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Environmental and socioeconomic assessment of impacts by mining activities—a case study in the Certej River catchment, Western Carpathians, Romania

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Abstract

Background, aim and scope In the region of the Apuseni Mountains, part of the Western Carpathians in Romania, metal mining activities have a long-standing tradition. These mining industries created a clearly beneficial economic development in the region. But their activities also caused impairments to the environment, such as acid mine drainage (AMD) resulting in long-lasting heavy metal pollution of waters and sediments. The study, established in the context of the ESTROM programme, investigated the impact of metal mining activities both from environmental and socioeconomic perspectives and tried to incorporate the results of the two approaches into an integrated proposition for mitigation of mining-related issues.

Study site The small Certej catchment, situated in the Southern Apuseni Mountains, covers an area of 78 km^2. About 4,500 inhabitants are living in the basin, in which metal mining was the main economic sector. An open pit and several abandoned underground mines are producing heavy metal-loaded acidic water that is discharged untreated into the main river. The solid wastes of mineral processing plants were deposited in several dumps and tailings impoundment embodying the acidic water-producing mineral pyrite.

Methods The natural science team collected samples from surface waters, drinking water from dug wells and from groundwater. Filtered and total heavy metals, both after enrichment, and major cations were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Major anions in waters, measured by ion chromatography, alkalinity and acidity were determined by titration. Solid samples were taken from river sediments and from the largest tailings dam. The latter were characterised by X-ray

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fluorescence and X-ray diffraction. Heavy metals in sediments were analysed after digestion. Simultaneously, the socioeconomic team performed a household survey to evaluate the perception of people related to the river and drinking water pollution by way of a logistic regression analysis.

Results and discussion The inputs of acid mine waters drastically increased filtered heavy metal concentrations in the Certej River, e.g. Zn up to 130 mg L^{-1}, Fe 100 mg L^{-1}, Cu 2.9 mg L^{-1}, Cd 1.4 mgL^{-1} as well as those of SO_4 up to 2.2 g L^{-1}. In addition, river water became acidic with pH values of pH 3. Concentrations of pollutant decreased slightly downstream due to dilution by waters from tributaries. Metal concentrations measured at headwater stations reflect background values. They fell in the range of the environmental quality standards proposed in the EU Water Framework Directive for dissolved heavy metals. The outflow of the large tailing impoundment and the groundwater downstream from two tailings dams exhibited the first sign of AMD, but they still had alkalinity.

Most dug wells analysed delivered a drinking water that exhibited no sign of AMD pollution, although these wells were a distance of 7 to 25 m from the contaminated river. It seems that the Certej River does not infiltrate significantly into the groundwater.

Pyrite was identified as the main sulphide mineral in the tailings dam that produces acidity and with calcite representing the AMD-neutralising mineral. The acid–base accounting proved that the potential acid-neutralising capacity in the solid phases would not be sufficient to prevent the production of acidic water in the future. Therefore, the open pits and mine waste deposits have to be seen as the sources for AMD at the present time, with a high long-term potential to produce even more AMD in the future.

The socioeconomic study showed that mining provided the major source of income. Over 45% of the households were partly or completely reliant on financial compensations as a result of mine closure. Unemployment was considered by the majority of the interviewed persons as the main cause of social problems in the area. The estimation of the explanatory factors by the logistic regression analysis revealed that education, household income, pollution conditions during the last years and familiarity with environmental problems were the main predictors influencing peoples' opinion concerning whether the main river is strongly polluted. This model enabled one to predict correctly 77% of the observations reported. For the drinking water quality model, three predictors were relevant and they explained 66% of the observations.

Conclusions Coupling the findings from the natural science and socioeconomic approaches, we may conclude that the impact of mining on the Certej River water is high, while drinking water in wells is not significantly affected. The perceptions of the respondents to pollution were to a large extent consistent with the measured results.

Recommendations and perspectives The results of the study can be used by various stakeholders, mainly the mining company and local municipalities, in order to integrate them in their post-mining measures, thereby making them aware of the potential long-term impact of mining on the environment and on human health as well as on the local economy.

Keywords Acid mine drainage (AMD) · Heavy metal · Mining impact · Multidisciplinary study · Romania · Risk perception · Water quality

1 Background, aim and scope

Metal mining is a long-standing human activity, which contributes indisputably to the progression of our civilisation and its economical growth. However, mining activities also result in apparent environmental impacts to waters, landscape and the atmosphere (Younger 1997). They also influence strongly the economic wealth of the area and act on its social life. Both the environmental and socioeconomic impacts of mining are well documented in numerous areas worldwide (e.g. Boni et al. 1999; Balistrieri et al. 1999; Hudson-Edwards et al. 1999; Dold and Fontboté 2002; Espana et al. 2005).

Acid mine drainage (AMD) is the key impact to aquatic ecosystems which stems from mining of sulphide-bearing ore deposits. Water draining from mine workings, such as adits, open pits, tailings impoundments and mine waste deposits may turn acidic, caused predominantly by the oxidation of sulphide minerals associated with the ores extracted. In the context of the long-term behaviour of waste ore deposits containing pyrite, it is important to consider the factors governing the pyrite oxidation. In this abiotic and microbial mediated reaction, O_2 and Fe(III) ion act as electron acceptors (Nordstrom and Southam 1997).

$$FeS_2 + {}^7\!/_2 O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

$$Fe^{2+} + {}^1\!/_4 O_2 + {}^5\!/_2 H_2O \rightarrow Fe(OH)_3 + 2H^+ \tag{2}$$

$$Fe(OH)_3 + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O \tag{3}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

In an oxygenated zone, e.g. on surfaces of tailings, reactions (1) and (2) will prevail, if the acid produced cannot be neutralised by bases, such as calcite or weatherable silicates. At a low pH condition, in which the Fe (III) remains mobile, reaction (4) will enhance the sulphide oxidation (Dold and Spangenberg 2005). Reaction (4) also occurs in acidic anoxic zones, where Fe(III) minerals are dissolved. Therefore, the pyrite oxidation in waste dumps exhibiting a lack of acid-neutralising capacity tends to produce increasingly stronger acidic water within a time scale of years and decades, 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 of a given mine waste by stoichiometric calculation, thereby taking reactions (1), (2) and (4) as acid producers and weathering reactions of carbonates as acid neutralisers. In literature, several such acid–base accounting (ABA) methods exist (Jambor 2003). These are all approximations since the contributions of silicate weathering reactions are difficult to determine and acid production potential by pyrite oxidation alone is considered.

