

ENVIRONMENTAL POLLUTION BY MINING ACTIVITIES – A CASE STUDY IN THE CRIȘ ALB VALLEY, WESTERN CARPATHIANS, ROMANIA

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Abstract. In the region of the Apuseni Mountains, a part of the Western Carpathians in Romania, mining activities have a long-standing tradition. But they also resulted in an apparent major acid mine drainage combined with a heavy metal pollution in surface waters. The acid mine drainage (AMD) production is due to enhanced pyrite oxidation in ore pits and deposits of ore.

The Criș Alb catchment covers an area of 4200 km². The mining activities are concentrated in the upper basin, in which an open pit and several abandoned under ground mines are producing AMD that is discharged untreated into tributaries. Solid wastes of the mineral processing plants were deposited in several dumps and tailings dams.

During several field campaigns, water was collected mainly from surface waters, dug-wells, piezometers and impoundments. Solid samples were taken from river sediments and of the biggest tailings dams.

Inputs of tributaries polluted with acid mine waters only slightly increase concentration of heavy metals and sulphate in the upper Criș Alb River. Water in the main river water remains neutral. These results contrast with those found in the neighbouring Certej catchment, where mining activities result in a strong acidic and heavy metal pollution. Metal concentrations measured at the upper station and in tributaries upstream mining areas reflect roughly background values. They fall in the range of the environmental quality standards proposed by the EU Water Framework Directive. Outflow of the big tailings dams and tributaries downstream old mines exhibit the first sign of acid mine drainage production. However, most heavy metal concentrations fall nearly to background values. These waters still have an acid neutralizing capacity. Metal concentrations in sediments taken in the active river channel display a decreasing trend downstream. The sequential extraction essay demonstrates that the mineralogy of the primary material deposited and the pH will be changed when waste ore deposits react with oxygen diffusing into the tailings.

In general, Criș Alb river water exhibits only a small impact by mining activities, although hot spots of acidic mine waters inputs exist in the upper valley and heavy metals in particles accumulate in river sediments.

The results of this study can be used by various stakeholders, mainly the mining companies, local municipalities and environmental protection county authority bodies in order to integrate them in their post-mining measures, making them aware by the potential long-term impact of mining on the environment and human health.

Key words: Mining impact, water quality, heavy metals, acid mine drainage

INTRODUCTION

Metal Mining is an essential human activity to provide rough materials for our society. Although the ore extraction itself directly affects a relatively limited area of terrestrial land, its impacts on the environment, as well as on public health, may be found at greater distances from the source and for a

long time period. Mining activities also influence strongly the economic wealth of the area and act on its social life. Both the environmental and socio-economic impacts of mining are well documented in numerous areas worldwide, nowadays (Boni *et al.* 1999, Balistrieri *et al.* 1999, Hudson-Edwards *et al.* 1999, Dold and Fontboté 2002, Espana *et al.* 2005).

In terms of water contamination stemming from metal mining, acid mine drainage (AMD) represents the key impact in areas exhibiting sulfide-bearing ore deposits. AMD is predominantly caused by the abiotic and microbial mediated oxidation of pyrite associated with ores extracted (Edwards *et al.* 2000, Dold and Spangenberg 2005). Water draining from mine working, such as adits, open pits, tailings impoundments, tailings and mine waste deposits, may turn acidic, if the acid neutralizing capacity in the water or in the solid deposits is not sufficient. AMD is characterised by low pH-values, high concentrations of dissolved heavy metals, non-metals and sulfate. Large waste dumps and tailings containing a surplus of pyrite tend to produce AMD within a period of hundreds of years, depending on specific environmental factors, such as the mineralogy and hydrology in the deposit and the climatological condition. In principle, it is possible to estimate the AMD production potential by stoichiometric calculations of a given waste ore dump by taking the pyrite oxidation as acid producer and the weathering reactions of carbonates and silicates as acid neutralizer. In the literature, several such acid-base accounting methods exist (Jambor 2003), but there are all approximations since the contributions of silicate weathering reactions are difficult to determine.

Natural waters heavily charged with AMD exhibit toxic concentrations of heavy metals, which will impair the aquatic life (Soucek *et al.* 2000) and groundwater fed by rivers. Recently, the European Union has set environmental quality standards (EQS) for dissolved concentrations of cadmium, lead and nickel in surface waters (EC 2006). Those of chromium, copper, and zinc remain in discussion (Crane *et al.* 2007). Waters draining mines also carry suspended solids, undissolved minerals and precipitates of iron and aluminium, to which dissolved metals will sorb when unpolluted tributaries gradually neutralize the acidic river water. Surface runoffs from bare impoundments and waste dumps also contribute to the load of suspended matter. All these particles containing harmful metals are transported downstream and may accumulate in the river channel or disperse to floodplains depending on the flow regime (Miller 1997, Hudson-Edwards 2003, Förstner 2004). In these fluvial deposits metals can be stored for tens or hundreds of years, a real long-term environmental problem (Macklin 1996). Tailings failure, when suddenly huge amounts of fine-grained materials are sliding downwards from unconsolidated dams, may represent a high risk for settlements and people living nearby. These slurries will also affect river channels and floodplains (Macklin *et al.* 2006).

In Romania, a country with a long tradition of mining, investigations on mining impacts just have evolved recently. West-European research groups in collaboration with Romanian institutes have undertaken studies concerning water pollution caused by ore extraction activities (Fornay *et al.*, 2000, Milu *et al.*, 2002, Bird *et al.*, 2003, Macklin *et al.*, 2003, Bird *et al.*, 2005). There are also a number of studies investigating the economic impact of restructuring industrialized areas due to

the political turn in the nineties of the last century (Chiribuca *et al.*, 2000 and Popescu *et al.*, 2003a).

The objective of the present study was to investigate and evaluate the water pollution in the mining impacted upper Criş Alb catchment and to assess its effect to the entire Romanian Criş Alb basin. This work presents a complementary study to that performed in the neighbouring heavily impacted Certej River catchment (Zobrist *et al.*, 2008), where another survey addressing the socio-economic issue of mining was carried out (Dogaru *et al.*, 2008). Results obtained from both studies are incorporated into a proposition for mitigation of mining activities related impacts. The project also exhibits a research capacity development aspect and a know-how transfer to the Romanian participants.

