Toxic Elements in Anthropogeneous Sediments of the Banská Štiavnica/Hodruša Ore District - a Bioavailability Study

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Abstract. A bioavailability study was done in the historical Banská Štiavnica/Hodruša epithermal vein precious and base metal ore district on anthropogeneous sediment samples taken from selected sites (tailing ponds, dumps, streams, alluvial plain). 5-step sequential extraction technique was applied to determine the bioavailability of Ag, As, Ba, Bi, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Zn and Cd in 11 samples. Bond of principal and associated ore elements on the studied mineral fractions (1. water soluble, 2. ion-exchangeable and carbonate, 3. reduceable – Fe-Mn oxides, 4. sulphide and organic, 5. non soluble) and relative bioavailability was specified. According to the total and extractable contents of studied elements the association of risk elements was set for the Banská Štiavnica/Hodruša area: Pb, Zn, Cu, Ag, Mn ± Cd.

Key words: anthropogeneous sediments, historical ore district, bioavailability of toxic elements, sequential extraction.

Introduction

Historical ore districts throughout the world are often affected by the activities connected with ore mining, processing and smelting. Highly anomalous total concentrations of potentially toxic elements – major and minor ore constituents – are present in the weathered rocks, soil and sediments. However, strongly enhanced total metal contents do not necessarily endanger the environment, if they are not bioavailable (e.g. sulphide minerals encapsulated in quartz or other chemically inert minerals).

Bioavailability is the proportion of total metals, that are available for incorporation into biota (bioaccumulation – du Bray et al., 1995).

In order to estimate potential risk elements association, a bioavailability study on anthropogeneous sediments of the Banská Štiavnica/Hodruša ore district was done (Marsina et al., 2001) in the frame of the project „Metallogenic evaluation of the Slovak republic" (Lexa, 1998).

The study area

Banská Štiavnica precious and base metal ore district is one of the largest in the Carpathian arc. It is situated in the central zone of the biggest andesite stratovolcano in the whole Carpatho-Pannonian area (diameter almost 50 km), including a caldera (20 km in diameter), resurgent horst and an extensive subvolcanic intrusive complex. Extensive and long living hydrothermal systems gave rise to one of the richest mining districts in Europe. There are about 120 veins at the area of 100 km^2 bearing low sulphidation epithermal precious and base metal mineralisation. Quartz veins are up to several km long, with carbonates and K-feldspars as gangue minerals and predominantly sulphides – chalcopyrite, galena, sphalerite, pyrite (minor sulphosalts) – as ore.

Banská Štiavnica area is well known for its historical mining activities which have begun more than two thousands years ago by Celtic people. Mining spectacularly flourished in the 18th century. An estimate of the total output of mines based on mining archive data stands at 80 tons of gold and 4 000 tons of silver. Base metal production (mainly sulphides) dominated during the 20th century from deeper parts of veins. Roughly 70 000 t of Zn, 55 000 t of Pb and 8 000 t of Cu was produced (Lexa et al., 1999).

Methodology

In the first stage 16 samples of anthropogeneous sediments from selected sites (tailing ponds, dumps, streams, alluvial plain) were taken and analysed for total contents of 23 elements and compounds in the Geoanalytical laboratories of the Geological Survey of Slovak republic – Spišská Nová Ves by AAS – atomic absorption spectrometry, ICP - AES - inductively coupled plasma-atomic emission spectrometry, XRF – X-ray fluorescence spectrometry, high-temperature oxidation, gravimetry and volumetry. The fraction <0,125 mm of stream and alluvial plain sediments was analysed. In the case of tailing pond sediments and weathered material from dumps, the whole sample analysis was done.

In the second stage 5-step sequential extraction technique after Tessier et al. (1979), modified by Fiedler et. al. (1994) was used to determine the bioavailability of Ag, As, Ba, Bi, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Zn and Cd in 11 anomalous samples.

Sequential extraction techniques (speciations) help to explain the physicochemical processes of the metal fixation, mobility and transport. There are two meanings of the speciation:

