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ORIGINAL ARTICLE

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# Environmental and health risk assessment in abandoned mining area, Zlata Idka, Slovakia

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**Abstract** The Zlata Idka village is a typical mountainous settlement. As a consequence of more than 500 years of mining activity, its environment has been extensively affected by pollution from potentially toxic elements. This paper presents the results of an environmental-geochemical and health research in the Zlata Idka village, Slovakia. Geochemical analysis indicates that arsenic (As) and antimony (Sb) are enriched in soils, groundwater, surface water and stream sediments. The average As and Sb contents are 892 mg/kg and 818 mg/kg in soils, 195 mg/kg and 249 mg/kg in stream sediments, 0.028 mg/l and 0.021 mg/l in groundwater and 0.024 mg/l and 0.034 mg/l in surface water. Arsenic and Sb concentrations exceed upper permissible limits in locally grown vegetables. Within the epidemiological research the As and Sb contents in human tissues and fluids have been observed (blood, urine, nails and hair) in approximately one third of the village's population (120 respondents). The average As and Sb concentrations were 16.3 μg/l and 3.8 μg/l in blood, 15.8 μg/l and 18.8 μg/l in urine, 3,179 μg/kg and 1,140 μg/kg in nails and 379 μg/kg and 357 μg/kg in hair. These concentrations are comparatively much higher than the average population. Health risk calculations for the ingestion of soil, water, and vegetables indicates a very high carcinogenic risk ($>1/1{,}000$) for as content in soil and water. The hazard quotient [HQ = average daily dose (ADD)/reference dose (RfD)] calculation method indicates a HQ > 1 for groundwater As and Sb concentrations.

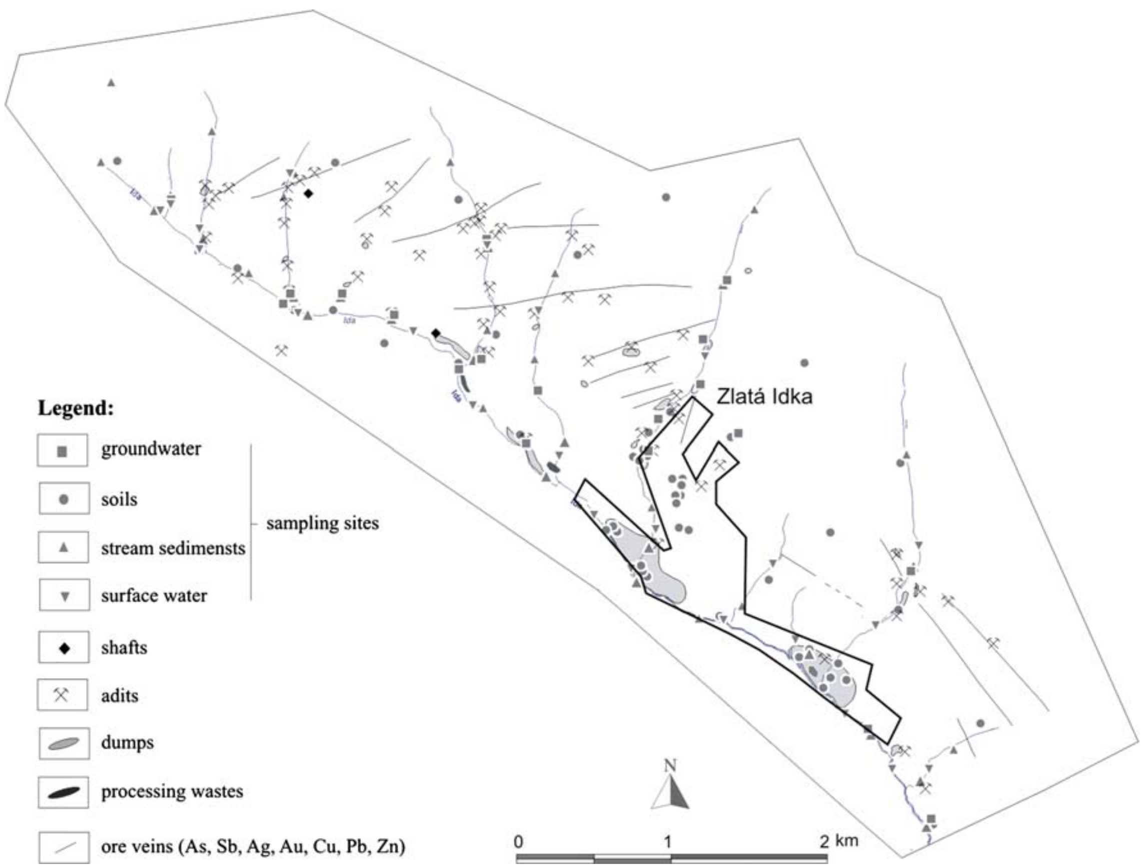
**Keywords** Mining activities · Contamination · Potential toxic elements · Environmental risk · Health risk · Slovakia

## Introduction

In Slovakia as well as in other areas in the world there exist dozens of places with strongly contaminated environment where mining activities took place over the centuries, so called abandoned mining areas. Numerous papers concerning the problems of mining tailings and waste and describing the problem of soil, groundwater and sediment contamination have been recently published (e.g. Hudson-Edwards et al. 1999; Donahue et al. 2000; Williams 2001; Aykol etal. 2003; Wennrich et al. 2004). These works deal mostly with evaluation of possible adverse effects from mining site contamination and its potential influence on quality of environment and health status of inhabitations.

The environment, in addition to the living style (the way of life and employment), genetic factors and medical care quality, is one of the most significant factors influencing population health. Its importance and impact are becoming increasingly evident in heavily polluted regions where a geographically significant illness may occur. The Spišsko-Gemerské Rudohorie Mts. is located within such a region. For this reason, this region has been chosen as a pilot area for regional geomedical research (Rapant 1998; Rapant et al. 2002). Recently, in this region, a methodical approach for analysing the geochemical environment and conducting contaminant impact assessment has been completed and verified in relation to population's health. The causal relationship between the trace elements and human health was determined based on mutual medical (Dietzová 2003) and geochemical (Cicmanová–Rapant 2002) research into one of the most geogenically contaminated villages of the region—Zlatá Idka. The very high level of environmental pollution was caused by several centuries of mining activities. The elevated environmental and health risk of the village is associated with the potentially toxic elements As and Sb which exceed the upper permissible limits in soils, stream sediments, groundwater and surface water. These limits have also been exceeded in potable groundwater that is the source of the village's water supply and in orchard and garden soils in which fruits and vegetables are grown for local consumption.