STUDY AREA

The Criş Alb River has its sources in the Metaliferi Mountains belonging to the Southern Apuseni Mountains in the Western Carpathians and flows towards the west into Tiza River in Hungary. The basin covers an area of 4200 km² (Fig. 1 and 2). The medium river discharge in the upper Criş Alb is about 1.6 m³sec⁻¹, increasing to 24 m³sec⁻¹, near the Hungarian border. About 123 000 inhabitants are living in the basin, in which mining was by far the most important economic sector. It was flourishing during the seventies to the nineties in the last century.

Ore deposits in the Criş Alb basin are situated in the upper basin. Geologically, they are associated with the Neogene volcanism, with a large mineralisation in the south-western part. The main exploitation for gold-silver ores is located in the Barza area, for copper in the Valea Morii (Arsului) open pit (a porphyry-copper system) (Fig. 2) and for lead and zinc, in the Brusturi area (Fig. 1). The exploitation was undertaken until 2006 in a dense network of underground galleries presently abandoned. These galleries still provide AMD that flow into Criş Alb River or its tributaries. Smaller mine operation sites are situated in the southern side valleys (Ruda-Brad) (Fig. 2) and were closed several decades ago. The ore mineralogical composition in the Barza area is represented mainly by native gold, pyrite, sphalerite, galena, chalcopyrite and native arsenic. Native gold in visible form is associated with calcite and polymetallic sulfides. In the Valea Morii area, the main mineralogical composition causes a grey-greenish rock colour and is represented by chalcopyrite, pyrite and magnetite (Popescu 2003b). Ore minerals were enriched by flotation in a processing plant near Brad and its waste was transported to tailings dams. The Ribiţa and Rovina tailings impoundment, the two largest one, contain each around 9 million m³ of fine-grained waste ores embodying the acidic water producing mineral pyrite. A volume of around 900 000 m³ is located in several waste dumps south-east of Ruda-Brad town, another source of metals for local rivers.

METHODS

SAMPLING

From 2005 to 2007, an interdisciplinary-team of geographers and chemists performed four field-campaigns, focusing on four different goals to get a broader view on the mining impact related questions. Two sampling campaigns were accomplished with Swiss partners of the project, also taking samples at key locations for the analytical quality control or special analyses.

Waters in the main river and its tributaries, acid mine inputs and ground water pumped from piezometers in the Rovina tailings, were collected 1 to 3 times at locations displayed in Fig. 1 and 2 and characterised in Table 1, during low and medium water discharge condition. pH was measured *in situ* by a calibrated pH meter (WTW Multiline P4 with SenTix electrode) and a sample for heavy metals was filtered through 0.45 µm cellulose acetate filter by using a syringe. Samples for filtered and total heavy metals were filled in polyethylene bottles containing the necessary volume of nitric acid suprapure to get a pH of 2. A third sample was taken for analysing the major ions. At selected sites, the technique of diffuse gradient in thin film (DGT) was applied for measuring pure dissolved heavy metals (Odzak *et al.*, 2002). A DGT deployment unit (DGT Research LTD Lanchester, GB) consists of two layers, the inner one is a resin Chelex-100, 4 mm thick, the outer one is a diffusive gel DGT crosslinker with open pore (allylglycidylagarose) 8 mm thick and a membrane filter 0.145 mm thick closes on top (Zhang and Davison 1995). DGT devices were placed directly in the river and retrieved after two days. Water samples from the dug wells, which provide the drinking water for one or several households, were taken with the vessel and cord used by the people to get their water. They were collected once in wells situated in a distance from 5 to 20 m polluted tributaries. All equipments for heavy metals sampling were cleaned with nitric acid in the lab and transported separately in clean plastic bags (Benoit 1994).

Solid tailings samples were taken by a polyethylene shovel at different spots of the main tailings dam. River sediment samples were collected from bar surfaces using a stainless steel shovel and stored in paper bags. At each station, 10 sub samples on a radius of 10 m were taken to yield a collective sample of 200 g.

ANALYSES

Low concentration samples of heavy metal were enriched by elution of the sorbed diethyldithiocarbamate metal complex from a phenyl resin sorbent (Eawag method modified from King *et al.*, 1985, Selina *et al.*, 2006). Heavy metal, arsenic and major base cations in water samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) according to ISO 11885. Recovery rates of extraction varied between 87 and 101 %.

The DGT resin gel layers were removed from the holders by pre-cleaned plastic tools in a clean box (SKANAIR) and transferred to 12-mL pre-cleaned tubes, containing 2 mL of 1M nitric acid (Merck, Suprapur). Heavy metals eluted after 24 h were analysed by inductively coupled plasma-optical mass spectrometry (ICP-MS) (Perkin-Elmer ELAN DRC II). Equations used to calculate the metal concentration in the river from the mass of ions accumulated are based on Fick's first law of diffusion (Zhang and Davison 1995).

Chloride, sulfate and nitrate were determined by ion-chromatography (Metrohm) according to ISO 10304-1. Alkalinity was obtained by titration to pH 4.5 by 0.1 M hydrochloric acid, acidity was titrated with 0.1 M sodium hydroxide to pH 4 (Totsche *et al.*, 2006). For comparison, selected samples were analysed at Eawag, where ICP-MS was used for heavy metals. The other elements were determined by the methods cited above. In addition, the plausibility of the analytical data was checked, including the ion balance for major anions.

A time dependent sequential extraction procedure was applied to acquire information regarding the speciation of minerals (Dold 2003), especially iron(III)-oxyhydroxides in tailings profile samples and metals bound to minerals, which could be liberated from reactive tailings. A 1 g sample was first extracted with 50 ml deionised water for 1 h to yield the water-soluble fraction E1; then with 1M ammonium-acetate, pH 4.5 for 2 h (exchangeable fraction E2); afterwards with 0.2 M NH₄-oxalate, pH 3.0 in the dark for 1 h (ferric-oxyhydroxides fraction E3) and finally, with 0.2 M NH₄-oxalate, pH 3.0, heat in water bath 80 °C for 3 h (ferric-oxides fraction E4). Dissolution-time curves were developed by taking 10 mL sub-samples with syringes at several intervals from 5 to 240 minutes. Metals from extracts were filtered (0.45 µm) and measured using the ICP-MS. The percentage of the extracted metal content was calculated considering the aqua regia extractable metal content as 100%.