1. It indicates a procedure, which distinguishes specific elemental form (monoatomic / molecular) or confi-

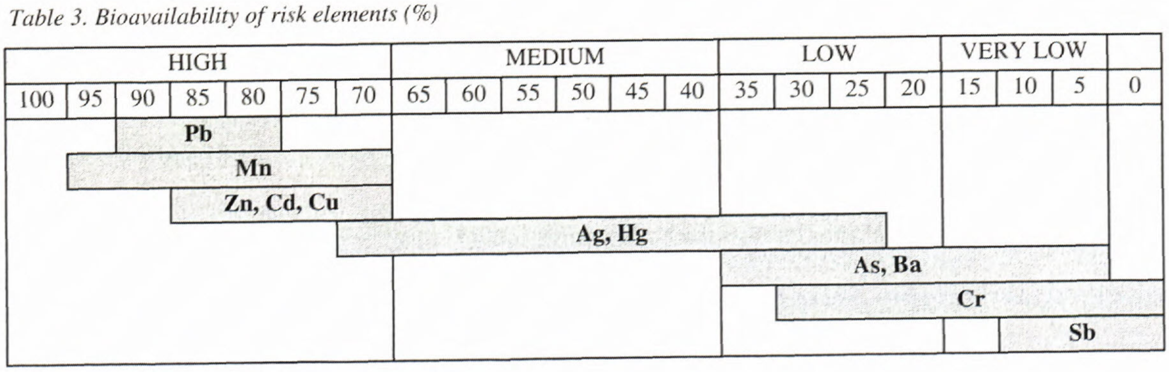
Table 1. Association of risk element contents with studied mineral fractions

SAMPLE	FRACTION	ELEMENT CONTENTS IN FRACTIONS (mg.kg-1) Ag	As	Cd	Cr	Cu	Mn	Pb	Sb	Zn
1	*1*	-0.5	0.4	-0.5	-1	-1	43	3	-0.1	4
	2	-0.5	-0.1	**3.1**	-1	28	**3 557**	2	-0.1	**443**
	3	**67.2**	**9.6**	**4.6**	-1	**80**	**13 190**	**735**	0.8	**589**
	4	1.3	0.9	0.6	-1	28	265	24	-0.1	157
	5	**24.2**	**67.9**	0.5	**17**	**42**	*0 ?*	73	**19.2**	355
2	*1*	-0.5	-0.1	-0.5	-1	-1	18	3	-0.1	4
	2	-0.5	-0.1	**13.9**	3	136	**6 826**	**900**	-0.1	**2 204**
	3	**2**	2	3	8	81	**2 054**	**616**	0.3	595
	4	1.1	3.5	**16**	2	**1 134**	299	77	-0.1	**3 088**
	5	**4.9**	**22.7**	8.9	**22**	**391**	**2 513**	273	**12.4**	**1 247**
3	*1*	-0.5	-0.1	-0.5	-1	-1	6	4	-0.1	2
	2	-0.5	-0.1	**10.9**	-1	98	**4 192**	**943**	-0.1	**1 544**
	3	**1.5**	1.4	4	4	63	**1 192**	**816**	0.3	784
	4	0.7	2	**14.8**	-1	**753**	171	190	-0.1	**2 678**
	5	**2.6**	**16.4**	7.8	**15**	**237**	839	262	**11.7**	**1 130**
4	*1*	-0.5	0.2	-0.5	-1	-1	45	-2	0.4	12
	2	-0.5	-0.1	3.8	-1	-1	614	-2	-0.1	132
	3	-0.5	-0.1	**60**	**20**	-1	**90 240**	9	3.6	**19 200**
	4	-0.5	5.4	5.7	**26**	**122**	1 865	**116**	1.2	3 042
	5	-0.5	**145**	0.8	**20**	45	2 406	42	**54.8**	4 864
5	*1*	-0.5	0.1	-0.5	-1	5	56	13	-0.1	45
	2	-0.5	-0.1	**1.5**	-1	79	245	**439**	-0.1	**160**
	3	**10.8**	6.2	0.7	-1	**134**	**1 619**	**1 564**	1.1	**300**
	4	1.2	0.3	-0.5	-1	58	92	94	-0.1	121
	5	**6**	**47.9**	0.4	**29**	**174**	**898**	**1 020**	**16.7**	**229**
6	*1*	-0.5	-0.1	-0.5	-1	5	20	33	-0.5	16
	2	-0.5	0.1	14.4	-1	221	**868**	**4 470**	0.6	2 484
	3	**12.7**	4.5	13.7	-1	761	**675**	**8 630**	0.9	2 518
	4	0.5	2.4	**41.9**	-1	**11 260**	72	2 476	-0.1	**8 660**
	5	**38.6**	**55.5**	**50.9**	**13**	**7 967**	355	**7 577**	**12.3**	**10 260**

Table 2. Association of risk elements with studied mineral fractions:

1. Water soluble fraction:	None
2. Ion-exchangeable and carbonate fraction	**Mn, Pb, Zn, Cd** (Cu)
3. Reduceable fraction (metals associated with Fe-Mn oxides)	**Ag, Mn, Pb, Zn, Bi** (Cu, Cd, As)
4. Sulphide and organic fraction	**Cu, Zn Cd** (Ag, Pb, As, Bi)
5. Non soluble fraction (metals fixed in crystalline lattices)	**Sb, Cr**

Table 3. Bioavailability of risk elements (%)



guration of the element. Distinguished forms represent various chemical individuals (ions, complexes, organometallic compounds etc.)

