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# Environmental Contamination by Heavy Metals in Region with Previous Mining Activity

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**Abstract** Due to its status as one of the most contaminated regions in Slovakia, 45 soil and plant samples were collected in the Middle Spis region. In soil, the exchangeable soil reaction, humus content and heavy metals content (Zn, Cd, Cu, Pb, Hg) were determined. Total content of heavy metals (TC-HMs) and content of mobile forms (MF-HMs) in soil, as well as metal content in plants, were determined by atomic absorption spectrometry. The concentration ranges for total Zn, Cd, Cu, Pb and Hg in soil were 33.1–953, 0.65–6.73, 11.0–913, 26.5–165 and 0.28–415 mg/kg, respectively. The overall concentration ranges of these metals in plants of two types (*Athyrium filix-femina* L. and *Poaceae* herbs) were 12.4–158.6, 0.10–1.63, 3.34–85.7, 0.09–29.7 and 0.01–12.8 mg/kg, respectively. Despite the values of Zn, Cd, Cu, Pb and Hg content in the soil exceeding limit values, only the Hg content in plants presented an ecological risk.

**Keywords** Soil–plant transfer · Heavy metals · Environment · Hygienic state

Heavy metals are major contaminants with a negative impact on the environment. They occur in soil in various concentrations and forms (Bystricka and Tomas 2009). Soils contaminated by heavy metals have been the source of serious concerns in recent decades. The main concerns include potential risk to human health through direct intake, bioaccumulation through the food chain and impacts on the ecological system (Naveedullah et al. 2013). Heavy metals include several non-essential chemical elements (Cd, Pb, Hg etc.), which are toxic even at relatively low concentrations (Çelik and Oehlenschläger 2007). Cadmium (Cd) is one of the cumulative metals (it is mainly accumulated in the liver and kidneys). In the body Cd is bound with selected enzymes, and therefore Cd inhibits their activity. Cadmium exhibits teratogenic and carcinogenic effects, causes damage to the sexual organs and affects blood pressure (Velisek 2002). Accumulation of lead (Pb) can damage the central nervous system, kidneys and blood system (Liu et al. 2014). It has been shown that Pb can disturb haemoglobin synthesis; a prolonged period of Pb exposure causes kidney problems and high blood pressure in adults and delays physical and mental development in children (Chen et al. 2014; Rahman et al. 2014). Mercury (Hg) occurs in three basic forms: elemental (vapors cause lung damage); inorganic (causes kidney failure, vomiting and collapse); and organic (methylmercury is the most toxic form: exposure affects brain development and co-ordination; it also affects liver, heart and kidneys, and is teratogenic) (Hronec et al. 2002; SCU 2013; Hailemariam and Bolger 2014).

Heavy metals also include essential trace elements (Cu, Zn etc.), which are toxic at excessive occurrence in ecosystems. Copper (Cu), at optimal concentration, is an essential element for plants and animals. However, excessive intake has a negative effect on the gastrointestinal and respiratory systems with a statistically significant carcinogenic effect (Makovnikova et al. 2006). Zinc (Zn) is an essential element for plants as well as animals, but exposure to elevated levels of zinc and zinc-containing compounds can result in a variety of adverse effects in the gastrointestinal, hematological and respiratory systems (Dabrowski and Sikorski 2005; Nriagu 2011).

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Heavy-metal soil pollution has become a severe problem in many parts of the world. Although heavy metals may occur naturally in soil, additional contributions come from anthropogenic activities such as agriculture, urbanization, industrialization and mining (Facchinelli et al. 2001). According to numerous studies, pollution of the environment with heavy metals is mainly derived from anthropogenic sources (Wei and Yang 2010). The main sources include emissions from smelters. Slovakia is tainted by mining and the related processing of iron ores in Middle Spis. A smelter for the processing of raw materials for copper production located in Krompachy operated (with several breaks) from 1843. According to the data, in 1952 there were almost 12,000 t of solid pollutants emitted by the smelter in Krompachy (Banasova and Lackovicova 2004; Hronec et al. 2010). In recent years this activity has stopped and all mines have been closed. The production of mercury in the Rudnany iron mines was the most serious source of pollution in this region. According to production data, the highest annual emission of solid pollutants was measured in 1988 (2406 tonnes, of which 6.40 t was Hg). At the present time, mining activity has ceased, and the mines and enterprises have been liquidated (Hronec et al. 2010; Krokusova and Cech 2010).