Dried river sediments were sieved in the lab and the fraction <100 µm was analysed for heavy metals by ICP-OES after digestion with nitric acid according to ISO 15587-2. Dried solid samples gained from the Ribiţa tailings were milled to produce a grain size fraction <70 µm. They were analyzed by X-ray fluorescence and X-ray diffraction at the mineralogical lab of the University Lausanne.

RESULTS AND DISCUSSION

RIVER AND GROUNDWATER

Values reported for heavy metals as well as for the major anions at the headwater station of Criş Alb, R1, and non-mining tributaries, VA2 and B1, represent background concentrations (Table 2). They fall in the scope that can be expected from the mineralogical and geological settings of the region. Heavy metals concentrations are about in the range of the European quality standards for rivers (Table 3).

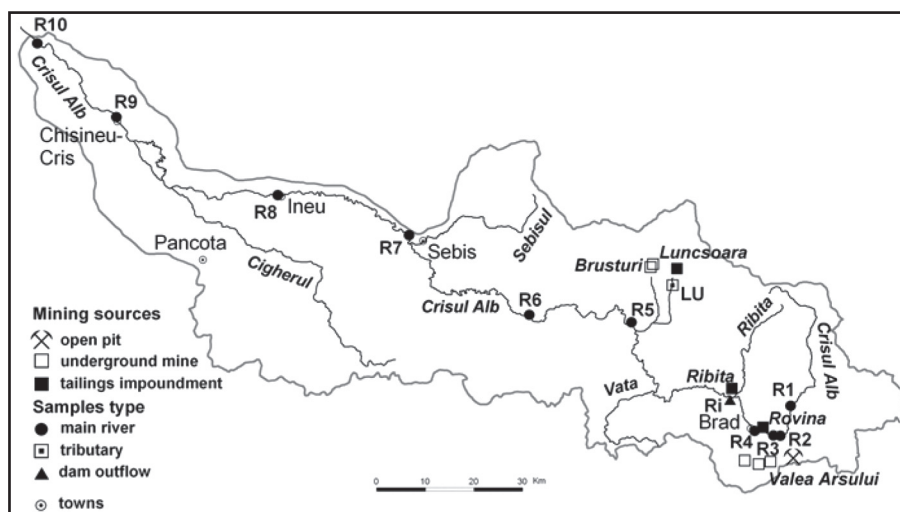


Fig. 1 Crișul Alb river basin - sampling stations on the main river, mining sources and locations

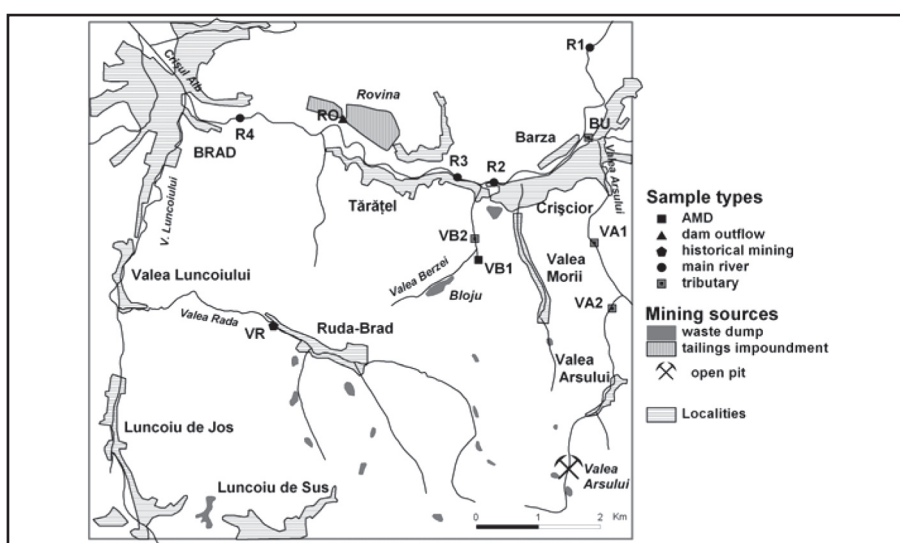


Fig. 2 Upper Crișul Alb River basin - sampling stations, mining sources and locations

Table 1 Description of water sampling sites

Designation of sites in Figs 1 and 2	Description
R1 to R10	Main river Criș Alb
BU	Tributary Bucuresti, left side tributary of Criș Alb
VA1-VA3	Tributary from mining sector Arsului (open pit) to Bucuresci river
VB1-VB2	Tributary from mining sector Barza to Criș Alb
B1	Tributary Brad to Criș Alb
VR	Downstream historical mines, tributary to Criș Alb
LU	Tributary Luncșoara to Halmagiu, right side tributary of Criș Alb, downstream tailings dam
Ro	Outflow Rovina tailings
Ri	Outflow Ribita tailings
Ri1	Piezometer Ribita tailings
AMD	Acid mine drainage, mine water coming from Barza mining sector
WCA1-WCA2	Well, Barza catchment, near VB2
WCA3	Well, Arsului river, upstream VA3

Table 2 Mean concentrations of major ions and of metals in filtrated fraction (except for wells WCA1 to WCA3, piezometer Ri1), units are per litre, n=1 to 2, depending on station. n.d.= not determined. Dist: Criş Alb River distance from source, Q: average water discharge [$\text{m}^3 \text{s}^{-1}$]