AMD, essentially diluted sulphuric acid, also dissolves toxic heavy metals and non-metals (Marchand and Plumb 2005), which impair the downstream aquatic life and groundwater fed by rivers. Recently, the EU has set environmental quality standards (EQS) for dissolved concentrations of Cd, Pb and Ni in surface waters (EC 2006). Those of Cr, Cu and Zn 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 neutralise 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 river flow regime (Miller 1997; Hudson-Edwards 2003). Tailings dam failure, when suddenly huge amounts of fine-grained materials are sliding downwards from geotechnically unstable 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).

Socially oriented studies, on the other hand, have focused mainly on assessing the socioeconomic status of mining-dependent areas and on the socioeconomic costs and effects of mine closure and future development patterns (Chiribuca et al. 2000; Andrews-Speed et al. 2005; Du Plessis and Brent 2006). In recent years, increasing interest has emerged in studies of environmental risk perception and in exploring factors most influencing peoples' responses to environmental problems, which are based on individual and community-related investigations (Grasmück and Scholz 2005; Dogaru et al. 2009). They have made evident that there are often differences between public perception of environmental risks and findings of experts. This discrepancy is a subject of concern in environmental risk management studies (Bickerstaff 2004; Power and McCarty 2006; Dogaru et al. 2009).

In Romania, a country with a long tradition of metal mining, investigations on mining impacts on waters have evolved just recently (Florea et al. 2005). Mainly, West-European research groups in collaboration with Romanian institutes have undertaken studies concerning water pollution caused by ore extraction activities (Fornay and Hallbauer 2000; Cordos et al. 2001; Milu et al. 2002; Bird et al. 2003; Macklin et al. 2003; Bird et al. 2005). Chiribuca et al. (2000) and Popescu et al. (2003) have investigated the economic impact caused by restructuring industrialised areas due to the political turn in the country occurring in the 90 s of the last century.

The objective of the present study is to investigate and evaluate the water pollution in the mining impacted Certej catchment and to assess the perception of inhabitants related to the poor water quality of the river and to their drinking water. Results gained by the natural science and socioeconomic approaches are incorporated into an integrated proposition for mitigation of mining activity-related impacts. The study area chosen represents an important hot spot of mining in Romania, where environmental protection norms have been little enforced. The project also exhibits a research capacity development aspect and a know-how transfer to the Romanian participants.

2 Study area

The small Certej catchment is situated in the Metaliferi Mountains, belonging to the Southern Apuseni Mountains in the Western Carpathians. It covers an area of 78 km^2 (Figs. 1 and 2). The Certej River, 18 km long, is a tributary to the Mures River, which flows into the Danube River. The average water discharge in the river not gauged is estimated to be about 0.8 to 1 m^3s^{-1}. About 4,500 inhabitants are living in the basin, in which mining was by far the most important economic sector which flourished during the seventies to nineties in the last century.

Geologically, the Certej valley is underlain by a sequence of Cretaceous black shales and thinly bedded sandstones, which have been intruded and overlain by a

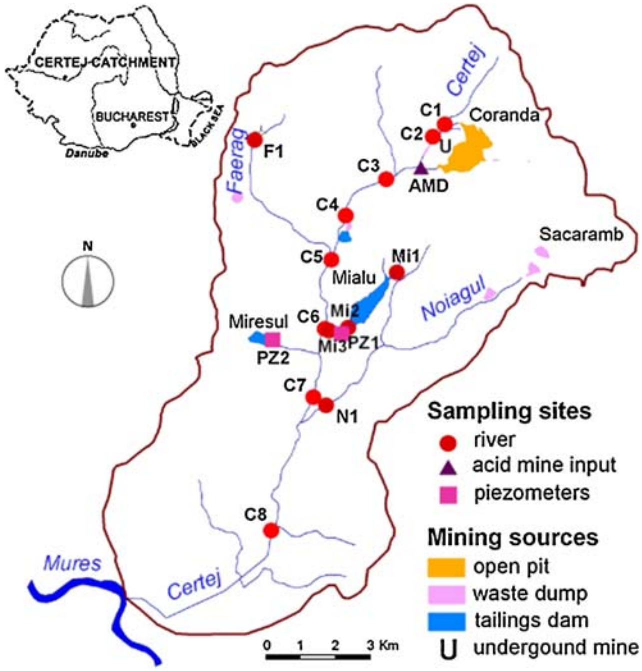

Fig. 1 Certej River catchment, sampling stations and mining sites

number of Neogene andesitic sills and associated andesitic flows and sediments. Precious metals are mostly hosted in steeply dipping veins in andesite stocks and lava flows. Magmatic rocks found in the Coranda open pit contains an impregnate type of polymetallic sulphides and veins of gold–silver. Gold is mainly associated with pyrite, but also found in sphalerite and galena (Frei 2006). Ore deposits in the valley were exploited at different places (see Fig. 1). In the open pit Coranda, by far the largest mine in the catchment, gold ore was exploited until 2006. Smaller underground mines situated near Coranda pit were abandoned earlier, but they still provide acidic waters that flow into Certej River. Smaller mine operation sites situated in the Noiagul side valley closed several decades ago. After processing the ore, residual material was transported to waste disposal sites. The largest is the Mialu tailings impoundment and contains 4.6 million m^3 of fine-crushed waste ores embodying the acidic water-producing mineral pyrite. It was used (actively) from 1984 to 2006. Miresul, a medium-sized and older tailings impoundment was active from 1972 to 1981. Now it is covered with plants and its seeping groundwater is monitored (PZ2). In 1971, a sliding from the tailings dam just upstream of Certeju de Sus caused a major accident to people with flooding of the river channel and subsequent deposition of slurry down to the confluence with Mures River.

