EFFECTS OF PAST MINING ON THE QUALITY OF WATER RESOURCES IN SARDINIA

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ABSTRACT

This paper reports the results of hydrogeochemical surveys carried out in Sardinia, a Mediterranean region with a mining history dating back to pre-Roman times. Among different ore deposits occurring in the region, the largest base-metal deposits were located in the Arburese-Fluminese-Iglesiente districts (SW Sardinia), with galena and sphalerite being the prominent exploited minerals. At some locations, pyrite, chalcopyrite, antimonite, barite and fluorite were also exploited intensively. Peaks in Pb-Zn production were reached in the 1950-1960 decades. The decline of mining industry led to the closure of most mines over the 1970-1990 period. This resulted in estimated 170 abandoned mines and 200 million tons of mining-related wastes.

Because environmental regulation of mining activities has been introduced relatively recently, the Regional and National Authorities did not plan any action for limiting the potential adverse effects of mine closure on the water systems. Nowadays, several drainages from flooded mines (flow range: <0.1 to 30 L/s) and diffused seeps from the mining residues left on the ground are the main mining-related sources of contamination in Sardinia. At specific sites, mine drainages show different physical-chemical characteristics (acid and near-neutral pH) and dissolved concentrations of contaminants (e.g. Zn, Cd, Pb, Ni, As, Sb) that span over several orders of magnitude, mainly depending on the composition of ore and hosting rocks.

Due to the proximity of mining sites to water resources, and land that is within reach of animals and humans, the major risks to human health are associated with the direct discharge of contaminated waters into the aquatic recipients and soils located downstream of the abandoned mines. The contamination level increases during the rain season, especially under storm events that have been occurring more frequently since the past decade. In fact, high runoff promotes erosion and increases the weathering of mining residues. These processes result in a higher dispersion of toxic and harmful elements that pose serious environmental hazards, especially to the aquatic system.

These results should help the Regional and National Authorities to address the increasing public awareness of health-related environmental issues and present regulations on the quality of water resources. Also, they might be useful elsewhere for planning remediation actions at abandoned mining sites. Lessons learnt by past mining in Sardinia indicate that a correct disposal and management of the mining residues should be mandatory since the beginning of exploitation and processing at each mine. This would allow to reduce the environmental hazards during mining as well as the cost of rehabilitation after mine closure.

1. INTRODUCTION

Abandoned mining sites pose physical safety and environmental hazards recognized by the United Nations as one of the major outstanding environmental problems related to mining (UNEP, 2001). Mining activities have a relevant influence on the quantity and quality of water resources in the surrounding environment. Dewatering during exploitation leads to drawdown the water table with consequent disappearance of certain springs or decrease in their flow. The rebound after the mine closure may degrade the quality of groundwater (e.g. Gandy and Younger, 2007), which is no more suitable for a valuable use. The deterioration of water quality caused by residues of ore exploitation and processing has been recognized worldwide (e.g. Neal et al., 2005; Wolkersdorfer and Bowell, 2005; Peplow and Edmonds, 2006). Therefore, the chemical contamination of water systems at abandoned mining sites demands investigation strategies capable of describing sources and pathways of contaminants and containment strategies devoted to limit the diffusion of toxic components.

Industrial mining activities in Sardinia (Italy) started in the 1850-1870. The largest Zn-Pb deposits were located in the Arburese-Fluminese-Iglesiente districts (Figure 1). At Funtana Raminosa (FR in Figure 1), the main exploited minerals were chalcopyrite, galena and sphalerite. Relevant Sb deposits were located in SE Sardinia (SU in Figure 1).

The cessation of mining activities over the 1970-1990 period left 169 abandoned mines and an estimated volume of mining wastes of $71*10^6$ m^3; these contaminated materials are spread over a 19 km^2 surface (RAS, 2003). About 67% of the abandoned mines and 90% of wastes occur in the Arburese-Fluminese-Iglesiente districts (Figure 1).