The aim of this study was to determine the level of ecosystem loading by selected heavy metals (Zn, Cd, Cu, Pb and Hg) originating from the Krompachy smelter and Rudnany iron mines in the area in the Volovske Hills of the Middle Spis region.

## Materials and Methods

Samples of soil and plant material were collected from the same 45 sampling sites (SS) (34 SS – forest, 11 SS – permanent grassland and pastures) in an area of approximately 156 km$^2$ in the Volovske Hills of the Middle Spis region (Fig. 1), using GPS. The Volovske Hills are situated in the eastern part of Slovakia. The predominant soil types in the investigated area are Haplic Cambisols (cation exchangeable capacity (CAC): 110.0 mmol/kg, degree of saturation (DS): 60 %) and Rendzic (CAC: 470.0–500.0 mmol/kg, DS: 99 %) – Haplic Leptosol (Skeletic) and Cambic Rendzic Leptosol (Skeletic). The whole area is covered by Clay Loam soils. Haplic Fluvisols are present near streams flowing through the observed area (Curlik and Sefcik 1999; RUSES 2013).The observed area is located between two important emission sources of environmental pollution. Rudnany, as a previous source of environmental pollution, was the basic point for determining the sampling sites. The second important source of environment pollution was Krompachy. Both sources were the dominant cause of the environmental contamination of this region by mining activity. The exact


**Fig. 1** Sampling sites in research area

sampling site location was given by radius penetration (1, 2, 3, 4, 5, 6, 8, 10, 12, 14 and 16 km, resp.) with vectors (N, E, S, NE, NE, NW, SE, ESE and SSE, resp.). The spatial deployment of sampling sites in basic directions and in different distances from the pollution source was assessed using Arc Gis 3.2 (ESRI Inc., Redlands, CA, USA) with spine interpolation. The strategy of sample collection (Fig. 1) was based on predominant wind directions (prevailing westerly to northwesterly winds) (Arvay et al. 2015). Soil samples were taken at a 0–10 cm horizon; plant samples were collected from the same sampling sites.

In the forest ecosystem, samples of dominant plant species (*Athyrium filix-femina* L.) and in permanent grassland, herbs from the plant family *Poaceae* were collected. The aboveground phytomass of the investigated plants was collected and analysed.

Content of organic carbon ($C_{OX}$, %; volumetric method; $H_2SO_4$: Merck, DE; $K_2Cr_2O_7$: Merck, DE; $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$: Merck, DE) and content of humus (Hum, %) calculated from value of $C_{OX}$ content; values of active soil reaction (pH/$H_2O$) and exchange soil reaction (pH/$CaCl_2$, $CaCl_2$: CentralChem, SK; Metrohm 691 pH Meter, Metrohm Ltd., Herisau, CHE) were determined according to Fiala (1999) . The content of mobile forms of Zn, Cd, Cu and Pb was determined in soil by extraction with $NH_4NO_3$ (c = 1 mol/dm$^3$, $NH_4NO_3$: Merck, DE). The total content of Zn, Cd, Cu and Pb, including all metal forms with exception of silicate forms, was determined by extraction with *aqua regia* (HCl: CentralChem, SK, $HNO_3$: Merck, DE) after sample mineralization (1 g fine earth II + 10 mL *aqua regia*) by microwave digestion for 70 min (MARS X-Press, CEM Corp., Matthews, NC, USA). Total Hg content was determined using the AAS method with cold Hg vapor detection. Mineralization of plant samples was performed by microwave digestion before determination of metal concentrations (Arvay et al. 2014).

