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Contamination of potentially toxic elements in streams and water sediments in the area of abandoned Pb-Zn-Cu deposits (Hrubý Jeseník, Czech Republic)

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Abstract. The deposits, located in Nová Ves and Zlaté Hory were well known and important sources of metal ore in Jesenniky region in the past. Especially the one in Nová Ves, which is recently the most important hydrothermal deposit of venous type in the whole area. The mining activity, aimed on lead and zinc minerals was practically permanent here from the middle-age to 1959. On the other hand, the site in Zlaté Hory is the most important ore deposit in Czech Silesia. The non-venous types of polymetallic, copper and gold deposits, evolved in the complex of metamorphic devon rocks are located on south and south-west directions of the area. Long and permanent mining industry caused remarkable changes in the local environment, creating mine heaps and depressions. The probability, that dump material contains potentially toxic substances that could be possibly leaked into surrounded environment is high.

This contribution presents the part of complex study results, aimed on evaluating of potential environmental impacts in above mentioned locations. It aims on contamination, caused by potentially toxic heavy metals (Pb, Zn, Cu, Ni, Fe, Mn, Co, Cd, Cr and As) at the sites, exposed to mining activity in the past. The study focus on the contamination of these sites and evaluate them as potential risk for surrounded environment.

1. Introduction

The Pb-Zn deposit in Nová Ves is the most important hydrothermal ore deposit of venous type in Jeseníky region from historical point. The mining activity was performed on eastern and south-eastern slopes of Soukenná (1026 m a. s. l.). The mining of polymetallic ores was well-known there from the Middle Age [1,2,4]. On the other hand, the mine region in Zlaté Hory is the most important ore deposit in Czech Silesia. The non-venous types of polymetallic, copper and gold deposits are situated here. Příčný hill, with altitude of 975 m a. s. l. is the highest peak of Zlatohorská highland. On this site, the rests of mining activity are still significantly present [3].

The historical dump-fields and mining enclaves in these areas could be on the present a potential risk for surrounded environment, which is a main topic of this work.

2. Materials and Methods

The main aim of the study includes the complex research of model areas (Soukenná and Příčný hill). The sampling sites were selected after the reconnaissance of terrain conditions, with the main focus on the description of interactions between the environment and mining enclaves. Figures 1 and 2 show individual localities of interest and sampling sites, marked as A (Soukenná) and B (Příčný hill).

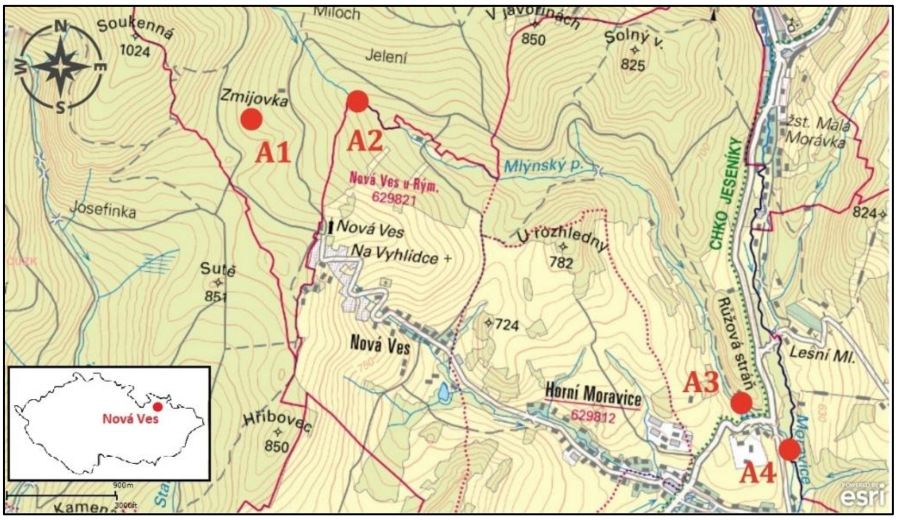

Figure 1. A1 – "Hereditary adit" (the name has just an informal character, since any project documentation, connected with this site was not available), A2 – Mlýnský brook, downstream from the junction with small creek (The creek flows from Dědičná shaft), A3 – Mlýnský brook, before reaching Moravice river, A4 – Moravice river, after the conjunction with Mlýnský brook.