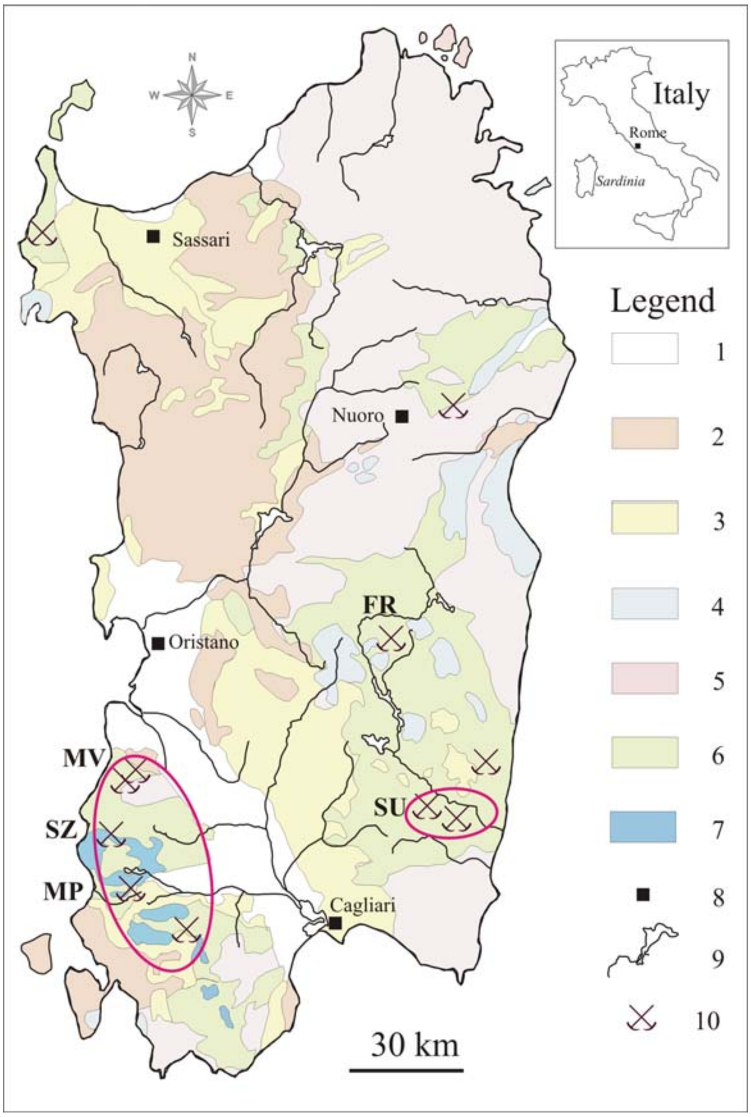

Figure 1. Schematic geologic map of Sardinia showing locations of relevant mining sites. Legend: 1 Recent sediments; 2 Basaltic (Plio-Pleistocene) and andesite prevailing volcanic sequences (Oligocene-Miocene); 3 Marly sandstone, siltstone, limestone and conglomerate (Miocene); 4 Limestone and dolostone (Dogger-Malm); 5 Granitic rocks (Carboniferous); 6 Palaeozoic basement; 7 Limestone and dolostone (Cambrian); 8 Towns; 9 Main rivers, streams and reservoirs; 10 Abandoned mines, MV: Montevecchio (Zn-Pb, Arburese), SZ: Su Zurfuru (Zn-Pb, Fluminese), MP: Monteponi (Zn-Pb, Iglesiente), FR: Funtana Raminosa (Cu, Barbagia Belvì), SU: Su Suergiu (Sb, Gerrei).

Climatic conditions in the region are characterized by long periods of heat and drought, usually extending from May to September, interrupted by relatively short rainy periods, with occasional heavy rain events. Mean annual rainfall ranges from 400 mm near to the coast to 900 mm inland, with a mean of 50 rainy days per year; the mean annual temperature is 15°C (RAS, 1998). River waters collected in artificial basins represent about 70% of the water supply for agricultural, industrial and domestic uses for a population of approximately 1.6 million people. The availability of water from reservoirs is very low in the Iglesiente (SW Sardinia), while the Cambrian carbonate formations host important aquifers due to intense fracturing and karst processes. It must be pointed out that the same formations also host large abandoned mines now flooded. Due to the increase of domestic water demand and the difficulty of alternative water supply in the Iglesiente, the groundwater hosted in flooded mines is considered a strategic water resource by the Regional Authorities.