The content of heavy metals (HMs) in soil and plant samples was determined using the AAS (atomic absorption spectrometry) method: Cd and Pb: Graphite Furnace AAS; Zn and Cu: Flame AAS (VARIAN AASpectr DUO 240FS/240Z/UltrAA equipped with a D2 lamp background correction system, using an air-acetylene flame, Varian, Ltd., Mulgrave, VIC, AUS) and Hg: Cold Vapor AAS (AMA 254, Altec s.r.o, Prague, CZE). The measured results were compared with the multielemental standard for GF AAS (CertiPUR®, Merck, DE). Concentrations of Zn, Cd, Cu, Pb and Hg were assessed at wavelengths of 213.9, 228.8, 324.8, 217.0 and 253.65 nm, respectively. The respective limits of detection (LOD) for Zn, Cd, Cu and Pb were 0.3, 0.05, 0.1 and 1.0 mg/kg; and their respective limits of quantification (LOQ) were 0.9, 0.15, 0.3 and 3.0 mg/kg. The detection limit for Hg (AMA 254) was 1.2 ng/kg dry matter (DM).

The measured concentrations of metals in soil samples were compared with Slovakian limit values, as given by Act No 2003 for agricultural and forest soil, as well as with the background values for world soils according to Hooda (2010). Contents of mobile forms of heavy metals were evaluated according to critical values (limit values for risk elements as they relate to the agricultural soil and plant) given by Slovakian Act No. 220/2004. Contents of heavy metals determined in plant samples were evaluated according to maximum allowed amounts given by Slovakian Government Decree438/ 2006.

Descriptive statistics regression and correlation analysis (Microsoft Excel, Redmond, WA, USA) were used to evaluate the degree of metal contamination and relationship between contamination of soil and plants. Obtained results were evaluated using F-test, with significance set at $p < 0.05$.

## Results and Discussion

The following information about the investigated location was obtained based on results of soil sample analysis evaluated using descriptive statistics. The observed parameters are used as criteria for the evaluation of agricultural soil properties. This evaluated group of soil samples (SS) included 34 from the forest ecosystem and 11 from the permanent grassland (PG) and pasture ecosystems (Table 1).

The average values of $C_{OX}$ were 1.69 % (permanent grasslands and pastures) and 4.86 % (forest ecosystem), respectively. The content of organic carbon ($C_{OX}$) in soils is largely conditional upon the processes of soil formation. Kanianska et al. (2014) compared 6 different soil types. The $C_{OX}$ content were from 1.4 % in soil type Podzol (land-use category forests) to 6.2 % in soil type Dystric Cambisol Pastures (land-use category pastures).

The evaluated soils ranged in humus content from low (1 %–2 %) to very good humus supply (10.2 %–34.6 %) for both the FE and PG + P soils. Both the percentages of $C_{OX}$ and humus were approximately 1.8 times greater in the FE soil than in the PG + P soli. The average values for pH indicated similar acid soil reaction values for soils from the two areas (Declaration 2005; Bielek 1996). Soil reaction is one of the factors that most affects the behaviour of heavy metals in soil (Arvay et al. 2012).

Total concentrations of heavy metals (TC-HMs) were compared with limit values for the investigated metals according to Act No. 188/2003 and the background values for world soils according to Hooda (2010). The content of mobile forms (MF-HMs) of Cd, Cu, Cr and Ni (no limits are given for Hg), determined in soil extracts by $NH_4NO_3$, were compared with the critical values. The obtained results are presented in Table 2.

From the aspect of ecotoxicity, Cd and Hg are the most hazardous metals. Determined total contents of Cd in soil were higher than the limit value in 43 of 45 samples. In 17 sampling sites, Cd content was more than five-fold higher, and at 1 site even more than 6-fold (Fig. 2). The Hg contents ranged from 0.28–415 mg/kg (800 times higher content in comparison with limit, while the average value exceeded the limit value 65-fold) (Fig. 3). In the case of Zn (Fig. 4) and Pb (Fig. 5) the situation is less critical, but limit values were exceeded at 28 sites for Zn and 12 sites for Pb. The average Cu content exceeded its limit value nearly twofold. The range for Cu was 11.00–913 mg/kg (Fig. 6).