**Fig. 1** Zlatá Idka area–sampling sites and location of mining and ore treatment sites




## Area description

### Geological setting

Zlatá Idka village is situated in the eastern part of the Slovak Republic within the Spišsko-Gemerské Rudohorie Mts. (SGR). Geologically, the Zlatá Idka village area belongs to the Inner Western Carpathians and is a part of the Gemericum unit. The bedrock is made of low-metamorphosed Early Paleozoic volcano-sedimentary formations. The formations are composed of sericitic–quartz phyllites and metarhyolite tuffs (Bajaník et al. 1984). The Zlatá Idka village area represents the easternmost segment of the so-called antimony ore stripe within SGR with vein deposits of Ag–Au–Sb ores. The ore mineralization occurs prevailingly in vein structures of acid volcanoclastics and is related to the presence of younger (Permian?) granite. The total length of the ore field with its ore veins is about 9 km and the width is approximately 1 km. The individual ore veins that strike SW–NE reach lengths of 200–500 m (Fig. 1).

Their thickness varies between 0.5 and 4 m and they are developed to a maximum depth of 350 m. The ore bodies are heavily disrupted by tectonics and segmented into lenses (Rozložník 1984). The matrix of the ore is quartz-siderite ore composed almost exclusively of quartz. The accessories minerals are sulphides—mainly jamesonite, arsenopyrite, chalcopyrite, sphalerite, galenit and Sb minerals—antimonite and tetrahedrite.

The mining activity within the Zlatá Idka village area dates back from the fourteenth century. Between the fourteenth and seventeenth century, gold was exploited. In the eighteenth and nineteenth centuries, silver was mined. Gold, and later antimony, were extracted as by-products. During this time period, several smelters for gold processing were established. With a gradual exhaustionof resources, silver exploitation declined and by the end of the nineteenth century and Sb-ores were mined. The entire area of the Zlatá Idka village is characterized by a high deterioration of the bedrock due to the mining activities (galleries and shafts). Waste rock dumps are located near the adits of former mining sites. In the village, silver and antimony ores were processed within several smelters. The main ore processing method included amalgamation with mercury in rotational cylinders. Ore concentrates, chemicals, roasters, amalgam works and amalgam mud were stored at the smelter facilities. The tailings and mining waste were used to level the morphology of the village. This includes using tailings or mining waste as garden soil at residents homes. All these loads from the former mining activities in the village represent high pollution sources of the geological environment, mainly due to the potential toxic elements, dominated by As and Sb.

## Health status of residents

The Zlatá Idka village is a typical rural settlement. The population of the village averages approximately 350 inhabitants. Each house has a garden covering several acres that is used to grow vegetables and fruits for personal consumption. The majority of inhabitants are employed in Košice, a regional industrial and economic centre located 30 km to the East. Very few of the inhabitants are employed in typical village industries such as service, tourism and agriculture. A review of basic demographic and health indicators of the Zlatá Idka village inhabitants in comparison with the overall data of the Slovak population is presented in Table 1 (Letkovičová et al. 2001). The data are standardized for a time period of 5 years (1993–1997) and calculated as rates per 100,000 inhabitants. The table data clearly indicate that the majority of the health indicators exhibit distinctly more unfavorable values when compared with the average Slovak data. This trend is observable primarily in the cases of fatalities due to the neoplasms and heart attacks. As a consequence, Zlatá Idka village exhibits very unfavorable mortality indicators, such as

**Table 1** Comparison of selected calculated standardised health indicators between the Zlatá Idka village inhabitants and the average Slovak population values (years 1993–1997)

| Indicator | Slovak Republic of indicator's values distribution | | | ZLATÁ IDKA | |
|---|---|---|---|---|---|
| | Below average | Average | Above average | Value | Class |
| Gross mortality per 1,000 inhabitants | 8.2 | 9.6 | 11.2 | 14.08 | Above |
| Men gross mortality per 1,000 inhabitants | 9 | 10.6 | 12.4 | 17.19 | Above |
| Women gross mortality per 1,000 inhabitants | 7.2 | 8.7 | 10.2 | 18.16 | Above |
| Standardized mortality ratio. SMR men | 85 | 99.9 | 115 | 120.48 | Above |
| Standardized mortality ratio. SMR women | 85 | 99.9 | 115 | 92.31 | Average |
| Percentage of previous deaths inhabitants < 65 years | 23.2 | 24.9 | 28.2 | 40.00 | Above |
| Percentage of previous deaths men < 65 years | 30.9 | 32.2 | 35.8 | 5.00 | Above |
| Percentage of previous deaths women < 65 years | 14.3 | 16.4 | 19 | 30.77 | Above |
| Directly standardized mortality | 966 | 1,076.5 | 1,186 | 1,401.5 | Above |
| PYLL per 100,000 inhabitants | 3,787 | 4,267 | 4,747 | 7,418.04 | Above |
| PYLL per 100,000 men | 5,400 | 6,270 | 7,140 | 8,641.75 | Above |
| PYLL per 100,000 women | 1,892 | 2,372 | 2,852 | 12,121.75 | Above |
| Mortality by neoplasm per 100,000 inhabitants | 174 | 199.1 | 224 | 455.3 | Above |
| Mortality by leukaemia per 100,000 inhabitants | 0 | 3.5 | 6.2 | 0 | Below |
| Mortality by lungs malignant tumours per 100,000 inhabitants | 32.9 | 44.7 | 50.2 | 11.8 | Above |
| Mortality by digestive system malignant tumours per 100,000 inhabitants | 56.8 | 71.9 | 79.8 | 56.9 | Average |
| Mortality by heart attacks per 100,000 inhabitants | 182.3 | 262.3 | 2775 | 739.9 | Above |
| Percentage of spontaneous abortions from all conceptions | 5.1 | 5.9 | 6.8 | 22.22 | Above |

