data according to: **FRAMEWORK (2010)**

Estimated daily intake (EDI; synonym: ADI – acceptable daily intake) represents the amount of a substance in food or drinking water that can be consumed daily over a lifetime without presenting an appreciable risk to health **(EFSA 2010, 2015, 2019)**.

The determined average EDI values (in μg/kg BW) ranged from 0.151 (Ni – Nižný Hrušov) to 12.2 (Zn – Kamenná Poruba). Overall, it was for Zn that the EDI values were the highest for all monitored localities. EDIs were not calculated for Brekov (Zn, Cd) and Nižný Hrušov (Cd). EDI values were compared with Tolerable daily intake. TDI was calculated for easier comparison from UL (Tolerable Upper Intake Level; UL = 25 mg Zn/person/day), TDI (Tolerable Daily Intake; TDI = 2.8 μg Ni/kg BW/day), PTWI (Provisional Tolerable Weekly Intake; PTWI = 25 μg Pb/kg BW/week), and TWI (Tolerable Weekly Intake, TWI = 2.5 μg Cd/kg BW/week).

Even though high concentrations of Pb (exceeding the maximum limits from 4 to 148%) were detected in potatoes from four monitored locations and high concentrations of Cd were detected from three locations (exceeding the maximum limits from 35 to 72%), the EDI values for all risk elements were several times lower than their Tolerable daily intake (EDI/TDI < 1). Only in the case of potatoes from the locality Kamenná Poruba was the average value of EDI (Cd) higher than the TDI for this risk element. Max. EDI (0.410) exceeded TDI (Cd) by 14.8%. For comparison, according to **Orellano *et al.* (2020)**, the EDI (in mg/kg) in adults consuming native potatoes (from Andean locations in Junín, Peru) is 8.81E-03 – 1.44E-02 (Zn), 1.73E-04 – 6.20E-05 (Pb), and 1.95E-05 – 4.00E-05 (Cd). **Nowakovski *et al.* (2021)** determined the EDI (Cd) in mushrooms from 0.0001 to 0.0234 mg/day; **Antoine *et al.* (2017)** for 13 types of Jamaican-grown food crops determined EDI 0.010 – 0.240 μg Cd/kg BW and 0.002 – 0.064 μg Pb/kg BW, **Dee *et al.* (2019)** within the framework of the health risk assessment of risk elements from smoked Corbicula fluminea give the EDI for Cd (Pb, and Zn) 0.28 (0.74, and 20.91) μg/kg BW, **Ullah *et al.* (2017)** give the EDI of risk elements through the consumption of eight fish species as follows: 0.0008 mg Cd/day/person and 0.0293 mg Pb/day/person.

The Target hazard quotient (THQ) was recognised as a suitable parameter for assessing the risk associated with the consumption of food contaminated with risk elements **(Dee *et al.*, 2019)**. THQ for Zn, Ni, Cd, and Pb (Table 6) was calculated according to eq. 10. THQ values are in the range of 0.0075 (Zn, Nižný Hrušov) to 0.732 (Cd, Kamenná Poruba). Overall, THQ was highest for Cd in three of the five monitored locations. THQ (Cd) values are not calculated for Brekov and Nižný Hrušov. There are studies in which THQ > 1. A high HQ for Pb was observed in *I. batatas* (7.12) and *A. hybridus* (2.46), which represents a significant carcinogenic health threat to consumers **(Kacholi, Sahu, 2018)**. **Orellana *et al.* (2020)** reported mean THQ values for Cd, Pb, Fe, and Zn of 0.033, 0.087, 0.098, and 0.046, respectively, and for adults, these values were 0.027, 0.070, 0.079, and 0.037. **Musilova *et al.* (2022)** determined significantly higher THQ values in potatoes compared to carrots and tomatoes. The lowest THQ values were for Ni (3.521E-05), and the highest THQ values were for Pb (0.4808) and Hg (0.7363).