The occurrence of high contents of heavy metals confirms the existence of former emission sites in Rudnany, Krompachy and Nizna Slana and also local mineralized zones (Porac, Slovinky, Krompachy, Gelnica) (Hronec et al. 2010). The background values for Cu, Pb and Zn according to Hooda (2010) were exceeded at 32, 41 and 42 sites, respectively. Cadmium and mercury were more than twofold higher than background values at all sites.

The critical value for the mobile form of Pb was exceeded at 33 sites, and even as high as > 20-fold at one site. A different situation existed in the case of Zn, Cd and Cu, but limit values were also exceeded at many sites (i.e., 14, 11 and 4 sites for Zn, Cd, and Cu, respectively). Limit-exceeding hazardous element content in soil does not always initiate their transfer into the plant, but multiple exceedances of the limit usually cause plant contamination.

**Table 1** Selected parameters of soil quality

| | $C_{OX}$ (%) | | Humus (%) | | $pH/H_2O$ | | $pH/CaCl_2$ | |
|---|---|---|---|---|---|---|---|---|
| | FE | PG + P | FE | PG + P | FE | PG + P | FE | PG + P |
| Minimum | 1.02 | 1.05 | 1.75 | 1.82 | 4.16 | 4.42 | 3.08 | 3.97 |
| Maximum | 20.1 | 5.90 | 34.6 | 10.2 | 8.40 | 7.73 | 7.54 | 7.08 |
| Average | 4.86 | 2.69 | 8.37 | 4.63 | 6.34 | 6.14 | 5.64 | 5.67 |
| Median | 3.72 | 2.11 | 6.41 | 3.63 | 6.33 | 6.05 | 5.60 | 5.59 |
| SD | 3.71 | 1.67 | 6.39 | 2.88 | 1.19 | 1.02 | 1.27 | 1.15 |
| Mode | 2.04 | – | 3.51 | – | 7.61 | – | – | 6.87 |

*FE* Forest ecosystem, *PG + P* Permanent grasslands and pastures

**Table 2** The content of mobile forms and total content of heavy metals in soil (in mg/kg)

| | Zn | | Cd | | Cu | | Pb | | Hg |
|---|---|---|---|---|---|---|---|---|---|
| | MFs | TCs | MFs | TCs | MFs | TCs | MFs | TCs | TCs |
| Minimum | 0.02 | 33.1 | 0.03 | 0.65 | 0.04 | 11.0 | 0.01 | 26.5 | 0.28 |
| Maximum | 5.43 | 953 | 0.24 | 6.73 | 2.21 | 913 | 2.15 | 165 | 415 |
| Average | 1.33 | 191 | 0.08 | 2.97 | 0.35 | 109 | 0.29 | 60.8 | 32.8 |
| Median | 0.72 | 144 | 0.07 | 2.63 | 0.18 | 41.1 | 0.15 | 52.8 | 3.04 |
| SD | 1.55 | 165 | 0.04 | 1.59 | 0.51 | 178 | 0.41 | 33.8 | 93.9 |
| Limit values[a] | | 150 | | 1.00 | | 50.0 | | 70.0 | 0.5 |
| Background values[b] | | 70.0 | | 0.30 | | 25.0 | | 29.2 | 0.14 |
| Critical values[c] | 2 | | 0.1 | | 1.0 | | 0.1 | | no limits |

[a] Limit values for Slovak soils according to Act No.188/2003 Coll. of laws

[b] BV – The background values for world soils according to Hooda (2010)