The below-average value represents 30th percentile of health indicator and the above-average value represents 70th percentile of health indicator for all Slovak inhabitants. The 30th–70th percentile is considered to be the health indicators average

*SMR* Standardized mortality ratio in %

gross mortality, directly standardized mortality and indicators of the previous deaths (potential years of lost life). Of the 18 presented health status indicators of the Zlatá Idka village population, in only one case, mortality by leukemia, does the indicator value exceed the mean Slovak population. In two cases, the number of deaths by diseases of digestive system and indirectly standardized women mortality, the health status indicators were comparable with the mean Slovak population.

## Materials and methods

### Geochemical research

Between 2000 and 2002, the Zlatá Idka village region soils (A–horizon), stream sediments, groundwater and surface waters were sampled and analyzed (Fig. 1). The research was realized in accordance with the International Geological Correlation Programme IGCP 360 Baseline Geochemical Mapping methods (Darnley 1994). Laboratory analyses were completed at the accredited Geoanalytical Laboratories of Geological Survey of Slovak Republic, Regional District Spišská Nová Ves (ICP, AAS, in more detail: detection limits, analytical methods and equipment (Vrana et al. 1997). Total contents of major elements, microelements, organic pollutants (EOX, PAU, PCB and OCP) were determined. Chemical analyses results (total contents) of previous geochemical studies (Geochemical Atlases and Environmental-Geochemical maps 1: 50 000, Rapant et al. 1999) were also utilized to characterise regional geochemical background. Both archive data (approximately 50%) and new analyses are used for geochemical characterization of the investigated area.

The chemical composition of groundwater, surface waters, soils and stream sediments from Zlata Idka area and its comparison to the national Slovakian average values (data from Geochemical atlas) are summarized in Table 2. Organic pollutants concentrations were primarily below the corresponding limit values of the non-polluted environment, or below analytical detection limits. The mobility and potential bioavailability of the high-risk elements, As and Sb, were determined using five-step sequential extraction (Quevalier et al. 1997; Rauret et al. 1999; Mackových et al. 2003). Table 3 presents the percentage of individual fractions—speciations for As and Sb in soils and stream sediments.

The scale of chemical elements distribution in the individual environmental compounds was wider than the range presented in Table 2. Chemical analysis of inorganic matter included 30 to 35 elements. In addition to the elements presented in Table 2, Ba, Be, Li, Sr, B, Bi, Ga, K, Mg, Na, Rb, Sn, Ti, W, Zr. Mo, Se, Sn, V, Ni, Co and other elements were also analyzed. However, their values did not exceed the limit values of environmental standards, therefore they were not evaluated. The vegetable samples were collected from

**Table 2** Concentrations range, mean concentrations, standard deviations and number of samples exceeding limit values in Zlatá Idka village with comparison Slovakian average values

| Environment | Statistics | Total element concentration (mg.kg$^{-1}$; mg.l$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | As | Cd | Cr | Cu | Hg | Pb | Sb | Zn |
| Soils | Range | 37–13 040 | 0.15–23.2 | 13–221 | 19–2 019 | 0.12–110.6 | 12.6–23 900 | 7.4–13 610 | 34–89 |
| | Mean | 892.68 | 2.79 | 69.43 | 156.66 | 3.70 | 1 283.1 | 818.75 | 66.80 |
| | SD | 2 224 | 4.27 | 35.13 | 364.13 | 16.62 | 4 325 | 2 184 | 23.23 |
| | n/ne | 46/46 | 46/30 | 30/1 | 30/16 | 45/31 | 31/20 | 46/46 | 5/0 |
| | SAD | 10.4 | 0.4 | 90 | 26 | 0.23 | 29 | 1.8 | 72 |
| Stream sediments | Range | 4.9–974 | 0.05–9.2 | 20–90 | 8–93 | 0.05–4.78 | 5–1 339 | 1.3–4 880 | 40–501 |
| | Mean | 195.06 | 2.33 | 46.40 | 29.00 | 0.534 | 175.78 | 249.70 | 141.72 |
| | SD | 250.0 | 2.32 | 14.84 | 22.01 | 1.07 | 285.9 | 798.4 | 104.11 |
| | n/ne | 38/23 | 38/24 | 32/0 | 32/9 | 38/11 | 32/11 | 38/32 | 22/7 |
| | SAD | 10.75 | 0.34 | 79.37 | 31.99 | 0.300 | 20.35 | 3.28 | 115.79 |
| Ground water | Range | 0.0005–0.24 | 0.0002–0.0007 | 0.0003–0.0069 | 0.0003–0.004 | 0.0001–0.0013 | 0.0005–0.006 | 0.0001–0.115 | 0.0005–0.082 |
| | Mean | 0.0277 | 0.0002 | 0.0010 | 0.0012 | 0.0002 | 0.0025 | 0.0207 | 0.0187 |
| | SD | 0.061 | 0.00 | 0.00 | 0.00 | 0.002 | 0.001 | 0.044 | 0.031 |
| | n/ne | 20/7 | 20/0 | 18/0 | 18/0 | 20/1 | 18/0 | 20/6 | 9/0 |
| | SAD | 0.0019 | 0.00138 | 0.00125 | 0.00189 | 0.00014 | 0.0011 | 0.0008 | 0.2672 |
| Surface waters | Range | 0.0005–0.1035 | 0.0002–0.0007 | 0.0003–0.0058 | 0.0003–0.002 | 0.0001–0.0002 | 0.0005–0.005 | 0.0002–0.143 | 0.0005–0.045 |
| | Mean | 0.0238 | 0.0004 | 0.0023 | 0.0013 | 0.0001 | 0.0014 | 0.0337 | 0.0105 |
| | SD | 0.038 | 0.001 | 0.002 | 0.00 | 0.00 | 0.00 | 0.04 | 0.016 |
| | n/ne | 23/14 | 23/0 | 20/0 | 20/0 | 23/0 | 20/0 | 23/14 | 13/0 |
| | SAD | – | – | – | – | – | – | – | – |