Sta	Dist	Q	pH	Ca	Mg	Na	K	SO ₄	Cl	NO ₃	Alk	Mn	Fe	Zn	Cu	Ni	Co	Cr	Pb	Cd	As
	km			mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	meq	µg	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
R1	28	1.6	8.0	54	6.6	5.2	1.7	22	3.3	0.9	1.5	22	52	7	23	10	7	<1	2	0.05	1
R2	32	3.4	7.8	n.d.	n.d.	n.d.	n.d.	35	18	3.4	2.5	212	4	106	50	6	7	<2	3	0.7	n.d.
R3	33		7.8	n.d.	n.d.	n.d.	n.d.	49	6.5	3.2	2.5	234	77	70	66	6	1	4	2	0.2	n.d.
R4	36		7.9	56	9.1	7.4	2.4	49	7.2	2.6	2.6	113	11	26	39	18	4.5	<1	5	0.5	0.8
R5	73		8.0	n.d.	n.d.	n.d.	n.d.	69	13	2.6	2.7	71	57	35	19	6	1	<2	3	0.2	n.d.
R6	97	20	8.2	49	7.2	7.1	2.2	33	6.0	1.5	1.4	82	46	13	8	14	6	10	3	0.4	4
R7	130		8.0	n.d.	n.d.	n.d.	n.d.	41	2.6	2.3	1.5	160	525	35	12	6	1	17	11	0.4	n.d.
R8	156		7.8	42	7.0	8.7	2.3	40	14	0.9	2.1	49	53	25	12	15	2	1	0.7	0.06	3.9
R9	192	24	7.9	n.d.	n.d.	n.d.	n.d.	35	13	2	0.84	19	19	60	40	6	<1	<2	4	0.2	n.d.
R10	215		7.9	48	7.9	9.8	2.4	33	9.9	1.9	2.2	44	10	51	6	17	2	3	3.	0.2	5
BU			7.5	n.d.	n.d.	n.d.	n.d.	1200	0.7	1.8	2.4	520	10	52	188	<6	6	<2	2	0.7	n.d.
VA1			4.0	280	350	19	5.0	3100	9	5.7	n.d.	18000	410	11000	32000	130	440	<0.5	<5	100	n.d.
VA2			7.7	79	14	13	3.6	87	3	1.7	n.d.	12	10	22	8	23	5	<0.5	<5	0.1	5.3
VA3			4.5	136	85	11	3.4	962	3.4	2.4	n.d.	11000	95	3300	4900	47	110	3	6	94	3.9
VB1			7.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	370	80	260	12	<6	11	<2	2	1.9	n.d.
VB2			4.6	240	66	21	3.2	1060	8	3.3	n.d.	5300	940	2200	310	43	39	5	2	11	5
AMD			3.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14400	28000	5700	190	6	1	21	4	375	n.d.
B1			8.2	54	20	6.4	0.7	22	2.3	1	n.d.	29	<11	4	7	18	3	2	<5	<0.05	5
VR			8.3	100	15	14	6.3	220	6.4	1.8	n.d.	20	<11	1	1	20	3	2	<5	<0.05	10.3
LU			8.1	25	3.0	2.5	1.2	15	1.2	2.0	n.d.	16	<11	7	4	7	3	2	<5	<0.05	6.6
Ro			7.1	68	16	16	8	200	7	11	2.0	110	190	11	0.2	0.25	0.26	0.4	0.2	<0.01	7
Ri			7.4	3109	46	22	8.2	740	6.4	0.9	1.5	270	8	2	1	0.24	0.3	0.03	0.04	0.06	18
Ri1			7.0	540	70	19	17	1400	5	2	5.0	2500	6100	30	1.2	2	3.2	0.1	0.2	0.05	110
WCA1			6.7	56	12	12	1.5	22	3.1	2.9	3.8	6	50	46	6	4	1.9	8	2	<0.5	2.6
WCA2			6.5	39	7.4	9.4	1.2	46	3	1.8	2.1	4	50	64	0.5	4	0.8	7	2	0.6	2.1
WCA3			6.5	31	5.8	11	1.8	46	3.2	1.7	1.9	20	100	24	3	3	1.9	10	3	<0.5	2.6

Table 3 European Quality Standards (QS) for inland surface waters (EC 2000/60, 2006) and for drinking water (EC 98/83, 1998) and LAWA target values for river sediments (LAWA, 2007)

	SO ₄	NO ₃	Mn	Fe	Zn	Cu	Ni	Co	Cr tot	Pb	Cd	As
	mg L ⁻¹	mg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹
QS surface water (filtered samples)	-	-	-	16 ^{a)}	7.8 ^{a)}	8.2 ^{a)}	20	-	8.1 ^{a)}	7.2	0.08 -0.25	-
QS drinking water	250 ^{b)}	50 ^{b)}	50 ^{b)}	200 ^{b)}	-	2000	20	-	50	10	5	10
					mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	-	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	
Target values in river sediments					400	80	120	-	320	100	1.2	-

^{a)} proposed (Crane *et al.*, 2007)

^{b)} Indicator values

Heavy metal contaminations in the Criş Alb basin, combined with high sulfate concentrations and low pH values, are only found in two side valleys, Valea Arsului and Valea Barza. VA1, the outflow of the open pit mined for copper situated in Valea Arsului, exhibits clearly high dissolved metal contents. As extreme, copper (Cu) is about three to four orders of magnitude higher than in unpolluted water. On the other side, contents of chromium (Cr) and lead (Pb) are low in VA1. Sample AMD, representing the drain of underground galleries and waste dumps in Valea Barza, shows high manganese (Mn), iron (Fe), zinc (Zn) and cadmium (Cd) concentrations. Due to the high contents of dissolved iron and particulate Fe, waters from AMD and VB2 display an ochre-brownish colour, the distinct and classical optical sign of mining pollution. The extreme high Cu content in VA1 produces even a greenish colour in the river.

These high concentrated mining inputs are diluted downstream, therefore, concentrations of pollution indicators in VA3 and further downstream BU or in VB1 decrease. Finally, in the upper part of the main river Criş Alb, stations R2 to R4, concentrations of the AMD indicators fall nearly back to the regional background values. pH values and alkalinities measured indicate no significant input of acidic waters, signifying the buffer capacity of river water is not impaired. Only Mn, Zn and Cu still exhibit slightly higher concentrations making evident the mining pollution inputs.