[c] Critical values for Slovak soils according to Act No 2004/2004

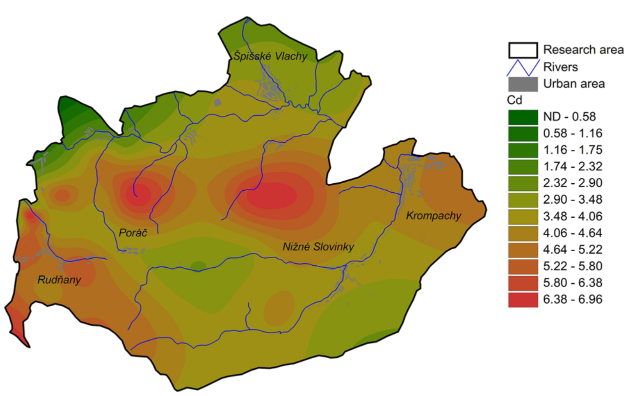


**Fig. 2** Total content of Cd in soil (mg/kg)

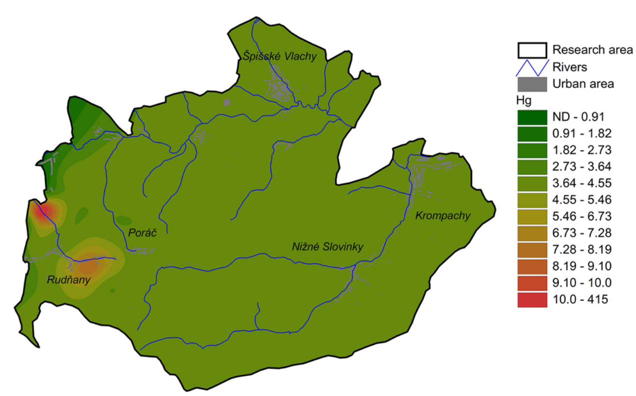


**Fig. 3** Total content of Hg in soil (mg/kg)

Middle Spis is an area with high content of metals and metalloids in soil due to pedological anomalies. The smelter in Krompachy and iron mines in Rudnany were in the past the determining sources of environmental contamination by solid pollutants (Hronec et al. 2010). The gravity of the situation has been confirmed in many studies focused on the monitoring of environmental contamination in this area of Slovakia. Tomas et al. (2004) reported ranges in 16 soil samples for Cd, Cu and Hg of 0.076–3.20, 1.76–9.65, and 0.566–111 mg/kg, respectively, at distances of 5, 7 and 10 km from the Rudnany iron mines and Krompachy copper smelter. In 2012 in the cadastre of the village of Rudnany, respective soil concentration ranges for Cu, Zn and Hg in relation to sampling site were 70.2–113, 63.7–128, and 5.62–19.4 mg/kg in the village; while means were 129 ± 13.5, 77.0 ± 2.94, and 1.0 ± 0.91 mg/kg in the eastern direction, and 1287 ± 140, 832 ± 13.4, and 99.0 ± 5.07 mg/kg at the tailing pond of the Hg processing plant (Angelovicova and Fazekasova 2014). The level of soil pollution by heavy metals in the vicinity of the smelter