*SD* standard deviation, *n* number of observation, *ne* number of specimens exceeding Slovak national limit values (see–limit values in Fig. 2), *SAD* Slovak average data—arithmetic means from Geochemical atlas

**Table 3** Percentage of individual As and Sb fractions in soils and stream sediments from Zlatá Idka vil

| Element | Environment | Total contents (mg.kg$^{-1}$) | | | Fraction (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *x* | Minimum | Maximum | I | II | III | IV | V |
| As | Soil | 2,051 | 171 | 13 040 | 2.42 | 1.9 | 38.92 | 5.46 | 52.15 |
| | Stream sediment | 186 | 162 | 974 | 2.04 | 0.62 | 38.30 | 8.68 | 50.45 |
| Sb | Soil | 2,043 | 76 | 13 610 | 2.26 | 0.15 | 5.15 | 2.26 | 89.59 |
| | Stream sediment | 258.4 | 62.5 | 616 | 4.79 | 0 | 2.24 | 3.58 | 89.98 |

Data represent means from 14 soil and 9 stream sediments samples
*I* water soluble, *II* ion-exchangeable and carbonate, *III* reducible, *IV* organic-sulphide, *V* residual, *x* arithmetic mean

the most contaminated gardens and analyzed (ICP-OS, AAS) in the Geoanalytical Laboratories of GS SR, Regional District Spišská Nová Ves. The vegetable samples were digested in concentrated nitric acid at higher temperatures. The analytical results and the corresponding Slovakia national limit values are presented in Table 4.

The European Union (EU) (Anon 1994) and the Slovak Republic (Anon 1998) methodological regulations for assessment and management of risk were used for calculation and map construction of the environmental risk (ER) from the geological environment contamination. In terms of the above methodological approaches the environmental risk from individual contaminant is given by ratio between its concentration in the environment—PEC (predicted environmental concentration) and concentration, which it is supposed not to pose any threat to organisms or ecological systems—PNEC (predicted non effect concentration). Based on the above, the environmental risk from one contaminant can be expressed by numerical coefficient ($Q_{\mathrm{ER}}$) and sum $Q_{\mathrm{ER}}$ of all contaminants by index ER ($I_{\mathrm{ER}}$) according to the following formula (Rapant 2002):

$$Q_{\mathrm{ER}i} = \frac{\mathrm{AC}_i}{\mathrm{RC}_i} - 1, \quad I_{\mathrm{ER}} = \sum_{i=1}^{n} Q_{\mathrm{ER}i}$$

$Q_{\mathrm{ER}i}$: environmental risk quotient of *i*-element, which exceeds the limit (risk) concentration
$\mathrm{AC}_i$: analytical concentration of *i*-element
$\mathrm{RC}_i$: limit (risk) concentration of *i*-element
$I_{\mathrm{ER}}$: environmental risk index of specimen analysed

As a PEC concentration we used analytical data from geochemical research and as a PNEC concentration we used Slovakian limit values for non-polluted environment (limit values–see Fig. 2). In the case that the analysed contaminant element does not exceed risk (limit) concentration, the $Q_{\mathrm{ER}i}$ value of that contaminant equals 0. By the mathematical-statistical approaches commonly used in geochemistry (inverse distance and moving median) the maps of ER assessment were compiled for individual environmental compounds—particularly for groundwaters, stream sediments and soils (Rapant-Kordík 2003). By combination of the above maps, the map of ER assessment of the contamination of the geological environment in the Zlatá Idka village, was constructed.

## Epidemiological research

Arsenic and Sb concentrations were analyzed in the blood, urine, nails and hair of approximately one-third (120) of the Zlatá Idka village residents (age 10–90 years). Medical examinations of randomly selected village residents were conducted to determine the status of their general health and their dental health and to detect any pigmented alterations on skin. The human tissues and fluids samples were analyzed using graphite furnace atomic absorption spectroscopy (GFAAS) at the State Health Institute in Košice (SpectrAA Zeeman 220, Varian).

Before conducting the study, the residents of the village were informed about the objectives of the research, and the project was widely supported by the local municipal administration. However, a complete set of biological samples was not obtained for the selected population due to objective reasons, such as children's fear of puncture, lack of hair, urine during menstruation, population migration, etc., or subjective reasons, such as failure of the subjects to submit hair and nail samples. One hundred and seventeen blood samples, 116 urine samples, 71 hair samples and 73 nail samples were collected from unique villagers. The analytical results of the As and Sb analyses for the biological samples of the monitored population of the Zlatá Idka village are presented in the Table 5.

The Spearman's correlation coefficient was used to evaluate the association between the concentration of As and Sb in the biological samples and in garden soils. When several subjects resided at the same residence, the same garden soil element concentration at that home was used for all residents in the correlation analysis. The values of Spearman's correlation coefficients (R) and corresponding p-value (p) are given in the Table 6.