Dissolved heavy metal concentrations in the tributary Valea Ruda (VR), downstream mines exploited in the 19th century and in tributary Lunçsoara (LU), downstream an old tailings also fall in the range of background contents reported. However, the somewhat high sulfate (SO₄) concentration indicates still the continuing impact of AMD input. In the case of the tailings outflows of Rovina and Ribiţa, Ro and Ri, and in the groundwater samples from the piezometer in Ribiţa tailings, Ri1, higher calcium (Ca) and SO₄ concentrations demonstrate that an oxidation of pyrite is proceeding in the tailings. The neutral pH and the alkalinity indicate that the sulphuric acid produced is still neutralized by calcareous minerals

present in the deposit. In the tailing outflow dissolved heavy metal concentrations are still low. But in the groundwater of the tailings Ribiţa, Ri1, the high SO₄ content and dissolved Fe, as well as, Mn concentrations clearly make evident an oxidation of pyrite. Concentrations of the other heavy metals are relatively low, suggesting their low mobility at present condition in tailings. It may be worthwhile to mention the high arsenic (As) content in piezometers water, 110 µg L⁻¹, confirmed in a second piezometer, data not shown. This finding is concordant with the observation that the outflow of Ribiţa tailings also contains a somewhat higher As concentration.

Stations in the lower part of Criş Alb river, R5 to R10, exhibit dissolved metal and SO₄ concentrations that fall in the range of unpolluted tributaries. They also show an alkalinity and pH values characterizing natural waters. Smaller increases in heavy metals and chloride in the lower basin, km 130 to 219, may also be due to the inputs from urban areas in the valley.

As conclusion, Criş Alb River does not show a significant impact by mining, although some tributaries exhibit clearly such a pollution. Longitudinal profiles of dissolved heavy metals and anions, see Fig. 3 and 4, display a step-up in concentrations of typical mining pollutants, such as SO₄ and Mn. But the increase is small and does not decline clearly downstream polluted inputs. These findings contrast to those in a neighbouring valley, where the main river, Certej, is heavily polluted by AMD inputs (Zobrist *et al.*, 2008) or those reported in the Corna River, Roşia Mountain (Florea *et al.*, 2004). However, for a clear statement on the chemical state of Criş Alb and its compliance with the EU quality standards, more measurements would be needed at a few stations, coupled with a tight quality control in sampling and analytics. Concerning loads of pollutants, to a first approximation, most of them increase about in the same range as the water discharge in the river is rising. For assessing correctly pollutant loads of total heavy metals, sampling during flood events would be needed, since fine and contaminated river sediments accumulated during low flow condition are preferably transported when the water discharge rises fast.

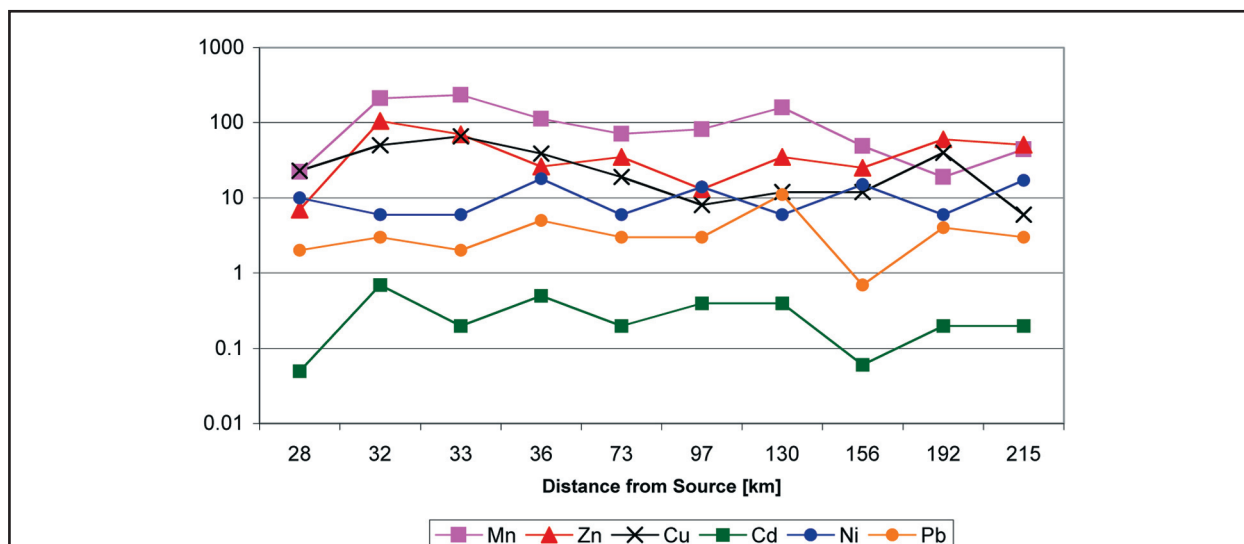


Fig. 3 Longitudinal profiles of filtered heavy metal concentrations (log scale) in Criş Alb River

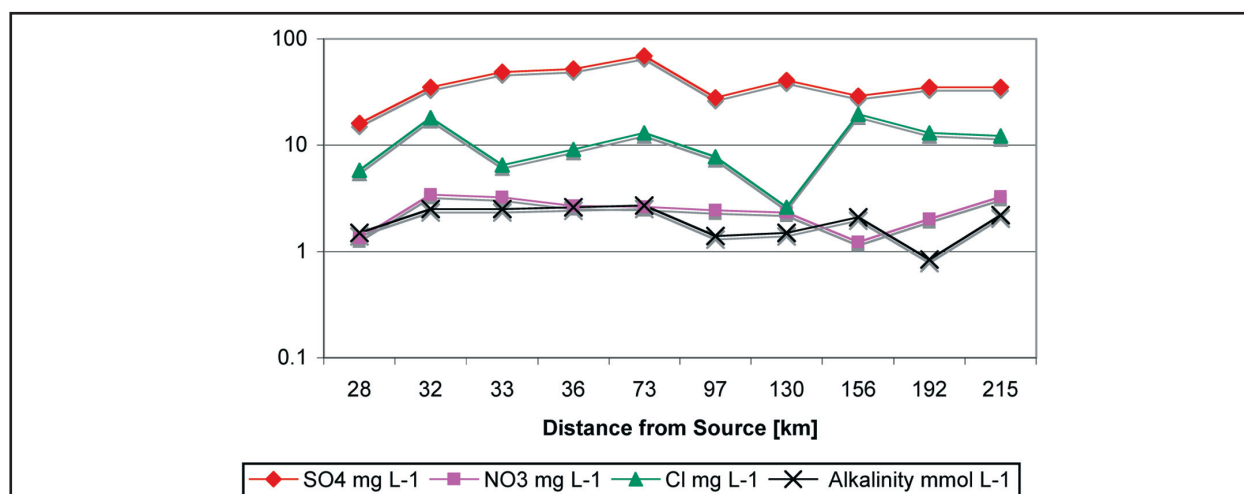


Fig. 4 Longitudinal profiles of major anions concentrations and alkalinity (log scale) in Criş Alb River