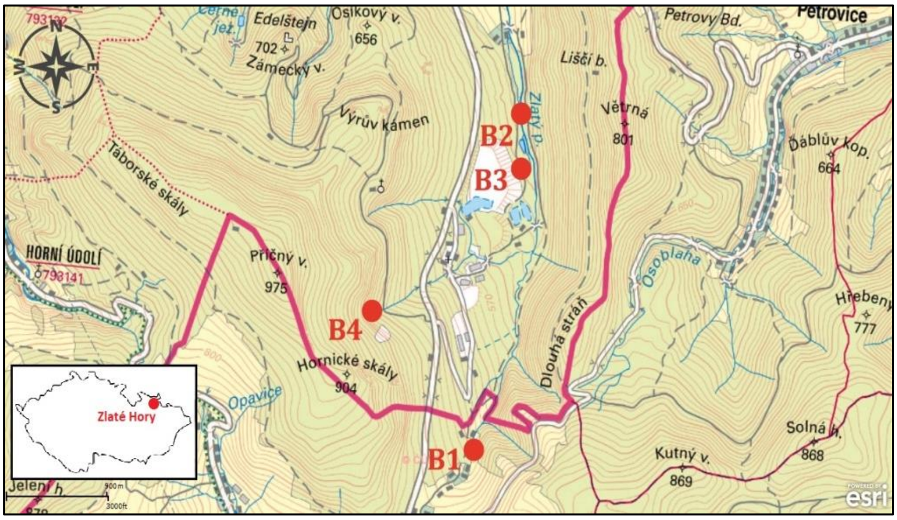

Figure 2. B1 – The spring site of Zlatý brook (in the valley under Příčný hill), B2 – Zlatý brook, B3 – small creek (confluent of Zlatý brook), B4 – Cascade of Modrý brook (this brook springs at Příčný hill).

Surface water and water sediments were regularly sampled every second month within the period of January – November 2016. The analyses of samples were performed in laboratories of VSB – Technical University in Ostrava by flame absorption, using atomic absorption spectrometer VARIAN AA 280 FS. Samples of soil sediment were dried at (105 °C) to gain equal weight and afterward grained to fine powder. After adding laboratory wax and pressing, the samples were analysed by roentgen fluorescent spectrometer WD-XRF. The final results of water were correlated with law norm ČSN 75 7221, whereas the evaluation of sediments was realised according to Czech Ministry of Agriculture, law no. 9/2009 Coll., on fertilizers, auxiliary soil substances, auxiliary plant preparations and substrates and on agrochemical testing of agricultural soils (Fertilizers Act), as amended, and other related acts.

3. Results

All the values in this chapter are representing the highest measured contents for individual areas.

After the correlation of obtained results from surface water of Soukenná (table 1) with law norm ČSN 75 7221, the high concentrations were found for Zn and Cu. The highest concentrations of Zn (0.663 mg l^{-1}) were found at sites A1 and A2, what indicates a strong water pollution. At sampling site A2, the values decreased in the second period of research indicate decreased level of water pollution. The values, indicating the strong water pollution were also recorded for Cu (0.147 mg l^{-1}) at the same sites, however only in September. During the rest of research period, the concentration of copper decreased. There was not found any significance in the contents among the other investigated elements (Pb, Fe and Mn), indicating the water pollution. The contents of Zn and Cu at sampling sites A3 and A4 were lower, following the water flow to Moravice river.

Higher concentrations of investigated elements and consequently higher pollution was detected in Příčný hill (figure 2). The highest contents of potentially toxic elements (Zn, Cu, Fe and Mn) were found at sampling site B3. The contents of Zn and Mn reached here very high levels (0.447 mg l^{-1}; 5.93 mg kg^{-1}). Those elements show high values almost in each sample. The concentrations of Cu and Fe also reached in one sample values, indicating the pollution of water (0.292 mg l^{-1}; 9.02 mg l^{-1}). The sampling point B2 indicated in some measurements high water pollution, especially for Cu; Zn and Mn (0.124 mg l^{-1}; 0.123 mg l^{-1}; 0.638 mg l^{-1}).

In the case of one specific measurement, the water indicates even a very high level of water pollution. Accordingly to results, the water indicates water pollution also at sampling sites B1 and B4. Increased contents of Cu and Zn were found in a few samples (0.041 mg l^{-1}; 0.050 mg l^{-1}), as well as Fe in one sample (0.630 mg l^{-1}). Those values indicate the moderate water pollution.

Table 1. The pollution limits for surface water, according to law norm ČSN 75 7221, defined in water quality classes (I. – V.). • I. class: without pollution • II. class: light pollution • III. class: high pollution • IV. class: strong pollution • V. class: very strong pollution. The presented values are in mgl^{-1}.

