

## Contamination of the Soil and Water Environment by Heavy Metals in the Former Mining Area of Rudňany (Slovakia)

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### Abstract

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Contamination of soil and water environment by heavy metals in a former mining area and their effect on the soil characteristics were determined. Soil samples were collected in the village of Rudňany which is, according to environmental regionalization, classified as an environmentally loaded and unhealthy area. Soil samples were collected in 2011 at eight fields situated at different distance from the pollution source. Total contents of heavy metals (Cu, Pb, Zn, Hg), soil reaction (pH), organic carbon (C<sub>ox</sub>), activity of urease (URE), acid phosphatase (ACP), and alkaline phosphatase (ALP) were determined in soil samples. Water samples were collected in Rudniansky creek, which flows through the village. The contents of heavy metals (Cu, Pb, Zn, Hg) were determined in water samples. High contents of heavy metals in soil and water result from long-term mining and smelting activities predominantly focused on copper and mercury production. Numerous heaps of waste material and tailing ponds are the main pollutant sources representing a great threat to the environment, as these pollutants can accumulate in plants and enter the food chain. Extremely high and above-limit values of copper and mercury were determined in the sampled soils. According to the index of geoaccumulation, copper has been shown as a serious contaminant in some soil sampling fields, which were determined as strongly contaminated. In terms of the geoaccumulation index, all sampling fields were evaluated as very strongly contaminated by mercury. We found significant positive correlation between zinc, lead, and copper contents in soils, which is a likely sign of the same source of pollution. A nonsignificant but positive relationship between soil reaction and heavy metals and a negative correlation between soil pH and organic carbon were observed. A high degree of soil pollution was reflected in soil biological properties. Activity of soil enzymes significantly decreased with increasing heavy metals content in soils. Rudniansky creek was polluted only by copper and mercury. The highest and above-limit values of these metals were determined at the point where the stream leaves the village (in a downstream direction).

**Keywords:** copper; environmental loads; soil enzymes; soil and water pollution; toxic elements

Environmental pollution by heavy metals which adversely affect soil quality and pose a threat for human health requires a rapid and comprehensive solution. Numerous anthropogenic sources of pollutants can contaminate the soil and water environment, including inputs from waste waters flowing from mines and waste storage, runoff of pesticides from agricultural land or atmospheric deposition (SONG *et al.* 2010). Increasing industrialization has been accompanied throughout the world by the extraction and distribution of mineral substances from their natural deposits. In the process of mining

and smelting activities, many kinds of risk elements enter the environment, causing serious environmental problems.

Rudňany village, as a part of the former mining Middle Spiš area, has been polluted in the long-term by heavy metals. The extraction and subsequent processing of mercury, copper, and barite were a major source of pollution in this region. In recent decades there has been increasing interest in high concentrations of heavy metals in the environment due to the fact that they can persist in soils for tens of thousands years (McGRATH 1984); as they are non-

biodegradable, they can accumulate to reach toxic levels in soil, water, and biota (KUMAR *et al.* 2007).

Groundwater contamination by heavy metals is often associated with mining activities and the subsequent processing of ores. Heavy metals enter the surface water in dissolved form and in association with substances washed off the ground, where they can migrate over long distances (FRANKOWSKI *et al.* 2009). Polluted water sources may become the source of undesirable substances, which are dangerous for human health causing various cancers, cardiovascular or neurological diseases (GALUŠKOVÁ *et al.* 2010).

Soil contamination by heavy metals is a significant problem, which leads to changes of soil characteristics and limits productive and environmental functions. Polluted soils are no longer appropriate for agricultural production, because they are unable to produce healthy food. Assessment of soil pollution by heavy metals in Slovakia is determined by limit values of risk elements, which were set by law (Act No. 220/2004).

It has been repeatedly shown that heavy metals have a negative impact not only on the size, activity and diversity of soil microbial communities (CHANDER *et al.* 2001), but they also affect soil enzymes (BELYAEVA *et al.* 2005). Soil enzyme activity is a reliable indicator reflecting the biological situation in soils and it is possible to very quickly obtain credible results of soil pollution. Reaction of enzymes to soil pollution is faster in comparison with monitoring of the chemical and physical properties (HINOJOSA *et al.* 2004).