Concentrations measured in groundwater sampled from wells, used by people as drinking water, present no signs of mining pollution, although wells are at a distance of 5 to 20 m to the polluted rivers in Valea Arsului and Valea Barza. All ions measured comply chemically with the EU quality standard for drinking water (Table 3). The remarkable differences in the water composition between the nearby polluted river and well water prove that the heavily polluted tributaries do not infiltrate detectably into the aquifers feeding the wells. Probably, the groundwater stems from the valley slopes, where local pollution sources, such as septic tank, could exist.

The technique of diffuse gradient in thin film (DGT) offers the possibility to determine the dissolved metal species that are in dissolved form (metal complexes of inorganic and small organic ligands), so called DGT labile species. These dissolved species are considered to be bioavailable and play

the key role when assessing the toxicity of heavy metals to aquatic life. The conventional distinction between particulate and dissolved compounds, obtained by a filtration with a 0.45 μm filter, also includes fine inorganic and organic colloids in the dissolved fraction.

In the evaluation of the DGT campaign (Fig. 5) at five sites along the Criş Alb River, we assigned the metal concentration measured in the DGT probe as dissolved fraction, the difference between the 0.45 μm filtrate and the DGT content as colloid fraction and the difference between the total and filtrate as particulate fraction. For copper, dissolved fractions amount to 10-22 % of the total concentrations. The colloid fractions cover 25-40 % and particulates comprehend 35-65 %. It may be interesting to note, that at the slightly impacted sites, R4, R6, R8 and R10, the sum of the dissolved and colloidal fractions, the conventional defined dissolved fraction, exceed the European

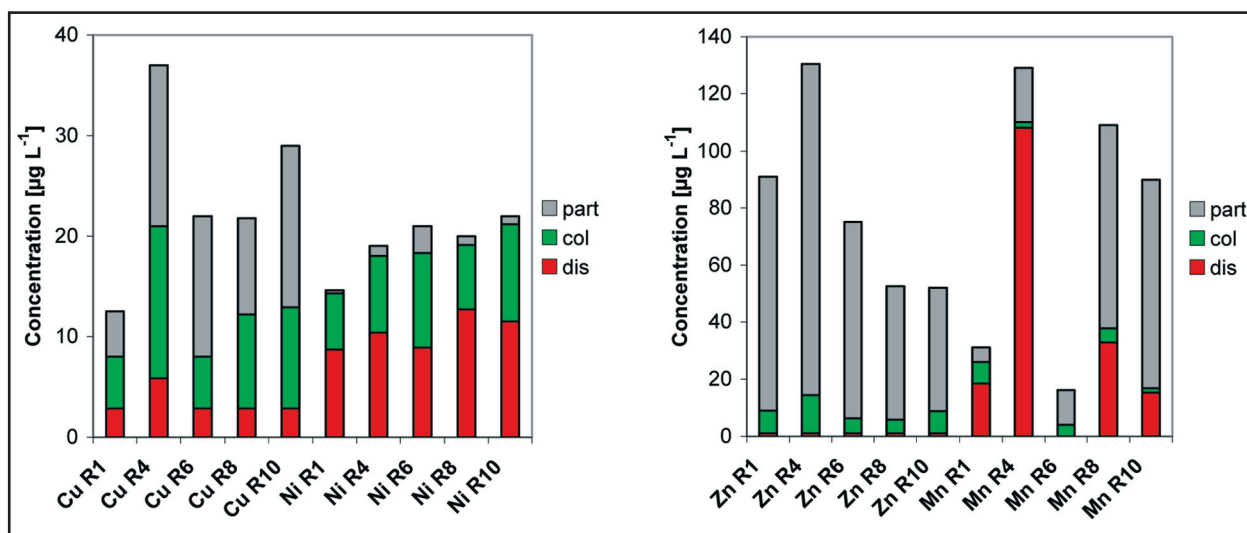


Fig. 5 Distribution of total heavy metal contents in dissolved, colloidal and particulate fraction in selected site on Criş Alb River

quality standard for Cu, whereas the DGT dissolved values fall below. In the case of nickel (Ni), 40-65 % of the total contents are in the dissolved form, 30-45 % exist as colloids and only 3-10 % as particles. Only a small part of Zn is found in dissolved form (1-2%), the biggest fraction is in the particulate fraction (83-90%) and 7-15% being colloids. Results for Mn indicate a site dependent distribution. At the background site R1 and at site R4, the dissolved fractions dominate. Latter site is situated near to AMD inputs exhibiting a high conventionally defined Mn concentration. Downstream, at sites R8 and R10, the particulate fraction is biggest. Results at site R6 may be erroneous. For Fe and Cr the particulate fraction is dominating (result not shown) and for Cd, concentrations were below detection limit at time of analysis.

SOLIDS

River sediments

Heavy metals content of Zn and Cu in river sediments increases significantly after the confluence with the mining polluted tributaries coming from Valea Arsului and Valea Barza (Fig. 6). The Pb content shows one peak at station km 73 (R5), which may be attributed to a local source. The other metals, Ni, Cr, and Cd (not shown) only display some variation in the longitudinal profile, but no significant increases or peaks can be allotted. Metal contents measured are assessed by the target values set by German Association for Water (LAWA) to protect the aquatic biota in sediments (Table 3). Concentrations of Cd measured surpass the target value of 1.2 mg kg^{-1} by a factor of about 3. Peak contents for Cu and Pb are about 50 % higher than the corresponding target values. Sediment concentrations of the other metals, Zn, Cr, and Ni, go beyond corresponding targets. Downstream, for most metals a general decreasing trend in concentrations can be noticed. This one-time measurement indicates that sediments of the Criş Alb River are not charged distinctly with heavy metals from

mining, except Cd, although tributaries from the mining areas in the Barza and Arsului valley exhibit concentrations of Cu, Zn and Pb above target values.