2. It determines individual elemental forms differing in physicochemical conditions as solubility and extractibility by various solvents. Sum of the element contents extracted in single solvents represent the total content of the element in the sample.

5-step sequential extraction technique after Tessier et al. (1979), modified by Fiedler et. al. (1994) was applied in our study. Following elemental forms/fractions were determined and solvents used:

1. ***water soluble fraction*** – elements predominantly in form of inorganic salts.

distilled water

2. ***ion-exchangeable and carbonate fraction*** – elements mainly adsorbed on inorganic salts and carbonates, released into the water, if neutral conditions change into slightly acid conditions.

0,11 M acetic acid

3. ***reduceable fraction*** - metals associated with Fe-Mn oxides, which are thermodynamically unstable and release elements into the water by the redox potential changes.

0,1 M hydroxylamine hydrochloride

4. ***organic and sulphide fraction*** – elements bound in organic matter and sulphides. They are released into the water as a consequence of the organic matter oxidation and degradation / decomposition of the sulphides by the changing physicochemical conditions.

8,8 M hydrogen peroxide
1M ammonium acetate

5. ***non soluble fraction*** - elements fixed in crystalline lattices of primary and secondary minerals

mixture of HNO_3, HF and $HClO_3$

Certified reference material of the stream sediment CRM 601 was used for the quality control testing by comparing measured and certified values. The above material was prepared by the European commission for reference material (BCR).

Discussion of the results

The results of the bioavailability study are discussed on the basis of 6 samples representing various contamination sources and their pathways. Association of risk element contents with studied mineral fractions is shown in Table 1.

Sample 1: sediment from tailing pond „Suchý tajch" with material from earlier precious metal ore processing with the highly anomalous contents of Ag, Mn and anomalous content of Pb and Zn, associated with fractions *3 (Fe-Mn oxides)* and 2 (carbonates). Sulphides do not play an important role in this type of sediments.

Sample 2, 3: sediments from tailing ponds „Lintich" and „7 žien" with material from later base metal ore processing with the highly anomalous contents of Cu, Cd, Mn, Pb, Zn, associated with fractions *4 (sulphides and organics), 2 (carbonates)* and 3 (Fe-Mn oxides). In the contrary to the sample 1 sulphides are the dominant mineral fraction in these sediments.

Sample 4: stream sediment from outflow of the main dewatering gallery „NOŠ" with material from the Banska Štiavnica/Hodruša ore district with the highly anomalous contents of As, Cd, Sb, Mn, Zn associated with fractions *3 (Fe-Mn oxides)* and *4 (sulphides and organics).* Several km transport of the material caused dissolving of carbonates and higher contents of Zn Cd, Mn (due to better mobility) compared to Cu, Pb.

Sample 5: alluvial plain sediment from the river Štiavnica watershed which drains the ore district with the highly anomalous contents of Ag, Pb, Cu and anomalous content of Zn, associated with fractions *3 (Fe-Mn oxides),* 2 (carbonates) and 4 (sulphides and organics) represent the „classical " principal ore element association.

Sample 6: weathered mineralised rock debris from the dump near the „Nová šachta" (New shaft) with ore material from later base metal ore processing with the highly anomalous contents of Ag, Bi (66.8 $mg.kg^{-1}$), Cd, Cu, Pb, Zn and anomalous content of As, associated with fractions *3 (Fe-Mn oxides), 4 (sulphides and organics)* and 2 (carbonates) represent the base metal ore enriched in Cu (copper is characteristic for the deeper parts of the ore veins), Ag and Bi (present in sulphosalts, Kovalenker et al., 1991).

Association of risk elements with studied mineral fractions summarises Table 2, bioavailability of risk elements in the Banská Štiavnica/Hodruša ore district is shown in Table 3.

Conclusion

The results show the variability of the anomalous element distribution in anthropogeneous sediments of the researched area.

According to the total and extractable contents of studied elements the following association of risk elements was set for the Banská Štiavnica/Hodruša area:

Pb, Zn, Cu, Ag, Mn ± Cd

The number of studied samples allowed us to point only on some contamination sources of the ore district. It is obvious, that quantitative risk assessment at the Banská Štiavnica/Hodruša ore district will require additional exact data on bioavailability of the risk elements in various media.

The applied 5-step sequential extraction technique has shown good results and could be recommended for further research.

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