Drinking water in the valley mainly stems from privately dug wells and, to a smaller part, from the communal water supply of Certeju de Sus.

3 Methods

3.1 Sampling

From 2005 to 2007, the natural science team (geographers, chemists and a geologist) performed six field campaigns, emphasising each time a specific goal to get a broader view on the mining impact-related questions. Three 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 groundwater pumped from the piezometer downstream from the two largest tailings impoundments were collected one to four times at locations displayed in Fig. 1 during low and medium water discharge condition. In situ, pH was measured 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 dissolved and total heavy metals were filled in polyethylene bottle containing the necessary volume of nitric acid suprapure to get a pH of 2. A third sample was taken for analysis of the major ions. 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 one to two times at locations displayed in Fig. 2. These dug wells are situated in a distance from 7 to 25 m of Certej River.

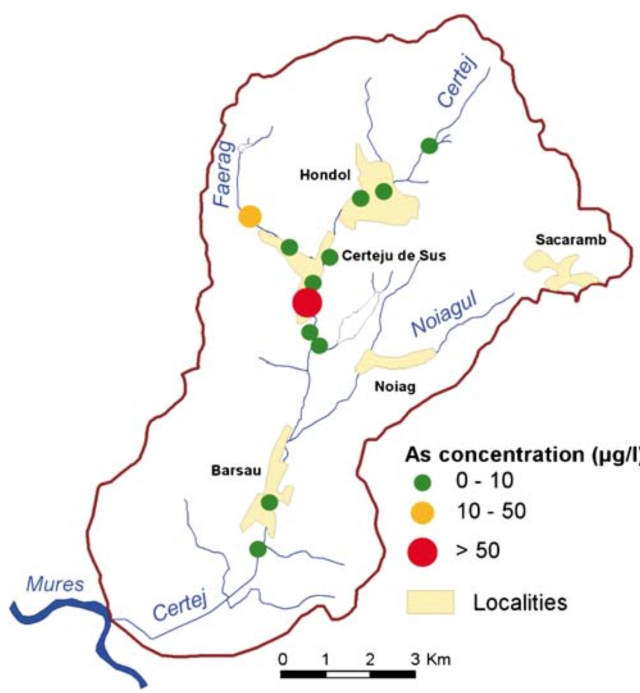

Fig. 2 Localities in the Certej River catchment, well water sampling sites and their arsenic concentrations

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

Polyethylene equipment for heavy metals sampling were cleaned with nitric acid in the lab and transported separately in clean plastic bags (Benoit 1994). In all sampling operations, prevention measures were taken to avoid contamination of samples by heavy metals.

The socioeconomic team performed surveys by interviewing people and discussed mining impact issues with local stakeholders, medical persons and the mining company. The main survey included 103 households and was performed in the three villages situated in the main valley (see Fig. 2). It was designed to obtain data on the mining-dependent economic condition of the people and to estimate their perception related to the water quality of the Certej River and of the drinking water.

3.2 Analyses

Low concentration samples of heavy metals were enriched by elution of the sorbed diethylydihiocarbamate metal complexes from a phenyl resin sorbent (Eawag method modified from King and Fritz 1985; Senila et al. 2006). Heavy metals, arsenic and major base cations were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) according to (ISO 11885 1996). Recovery rates of extraction varied between 87% and 101%. Cl, SO_4 and NO_3 were determined by ion chromatography according to (ISO 10304-1 1997). Alkalinity was obtained by titration to pH 4.5 with 0.1M HCl; acidity was titrated with 0.1M NaOH to pH 4 (Totsche et al. 2006). All samples were analysed at the ICIA lab. For comparison and complementary examinations, selected samples were analysed at Eawag, where inductively coupled plasma mass spectroscopy (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 of the major anions and cations.

Air dried solid samples of the tailings were milled to produce a grain size fraction <70 µm. They were analysed by X-ray fluorescence and X-ray diffraction at the mineralogical lab of the University Lausanne. Total carbon content, a proxy for calcareous minerals, was measured by a total organic carbon (TOC) analyser (liquidTOC) (Frei 2006). 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 2002).

A logistic regression analysis (Turgeon et al. 2004) was applied to evaluate the responses to the questions set up in the household survey in respect to the pollution of the Certej River and of the drinking water. In this analysis, the socioeconomic and local environmental characteristics (see Table 6) represent the independent variables (predictors). The water quality is defined as a dependent binary variable, by attributing a value of 1 for highly polluted water if the person considered it so and a value of 0 otherwise. All predictors are also converted to binary values. Equation (5) expresses the general form of the logistic regression.

$$\log(odds) = C + \sum_{i=1}^{n} B_i X_i \tag{5}$$

odds	how likely it is that the observed values of the dependent variable may be predicted from the observed values of the independent variable X
logits (log odds)	the natural logarithms of the odds ratio
C	intercept
B	the coefficient of the variable
X	the independent variables (see Table 5)

In the logistic regression, the log odds is defined as the ratio of two probabilities that an event occurs to a probability (p) and that it fails to occur with a probability ($1 - p$), and is a linear combination of independent variables. It allows elucidating by a stepwise procedure which of the independent variables presents the main explanatory factors for a given question, i.e. the model to be tested.