Tailings

Several tailings samples were collected from different parts of the Ribiţa tailings dam in order to get a general view of the mineralogy occurring in waste deposited and its change with time. XRD analysis indicates, that original waste (primary material), put in at the time the dam was build up (active), contains mainly silicates (quartz and muscovite), some pyrite and traces of calcite, gypsum and sphalerite. Samples from the oxidised zone (secondary material) contain jarosite in addition. The elemental composition, obtained by X-ray fluorescence, indicates an average pyrite content of 4.8%.

The dissolution kinetics was performed for two samples in a representative depth profile (Ri10A and Ri10B) of Ribiţa tailings. Sample Ri10A spans the first 22 cm of the profile and exhibits partially ochre coloured bands. A paste of this material shows a pH value of 3.1, indicating an oxidised and acidified zone. Sample Ri10B characterizes the deeper greyish zone with primary material, its paste pH is 7.8.

The kinetic study performed in connection with the sequential extraction reveal that the evolution of water and acetate dissoluble fractions of metals (E1 and E2) proceeds within 5 to 10 minutes, whereas both oxalate extractions (E3 and E4) need the time indicated in the procedure to clearly level-off (figures not shown). The evaluation of the results obtained in our extraction study (Fig.7) is based on the work of Dold (2003). Total metal contents in the two samples of the profile vary somewhat, but can be regarded as nearly equal for the evaluation of the sequential extraction data, except for Mn, As and Zn. However, when comparing the relative partition of the four fractions and the amount extracted, Fig.7, distinct differences arise between the oxidized solids (second-

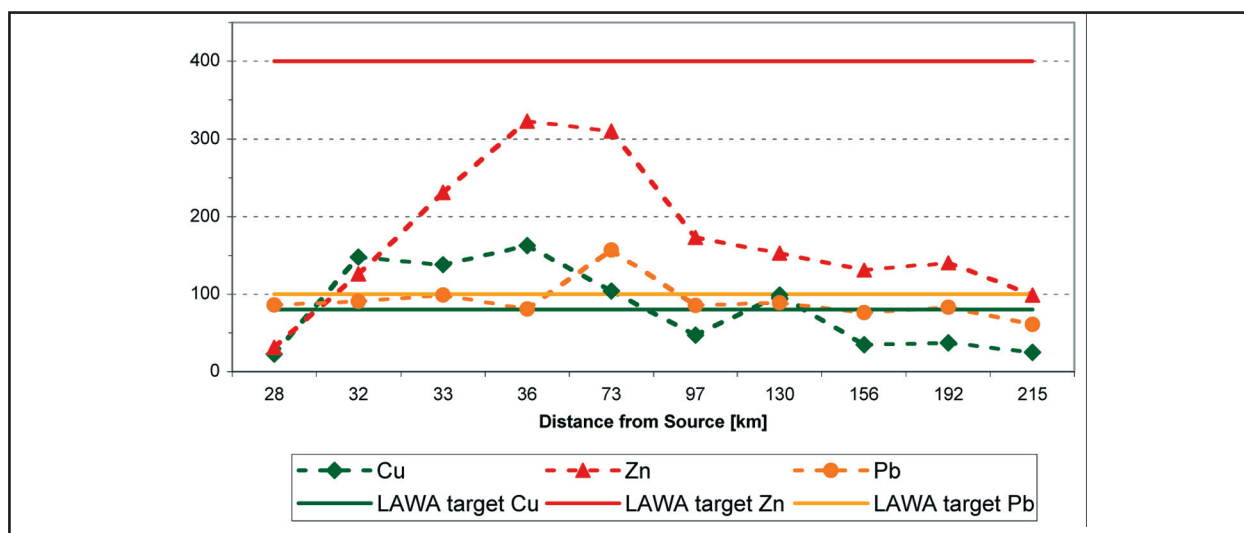


Fig. 6 Longitudinal profiles of heavy metal concentrations in river sediment samples from Criş Alb River

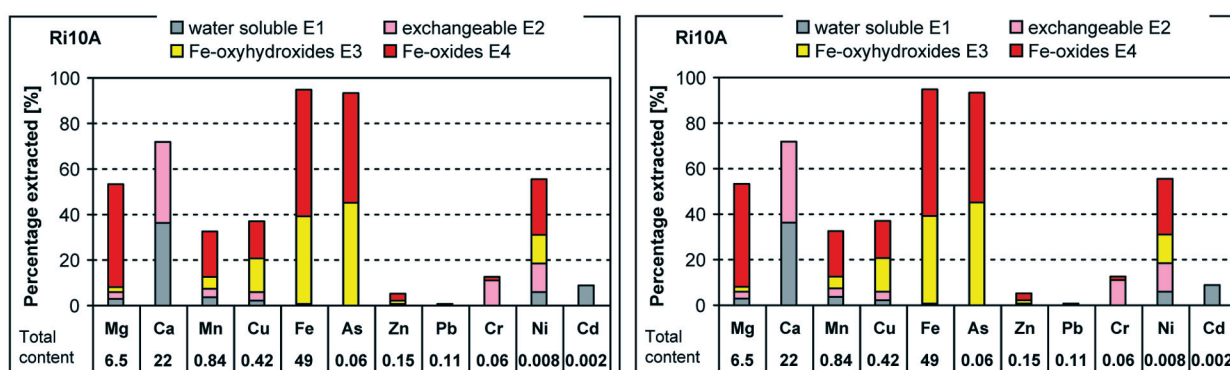


Fig.7 Selective extraction of metals in the Ribița tailings profile, Ri10A, oxidized and acidic top layer, Ri10B original and neutral deposit below 22 cm. Total metal content in g kg⁻¹