Mining and smelting activities in the Rudňany area have influenced the geological landscape structure (formation of mines, heaps of waste material, and ponds of sewage sludge) but predominantly caused pollution of the environment (BREHUV *et al.* 2005). The processing plant for mercury and barite along with the heating plant were the main sources of pollution in Rudňany village. The largest volumes of mercury ores were mined and processed at the end of the 1980s. Before the attenuation of production, plants emitted into the air 4 t of mercury per year (HANČUĽÁK *et al.* 2006). Copper contamination of the whole Middle Spiš region is the result of long-term mining and processing of copper ores. Produced waste material was stored on the numerous heaps and in the tailing pond.

The aim of the study was to determine (1) the level of soil pollution by heavy metals according to the index of geoaccumulation and, (2) the influence of soil pollution on soil chemical and biological properties. The study also aims to determine the level of water pollution in Rudňany village, which belongs to the most polluted former mining areas in Slovakia.

## MATERIAL AND METHODS

**Study area.** The research was conducted in Rudňany village (48°52'774" N; 20°41'165"E), which belongs to the most polluted, environmentally loaded, and unhealthy areas of Middle Spiš. The Rudňany cadastral area covers 13.4 km<sup>2</sup> and the altitude ranges from 475 to 959 m a.s.l. Climate and soil characteristics of sampling fields are listed in Table 1. Predominant soil types are Cambisols, but on the creek floodplain the subtypes of Fluvisols are developed. Rudňany village is one of the most significant deposits of siderite formation, the source of mercury and copper sulphides.

**Soil sampling.** A set of 24 soil samples (0.15–0.20 m) in total from 8 locations (3 samples from each field) were collected in April 2012 from grasslands in the cadastre of Rudňany village (Figure 1). Samples were taken next to the heap of waste material (locality 4), next to the tailing pond and mercury processing plant (locality 7), two samples were taken in the southern part of the village (locality 1, locality 2) out of potential pollution sources, and one sample was taken in the central part of the village (locality 3). Some samples (locality 5, locality 6) were taken in the northern direction from the heap of waste material and in the eastern direction from the tailing pond (locality 8). Soil samples were homogenized, dried at room temperature, sieved to < 2 mm, and stored in plastic bags until analysis. Total content of copper, lead, and zinc was determined by atomic absorption spectrometry (AAS). For the estimation of copper, lead, and zinc contents, the soil samples were extracted by a solution of nitric acid (68%) (5 min shaking). Total content of mercury was determined by DMA 80 apparatus (Milestone Systems, Beaverton, USA). Assessed values of heavy metals in soils were compared to the limit values of Slovak soils (Act No. 220/2004). Soil reaction was determined in a soil solution (5 g of soil mixed with 25 ml of 0.01M CaCl<sub>2</sub>) using a pH meter inoLab pH 720-WTW (WTW GmbH, Weilheim, Germany). Organic carbon was measured according to the Jodlbauer method (PETERBURSKIY 1963). Urease activity (URE) was measured using a method described by CHAZIJEV (1976). Acid (ACP) and alkaline (ALP) phosphatase were measured according to a method described by Chazijev (method modified by GREJTOVSKY 1991). STATISTICA 10 software was used for all data analyses. The level of significance between soil properties was calculated using Spearman's correlation coefficient.

**Water sampling.** Water samples were collected at five localities of Rudnianský creek (Figure 1). Sampling points were deployed in the downstream

Table 1. Characteristics of sampling fields

Locality	Climatic regions*	Mean temperature (°C)		Mean precipitation during vegetation period (VI–IX) (mm)	Soil type	Soil texture
		January	vegetation period (VI–IX)			
1	cold and wet	–4 to –6	12–13	60–50	Cambisols on crystalline rocks	moderate heavy to light soils
2	cold and wet	–4 to –6	12–13	60–50	shallow Cambisols on crystalline rocks	moderate heavy to light soils
3	slightly cold, slightly wet	–3 to –6	12–14	100–0	Pseudogley Cambisols	moderate heavy to light soils
4	slightly cold, slightly wet	–3 to 6	12–14	100–0	Pseudogley Cambisols	moderate heavy to light soils
5	very cold, very wet	–2 to 5	13–15	100–0	shallow Cambisols on crystalline rocks	moderate heavy to light soils
6	very cold, very wet	–2 to 5	13–15	100–0	Cambisols on crystalline rocks	moderate heavy to light soils
7	slightly cold, slightly wet	–3 to 6	12–14	100–0	Pseudogley Cambisols on flysch	heavy to very heavy
8	slightly cold, slightly wet	–3 to –6	12–14	100–0	Pseudogley Cambisols on flysch	moderate heavy