4 Results

4.1 Surface waters

Measured concentrations of chemical species in filtrated samples of surface waters are summarised in Table 1. Values reported for heavy metals as well as for the major anions at the headwater stations C1, F1 and Mi1 (in italics in Table 1) represent background concentrations. They were in the range expected from the mineralogical and geological settings of the region. With the exemption of the Zn concentration at C1, they complied with the European quality standards in rivers (see Table 3). Concentrations of SO_4, Fe, Mn, Ni, Cu and As in the tributary Noiagul, station N1, went beyond the background values. This small pollution reflects the impact of small mines and their waste dumps that were operated in the valley from approximately

Table 1 Mean concentrations of major ions and of metals in filtrated fraction (except PZ 1 and 2, n=1 to 4 depending on station)

Station	pH	Ca	Mg	Na	K	Aci	SO_4	Cl	NO_3	Alk	Mn	Fe	Zn	Cu	Ni	Co	Cr	Pb	Cd	As
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	meq L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	meq L^{-1}	mg L^{-1}	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}
C1	*7.6*	*36*	*7*	*9*	*1*		*50*	*3*	*1*	*1.8*	*0.02*	*0.03*	*0.05*	*6*	*5*	*1*	*0.5*	*1*	*0.1*	*n.d.*
C2	3.0	190	260	9	2	7	1,800	5	3		70	98	83	2,900	400	180	72	5	570	230
C3	3.1	290	210	14	3	8	2,200	10	5		68	100	74	1,800	350	n.d.	62	4	630	n.d.
C4	3.0	290	180	15	4	7	1,900	7	3		52	38	60	1,700	150	n.d	54	9	1,400	n.d.
C5	3.5	320	110	16	5	7	1,700	2	n.d.		50	12	50	1,100	150	n.d.	7	–	270	n.d.
C6	3.5	280	120	18	5	3.4	1,400	24	4		34	23	58	930	390	108	24	24	490	n.d.
C7	3.5	260	93	18	9	5	1,200	24	3		18	14	26	280	n.d.	n.d.	n.d.	31	150	n.d.
C8	5.2	220	62	24	10		900	22	2		22	0.6	29	270	430	130	2	92	300	2
AMD	2.9	320	350	14	4	10	2,700	3	0.2		110	370	130	2,300	19	310	19	5	660	580
F1	*7.8*	*46*	*9*	*8*	*1*		*67*	*2*	*0.5*	*1.7*	*0.11*	*0.04*	*<0.005*	*2*	*3*	*1*	*7*	*1*	*0.1*	*3*
Mi1	*7.1*	*31*	*23*	*4*	*1*		*76*	*2*	*0.1*	*1.8*	*0.002*	*0.01*	*<0.005*	*1*	*0.5*	*0.1*	*0.5*	*<1*	*<0.1*	*<1*
Mi2	6.7	360	45	27	30		1,100	32	1.2	1.0	8.4	13	0.84	3	51	12	2	2	2	110
Mi3	6.8	390	52	31	33		1,100	37	0.6	0.7	12	6	2.4	6	81	24	1	35	7	35
N1	7.8	160	23	49	11		460	29	6	2.6	0.35	0.13	0.022	8	13	4	1	1	0.1	22
PZ1	7.2	120	37	17	13		78	4	2.2	7.3	2.0	40	0.07	52	84	22	96	75	5	27
PZ2	7.0	150	63	26	6		290	8	0.7	6.0	2.8	8.8	0.06	9	25	10	10	3	0.1	45

Stations in italics reflect background locations

1750 to 1950. Mapping of heavy metal concentrations clearly visualises the very large differences in metal concentrations between Certej River, downstream from the first AMD, and the other surface and groundwaters (two examples see Fig. 3).

The longitudinal profiles of heavy metals, SO_4 and alkalinity, resp. acidity (Figs. 4 and 5) clearly depict, quantitatively, the strong pollution in the Certej River

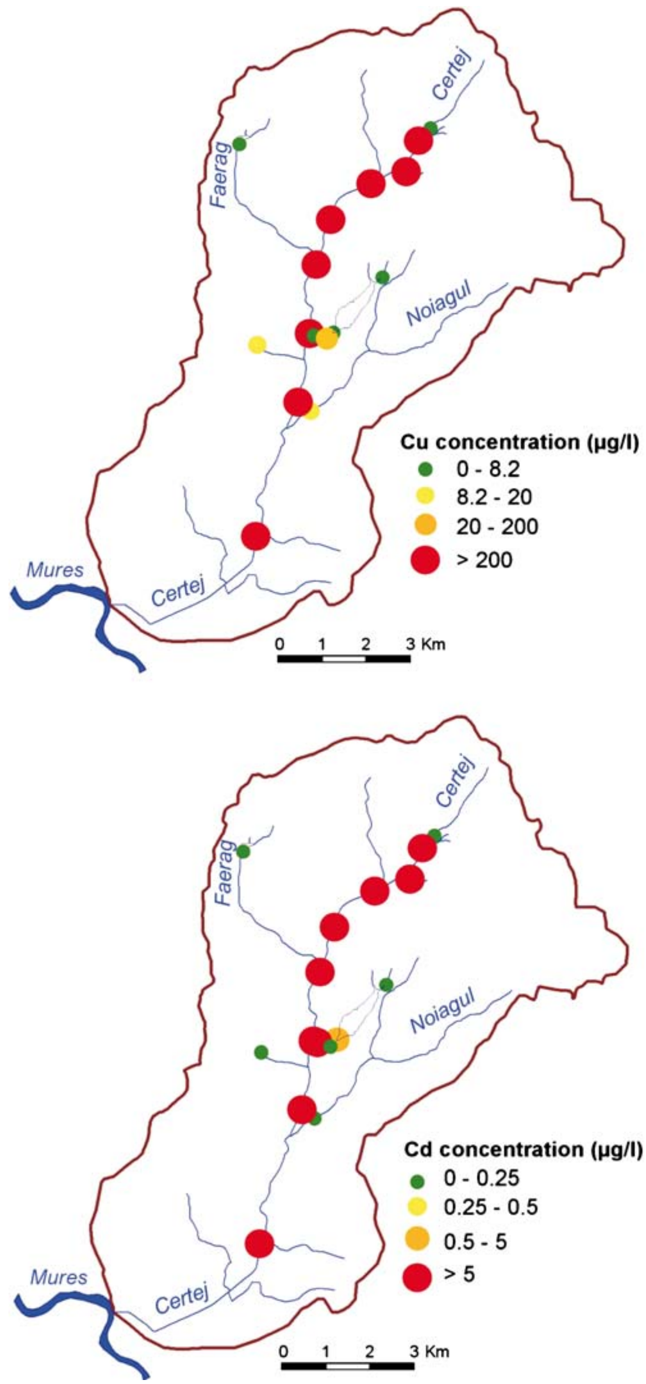

Fig. 3 GIS-based representation of filtered Cu and Cd concentrations in surface and groundwaters