**Table 4** Potential toxic elements contents in the vegetables specimens from Zlatá Idka vil (fresh weight)

| Sampling site | Vegetables | As | Cd | Cr | Cu | Hg | Ni | Pb | Sb | Zn | Soil | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Sb | As |
| LV | | 0.5 | 0.1 | 0.5 | 10 | 0.05 | 0.5 | 1 | 0.3 | 10 | | |
| House Nr. 239 | Kohlrabi | 0.50 | 0.011 | 0.13 | 0.76 | 0.00048 | 0.38 | 0.2 | < 0.03 | 2.06 | 24 | 370 |
| House Nr. 56 | Carrot | 1.50 | 0.023 | 0.16 | 0.75 | 0.00107 | 0.10 | 3.2 | 0.73 | 2.94 | 4 594 | 6 356 |
| | Beetroot | 1.38 | 0.032 | < 0.05 | 0.78 | 0.00043 | < 0.05 | 0.5 | 0.43 | 3.79 | | |
| House Nr. 57 | Carrot | 0.98 | 0.015 | 0.13 | 0.98 | 0.00068 | 0.07 | 1.3 | 0.06 | 2.15 | 4 504 | 5 626 |
| | Beetroot | 0.84 | 0.009 | < 0.05 | 1.02 | 0.00043 | < 0.05 | 0.3 | 0.21 | 7.92 | | |
| House Nr. 31 | Kohlrabi | 0.54 | 0.017 | 0.07 | 0.38 | 0.00050 | < 0.05 | 0.2 | 0.17 | 1.87 | 1 651 | 1 858 |
| | Carrot | 0.73 | 0.029 | 0.12 | 1.79 | 0.00128 | 0.14 | 0.2 | 0.11 | 2.70 | | |
| | Beetroot | 1.27 | 0.215 | 0.05 | 1.80 | 0.00113 | 0.07 | 0.5 | 0.64 | 9.63 | | |
| House Nr. 157 | Kohlrabi | 0.35 | 0.010 | < 0.05 | 0.61 | 0.00040 | 0.08 | < 0.1 | 0.08 | 2.11 | 247 | 376 |
| | Carrot | 0.47 | 0.014 | 0.12 | 1.00 | 0.00090 | 0.19 | 0.2 | 0.14 | 3.35 | | |
| | Parsley | 0.74 | 0.015 | 0.09 | 1.67 | 0.00139 | 0.17 | < 0.1 | 0.14 | 4.06 | | |
| House Nr. 200 | Kohlrabi | 0.24 | 0.018 | 0.11 | 0.41 | 0.00028 | 0.07 | 0.1 | 0.03 | 2.17 | 594 | 1 040 |
| | Beetroot | 0.53 | 0.023 | 0.05 | 2.22 | 0.00037 | < 0.05 | 0.1 | 0.08 | 8.34 | | |

Data in mg kg$^{-1}$ *LV* limit value according to Anon 1996 (Food code of Slovak Republic)

The potential influence of toxic element environmental contamination on the health status of the population in the Zlatá Idka village can be determined by calculating the human health risk. The mean concentrations of soil and groundwater (potable water) were calculated to represent the human health risk of the entire village (Table 2). The calculations were completed using two methods: United States Environmental Protection Agency (U.S. EPA) Risk Assessment Method (Anon 1999) and the Slovak regulation method (Anon 2001) for potable waters (Hazard Quotient Calculation—HQ = ADD/RfD). The calculations assumed 70 years of exposure, 70 kg body weight and intake by ingestion. The mean fluids intake was estimated to be 2 l per day. Health risk level was classified in accordance with U.S. EPA approach (Anon 1999).

**Fig. 2** Environmental Risk Assessment Map of the Zlatá Idka village

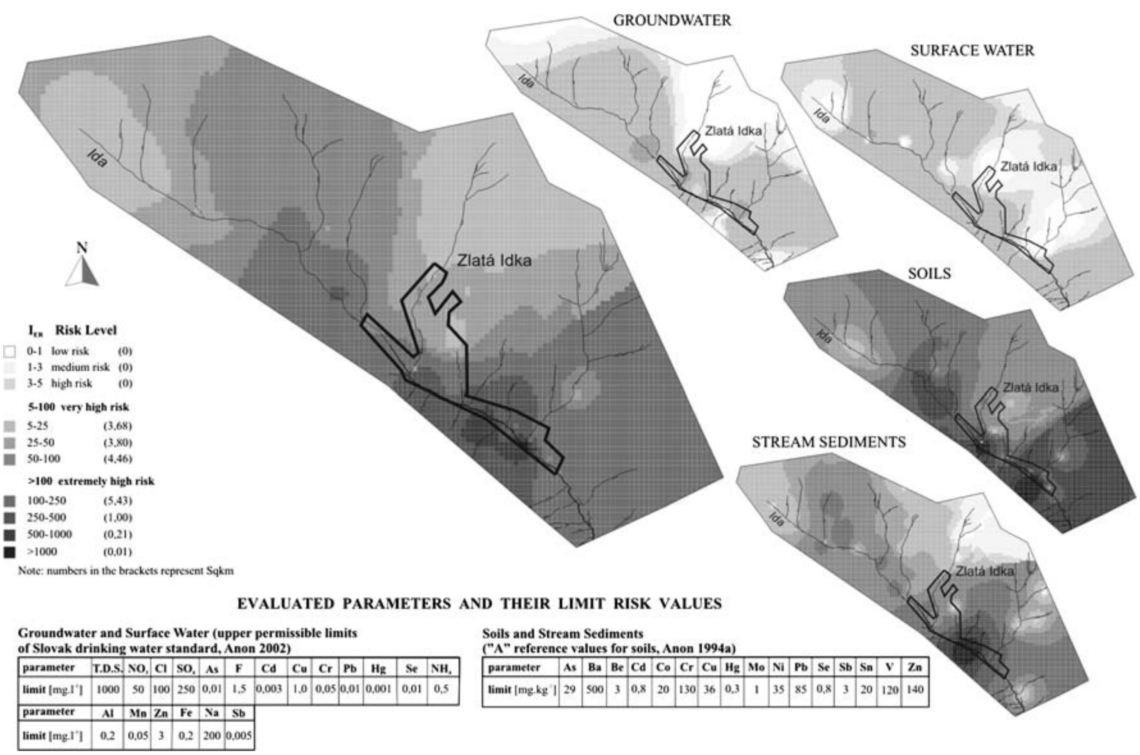


Table 5 General characteristic of the As and Sb content in human materials of the Zlatá Idka inhabitants

| Material | *n* | Mean | Median | MIN | MAX | LV | ne | TRD | TXD |
|---|---|---|---|---|---|---|---|---|---|
| As | | | | | | | | | |
| Hair | 71 | 379.1 | 255.7 | 17.3 | 3,051.5 | < 25 | 70 | [a] | [a] |
| Nail | 73 | 3,179.2 | 1,598.6 | 215.9 | 16,671 | < 1.08 | 73 | [a] | [a] |
| Urine | 116 | 15.8 | 12.0 | 0.8 | 59.2 | < 10 | 67 | 10–39 | > 40 |
| Blood | 117 | 16.3 | 7.0 | 2.3 | 125.4 | < 10 | 49 | 10–49 | > 50 |
| Sb | | | | | | | | | |
| Hair | 71 | 357.4 | 221.0 | 30.9 | 5072.8 | [a] | | [a] | [a] |
| Nail | 73 | 1,140.5 | 473.7 | 123.8 | 15225.6 | [a] | | [a] | [a] |
| Urine | 116 | 18.8 | 14.3 | 1.3 | 87.7 | < 20 | 37 | 20–34 | > 35 |
| Blood | 117 | 3.8 | 1.1 | 0.34 | 14.2 | < 10 | 12 | 10–199 | > 200 |