THQ describes the non-carcinogenic health hazard posed by exposure to the relevant toxic element. If THQ is < 1, non-carcinogenic health effects are not expected **(Antoine *et al.*, 2017; Dee *et al.*, 2019)**. A THQ value exceeding 1 suggests a likelihood that consuming a specific food product could have adverse health effects **(Nowakowski *et al.*, 2021)**.

The Hazard index (HI) is an overall risk index for monitored metals. If the HI value is less than one, the exposed population is unlikely to experience adverse health effects. The non-carcinogenic adverse effect caused by this exposure route or chemical is considered to be negligible. If the HI value exceeds one, adverse health effects may occur **(Li *et al.*, 2014; Onyele, Anyanwu, 2018)**.

HI for the four risk elements (Zn, Ni, Cd, and Pb) in the monitored locations were in the order: Nižný Hrušov (0.179) < Brekov < Štefanovce < Belá n/Cirochou < Kamenná Poruba (0.894). Despite the fact that no HI > 1, an increased risk of oral exposure to cadmium can be assumed. Its share in HI (THQ (Cd)/HI) represents up to 82% (Kamenná Poruba), or 84% (Štefanovce). It is also necessary to take into account that in our study we focused only on Zn, Ni, Cd, and Pb. It is assumed that other risk elements (Fe, Cu, Mn, Cr, etc.) are present in the soil, the intake of which by plants can contribute to higher HI.

Orellana *et al.* (2020) found exceeding limit values in potatoes for Pb. Consumption of potatoes from the studied areas posed no significant non-carcinogenic health risk to the population (HI values ranged from 0.319 to 0.828 for children and from 0.256 to 0.666 for adults). **Hu *et al.* (2017)** evaluated the HI for eight risk elements (Cr, Pb, Cd, Hg, As, Cu, Zn, and Ni) in the study area (Yangtze River Delta region in eastern China) for different age groups. HIs were in decreasing order: children (1.85×10^{-1}) > adults (1.10×10^{-1}) > seniors (7.72×10^{-2}). HI caused by As was the largest; Pb and Hg also had a large contribution to HI. The uptake of trace elements from the soil by plants is influenced by many factors, in addition to the concentration of elements in the soil, such as soil pH, organic matter, electrical conductivity, and plant species. **Aina *et al*. (2024)** evaluated the influence of different methods of soil treatment on the uptake and bioaccumulation of risk elements by vegetables (lettuce, carrot). The authors recorded high HI values (1.269 and 1.580) for lettuce fertilised with NPK and sewage sludge, which means that consumption of lettuce from these two soil treatments may be harmful and lead to potential non-carcinogenic diseases.

CONCLUSION

Even though the monitored localities Brekov, Nižný Hrušov, Kamenná Poruba, Štefanovce, and Belá n/Cirochou are located in the area with the most significant environmental pollution, the contents of risk elements in their mobile and pseudototal forms were lower than their limit or critical values. Based on the indices of risk elements, the soils from the Brekov and Belá n/Cirochou locations can be classified as the most polluted.

Based on CF, all plots can be classified as having a considerable degree to a very high degree of cadmium, moderate to considerable contamination according to C_{deg}, or a moderate to high contamination grade according to mC_{deg}. Based on PERI, the level of contamination with hazardous elements represents a moderate to significant potential ecological risk, while PLI values > 1 indicate a progressive deterioration of soil contamination with hazardous elements. We can conclude that Cd has the largest share of contamination.

Increased contents of Pb and Cd were accumulated in potatoes (more than twice the maximum limits for Pb). Based on the risk assessment according to EDI, THQ, and HI, the consumption of potatoes grown in monitored locations does not represent a significant non-carcinogenic potential health risk for the population. However, it is important to continue to check the condition of the soil. For example, changing its agrochemical properties, such as pH, organic matter content, and other factors, can cause the transformation of pseudo-total forms of risk elements into bioavailable ones. This increases their transfer and concentration in plants.

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