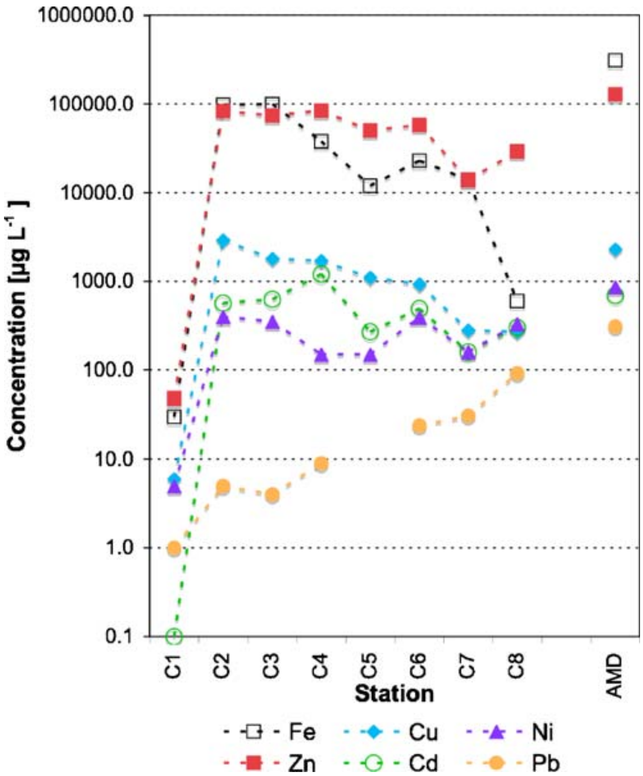

Fig. 4 Longitudinal profiles of filtered heavy metal concentrations (log scale) in Certej River and in the three averaged AMD inputs

caused by the mining operations in the last decades. Concentrations increased two to three orders of magnitude from background stations C1 to C2, situated downstream from the first AMD input. From station C2 to C7, the water exhibited an acid pH value of 2.9 to 3.5 and very high concentrations of Mn, Fe, Zn, Cu and Cd. They were only slightly lower than those in the three AMD outflows from underground mines near the open pit Coranda. The high concentrations of dissolved and particulate Fe (data not shown) resulted in an ochre-brownish colour in the river water, a distinct and classical optical sign of AMD pollution (hydrolysed Fe(III) hydroxide polymers). The creek downstream from the Mialu dam, stations Mi2 and Mi3, still exhibited a low alkalinity and a neutral pH value, but their high SO_4, Mn, Fe, Zn and As concentrations clearly indicated an input of AMD. Downstream Certej valley, at station C8, waters from non- or less polluted tributaries caused a minor dilution. Consequently, the pH value increased depending on the relation between waters originating from mines and non-polluted waters. The acidity also decreased; at higher discharge, the river water may even exhibit an alkalinity. However, most heavy metal concentrations still exceeded clearly the European quality standards in rivers (see Table 3). The single ICP-MS measurements in samples from C8 yielded the following concentrations: 4 µg L^{-1} for Se, 1 µg L^{-1} for Sb, 2 µg L^{-1} for U and 33 µg L^{-1} for B. The elevated concentrations of Se and Sb were due to the input of the Mialu creek, where respectively 21 µg L^{-1} and 8 µg L^{-1} were found. This observation is plausible since mined ores always contain other metal-bearing minerals (Frei 2006), which can also be dissolved. The Certej River inputs of heavy metals into Mures River will be substantial, despite the water discharge in Mures River being about 20 to 50 times larger than in the Certej River. Although not measured, chemical results made irreproachably provide evidence that the ecological condition in the Certej River also did not comply with the European Water Frame Work Directive. Data for pollutants measured before and after mining closure did not indicate any significant change, i.e. a decrease after ceasing mining activities.

Groundwater in the piezometers downstream from the Mialu and Miresul tailings exhibited a different water composition than background surface waters. The elevated alkalinity, Ca and Mg content, combined with a moderately high SO_4 concentration, indicated an acid production by pyrite oxidation, which is neutralised by carbonate minerals. The relatively high concentrations of Mn and Fe in unfiltrated samples were due to colloidal particles, although the water was only slightly turbid. Concentrations of other heavy metals were also above background values. This fact indicates the impact caused by leaching of heavy metal-containing minerals occurring in waste ore deposits. It may be worthwhile to note that the water on top of the piezometer tube, which is usually monitored by the Romanian monitoring institution, displayed a much lower electrical conductivity than water pumped from the middle