Element	I. class	II. class	III. class	IV. class	V. class
Zn	< 0.015	< 0.050	< 0.100	< 0.200	≥ 0.200
Cu	< 0.005	< 0.020	< 0.050	< 0.100	≥ 0.100
Fe	< 0.500	< 1.000	< 2.000	< 3.000	≥ 3.000
Mn	< 0.100	< 0.300	< 0.500	< 0.800	≥ 0.800
Ni			no available		

In the comparison with the pollution limits in law no. 9/2009 Coll, the results of sampling and analyses from locality Soukenná (figure 1) show, that the highest contents are detected for Zn (5,667 mg kg^{-1}) at sites A1 and A2. Describing the other important elements, that overreached the permitted limit at these sites, there could be stated, that Co, Cu, Ni and As have following contents in sediments: 39 mg kg^{-1}; 238 mg kg^{-1}; 90 mg kg^{-1}; 39 mg kg^{-1}. Sampling site A2 was also specific with high concentrations of Pb and Cd (6,338 mg kg^{-1}; 27 mg kg^{-1}). The sediment at site A3 is characterized by light increased contents of Pb and Zn (558 mg kg^{-1}; 627 mg kg^{-1}). The sediments at the site A4 satisfy the limits of potentially toxic element content (except the softly increased level of Pb). The results of element contents in sediments from locality Příčný hill (figure 2) indicate the conditions without the pollution at site B1, since there was not found any overreached concentration of toxic elements. However, the highest contents of Zn; Cu; Co; Cd; Ni and As were detected at site B3 (4,953 mg kg^{-1}; 2 562 mg kg^{-1}; 542 mg kg^{-1}; 27 mg kg^{-1}; 447 mg kg^{-1}; 40 mg kg^{-1}). The site B2 was also specific, by overreaching the limits within elements Cd; Zn; Ni and Cu (18 mg kg^{-1}; 3 659 mg kg^{-1}; 199

mg kg^{-1}; 202 mg kg^{-1}). The concentrations of Pb and Cd in mentioned sediments were increased very lightly (B3). The overview of all measured elements and concentrations is presented.

Table 2. The limit concentrations of potentially toxic elements in dried matter of surface water sediments, according to law norm no. 9/2009 Coll.

Element	Limit value
Zn	600
Ni	80
Pb	100
As	30
Cu	100
Hg	0.8
Cd	2.5
V	180
Co	30
Cr	no available

4. Discussion

According to obtained results, there can be stated, that localities of interest (Soukenná, Příčný hill) are appropriate areas for this research. The Pb-Zn deposit is located in Soukenná and the deposit of Pb-Zn and mainly Cu is located in Příčný hill.

In 2016, numerous analyses were performed (912) to investigate 10 elements in surface water and 9 elements in sediments from this site. The high concentration of Zn and Cu was found in surface water of Soukenná, what could be caused by soil conditions in local dump-field, where Cu is present in oxidation zone in the form of secondary mineral. Besides Pb and Zn, in sediments were also proved the presence of Co; Ni; Cu; Cd and As. Those elements are mostly occurred as additions in galena (PbS), sphalerite (ZnS) and pyrite (FeS_2), that are present in local dump-fields [5]. In area of Příčný hill, the samples of water and sediment contain Zn; Pb; Cu; Mn; Fe; Ni; Co and As in high concentrations. The local deposits consist mainly of sphalerite (ZnS), galena (PbS) and chalcopyrite ($CuFeS_2$) [6]. Those minerals contains the investigated elements, thus they could be the sources of contamination in water and sediments.

The high concentration of Pb could be expected only in sediments, what is caused by high accumulation factor of this metal. In water it is hard-soluble and thus cumulative – galena is the exception among sulphides, it is not a subject of chemical and biochemical oxidation [7,8,9]. Zn is obviously leached into water by erosion processes of zinc minerals and accumulates on the floor of rivers and basins, but a little amount could be soluble in water [9]. Metallic form of Cu binds in soil to organic compounds, or to clay, what results in the prior copper occurrence in upper soil layers. This causes the leaching of Cu into surrounded environment. In water, Cu could be transported for big distance from the source, but more frequently is fixed to sediment [10]. The high concentration of Fe can be explained by the high mobility of this metal. It enters a water by Fe-mineral erosion [11]. Mn occurs in water with Fe, thus the presence of Fe-minerals indicates also higher content of this element. It leach to water from soil and sediments [12,13]. The source of Ni could be natural – it can enter the water by dissolution of a bottom sediments, or could be present in a rainfall. It binds to compounds, consisting of Fe and Mn [14]. Co could be absorbed by particles of soil and sediments. In compact state, this element is stabile in water [15]. As occurs as a secondary element, especially in Cu, Ag and Pb ore minerals. It leaches to the environment by mining industry those. It effectively accumulates in river sediments [16,17]. Cd is one of the most toxic elements in nature. It is mostly present in Pb, Zn and Cu ore minerals. It is not present in the elementary form [18].

5. Conclusions

Based on the obtained results, there is no any significant evidence that the investigated sites could be refer as a risk for the environment. The study of potentially toxic elements on these areas (Soukenná and Příčný hill) is still in the progress. The further research, including analyses of soil and biomass is required, including the stabilization of sorption capacity and the sorbents. The evaluating of impact, caused by potentially toxic elements could be improved by the performing of these steps.

Acknowledgments
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