\*DŽATKO (1989)

direction (1 to 5). Collection and water treatment was performed using the methodological guidelines of the Ministry of Environment of the Slovak Republic (STN EN ISO 5667-1 2006). Samples were processed immediately after sampling, and content of mercury was determined in the laboratory by AAS. Content of other metals was determined by atomic AAS with inductively coupled plasma (AAS-ICP). Measured values of heavy metals in the water of Rudňanský creek were compared with the limit values (Act No. 269/2010), defining good quality of surface water.

**Index of geoaccumulation.** For quantification of the degree of contamination, the index of geoaccu-

mulation ( $I_{\text{geo}}$ ) was used. The index was calculated as follows:  $I_{\text{geo}} = \log_2 (Cn/1.5 \times Bn)$ , where  $Cn$  is the concentration of heavy metal in a sample and  $Bn$  is the geochemical background value (median), which was calculated from the geochemical database of Slovak soils (uncontaminated) (ŠEFCÍK *et al.* 2008). The background values are as follows (mg/kg): Cu = 18; Hg = 0.06; Pb = 18; Zn = 60. MÜLLER (1979) characterized seven categories of contaminated soil using the index of geoaccumulation: 1<sup>st</sup> class: background values  $I_{\text{geo}} \leq 0$ ; 2<sup>nd</sup> class: uncontaminated  $0 < I_{\text{geo}} < 1$ ; 3<sup>rd</sup> class: uncontaminated or slightly contaminated  $1 \leq I_{\text{geo}} \leq 2$ ; 4<sup>th</sup> class: slightly contaminated  $2 \leq I_{\text{geo}} < 3$ ;

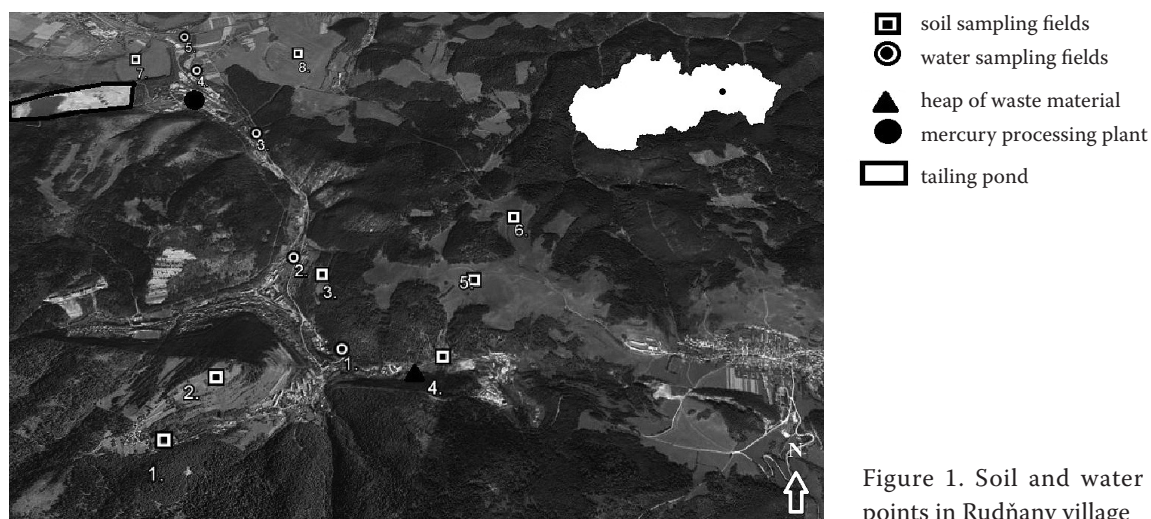


Figure 1. Soil and water sampling points in Rudňany village

5<sup>th</sup> class: moderately contaminated  $3 \leq I_{\text{geo}} < 4$ ;  
 6<sup>th</sup> class: strongly contaminated  $4 \leq I_{\text{geo}} < 5$ ; 7<sup>th</sup> class:  
 very strongly contaminated  $I_{\text{geo}} \geq 5$ .