Data in $\mu g\ l^{-1}$ for blood and urine and $\mu g\ kg^{-1}$ for hairs and nails
*n* number of respondents examined, *LV* limit value for normal occurrence, *ne* number of specimens exceeding LV, *TRD* therapeutic dose, *TXD* toxic dose, Limit values for As—Anon 1999a for Sb—Anon 2001a
[a] In the world up to present not adopted limits are not known for us

Table 6 Spearman's correlation coefficients and confidence levels α between As and Sb contents in soils and human materials of the Zlatá Idka inhabitants

| As | | *n* | R | *p* |
|---|---|---|---|---|
| Soil | Blood | 27 | 0.031 | 0.881 |
| Soil | Urine | 36 | 0.248 | 0.188 |
| Soil | Finger nail | 24 | 0.698 | 0.0001 |
| Soil | Hair | 25 | 0.295 | 0.157 |
| Sb | | *n* | R | *p* |
| Soil | Blood | 14 | 0.241 | 0.393 |
| Soil | Urine | 22 | 0.146 | 0.534 |
| Soil | Finger nail | 25 | 0.597 | 0.001 |
| Soil | Hair | 23 | 0.091 | 0.693 |

*n* number of correlated pairs, *R* Spearman's order correlation coefficient, *p* value

Evaluative scales used for carcinogenic and chronic risk level classification are reviewed in Tables 7 and 8, respectively. The results of the health risk calculations (carcinogenic and chronic effects) for individual compounds are presented in Tables 9, and 10.

The HQ of toxic risk from water consumption greater than one (HQ > 1) is assumed to represent the presence of risk. The contaminant exposure pathway was assumed to be through ingestion. The daily water intake was assumed 2 l.

Table 7 Scale for carcinogenic risk level assessment

| Risk level | Calculated neoplasm occurrence | Neoplasm occurrence risk |
|---|---|---|
| 1 | < 1 per 1,000,000 inhabitants | Very low |
| 2 | > 1 per 1,000,000 inhabitants<br>< 1 per 100,000 inhabitants | Low |
| 3 | > 1 per 100,000 inhabitants<br>< 1 per 10,000 inhabitants | Medium |
| 4 | > 1 per 10,000 inhabitants<br>< 1 per 1,000 inhabitants | High |
| 5 | > 1 per 1,000 inhabitants | Very high |

## Results and discussion

The Zlatá Idka village Environmental Risk Assessment Map (Fig. 2) indicates high ($I_{ER} > 5$) to extremely high ($I_{ER} > 100$) environmental risk due to contamination of environmental geological media. The most intense contamination has been documented for soils and stream sediments where almost the entire Zlatá Idka village area exhibits very high ($I_{ER} > 5$) and extremely high ($I_{ER} > 100$) environmental risk. The groundwater and surface waters from the northeast (NE) part of the area studied indicate low ($I_{ER} \leq 1$) and medium ($I_{ER} < 3$) environmental risks. Figure 2 indicates that the urbanized part of the village has high to extremely high ER in the soil, groundwater, stream sediments and stream water. The observed environmental risk is associated primarily with the As and Sb concentrations. In soil, As and Sb exceed their limit values of non-polluted environment in all of the analyzed samples. In stream sediments, As concentrations exceed their limit value (29 mg/kg) in more than 60 % of samples and the Sb exceed their limit value (3 mg/kg) in more than 84%

Table 8 Scale chronic risk level assessment

| Risk level | ADD/RfD | Chronic disease occurrence risk |
|---|---|---|
| 1 | ≤ 1 | No risk |
| 2 | > 1 ≤ 5 | Low |
| 3 | > 5 ≤ 10 | Medium |
| 4 | > 10 | High |

**Table 9** Calculation of the health risk from groundwater (by ingestion) in the Zlatá Idka area

| US EPA method (Anon 1999) | | | | | | | | HQ (ADD/RfD) |
|---|---|---|---|---|---|---|---|---|
| Element | CC (mg/l) | RfD (mg/kg-day) | ADD (mg/kg-day) | ELChR | ChRL | ELCR | CRL | |
| For village's mean contents | | | | | | | | |
| As | 0.0277 | 0.0003 | 0.00079 | 3E+00 | 2 | 1.1E−03 | 5 | 2.638 |
| Cd | 0.0002 | 0.001 | 0.0000057 | 6E−03 | 1 | – | – | 0.028 |
| Cr | 0.0010 | 1.0 | 0.000029 | 3E−05 | 1 | – | – | 0.00003 |
| Pb | 0.0025 | 0.09 | 0.000071 | 8E−04 | 1 | – | – | 0.00079 |
| Hg | 0.0002 | 0.0002 | 0.0000057 | 3E−02 | 1 | – | – | 0.0285 |
| Se | 0.0005 | 0.005 | 0.000014 | 3E−03 | 1 | – | – | 0.0028 |
| Cu | 0.0012 | 0.0371 | 0.000034 | 9E−04 | 1 | – | – | 0.00119 |
| Zn | 0.0187 | 0.3 | 0.00053 | 2E−03 | 1 | – | – | 0.00177 |
| Sb | 0.0207 | 0.0004 | 0.00059 | 1E+00 | 2 | – | – | 1.475 |
| For mean contents in previously exploited water supplies (old mine effluents) | | | | | | | | |
| As | 0.0670 | 0.0003 | 0.0019 | 6E+00 | 3 | 1.8E−01 | 5 | 6.33 |
| Sb | 0.0304 | 0.0004 | 0.00087 | 2E+00 | 2 | | – | 2.175 |