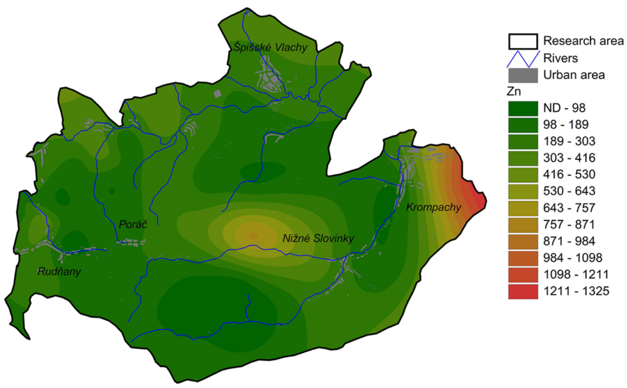


**Fig. 4** Total content of Zn in soil (mg/kg)

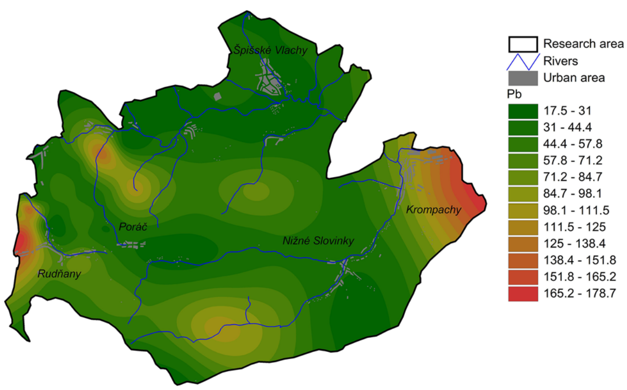


**Fig. 5** Total content of Pb in soil (mg/kg)

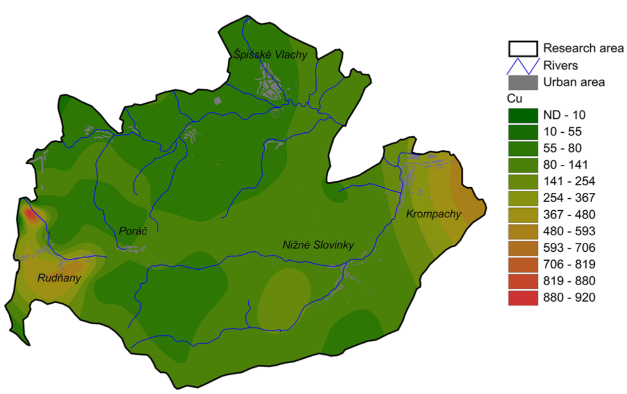


**Fig. 6** Total content of Cu in soil (mg/kg)

during 1987-1993 and after 10 years (in 2003) was assessed by Banasova and Lackovicova (2004). Cu and Zn contents in soils at the north-east exposed slope situated opposite the smelter at an altitude of about 525 m during the first period ranged from 74.1 to 444 and 179–720 mg/kg, respectively. In 2003, the determined Cu and Zn soil contents were 1310 and 306 mg/kg. Li et al. (2014) compared Zn, Cd, Cu and Pb concentrations in soils from mining areas in several countries. The respective metal concentrations (mg/kg) by country were: China – 1163, 11.0, 212 and 641; Spain – 466, 6.59, 121 and 882; Vietnam – 41.1, 135, 271 and 30.6; and India – 339, 3.82, 63.5 and 305.

The contamination status of the soils was assessed in two five-year cycles (1991-1995 and 1996-2000) and one three-year cycle (2001–2003) by Dobrikova and Salgovicova (2006). The most significant soil contaminants within the monitored region included Hg, Cu and Cd. During the first cycle, higher than permissible concentrations of Cd and Hg were measured overall in 36.7 % and 50.8 % of the soil samples, respectively. In the third cycle, Cd concentrations in all soil samples were below the maximum permissible concentration levels. The proportions of Hg-contaminated soil samples decreased to 58.8 %. In most cases, it was possible to confirm the exceedances of hygienic limits for monitored heavy metals.

Heavy metals cannot be degraded or destroyed but only accumulated in soil, water, and sediments (Akoumianakis et al. 2009; Harangozo et al. 2012; Naveedullah et al. 2013). Metal concentration found in contaminated soil frequently results in uptake by plants (Oves et al. 2012), their bioavailability can be influenced by change in soil properties (Vollmannova et al. 2002; Harangozo et al. 2012). The importance of determining the levels of hazardous trace elements in soils is given by their toxicity to plants and their entry into other organisms via food chains.

Samples of plant material were collected from the same sampling sites as the soil samples and contents of Zn, Cd, Cu, Pb and Hg were determined. The obtained results are described using descriptive statistics (Tables 3 and 4).

The determined Cd, Pb and Hg contents were compared with the maximum allowed amounts for undesirable substances given by Government Decree 438/2006 (no limits are given for Zn and Cu). An increased content of cadmium