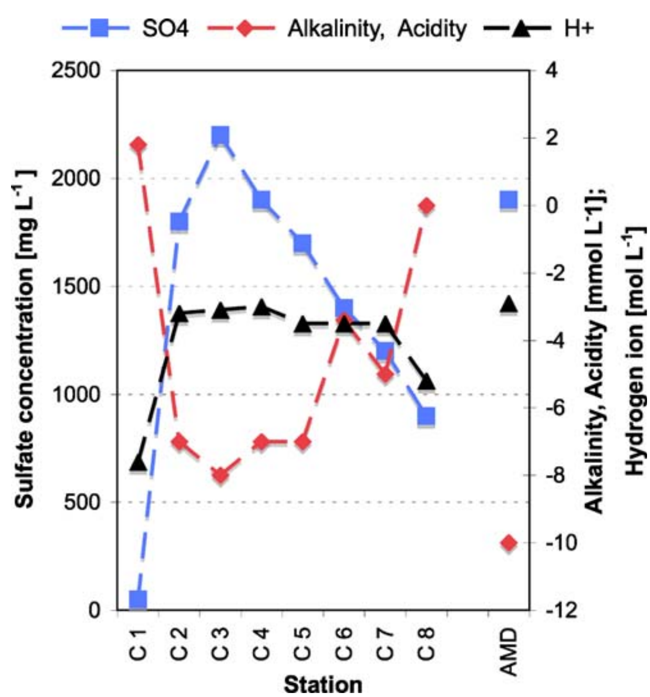

Fig. 5 Longitudinal profiles of sulphate, alkalinity–acidity and pH in Certej River and in the three averaged AMD inputs

Table 2 Concentrations in 11 dug wells near the Certej River, minimum, median and maximum

	pH	Ca	Mg	Na	K	SO_4	Cl	NO_3	Alk	Mn	Fe	Zn	Cu	Ni	Co	Cr	Pb	Cd	As
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	meq 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}
Min	6.5	46	8	10	3	10	6	2	1.5	5	10	10	1	2	<1	4	0.2	<0.1	1
Median	6.9	77	17	19	13	46	14	13	3.5	17	35	60	2	4	1	7	0.4	0.1	8
Max	7.5	370	40	48	47	950	87	48	7.2	170	600	1,000	5	32	3	13	0.6	0.9	62

part of the piezometer. This anomaly may suggest a density separation of more saline groundwater and groundwater diluted with rainwater.

4.2 Drinking water

Drinking waters taken from the 11 dug wells situated at a distance of 7 to 25 m from the heavily polluted Certej River exhibited a composition (Table 2) that differed greatly from that of the river. pH values were neutral and heavy metal concentrations were mostly low and near background values. The metallic water extraction equipment of the dug wells, sometimes not well maintained, might have caused heavy metal concentrations slightly above background. Most of these well waters, as well as the drinking water of the public water supply in Certeju de Sus (data not shown), complied chemically with EU quality standards for drinking water (Table 3). The two wells in Hondol showed SO_4 concentrations in the range of 900 mg L^{-1} and a low alkalinity, indicating pollution, probably caused by a small input of AMD. In two wells, As concentrations exceeded the quality standards for drinking water (see Fig. 2). The big differences between the water composition of river and well water proved that, at the time of sampling, the heavily polluted river did not infiltrate, or at most, slightly only, into the aquifer feeding the wells. Probably, the groundwater stems from the valley slopes, where local geogenic pollution sources could also exist. A hydrogeological study would be needed to clarify the condition of the groundwater used as drinking water.

4.3 Solids

Samples taken on the top of the Mialu tailings dam contained mainly silicates (quartz, K-feldspar and muscovite), some pyrite and little carbonates, shown by X-ray diffraction. Few samples also hosted traces of gypsum and sphalerite (Frei 2006). The elemental composition, obtained by X-ray fluorescence (Table 4) indicated a distinct average content of pyrite, 36 g kg^{-1}, (0.3 mol kg^{-1}, std. dev. 0.036) if all sulphur was taken as pyrite, and also a small amount of carbonates. The total carbon (TC), measured separately, indicated levels of carbonate, since the organic content of the material was negligibly small. Taken as calcite, the average of ten samples amounted to 36 g kg^{-1} (0.36 mol kg^{-1}, std. dev. 0.073). The conversion of all Ca displayed in Table 4 into calcite would yield 55 g kg^{-1}, a calculation which does not account for the Ca in silicates and gypsum. Data on the composition allowed performing an acid–base accounting (ABA) by assuming that the four protons produced by reaction (1) and (2) will be neutralised by four calcite to obtain a pH of 8.2. This procedure estimates roughly if the tailings impoundment material will produce an excess of acidity or if it will be able to neutralise the acidity produced. The stoichiometric calculation with given values of pyrite and calcite contents resulted in net acid production potential of 0.84 mol H^+ kg^{-1}, corresponding to a lack of (84 g calcite as acid-neutralising capacity per

Table 3 European Quality Standards (EQS) for inland surface waters (EC 2000/60 2006) and in 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]	–	2,000	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

Table 4 Element content in 15 samples taken on the Mialu tailings dam, analysed by XRF and LiquiTOC (Frei 2006), mean and standard deviation

	Si	Al	Ca	Mg	S	Mn	Fe	Zn	Cu	Ni	Co	Cr	Pb	Cd	As	TC
	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}
Mean	310	67	22	8.2	19.3	2.5	25	2	0.06	0.02	0.04	0.06	1	0.02	0.3	4.3
St. dev.	1.1	0.9	0.6	0.3	1.4	0.2	0.6	0.2	0.03	0.01	0.04	0.03	0.1	0.01	0.08	

kilogram, 95% confidence interval 38 g kg^{-1}). An extrapolation to the whole Mialu deposit would give a non-neutralised production potential of about 50,000 t sulphuric acid (about equivalent to a 0.1 m^3 s^{-1} flow of acidic water with a pH of 3 in a time frame of 300 years). The ABA calculation presents an upper limit of the acid production since the slow neutralising weathering reactions of silicates is not considered. Data on the composition of Mialu tailings dam samples also indicated approximately that of the rock in the Coranda ore deposit.

Heavy metals content of Zn, Cu, Pb and Cd increased distinctly in river sediments from the downstream station C3 and reached a peak at station C4 or C 5 (Fig. 6). Several factors might have caused this increase; higher sedimentation rate due to lower slope of the river bed, remaining inputs from the ore processing plant and a nearby tailings dam. In the upper part of the river, metal concentrations, except those for Cd, fell in the region of the target values set by the German Association for Water (LAWA) to protect the aquatic biota in sediments (see Table 3). At the downstream station C8, target values were still surpassed, except for Cu. In the Mures River, downstream from the confluence of Certej River, metal contents in sediments did not decrease to background values, but those for dissolved Zn and Pb diminished (data not shown). This fact suggests a pollution of Mures River by sediments and precipitates of dissolved heavy metals, both stemming from Certej River.

