Mineralogical and Geochemical Research in a Contaminated Environment near the Abandoned Poproč Sb Deposit (Slovakia)

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Abstract
The area surrounding the abandoned Poproč antimony deposit in Slovakia contains high concentrations of toxic contaminants, mainly sulfide-related minerals. Pollution resulting from historic mining was observed in the area adjacent to the Agnes mine adit, with Sb concentrations ranging from 4 700 – 10 000 $mg.kg^{-1}$; the maximum As concentration in soil samples was 56 900 $mg.kg^{-1}$. High levels of Sb, As, and other elements in the investigated area were associated with the locations of long-term outflows. This study focused on the migration of the toxic elements in environment, their binding on Fe-oxyhydroxides or other natural sorbents, and mechanisms by which these contaminants may enter the food chain.

Key words: abandoned Sb deposit, toxic contaminants, mobility, Slovakia

Introduction
The Poproč region has long been recognized as an important source of antimony in Europe; mining began in the 17th century and finished in the 20th century (Chovan et al. 1994). The abandoned Poproč Sb deposit is situated in the SE part of the Spišsko-gemerské Rudohorie Mts. (Slovakia). Geologically, the area consists of Paleozoic metamorphic rock complexes – graphitic and sericitic phyllites, metapsammites and metarhyolitic tuffs and granites. The Sb mineralization occurs as quartz-carbonate veinlets and impregnation in the host rocks. Antimony is the main ore mineral; others are pyrite, arsenopyrite, and various sulphides of Pb-Zn-Cu. The main non-metallic vein minerals are quartz, carbonates, tourmalines, albites, sericites, and chlorites. Extensive contamination related to the Sb deposit in Malé Karpaty Mts. was described by Veselský et al. (2003) and studied by Chovan et al. (2006). The study of arsenic and antimony bindings to ferrous ochres (Trtíková et al. 1999, Majzlan et al. 2007), concentrations and distribution of As and Sb in oxidation rims of destabilized sulphides of impoundment sediment, and experimental investigation of geochemical barrier media were important (Lalinská and Šottník 2007). Andráš et al. (2004) conducted investigations of biological and chemical oxidation. Rapid dissolution of Sb from impoundment sediment was studied at the nearby Dúbrava deposit by Maruška et al. (2000). The significant influence of long term mining activity and the potential effects of abandoned deposits on population health quality in the Zlatá Idka community (Spišsko-gemerské Rudohorie Mts.) were described by Rapant et al. (2007). Finally, a study of the Poproč area and its surroundings reported highly contaminated surface waters, soils, and stream sediments (Kaličiaková et al. 1996). The As in soil samples exceeded class C standards of the Ministry of Agriculture of the Slovak Republic No. 531/1994-540 by 400 times, all stream sediment samples exceeded class C As and Sb limits, and concentrations of Sb were 100 times higher than sanitary regulatory limits for drinking water (Government Directive No. 354/2006).

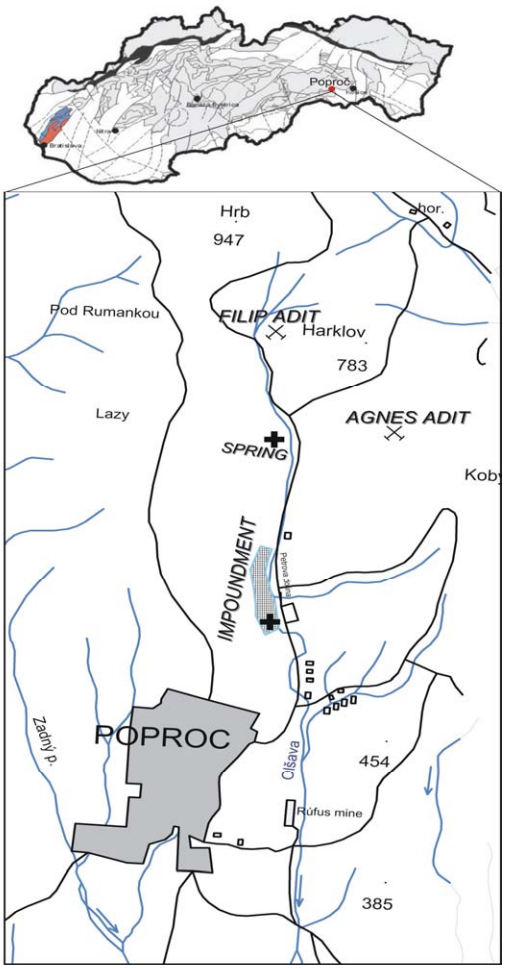
Methods
Samples were collected of geological materials and natural media (groundwater, surface waters, stream sediments, soils and ochres) and selected plant species (roots and shoots) in the field area shown in **Fig 1.** Samples were preferentially collected in areas near potential local contamination sources (outflow from mines, tailings ponds and theirs surroundings, and mining wastes). Samples of soils, stream sediments, impoundment material, and plant tissues were dried and homogenized under laboratory conditions by standard procedure. Special techniques were needed to selectively dissolve the solid ochre samples from the Agnes and Filip adits outflow. Selective dissolution analysis is based on the different dissolution rates of various mineral phases and compounds (Carlson and Schwertmann