## RESULTS AND DISCUSSION

**Heavy metals in soils.** All measured data on heavy metal content (Table 2) were compared to the limit values for Slovak soils (Act No. 220/2004). Extremely high and above-limit values of copper were determined at six out of eight localities. At the most polluted sampling point (locality 7) the content of copper exceeds more than 21 times the permissible limit value. The measured values differ depending on the distance of the monitored localities from the primary pollution sources (tailing pond, heaps of waste material and the mercury processing plant) (Figure 1). Copper is generally considered as the main pollutant in the Middle Spiš area due to its long-term mining and smelting. Limit values for lead and zinc were exceeded only at locality 7 and for Pb and Zn at localities 4 and 7, respectively. At locality 7, the value of lead was 1.5 times higher and the value of zinc 5.5 times higher than the limit value for Slovak soils. Ponds contain increased contents of lead and zinc, by-products in the processing of metal ores. Deposits of copper and mercury sulphides became the main source of mining and processing activities, and therefore large amounts of mercury and copper have been released to the environment as an undesirable side effect (BÁLINTOVÁ *et al.* 2012). The concentration of mercury was extremely high in all samples, differing considerably in dependence on the distance of the sampling point from the potential pollution source. The level of mercury exceeded the permissible limit value 5.7 times at the least polluted locality (locality 6) sampled at a considerable distance from the pollution sources, 141 times at the

locality 7 (a sampling position close to the tailing pond and mercury processing plant), and more than 66 times at the locality 4, next to the heap of waste material. Contents of mercury in the Rudňany village soils, which were several times higher than the permissible limit values, were measured by BOBRO *et al.* (2006). TAKÁČ *et al.* (2008) reported that high levels of mercury in the soils of Rudňany village and its neighborhood significantly reduced forest and agricultural production. High mercury content in the vegetation (DOMBIANOVÁ 2005) as well as in domestic animals (REICHNOVÁ & BENCKO 1995) was also found as a result of long-term environmental pollution in Rudňany village.

Values of chemical and biological properties of sampling fields are listed in Table 3. Soil reaction ranged from 4.6 (strongly acid) to 7.1 (neutral). According to the findings of BREHUV *et al.* (2005), high contents of heavy metals in the soil environment can cause changes in the soil reaction from acid to alkaline. We reported a tendency of increasing soil pH with increasing soil pollution. Organic carbon content ranged from 3.27 to 7.1% and there was no reported relationship with the sampling position.

Activity of soil enzymes was changing according to the soil pollution. Measured values of urease ( $0.15\text{--}0.63 \text{ mg NH}_4 \pm \text{N/g/24 h}$ ), acid phosphatase ( $50.2\text{--}250 \text{ } \mu\text{g P/g/3 h}$ ), and alkaline phosphatase ( $29.95\text{--}199 \text{ } \mu\text{g P/g/3 h}$ ) were low, which is typical for heavy metal polluted soils (HE *et al.* 2005). The lowest values of urease, acid and alkaline phosphatase were measured at the most polluted sampling fields (locality 7 and 4). It has been recorded repeatedly, that heavy metals exhibit a toxic effect on enzyme activities, which is observed as increasing soil enzyme activity with decreasing heavy metal content (WANG *et al.* 2007; KENDELER *et al.* 2012). Therefore, soil enzymes are suitable as bioindicators to determine

Table 2. Values of heavy metal contents (average  $\pm$  standard deviation) in soil (in mg/kg)

Locality	Cu	Pb	Zn	Hg
1	104 $\pm$ 9.4	26 $\pm$ 3.74	69 $\pm$ 5.35	18.9 $\pm$ 0.49
2	73 $\pm$ 2.82	31 $\pm$ 5.09	122 $\pm$ 6.37	5.9 $\pm$ 0.29
3	257 $\pm$ 44.3	27 $\pm$ 2.94	126 $\pm$ 5.35	32.7 $\pm$ 1.87
4	404 $\pm$ 6.12	25 $\pm$ 4.32	165 $\pm$ 8.04	33.5 $\pm$ 2.4
5	56 $\pm$ 5.71	19 $\pm$ 6.5	49 $\pm$ 4.1	11.3 $\pm$ 1.20
6	48 $\pm$ 10.67	61 $\pm$ 4.96	119 $\pm$ 4.32	4 $\pm$ 0.66
7	1287 $\pm$ 139.6	102 $\pm$ 4.54	832 $\pm$ 13.44	99 $\pm$ 5.07
8	129 $\pm$ 13.48	14 $\pm$ 3.55	77 $\pm$ 2.94	16 $\pm$ 0.91
Limit value*	60	70	150	0.7