This paper reports some results of hydrogeochemical surveys carried out in Sardinia. The information derived from our studies should help the Regional and National Authorities to address present environmental regulations, also, it might be useful in planning remediation actions at abandoned mining sites elsewhere.

2. IMPACT OF PAST MINING ON WATER SYSTEMS

Results on the composition of mine drainages in Sardinia show a large variability, as it can be seen from selected data reported in Table 1. Acid and/or near neutral mine drainages may occur at specific sites. Dissolved (i.e. <0.4 µm aqueous fraction) concentrations of contaminants span over several orders of magnitude, mainly depending on the composition of ore and hosting rocks. In this paper, a few case studies have been selected to show the mining impact on water systems in prominent areas affected by past mining.

Table 1. Composition of some mine drainages in Sardinia after a flushing time ≥10 years. Concentrations were determined on aliquots filtered through 0.4 µm. Locations of mines are shown in Figure 1.

mine	dominant ore	date	flow L/s	pH	TDS* g/L	SO_4 g/L	F mg/L	Fe mg/L	Mn mg/L	Zn mg/L	Cd µg/L	Pb µg/L	Sb µg/L
MV	Zn-Pb	2008	1	4.1	4.9	3.2	1.0	90	46	1200	9000	1800	<1
SZ	Zn-Pb	2008	1	7.6	0.8	0.3	2.4	5	3	19	42	14	<1
SU	Sb	2006	<1	7.8	2.9	1.9	0.5	<0.1	<0.1	0.1	0.3	1	300
FR	Cu	2005	<1	7.8	1.2	0.8	2.3	0.1	0.2	4.6	135	8	<1

* total dissolved solids; MV: Montevecchio; SZ: Su Zurfuru; SU: Su Suergiu; FR: Funtana Raminosa

Arburese District

In the Arburese (SW Sardinia, Figure 1), the Pb-Zn vein ores are hosted in Palaeozoic silicate-dominant rocks. These deposits are mainly comprised of galena and sphalerite; quartz, pyrite, marcasite, and other sulfide minerals, and local occurrences of siderite, ankerite and calcite are associated with the ore. The ore exploitation extended in a system of overlapping galleries for a depth of 600 m below ground level. The tailings, initially contained by dams, were periodically discharged into the local streams. At present, the dumped wastes are deeply eroded and most of the material has been transported and deposited on the stream banks. Since 1940, the largest flotation tailings impoundment was located at Montevecchio (Piccalinna). These tailings have grain size <63 µm; average metal contents are 7.2 wt. % Fe, 0.4 wt. % Zn, 0.2 wt. % Pb, 166 mg/kg As, 140 mg/kg Cu, 29 mg/kg Ni, 27 mg/kg Cd, and 15 mg/kg Co; approximately 80 % of Pb and 60 % of Zn are easily soluble when subjected to a sequential extraction procedure (Da Pelo, 1998).

Under dewatering conditions, the total flow of water pumped out of the Arburese mines was in the range of 55 to 70 liters per second (L/s). In 1973 (i.e. under active mining; Biddau, 1978), the pH was near neutral, concentrations of sulfate and metals were high (see Table 2). The closure of mines implied the shutdown of pumping systems, thereafter waters flowing out of galleries and shafts were observed since 1996. At the beginning, mine drainages showed dissolved (i.e. aqueous fraction <0.4 µm) concentrations of sulfate and metals much higher than those observed under dewatering conditions (Table 2). These high concentrations of Zn, Cd and Pb can be explained taking into account that the underground workings were kept dry during exploitation; flooding allowed the contact of water with sulfide minerals promoting their oxidation and mobilization of metals. Then, mine wastes and flotation tailings have been used to refill the underground workings; flushing of these materials was facilitated by their small grain size. Results of hydrogeochemical surveys carried out during the period 1996-2008 can be summarized as follows. The flow from the Montevecchio adits varied from 2 to 20 L/s depending on rainfall infiltration. The acidity produced by the oxidation of sulfide minerals (especially pyrite) has been not buffered at Montevecchio (pH: 3.6-4.3) due to the poor occurrence of carbonates in the ore and host rocks. As compared with values recorded at the first stages of rebound, a significant decrease (about 50%) in sulfate and metal concentrations was observed in 2008, nevertheless, a very high contamination level still persists after 13 years of flushing (Figure 2).