ary material) in the top layer of the tailings (Ri10A) and the not yet oxidised solids (primary material) in the next layer of the profile (Ri10B). In the oxidized layer relative and absolute amounts of ferric-oxyhydroxides and -oxides are bigger than in the bottom part. This augmentation may indicate a transformation from more resistant iron minerals to more soluble phases caused by oxidation. However, the low pH in the oxidized layer should facilitate a leaching of iron and therefore lowering the content of iron phases. Results obtained do not correspond to this expectation; the reason for the discrepancy remains unclear. The amount of water soluble and exchangeable Fe is negligibly small in both layers. Mn displays an opposite extraction behaviour than Fe. The relative and absolute amounts of fractions E2 to E4 decrease in the oxidized layer. This observation can be explained by a washing out of soluble Mn(II) from the acidic and oxidized layer Ri10A. Indeed, the amount of exchangeable Mn in the layer underneath, represented by the sample Ri10B, is substantial and the total amount of Mn in the oxidized layer is smaller than in the primary material. Furthermore, concentration in the

water sampled in the piezometer of the tailings dam (Ri1) is high. Cu exhibits the same behaviour as Mn, concerning the relative and absolute amount extracted. Therefore, it can be assumed that Cu is also leached out when primary material gets oxidized. The high amount of total Ca extracted in the first two extraction steps, E1 and E2, reveals that Ca is present as gypsum in the "water soluble" extract and as calcite in the "exchangeable" extract. The calcite content in the neutral bottom material surpasses that in the acidic and oxidized layer. Magnesium (Mg) is found in all four extracts, the highest part in E4, where a reductive dissolution in an acidic milieu is proceeding. At present, we have no knowledge of a mineral that will be dissolved under condition mentioned. Mg extracted clearly decreases in the first three extraction steps when going from primary to secondary materials. Zn and Pb exhibit small contents in both samples and from this part only a small part undergoes extraction. A single point, a distinct part of Pb in the bottom layer exists in an exchangeable form. Cr, Co Ni and Cd display even smaller total contents than Pb, impeding a reasonable evaluation. As, a non-heavy metal,

demonstrates a special behaviour. Most of the As present in the solids is extracted in fraction E3 and E4 indicating that As is bound to Fe-oxyhydroxides and Fe-oxides. The distinct lower As content in the oxidized layer (Ri10A) than in the primary material (Ri10B) and the high amount of extractable As in E3 and E4, *i.e.* mobilizable As, could explain the high As concentration observed in the water of the piezometer in Ribiţa tailings (Ri1).

The sequential extraction essay demonstrates that the mineralogy of the primary material deposited will be changed when it reacts with oxygen diffusing into the tailings. As consequence, the leaching behaviour of heavy metals also is modified. The most important governing factor for leaching is the acidic pH in the oxidized solids that favours this process.

CONCLUSIONS

The inputs of AMD stemming from the large open pit and several underground mines drastically impair the water quality of some tributaries to Criş Alb River. The acidic pH, high concentrations of dissolved heavy metal concentrations present a chemical condition in these river that go very far beyond the good chemical status required by the EU Water Frame Work Directive for running waters. Fortunately, the pollution level of the tributaries can only slightly be felt at the whole basin scale of Criş Alb.

Presently, the outflow of the large tailings dams, Rovina and Ribiţa are causing a moderate pollution. This is also the case for the old Rovina impoundment, inactive (abandoned) for around 25 years. It seems that the acid production in the deposit is staying in a non-impairing scope by natural factors only. This effect may be due to the mineralogical composition of the material deposited in the impoundment, *i.e.* the natural condition, assures a protection in terms of acid production, a natural attenuation effect. However, locally in the neighbourhood of the deposit, the AMD phenomenon is easily visible. In contrast, we hypothesize, that the most recent tailings impoundment Ribiţa, will not benefit from the same favourable conditions as Rovina, due to a different procedure of operation and kind of waste ore deposited. The sequential extraction experiment with material from a depth profile gained from Ribiţa tailings clearly shows an acidification is occurring changing the mineralogy and enhancing the leaching process of heavy metals. Therefore, we hypothesize that Ribiţa tailing could have the potential to represent a long-term environmental pollution issue in the future. More work is needed to clarify these two assumptions on the long-term behaviour of the two large tailings Rovina and Ribiţa.

The present study performed by the Romanian researchers shows a different pattern of mining impact than found in the neighbouring Certej basin, where mining provokes a heavy pollution of the main river (Zobrist *et al.*, 2008). or in the Corna River (Florea *et al.*, 2004). In the case of the Criş Alb, a natural attenuation (dilution) of heavy metal peaks in the

aquatic system is observed, emphasising the role of the natural background factors such as water discharge and geology and mineralogical composition.

Finally, it may be worthwhile to note, that due to several economical measures adopted by local authorities to increase foreign investments in the Brad area, mining is no more the main source of income for the inhabitants.

RECOMMENDATIONS AND PERSPECTIVES

Based on this study, a long-term survey can be established that will monitor: - The evolution of the AMD production in the tailings dam, - Changes in the water quality of the main river at 2 to 3 stations and of the polluted tributaries, - The chemical condition in the drinking water wells and in the groundwater downstream the waste ore deposits. - The fluxes of sediments in Criş Alb River, their composition and, last but not least, - Detailed essays to determine the acid production potential in Ribiţa and Rovina tailings. The water monitoring programme has also to include measurements during high floods events, *i.e.* heavy rain falls in order to properly determine the heavy metal load in the river.

However, pollution monitoring represents just a first step into a more elaborated plan to reduce existing mining impacts and to prevent that the huge AMD production potential in the waste ore deposits will be developed. At least, measures taken should slow down the AMD evolution. As natural attenuation measure, it is important to cover the bare tailings dams to prevent erosion of the fine material and to decrease the oxygen flux into the deposit. Proper consolidation of tailing dams is an additional issue. However, regulations and remediation actions of mining waste sites will face many difficulties (Gustavson *et al.*, 2007) and need a long-term and firm commitment of all stakeholders involved. Such a plan also incorporates the perception of the inhabitants towards the pollution problem and the environmental risk of mining. The latter aspect of mining activities should be considered thoroughly when mining activities would be re-opened due to a new and profitable technology employed by leading mining companies. In such a case, measures have to be taken from the very beginning on to prevent the production of AMD for all times.

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