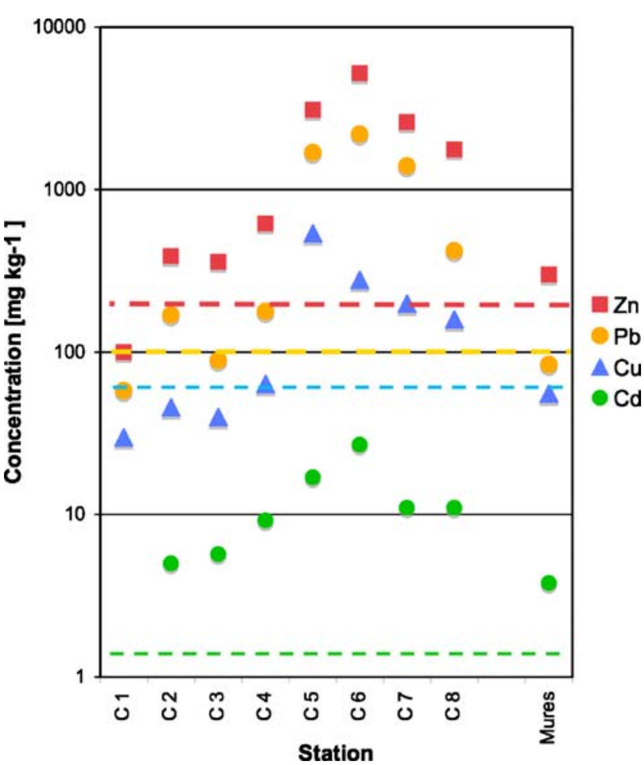

Fig. 6 Longitudinal profiles of heavy metal concentrations (log scale) in river sediments of Certej River and Mures River. *Dashed lines* indicate the target values according to LAWA

4.4 Socioeconomic study

This part summarises results of the extensive study performed by Dogaru et al. (2009). Answers related to the socioeconomic dependencies of the people to the mining industry revealed that 20% of the households had redundant mine workers and that 45% of the households were partly or completely reliant on financial compensation as a result of mine closure. For 64% of the respondents, mining was the major source of income. Mine closure and the high unemployment rate of 35% were considered as the main cause for social problems by 93% of the people. Of the interviewed families, 60% possess no arable land besides that surrounding their houses.

Table 5 adds further primary results obtained from the survey and factors considered in the perception study. It also designates the predictor variables and the dependent variables used in logistic regressions. Answers to the questions of the enquiry reflected the social structure and the economic situation in the region and how people assessed pollution and its impact. A statistical analysis indicated a relative spatial homogeneity of the data within the main river valley, suggesting that the study was reasonably representative.

The stepwise logistic regression revealed that, for the perception 'highly polluted river water', four predictors were most significant in explaining the opinion of the interviewed people (Table 6). They were: education, household income, pollution during last years before mine closure and familiarity with environmental problem. Out of the four education-level groups, the post-high school group was about seven times (odds ratio 6.97) more likely to

Table 5 Socioeconomic variables of the perception study, also denoting questions asked and answers given by 103 households

Class of variables and their content	Category	% of 103
Independent variables		
Socioeconomic characteristics		
Gender	Male vs. female	63
Age	<40 years	28
	40–59 years	17
	>60 years	54
Education	Secondary school	21
	Vocational school	33
	High school	28
	Post-high school studies	18
Household income per month	<1,000 RON[a] vs. more	60
Employment status	Unemployed	35
	Employed	29
	Retired	36
Issues attributed		
Observable effects in the river		
Colour, garbage, smell	Yes vs. no	40
Colour, garbage or colour, smell	Yes vs. no	36
Colour only	Yes vs. no	24
Change in pollution during last year before mine closure		
Certej River water quality	Deteriorated	11
	Unchanged	54
	Improved	35
Drinking water quality	Deteriorated	8
	Unchanged	84
	Improved	8
Intensity of pollution		
Taste of drinking water	Bad	25
	Fair	26
	Good	49
Likely to have a disease due to drinking water	Yes vs. no	12
Familiarity with environmental problem		
River water pollution mentioned as a problem	Yes vs. no	83
Water pollution mentioned as a potential risk to health	Yes vs. no	77
If mine still operational, river would be even more polluted	Yes vs. no	68
If mine still operational, drinking water would be even more polluted	Yes vs. no	40
Investment in mining would be a good opportunity	Yes vs. no	90
Dependent variables		
Degree of mining-induced pollution in the river	Highly polluted	48
	Not highly polluted	52
Degree of mining-induced pollution in the drinking water	Polluted	55
	Not polluted	45

[a] 1,000 RON correspond to about 285€

consider the River Certej as highly polluted than the high school graduates taken as a reference category. The other two education-level predictors exhibited also an odds ratio >1, but they were less significant ($p > 0.05$) and had low B values. This result supported the general view that more highly educated people show more concern with environmental problems. Regarding household income, respondents who reported a household income below 1,000RON per month were more likely to perceive the Certej River as highly polluted than the more affluent ones, although this effect was not significant at a 0.05 level. This income predictor was inconsistent with the general expectation that people with higher income usually show more concern with the environmental problems. The inverse relationship in the Certej catchment may be viewed as people associating their current economic condition with the precarious living neighbourhood. The other two explanatory variables were pollution in the last years before mine closure and familiarity with environmental problems. They showed an increased likelihood of predicting that locals perceive the Certej River to be highly polluted. People who believed that the water quality stayed the same or deteriorated compared to the period before mine closure were five to seven times more likely to perceive the water as being highly polluted than those who said that the water quality had improved since then. Also, people who reported that the mine would pollute more if it were still functioning were more likely to consider the river water to be highly polluted. These results were consistent with the fact that people perceive mining as a major source of pollution. The independent variables 'observable effects' were statistically insignificant in the analysis. In this model for the perception of the river water quality, 77% of the observations were correctly predicted (74% for those who considered the water as highly polluted and 80% for those who did not, e.g. who considered the river water as only being polluted). The outcome of the perception study agrees with the chemical data indicating a strong pollution of the river.