Table 2. Mine drainage at Montevecchio. In 1996 waters were filtered through 0.4 µm filters; information not available on the 1973 data.

	exploitation 1973*	closure 1996
pH	6.2	3.6
SO_4 (mg/L)	2000	5000
Zn	290	2400
Cd	1	24
Pb	1.2	2.6
Mn	4	88
Fe	**	130

* from Biddau (1978)

** not reported

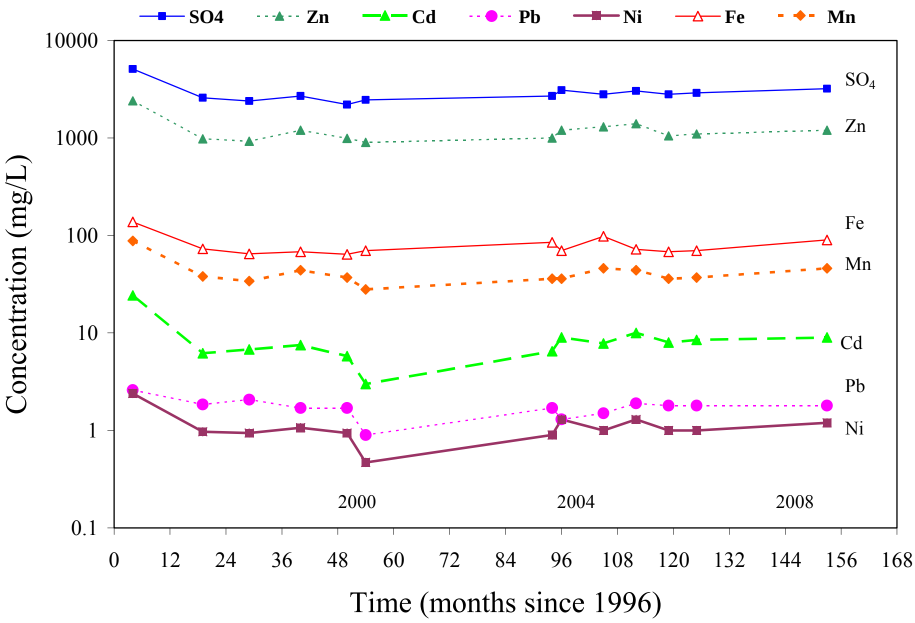

Figure 2. Temporal variations of dissolved sulfate and metals in water flowing out of the Montevecchio adit. Concentrations were determined on aliquots filtered through 0.4 µm. The pH values were in the range of 3.6 (in 1996) to 4.2 (in 2008). As compared to the first stage of rebound, a decrease of about 50 % in the dissolved load of sulfate and metals occurred.

Mine drainages from Montevecchio flow directly into the Rio Montevecchio. Additional contamination in the streams of the area derives from the weathering of mining-derived solid materials abandoned on the ground. This contamination is enhanced during heavy-rain events that cause high runoff. A decrease in dissolved metals occurs downstream at sites where uncontaminated tributaries flow into the contaminated streams. Despite the load of dissolved contaminants decreases from the mine sites downstream, the dispersion of toxic elements extends about 10 km eastwards to the Marceddì lagoon (see Table 3). Consequently, sediments in this lagoon have relevant concentrations in metals, i.e. mean values 1022 mg/kg Zn, 62.4 mg/kg Pb and 5.8 mg/kg Cd in the solid fraction <4 µm (Magni et al., 2006). This contamination might result in potential adverse effects on fishery that represents an important activity for the local community. Indeed, results of a year-round biomonitoring study on mussels carried out in the Gulf of Oristano showed that higher values of micronuclei frequency and DNA damage occurred in mussels from Marceddı` as compared to those detected in mussels from the control site (Magni et al., 2006). However, another investigation carried out in 2006 showed metal concentrations in fish and bivalve samples collected in the lagoon below the maximum values established by the European Community (no. 1881/2006); nevertheless, monitoring of the fish quality in this stressed environment has been recommended (RAS, 2007).