*CC* contaminant concentration, *RfD* reference dose, *ADD* average daily dose, *ELChR* excess lifetime chronic (noncarcinogenic) risk, *ChRL* chronic risk level, *ELCR* excess lifetime cancer risk, *CRL* cancer risk level, *HQ* hazard quotient, *CSF* cancer slope factor for As—1.5 mg/kg-day, *HQ* Slovak regulations (Anon 2001)

**Table 10** Calculation of the health risk from soils (by ingestion) in the Zlatá Idka area according to US EPA (Anon 1999)

| Element | CC (mg/kg) | RfD (mg/kg-day) | ADD (mg/kg-day) | ELChR | ChRL | ELCR | CRL |
|---|---|---|---|---|---|---|---|
| For village's mean contents | | | | | | | |
| As | 892.69 | 0.0003 | 0.000076 | 3E−01 | 1 | 1.04E−04 | 4 |
| Cd | 2.796 | 0.001 | 0.00000024 | 2E−04 | 1 | – | – |
| Cr | 69.43 | 1.0 | 0.0000059 | 6E−06 | 1 | – | – |
| Pb | 1 283.1 | 0.09 | 0.00011 | 1E−03 | 1 | – | – |
| Hg | 3.704 | 0.0002 | 0.00000031 | 2E03 | 1 | – | – |
| Se | 0.070 | 0.005 | 0.00000006 | 1E−06 | 1 | – | – |
| Cu | 156.67 | 0.0371 | 0.000013 | 4E−04 | 1 | – | – |
| Zn | 66.80 | 0.3 | 0.0000057 | 2E−05 | 1 | – | – |
| Sb | 818.75 | 0.0004 | 0.00007 | 2E−01 | 1 | – | – |

*CC* contaminant concentration, *RfD* reference dose, *ADD* average daily dose, *ELChR* excess lifetime chronic (noncarcinogenic) risk, *ChRL* chronic risk level, *CSF* cancer slope factor, *ELCR* excess lifetime cancer risk
*CRL* cancer risk level, *CSF* cancer slope factor for As 1.5 mg/kg-day

samples. Among the analyzed elements, As and Sb exhibit the highest risk in groundwater, where approximately one-third of the samples exceed limit values. Among the other potential toxic elements within the studied area, we observed copper (Cu), mercury (Hg), lead (Pb) and cadmium (Cd) enrichment in soils and stream sediments (Table 2).

Potentially toxic metal concentrations in soil, water and sediments in the Zlatá Idka area are similar to concentrations typically observed at Abandoned Mine Sites (AMS) (Thornton 1993). At AMS, soil and stream sediment As concentrations typically exceed 10,000 mg/kg (Alloway 1990; Fillippi et al. 2004) and groundwater samples typically exceed 0.5 mg/l (Moore-Ramamoorthy 1983; Lee-Chon 2003). The elements Pb, Cd, Cu and Zn display a similar pattern as As and Sb. The contents of Sb in soil and sediments in Zlatá Idka area are one of the highest among known AMS. In comparison with Slovak average As and Sb concentrations, the average As and Sb in individual geological components (soil, water, sediments) of the Zlatá Idka area (Table 2) have enrichment factors between 50 and 500.

The potential mobility and bioavailability of two most critical elements of the area—As and Sb in soils and stream sediments, were analyzed using five-steps sequential extraction Mackových et al. (2003). The total concentration of toxic elements was divided into five fractions: 1 water soluble, 2 ion-exchangeable and carbonate, 3 reducible, 4 organic-sulphide, 5 residual (Table 3). The first two fractions represent the potentially bioavailable contents and the fifth (residual) fraction represents the stable fraction. The bioavailability of the third and fourth fractions is limited and can be affected by changes in thermodynamic conditions such as pH, temperature and oxidation-reduction potential. The residual fraction contains a high proportion of total As and Sb (Sb, 90%; As, 50%). The reducible fraction also contains a high proportion of As (38%). Relatively mobile and bioavailable first two fractions represent in average only 2, 5–4% of the total As and Sb contents. Expressed in concentration levels (mg.kg$^{-1}$) these relatively low rates generally exceed limit values given by environmental standards based on total contents. Average As and Sb concentration in the water-soluble fraction of 14 soil samples collected from the vegetable gardens in Zlatá Idka village are 49.6 and 46.2 mg/kg, respectively. The metal concentration in the water soluble fraction of soils are considered to be bioavailable and significantly exceed limit values for non-contaminated soils ('Dutch List') and exceed limit values based on total concentration in Slovakian and international standards (e.g. Anon 1994a; Fergusson et al. 1998). Residents living in Zlatá Idka village are at risk from exposure to bioavailable metals when consuming locallly grown vegetables and from total metal contents in soils they are exposed through direct ingestion, dermal contact and inhalation. Based on the results presented above, it is evident that As and Sb soil contamination in the Zlatá Idka village represents a serious environmental hazard.