1981). Based on the Fe_{OX}/Fe_{DT} ratio in analyzed ochre samples, it was possible to evaluate the relative crystallinity of the Fe^{III} oxides and oxyhydroxides. Samples were dissolved by three different methods:

i. dissolution of Fe oxides and oxyhydroxides in hydrochloric acid
ii. dissolution of Fe oxides and oxyhydroxides in dithionate-citronate-bicarbonate (DCB)
iii. dissolution of Fe oxides and oxyhydroxides in ammonium acetate

Samples of soils, sediments, waters, impoundment material, ochre, and plant tissues were analyzed in the geochemical laboratories of the State Geological Survey of the Slovak Republic. Selected chemical parameters (As, Sb, Zn, Cu, Pb, Fe, Al, Mn) were analyzed by atomic absorption spectrometry in the <0.125 mm mesh size fraction.

Figure 1 *Schematic map of investigated area*



Results and Discussion

Chemical analyses of the various environmental media sampled confirm the previous field investigation findings that the area surrounding the abandoned Poproč Sb deposit is highly polluted.

Results of selected chemical analysis data for soils are shown in **table 1**. The most important contaminants in the area are antimony and arsenic; their association is in accordance with the fact that the two elements are chemically similar (WHO 1996, Filella et al. 2002). Their toxicology is also similar, and they are both carcinogenic (e.g. Jain and Ali 2000, Uexküll et al. 2005). Extremely high concentrations of Sb were recorded in the area surrounding the Agnes adit, with values ranging from 4 700 $mg.kg^{-1}$ to 10 000 $mg.kg^{-1}$. The highest As level measured 56 900 $mg.kg^{-1}$. These extreme Sb and As concentrations in soils near the Agnes adit are both a result of recent contamination. A 2 m thick layer of ochre precipitates was observed over a 200 m^2 area coming from the Agnes adit until the

year 2004 when stable conditions were provided. The ochre precipitate, which potentially contained similarly high concentrations of toxic elements were in the past mechanically removed by water outflowing from the Agnes adit, discharging to the catchment of the Olšava River. Chemical analysis of ochre samples collected from the Agnes adit and dissolved in HCl show high content of As and Sb in ochre material (**tab 2**); these toxic elements have long contaminated the surface water and stream sediments of the Olšava and Bodva Rivers.

Antimony, analogous to arsenic, has an ability to bind to plant tissues and can be phytotoxic (Foy et al. 1987). Considering the often-described mobility of these elements, their biosorption into organisms or biovolatilization in organisms (e.g. Flynn et al., 2003, Čerňanský et al., 2007) is important. Plant tissues were sampled in the area of interest and high concentrations of As and Sb were detected in selected plant species. Near the Agnes adit, the maximum As and Sb values of plant tissue were, respectively, 45,8 $mg.kg^{-1}$ and 1,9 $mg.kg^{-1}$ (dry weight).

Table 1 *Selected chemical parameters of soil samples from surroundings of Sb deposit Poproč*

Sample identification	mg.kg^{-1}					%			
	As	**Sb**	**Pb**	**Zn**	**Cu**	**Fe**	**Mn**	**Al**	**$(SO_4)^{2-}$**
Adit Filip	72	3720	274	122	54	4.23	0.174	7.97	0.13
Adit Filip-subs	298	86230	1723	352	155	4.29	0.106	6.92	0.11
Adit Agnes OU	11060	9254	25	135	48	17.0	0.262	4.73	0.14
Adit Agnes OA1	26380	4697	<5	1656	34	30.8	0.073	1.44	0.27
Adit Agnes OA2	56900	9993	<5	3272	52	35.6	0.020	0.07	0.24
Impoundment	1898	4747	351	71	15	0.92	<0.001	5.06	0.27
Impoundment (cover)	2800	4190	352	60	13	5.67	0.002	3.38	1.97

Table 2 *Ochre samples chemical analysis ($mg.kg^{-1}$)*

Chemical parameter	**Spring 300 m NW from adit Agnes**	**adit Agnes**	Chemical parameter	**Spring 300 m NW from adit Agnes**	**adit Agnes**
Fe	106 000	336 000	**Na**	8 540	1 360
As	8 600	34 000	**K**	1 720	420
Sb	5 200	6 100	**Ca**	10 600	2 460
Pb	104	97	**Mg**	6 070	830
Zn	160	831	**Al**	7 660	2 560
Cu	44	0	**S**	23 300	5 950
Mn	1 580	210			
Hg	0.4	1			
Cd	0	12			

Conclusions

The results of preliminary mineralogical and geochemical sampling near the abandoned Poproč Sb deposit reveal significant contamination of the surrounding environment. The most important toxic elements in the study area are As and Sb. High concentration levels measured in adit estuaries could be caused by inadequate mine closure/rehabilitation. Deposition of highly contaminated ochre precipitates near the Agnes adit and outflow are indicative of contaminated mine waters; inadequate recultivation has caused ochre precipitates (containing AS and Sb) to be resuspended and to flow into the Olšava river catchment. The next step should be research into geochemical and mineralogical mobility and the bioavailability of the main contaminants in the environmental media.

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