Table 3. Estimated amount of metals discharged daily into the Marceddì lagoon. Metals were determined on aliquots filtered through 0.4 µm.

source	Montevecchio	
recipient	Marceddì lagoon	
date	January 2003	June 2003
flow (L/s)	400	70
Zn (kg/day)	100	1.8
Cd	0.7	0.006
Pb	1.7	0.06
Ni	0.3	0.02

Fluminese-Iglesiente Districts

Ore bodies in the Fluminese-Iglesiente districts (Figure 1) consist of massive and lower grade sulfides hosted in Cambrian carbonate sequences; the most abundant ore minerals are sphalerite and galena, with variable pyrite contents; barite and fluorite are abundant at some locations; ore bodies near the surface are generally oxidized (Boni, 1994). In the Fluminese, drainage out of five adits was observed soon after the closure of mines in 1980-1990. These mine waters were near neutral to slightly alkaline (pH: 6.3-8.2), reflecting their circulation in carbonate rocks, and showed a wide range of metal concentrations depending on the dominant mineral assemblage at each mine. The highest concentrations of dissolved metals were observed for Zn (100 mg/L), Mn (18 mg/L), Fe (15 mg/L), Cd (0.3 mg/L) and Ni (0.3 mg/L). Although the discharge of these mine drainages into the local streams causes a deterioration of the water quality, the overall contamination level in this district is much lower than that observed in the Arburese.

In the Iglesiente district, rebound of mines did not cause outflows from adits and/or shafts up to present (2009). At the beginning of rebound (1997-1999), a marked increase in dissolved SO_4 (800 mg/L), Zn (57 mg/L), Cd (0.1 mg/L) and Fe (30 mg/L) was observed. In 2005, i.e. after 8-years of rebound, the groundwater sampled at the water table level in each mine showed dissolved concentrations of Zn, Cd, and Hg below the recommended values for drinking water, except at two sites showing Hg (1.9-2.3 µg/L) above the 1 µg/L limit (WHO, 2006). Relatively high levels of Pb (10-81 µg/L) were still present in groundwater at most mines. Speciation using the PHREEQC thermodynamic code (Parkhurst and Appelo, 1999) showed that the most abundant species of dissolved Pb was $PbCO_3^0$ (80-95%). Lead speciation did not vary under flooded or dewatered conditions, nor at low or high salinity; the $PbCO_3^0$ species is highly soluble and might explain the relatively high Pb observed in these mine waters under non acidic conditions.

It is important to recall that the groundwater hosted in flooded mines in the Iglesiente represents a strategic water resource. As compared with the beginning of rebound, the quality of groundwater in the aquifers of the Iglesiente mining district has significantly improved, especially in the upper aquifer (Cidu et al., 2007), so that this resource can be properly exploited up to the limit of the annual recharge. Indeed, groundwater from the Campo Pisano mine presently contributes to supply to the town of Iglesias (about 30,000 inhabitants). However, a greater exploitation might result in bad quality water being extract, thus monitoring will be required to predict any degradation in the mine groundwater quality.

Gerrei District

In the Gerrei (Figure 1), Sb deposits are hosted in Palaeozoic black schists and metalimestones. The mineralization consists of antimonite, scheelite, arsenopyrite, pyrite and gold, with calcite and quartz in the gangue (Funedda et al., 2005). Ores in these districts have been exploited and processed until 1960-1980. The mining residues left on the ground include flotation tailings and slag derived from Sb-processing. Some drainages from abandoned mining sites flow into tributaries of the southern Flumendosa River, which is a significant resource used for domestic purposes and for irrigation of a fertile plain.