\*Act No. 220/2004



Table 3. Biological and chemical soil properties of sampling fields

Locality	URE	ACP	ALP	pH	C <sub>ox</sub> (%)
	(mg NH <sub>4</sub> ± N/g/24 h)	(μg P/g/3 h)			
1	0.53 ± 0.045	86.5 ± 1.36	71 ± 6.48	4.6 ± 0.14	3.27 ± 0.05
2	0.45 ± 0.053	183 ± 4.54	188 ± 10.7	4.9 ± 0.08	4.4 ± 0.22
3	0.57 ± 0.07	148 ± 2.94	81 ± 2.9	7.1 ± 0.29	7.1 ± 0.45
4	0.48 ± 0.04	186 ± 2.82	179 ± 5.71	5.1 ± 0.08	5.1 ± 0.29
5	0.42 ± 0.04	50 ± 2.16	30 ± 2.16	5.2 ± 0.24	5.25 ± 0.16
6	0.63 ± 0.03	184 ± 2.82	119 ± 1.41	5.3 ± 0.08	4.1 ± 0.22
7	0.15 ± 0.03	64 ± 5.09	52 ± 2.44	7 ± 0.14	6.2 ± 0.45
8	0.52 ± 0.03	250 ± 8.98	199 ± 1.41	6.2 ± 0.29	4.9 ± 0.00

URE – urease; ACP – acid phosphatase; ALP – alkaline phosphatase; C<sub>ox</sub> – organic carbon

toxicological influence of various pollutants on soil quality (SHEN *et al.* 2005).

**Index of geoaccumulation in soils.** Using the index of geoaccumulation, the sampling fields were divided into seven classes, according to MÜLLER's (1979) seven members scale (based on the degree of contamination) (Figure 2). The degree of the copper contamination indicated significant differences between the fields. While the fields close to the tailing pond and heaps of waste material were evaluated as very strongly contaminated (class 7), fields at a greater distance from the main pollution source were classified as uncontaminated or slightly contaminated (class 3). Mine waste heaps caused moderate soil contamination (class 5) of localities 3 and 4 by copper. Lead values ranged in classes from uncontaminated to slightly contaminated (class 1–3). Zinc concentrations were extremely high only at locality 7 (class 5), other fields we evaluated as uncontaminated. Mercury was proven as the biggest pollutant; all sampling fields were evaluated as very strongly contaminated (class 7). Because of the mining and subsequent heat-treating of mercury ores, Rudňany village is considered as a highly environmentally hazardous area (BREHUV *et al.* 2005). ŠEFČÍK *et al.* (2008), who studied the pollution of Slovak soils using the index of geoaccumulation, noted that the area of Middle Spiš is moderately or highly contaminated by heavy metals, but Rudňany village is the main core of mercury pollution. It has been repeatedly shown that long-term mercury exposure is reflected in numerous diseases. Mercury tends to accumulate in the body, resulting in brain or peripheral nerves damage (POULIN & GIBB 2008).

**Correlations between soil characteristics.** Table 4 presents significant correlations between heavy metals and soil characteristics. According to DE WOLF and RASHID (2008), a significant correlation between heavy metals indicates the probability that their source

is identical. We have found significant positive correlation between zinc, lead, and copper. It has been repeatedly accentuated that the solid waste from the copper production contains the residues of lead and zinc (BÁLINTOVÁ *et al.* 2012) which explains the significant correlation between copper and zinc or lead ( $P < 0.01$ ) or between lead and zinc each other ( $P < 0.05$ ). Mercury gave significant positive correlation ( $P < 0.01$ ) only with copper. Waste material from the mercury production usually contains the residues of barium, chromium, iron, and antimony, which were not assessed in our study. Copper and mercury sulphides are the main elements of the ore deposits in Rudňany village. Disrupting of the bedrock contributed to their releasing into the environment and explains the significant positive correlation between them. We found an insignificant, but positive correlation between heavy metals and soil reaction and a negative correlation between soil