Three significant predictors estimated the perception 'polluted drinking water', education, household income and people who consider drinking water would be even more polluted if mines were still in operation. The model results indicated that these three categories were about three times more likely to consider drinking water to be polluted. Characteristics for pollution during the last years before mine closure and taste of drinking water were also tested, but none proved to be statistically significant. This model was able to correctly predict 66% of the observations, leading to the conclusion that the approach might not be able to estimate properly whether people in the Certej catchment believe their drinking water to be polluted by mining, or where there might be other independent variables, i.e. questions not included in the questionnaire, which could better explain the drinking water quality perception model. Indeed, the chemical data of the drinking water do not indicate polluted water in general.

Table 6 Results of the logistic regression analysis

Perception (model)	Predictors		*B*	*p*	Odds ratios
Highly polluted river water	Education	Secondary school	1.21	0.092	3.36
		Vocational school	0.92	0.141	2.51
		Post-high school studies	1.94	0.010	6.97
	Household income	<1,000 RON/month vs. more	0.78	0.137	2.17
	Pollution last years before closure	Deteriorated water quality	1.93	0.020	6.92
		Water quality stayed the same	1.69	0.002	5.42
	Familiarity environmental problem	If mines still operational, river would be even more polluted (yes vs. more)	1.63	0.003	5.11
		Constant (intercept)	−3.77	0.000	0.02
		Percent concordant=76.7%			
Polluted drinking water	Education	Secondary school	0.23	0.720	1.25
		Vocational school	0.04	0.941	1.04
		Post-high school studies	1.33	0.052	3.79
	Household income	<1,000 RON/month vs. more	1.18	0.009	3.25
	Familiarity environmental problem	If mines still operational, drinking water would be even more polluted (yes vs. more)	0.93	0.040	2.54
		Constant (intercept)	−1.14	0.030	0.32
		Percent concordant=66%			

Reference categories—high school; >1,000 RON/month; improved water quality; if mine still operational, water would be even more polluted

B regression coefficient, *p* significance level, *odds ratio* how much the likelihood of the outcome changes for a modification in one category vs. another, thus expressing the relative importance of the predictor in view to the reference category (examples see text)

5 Conclusions

The combined natural and socioeconomic study performed by the Romanian researchers revealed for the first time clear quantitative and qualitative evidence for the impact of mining activity in the Certej River valley.

The inputs of AMD from the large open pit and several adits drastically impaired the water quality of the river. The acidic pH and high concentrations of filtered heavy metal concentrations represented a chemical condition in the river that went way above the good chemical status required by the EU Water Frame Work Directive for running waters. Metal contents in sediments deposited in the middle and lower part of the river also indicated pollution. All these results contrasted to those found in the neighbouring Cris Alb catchment, where mining activities resulted in a spatially restricted impact only (Sima et al. 2008).

At present, the outflow of the large tailings dam Mialu only caused a moderate pollution. However, its AMD production potential due to the oxidation of pyrite incorporated in the tailings is enormous. It could even increasingly impair the water and sediment quality in the tributary to Certej River from a long-term perspective. The first sign of AMD production could yet be observed at the foot of the tailings dam where AMD outcrops.

In contrast to the polluted river, the groundwater taken from the dug wells for drinking water mostly exhibited a chemical quality complying with the EU drinking water standard.

The mining activities formed the main source of revenue for the inhabitants in the Certej catchment and still do it after closure. In spite of its benefit, people perceived conclusively that Certej River is highly polluted by mining, but their opinion on the pollution of drinking water was not so clear.

6 Recommendations and perspectives

Based on the natural science part of this study, a long-term survey should be established that will monitor the evolution of the AMD production in the tailings dam (Moreno and Neretnieks 2006), the changes in the water quality of the river, the drinking water wells and the groundwater downstream of the waste ore deposits and the changes in the fluxes and composition of sediments in Certej River. Such a programme, consisting of two or three sampling campaigns a year at key stations, should also include measurements during high floods events, i.e. heavy rainfalls. Additional observation piezometers should be installed to control the migration of possible contamination plumes in the groundwater.

However, pollution monitoring represents just a first step into a more elaborated plan to mitigate existing mining impacts. Few statements may trace the general direction to go on. At a minimum, measures should be taken to slow down the AMD evolution. Proper consolidation of tailings dams is an additional issue (Vrubel et al. 2007). However, regulations and remediation actions of metal mining waste sites (Gore et al. 2007) will face many difficulties (Gustavson et al. 2007) and need an adaptive management (Linkov et al. 2006) implying a long-term and firm commitment of all stakeholders involved (Fourie and Brent 2006). A mitigation plan also incorporates the perception of the inhabitants towards the pollution problem and the environmental risk of mining. It should also consider actions to ameliorate the tenuous economic situation of the inhabitants due to mine closures. Increasingly, there are good chances to find financial support for remediation of the tailings impoundments themselves, as they still represent a resource of metals that could be exploited in time of high and growing metal prices. Therefore, a first approach in this direction would be to investigate in detail if tailings impoundments exhibit economically recoverable metals. In the case of Mialu dam, it would be an important measure to retreat and redeposit the material in a safe way as the dam is constructed as an upstream impoundment, a highly dangerous technique predestined for dam failures, as already occurred in the area during the 1970s.

The Certej River catchment would be suitable for a case study project concerning mining rehabilitation, since a restricted number of clear cut problems have to be tackled in an area of limited size and easily understandable structure.

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