In this area, surface and ground waters have chemical composition varying from Na-Cl with low total dissolved solids (TDS 0.1-0.5 g/L) to Ca-HCO_3 with TDS in the range of 0.2 to 0.8 g/L. The waters that drain the mine sites generally have a distinguished Ca-SO_4 composition with TDS up to 3 g/L and show much higher dissolved concentrations of toxic or harmful elements. The highest concentrations of Sb and As occurred in the waters that drain the Sb mine of Su Suergiu (Figure 1).

Detailed sampling carried out under low flow condition at Su Suergiu showed Sb concentrations in the range of 0.4 to 7 µg/L in waters sampled out of the mined area, and up to 380 µg/L in waters from adits. The highest concentrations of dissolved Sb (up to 9600 µg/L) and As (up to 3500 µg/L) were observed in waters flowing out of the slag materials derived from the processing of Sb-ore. Dissolved Sb concentrations in the stream draining the Su Suergiu area, about 3 km downstream of the mine site, were 800 µg/L and 1200 µg/L, respectively under high (about 200 L/s) and low flow (3 L/s) conditions. Leaching tests on the slag wastes showed that these materials react very fast (Cidu et al., 2008b); this explains the high Sb concentrations observed in the stream draining the mine area under high flow conditions.

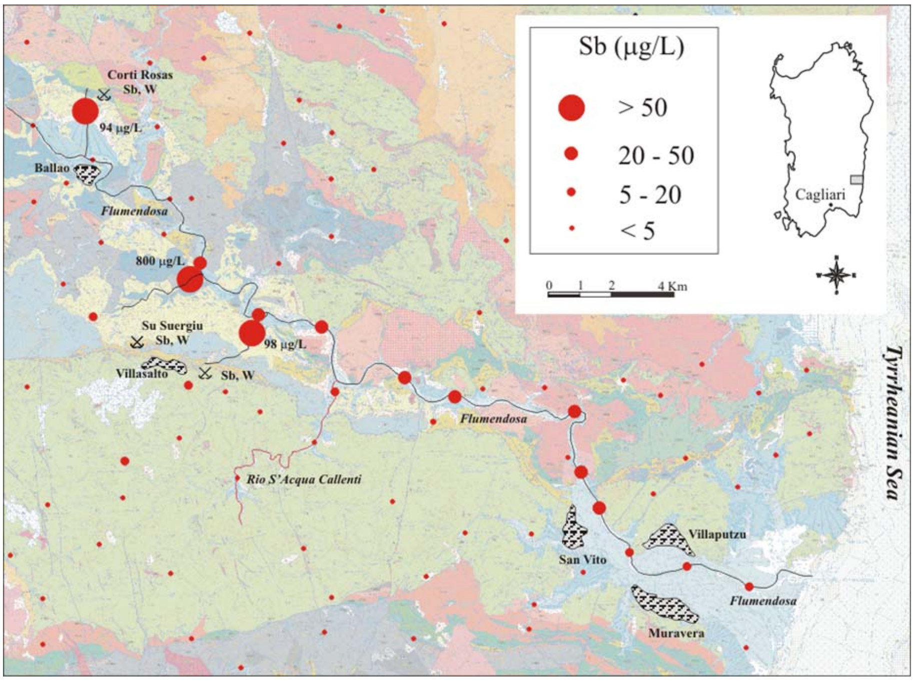

Figure 3. Concentrations of dissolved (i.e. aqueous fraction <0.4 µm) Sb in stream waters of the Flumendosa River catchment sampled under high flow condition (Cidu et al., 2008a).