The bioavailability of potentially toxic elements in soils was also examined by measuring metal concentrations in vegetable samples collected from residents gardens. Table 4 indicates that the increased concentrations of toxic elements that were found in the natural geochemical background of the Zlatá Idka village are also found in locally grown vegetables. The limit values of metals in vegetables were exceeded for several elements: As in nine of 13 vegetable samples, Sb in three of 13 samples, lead in two of 13 samples and Cd in one of 13 samples. Therefore, the uptake of toxic elements from the geological environment into the food chain has the potential to negatively effect the health of the Zlatá Idka village population because the inhabitants exclusively consume their own grown vegetables and fruits. The As concentration of vegetables grown in non-contaminated soils range between 0.001 and 0.08 mg/kg for fresh weight (FW) samples (Kabata-Pendias and Pendias 1999) and between of 0.04 and 0.08 mg/kg for dry weight (DW) samples (Fergusson 1990). Vegetables grown in contaminated soil have been found to have As concentrations that range between 0.26 and 1.1 mg/kg (FW), (Kabata-Pendias and Pendias 1999). For edible plants, the Sb content in non-contaminated areas range between 0.0002 and 0.0043 mg/kg (Fergusson 1990) and potato Sb concentrations are less than 0.002 mg/kg$^{-1}$ (DW). Comparison of metal concentrations of vegetables grown in Zlatá Idka village with literature values indicates that As and Sb contents in the vegetables from Zlatá Idka are in the upper range of metal concentrations compared to vegetables grown in areas documented to have elevated soil metal concentrations and in some cases are higher than published ranges. A number of factors influences the actual concentration of elements found in plants and the element transfer coefficients from soil to plants. In addition to the concentration of metals in soil, these factors include the type of plant, soil, plant tissue, the availability of the element in the soil, season, climatic conditions and the foliar uptake from settled aerosol (Fergusson 1990). These dependencies were not examined in this study. We restricted our observations to the potential bioavailability using five-step sequential analyses. Our sequential extraction analyses (Table 3) indicate that only about 2.5% of the total metal concentrations of As and Sb can be considered bioavailable and 90–95% of the total metal content is not bioavailable (fractions III, IV and V). This corresponds to very small soil–plant transfer coefficient values (contaminant in vegetables/contaminant in soil) for As and Sb. For As, the transfer coefficients range between 0.001 and 0.0002 for Sb, the Sb transfer coefficient range is only 0.0005–0.00005.

Correlation analysis (Table 6) results indicate that a statistically significant association was found between As and Sb contents in soil and human tissues. The highest correlation coefficient values are between soil and nails (Sb: 0.597, As: 0.698) and since the $p$ values are less than 0.05, the results are statistically significant.

Increased concentrations of As and Sb were also documented in biological materials of the Zlatá Idka village residents (Table 5). In extreme cases, the means of both analyzed elements, with the only exception of Sb content in blood, exceed the adopted naturally occurring limit values. The mean As and Sb values in urine and As in blood are within the range of therapeutic dose which can be applied for a short time period under strict medical supervision during a patient's hospitalization. The residents therapeutic As dose was exceeded in 33% of urine samples and 54% of blood samples. The therapeutic Sb dose was exceeded in 16.4% of the urine samples. Nearly all subjects extremely exceeded the As limit in hair and nails. The average Sb concentration in blood could be considered normal, with 10% of the subjects within the range of therapeutic dose. Based on the data presented above, it is apparent that the occurrence of the toxic metals in the biological materials of the Zlatá Idka village's population is atypical and undesirable. Also, comparison of As and Sb contents in human tissues and fluids of the residents of Zlatá Idka area with selected accessible information in literature (Anspaugh et al. 1971; Jervis and Tiefenbach 1974; Chattopadhyay et al. 1977; Bowen 1979; Landringan and Baker 1981; Foa et al. 1984; Ferguson 1990; Nieboer 2001), indicates that metal concentrations in the residents reach upper range of limit values characteristic for polluted areas and in the case of Sb they significantly exceed the published literature values. The data clearly indicate that the extremely elevated concentrations of elements in the environment can be transferred to biological tissues and fluids of the residents. The elements circulate in high concentrations in blood and are partially excreted via urine. However, the cumulative effect of the metals is best demonstrated by their accumulation in the hair and nails of the residents.

The elevated health risk for the residents of Zlatá Idka village from the contaminated environment is apparent from health risk calculations (Tables 9, 10). Ingestion of As from water was found to have the highest risk of neoplasms, while soil ingestion indicates a high-risk level. Table. 9, 10 indicate that a lifetime exposure (70 years) to As in drinking potable water for the residents of Zlatá Idka results in a cancer risk of 18 cases per 100 inhabitants, and from the average As content in village groundwater is 11 cases per 10,000 inhabitants The calculated risk of cancer occurrence from soil is 104 cases per 100,000 residents. The cancer risk rates are disturbing, however they are limited by the fact that the residents do not solely consume water from local supplies and they are not always present in the village and that most of the consumed food is produced from outside the village. Based on the HQ calculations, the non-acceptable HQ values (higher than 1) have been documented in water for As and Sb. Based upon the results presented above, the calculations of health risk from the geological environment contamination have proven that As and Sb contents pose a high potential health risk. It appears that As and Sb have a direct negative influence upon the health status of the Zlatá Idka village population, which is apparent in Table 1. The extreme metal concentrations of some of the samples display parameters of health indicators of Zlatá Idka inhabitants in comparison with the Slovak average data.

## Conclusion

The medical-geochemical research carried out in the Zlatá Idka village has documented increased concentrations of potential toxic elements, mainly As and Sb, in the geological environment (soils, waters and sediments). The environmental risk due to exposure of As and Sb in the geological environment was classified as very high ($I_{ER} > 5$) to extremely high ($I_{ER} > 100$). This is indicated by As and Sb concentrations in the locally grown vegetables and biological samples (blood, urine, hair and nails) of the village residents. The calculations of the health risk via ingestion of soil, water and vegetables have document a high carcinogenic risk from As with HQ values that exceed 1 for As and Sb. The increased concentrations of these metals in the village's environment poses a direct negative influence on the health status of the inhabitants. The health indicators show distinctly unfavorable values in comparison with the Slovak average parameters. To improve the health status of the inhabitants, a potable water cleaning plant (As and Sb withdrawal) was constructed. In addition, the population was informed about the high contamination of gardens soils and its unsuitability for growing plants for personal consumption. The methods used to document the association between the potentially toxic element concentrations in geological environment, food chain and biological materials of the Zlatá Idka village residents will be used for future research at the regional and national levels. The presented methodological approaches—calculations of health and environmental risk, where causality was verified by epidemiologic research, provided the opportunity for an early identification and minimization of adverse health effects from contaminated geological environment.

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