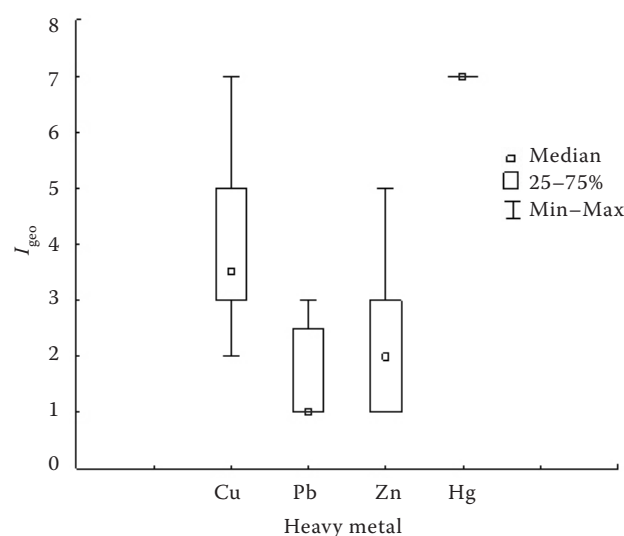


Figure 2. Box plot of the geoaccumulation index ( $I_{\text{geo}}$ ) of heavy metals in soils of Rudňany village

Table 4. Correlation between heavy metals and soil properties

	Cu	Pb	Zn	Hg
URE	−0.95**	−0.16	−0.40	−0.85**
ACP	−0.81*	−0.04	−0.05	−0.88**
ALP	−0.69	−0.19	−0.02	−0.81*
pH	0.30	0.33	0.48	0.33
Cox	−0.77	−0.76	−0.77	−0.12
Cu		0.96**	0.92**	0.95**
Pb			0.81*	0.05
Zn				0.14

URE – urease; ACP – acid phosphatase; ALP – alkaline phosphatase; \*, \*\*correlation is significant at  $P = 0.05$ ,  $P = 0.01$  level, respectively

reaction and enzymes. TAYLOR *et al.* (2002) consistently reported a negative correlation between the soil reaction and soil enzyme activity. CANG *et al.* (2009) showed a prominent effect of the soil reaction on the activity of acid phosphatase, but did not reveal any significant relationship between the soil reaction and the activity of alkaline phosphatase and urease. No correlation between organic carbon and heavy metal content was confirmed. Consistent with our results, LEITA *et al.* (1999) reported that organic carbon probably does not reflect the heavy metal soil contamination. WANG *et al.* (2007) found nonsignificant correlation between organic carbon and soil enzymes, which was probably due to the quality of the organic inputs into the soil. FRIEDLOVÁ (2010), who investigated polluted areas near sludge ponds, similarly found no direct influence of organic carbon on the contents of heavy metals. Spearman's correlation coefficient indicated that enzyme activities have a significant positive correlation ( $P < 0.01$ ) between each other and a significant negative correlation with some heavy metals. We reported a significant negative correlation ( $P < 0.01$ ) between soil urease and copper and also mercury. Acid phosphatase gave a significant negative correlation with copper and mercury and alkaline phosphatase only with mercury. It has been reported repeatedly that soil microbial activities, including urease, acid and alkaline phosphatase contents, were significantly lower in soils polluted by heavy metals (KHAN *et al.* 2010).

**Heavy metals in water.** Values of heavy metals in Rudnianský creek (Table 5) show that the creek is contaminated only by copper and mercury. An above-limit value of copper was measured at one sampling point (locality 4). It is probably caused by the tailing pond and the former mercury processing plant, which are located close to this locality. Proximity of the pollution sources and the penetration of toxic substances is probably the main reason of

Table 5. Measured values of heavy metals in water (in µg/l)

	Cu	As	Pb	Zn	Hg
Min	2	4	4.2	2.7	0.1
Max	23	6	5	18.2	3
Average	8	5	4.5	6.9	0.8
SD	7.6	0.6	0.3	6.5	1.1
Limit value*	20	20	20	100	0.1

SD – standard deviation; \*Act No. 269/2010

the high mercury content in the last three sampling points (locality 3, 4, 5). The limit value for mercury (0.1 µg/l) was exceeded three times at localities 3 and 5, and four times at locality 4. KLUKANOVÁ *et al.* (2010) found that swirling of the polymetallic dust, penetration of the polluted water from the tailing pond and heaps of waste material, and long-term loading by dust fallout coming from ores processing have been reflected in the pollution of Rudnianský creek. High values of copper and mercury, which several times exceed the permissible limit values, are the evidence of insufficient protection of the environment against the penetration of the toxic substances.

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