Contamination from Su Suergiu affects the Flumendosa River: the water sampled upstream of the contaminated tributary showed 4 µg/L Sb and 1.9 µg/L As, values below the limits established by the World Health Organization guidelines for drinking water (20 µg/L Sb and 10 µg/L As; WHO, 2006), while downstream of the confluence dissolved Sb was 32 µg/L and As 6.7 µg/L. Antimony contamination in the Flumendosa extended some 16 km downstream of the abandoned mines; an attenuation (15 µg/L Sb) was only observed close to the mouth (Figure 3).

3. CONCLUSIONS

The hydrogeochemical approach appeared to be a valuable tool for the understanding of contamination processes occurring at abandoned mining sites. The examples shown above indicate that drainages from flooded mines and seeps from the mining residues left on the ground are the main mining-related sources of contamination in Sardinia. The major risks to the water systems are associated with the direct discharge of contaminated waters into the aquatic recipients located downstream of the contaminant sources. The dispersion of toxic and harmful elements increases during the rain season, especially under heavy rain conditions. High runoff results in high concentrations of dissolved metals, especially Zn, Cd, Pb and Sb in the stream waters, due to the weathering of the exposed mining residues. Because a high quantity of fine material is observed at such conditions, the dispersion of contaminants is favored by transport via adsorption processes onto very fine particles (<0.4 µm) and/or associated to colloids (Cidu and Frau, 2009).

Taking into account the risk to human health due to the proximity of the Sardinian mining sites to water resources and land that is within reach of animals and humans, different actions aimed to reduce the contamination level are needed at specific sites. Among actions requiring relatively low investments, the physical stabilization of the contaminated solid materials would reduce rates of erosion processes; the creation of drain systems to diverting runoff on the waste dumps and impoundments could minimize the contact between water and the polluted materials. These actions would be appropriate for the Su Suergiu site because proved to be efficient in reducing significantly the dispersion of contaminants when used elsewhere in Sardinia. As an example, the stream receiving the drainages from tailings contained in drained impoundments at Funtana Raminosa (Central Sardinia) showed relatively low concentrations of metals (170 µg/L Zn, 7 µg/L Cd and 1 µg/L Pb; Cidu, 2007). Also, the collection of the mine drainages in artificial ponds prior to discharge into streams and soils will favor the decrease of dissolved contaminants via settlement of the fine particles and precipitation-sorption processes. Ideally, the extremely contaminated drainages should be 'cleaned' before discharge, and the highly contaminated solid residues should be removed or properly disposed. These actions will require much larger investments, including long-term costs for the management of decontamination plants and the disposal of treatment-derived residues.

The information derived from our studies should help the Regional and National Authorities to address present environmental regulations and might be useful in planning remediation actions at abandoned mining sites elsewhere. Lessons learnt by past mining in Sardinia indicate that a correct disposal and management of the mining residues should be mandatory at the active mines. This would allow to reduce the environmental risks as well as the cost of rehabilitation.

4. REFERENCES

Biddau, M. (1978) “Indagine chimica-idrologica sulle possibilità di utilizzazione delle acque edotte nel Sulcis-Iglesiente.” *La Programmazione in Sardegna,* **67/68**, 99-115 (in Italian).

Boni, M. (1994) “Ores in southwestern Sardinia.” In: Bechstädt, T., and Boni, M. (eds.), Sedimentological, stratigraphical and ore deposits field guide of the autochthonous Cambro-Ordovician of southwestern Sardinia. *Mem. Descr. Carta Geol.d’It., Serv. Geol. Naz,.* **48**, 155-184.

Cidu, R. (2007) “Influence of past mining on the quality of surface waters at Funtana Raminosa (Sardinia).” *Mine Water and the Environment*, **26**, 199-208.

Cidu, R., Biddau, R., and Nieddu, G. (2007) “Rebound at Pb-Zn mines hosted in carbonate aquifers: influence on the chemistry of ground water.” *Mine Water and the Environment*, **26**, 88-101.

Cidu, R., Caboi, R., Biddau, R., Petrini, R., Slejko, F., Flora, O., Aiuppa, A., Parello, F., and Valenza, M. (2008a) “Caratterizzazione idrogeochimica ed isotopica e valutazione della qualità delle acque superficiali e sotterranee campionate nel Foglio 549 Muravera.” In: *GEOBASI*, Ottonello, G. (ed.), pp 149-183. Pacini Editore, Pisa (in Italian).