**Table 3** Total content of Zn, Cd, Cu, Pb and Hg in *Athyrium filix-femina* L. (in mg/kg dry matter)

| | Zn | Cd | Cu | Pb | Hg |
|---|---|---|---|---|---|
| Minimum | 12.4 | 0.10 | 3.34 | 0.09 | 0.02 |
| Maximum | 73.7 | 0.91 | 85.7 | 17.3 | 12.8 |
| Average | 39.5 | 0.38 | 10.3 | 2.21 | 0.99 |
| Median | 38.3 | 0.35 | 7.61 | 1.10 | 0.06 |
| SD | 14.2 | 0.20 | 13.61 | 3.16 | 2.88 |
| Signif. $F_{MFs/HMp}$ | 0.12 | 0.64 | 0.02 | 1.08E−04 | |
| $R_{MFs/HMp}$ | 0.27 | 0.08 | 0.41 | 0.62 | |
| Signif. $F_{TCs/HMp}$ | 0.64 | 0.34 | 7.59E−06 | 0.79 | 0.29 |
| $R_{TCs/HMp}$ | 0.08 | 0.17 | 0.69 | 0.05 | 0.19 |

Signif. $F_{MFs/HMp}$ (Signif. $F_{TCs/HMp}$) – Correlation between content of mobile forms (total content) of heavy metals in soil and total content of heavy metals in plant materials; $R_{MFs/HMp}$ ($R_{TCs/HMp}$) – correlation coefficients

**Table 4** Total content of Zn, Cd, Cu, Pb and Hg in *Poaceae* (in mg/kg dry matter)

| | Zn | Cd | Cu | Pb | Hg |
|---|---|---|---|---|---|
| Minimum | 29.9 | 0.10 | 3.87 | 0.09 | 0.01 |
| Maximum | 158.6 | 1.63 | 28.6 | 29.7 | 0.13 |
| Average | 54.3 | 0.41 | 8.37 | 3.82 | 0.05 |
| Median | 38.5 | 0.26 | 5.46 | 0.62 | 0.04 |
| SD | 38.5 | 0.42 | 7.18 | 8.84 | 0.04 |
| Signif. $F_{MFs/HMp}$ | 0.53 | 0.22 | 1.16E−06 | 0.21 | |
| $R_{MFs/HMp}$ | 0.22 | 0.41 | 0.97 | 0.41 | |
| Signif. $F_{TCs/HMp}$ | 5.00E−03 | 0.42 | 2.86E−07 | 1.40E−03 | 0.99 |
| $R_{TCs/HMp}$ | 0.78 | 0.27 | 0.98 | 0.83 | 0.00 |

Signif. $F_{MFs/HMp}$ (Signif. $F_{TCs/HMp}$) – correlation between content of mobile forms (total content) of heavy metals in soil and total content of heavy metals in plant materials; $R_{MFs/HMp}$ ($R_{TCs/HMp}$) – correlation coefficients

(Cd > 1 mg/kg) was determined only in 1 plant sample despite high determined total contents of Cd in all soil samples (even in 11 soil samples the critical values for Cd were exceeded). The measured ranges for Zn and Cu in plants were 12.4–158.6 and 3.34–85.7 mg/kg, respectively. A significant correlation between the mobile form of metal in soil and its concentration in plant tissue was obtained only for Cu (Table 4). However, significant concentrations between total metal content in soil and metal concentration in plant tissue were obtained for Zn, Cu and Pb. Lead and Hg are the least mobile elements in the soil horizon. The content of Pb was higher than the limit value (Pb > 10 mg/kg) in only 2 samples, but a significant correlation between the content of Pb in plants and its total content in soil was confirmed (Tables 3 and 4). Mercury migration is affected by the type of sediment, especially by particle size and physico-chemical parameters such as pH and Eh (Dadova 2014). High levels of mercury in the soil were reflected in its high accumulation in plants, although no correlation between Hg content in plants and its soil content was confirmed. In samples from 12 sampling sites, higher Hg content than the maximum allowed by legislation (Hg > 0.1 mg/kg) was determined (even more than five times higher compared with the limit value).

Rich mineral reserves in Volovske Hills in the past led to intensive mining and industrial activity in the Middle Spis region. The area consequently became contaminated with heavy metals due to the mining and processing of copper and iron ores, and especially without the application of modern technology to minimize impact on the environment. Our results correspond with results of previous research on the environmental contamination of the Middle Spis region realized by several authors. These data confirm the permanent risk for ecosystems, as well as human populations, caused by harmful heavy metals in this region.

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