Cidu, R., Fanfani, L., Frau, F., Biddau, R., Cabras, R., and Da Pelo, S. (2008b) “The abandoned antimony-mines of SE Sardinia: impact on surface waters.” *Proceedings IMWA 2008*, June 1-5, 2008, Karlovy Vary, Czech Republic, pp 127-130.

Cidu, R., and Frau, F. (2009) “Influence of the fine-particle load in Mediterranean rivers and streams on the distribution of trace elements in filtered and non filtered aqueous fractions.” *Applied Geochemistry*, **24**, 611-623.

Da Pelo, S. (1998) “Mineralogia e geochimica ambientale di aree minerarie attive e dismesse.” *PhD thesis,* 95 pp, University of Cagliari, Italy (in Italian).

Funedda, A., Naitza, S., and Tocco, S. (2005) “Caratteri giacimentologici e controlli strutturali nelle mineralizzazioni idrotermali tardo-erciniche ad As-Sb-W-Au del basamento metamorfico paleozoico della Sardegna sud-orientale.” *Resoconti Associazione Mineraria Sarda*, **CX**, 25-46 (in Italian).

Gandy, C.J., and Younger, P.L. (2007) “Predicting groundwater rebound in the South Yorkshire Coalfield, UK.” *Mine Water and the Environment*, **26**, 70–78.

Magni, P., De Falco, G., Falugi, C., Franzoni, M., Monteverde, M., Perrone, E., Sgro, M., and Bolognesi, C. (2006) “Genotoxicity biomarkers and acetylcholinesterase activity in natural populations of Mytilus galloprovincialis along a pollution gradient in the Gulf of Oristano (Sardinia, western Mediterranean).” *Environmental Pollution,* **142**, 65-72.

Neal, C., Whitehead, P.G., Jeffery, H., and Neal, M. (2005) “The water quality of the River Carnon, west Cornwall, November 1992 to March 1994: the impacts of Wheal Jane discharges.” *Science of the Total Environment*, **338**, 23–39.

Parkhurst, D.L., and Appelo, C.A.J. (1999) “User’s guide to PHREEQC (version 2) – a computer program for speciation, batchreaction, one-dimensional transport, and inverse geochemical calculations.” *US Geol. Surv. Water-Resour. Invest. Rep. 99–4259.*

Peplow, D., and Edmonds, R. (2006) “Cell pathology and development effects of mine waste contamination on invertebrates and fish in the Methow river, Okanogan County, Washington (USA).” *Mine Water and the Environment,* **25**, 190-203.

RAS (1998) *Nuovo studio dell’idrologia superficiale della Sardegna,* Regione Autonoma della Sardegna, Assessorato della Programmazione, Bilancio ed Assetto del Territorio, Ente Autonomo del Flumendosa, Cagliari (in Italian).

RAS (2003) *Piano regionale di gestione dei rifiuti,* Regione Autonoma della Sardegna, 255 pp (in Italian).

RAS (2007) *Piano di monitoraggio ambientale degli stagni di S. Giovanni e Marceddì e della antistante fascia marino costiera compresa tra lo stagno di Marceddì e Capo della Frasca – relazione conclusiva,* Regione Autonoma della Sardegna, 11 pp (in Italian).

UNEP (2001) *Abandoned mines: Problems, issues and policy challenges for decision makers – Summary Report,* United Nations Environment Programme and Chilean Copper Commission, Santiago, Chile, <http://www.natural-resources.org/minerals/CD/docs/unep/abandoned_mines_report.pdf> (accessed May 26, 2009).

WHO (2006) *Guidelines for Drinking-water Quality. Third Edition,* World Health Organization, Geneva.

Wolkersdorfer, C., and Bowell, R. (eds.) (2005) “Contemporary reviews of mine water studies in Europe.” *Mine Water and the Environment*, **24**, Supplementary Material.

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