

# IMPACT OF THE CASARGIU MINE DRAINAGE (SW SARDINIA, ITALY) ON THE MEDITERRANEAN SEA

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## ABSTRACT

In Sardinia (Italy), Pb-Zn vein ores hosted in Palaeozoic silicate-dominant rocks of the Arburese mining district have been exploited in a system of overlapping galleries for a depth of 600 m below ground level. To keep the pits dry, a total flow in the range of 55 to 70 liters per second (L/s) of water was pumped out of the mines. In 1973 (i.e. under active mining), the pumped water at the Casargiu mine was circumneutral (pH 7.5) and concentrations of sulfate (1400 mg/L) and metals (e.g. 70 mg/L Zn, 1.2 mg/L Cd) were high. The mine closure in the 1980s implied the shutdown of pumping systems, thereafter drainage flowing out of the Casargiu shafts was observed since 1996. At the beginning, the mine water showed a pH of 6.0 and dissolved concentrations of sulfate (5000 mg/L) and metals (e.g. 1000 mg/L Zn, 2 mg/L Cd) much higher than those observed under dewatering conditions. These extreme concentrations 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, and the dissolution of efflorescent salts. The acidity produced by the oxidation of sulfide minerals (especially pyrite) has been in part buffered by the occurrence of calcite and ankerite minerals in the Casargiu ore.

As compared with values recorded at the first stages of rebound at Casargiu, a significant decrease (about 50%) in sulfate and metal concentrations was observed in 2009; nevertheless, a very high contamination level still persists at this site after 14 years of flushing.

Mine drainages from Casargiu (20-70 L/s) flow into the Rio Irvi stream. A decrease in dissolved metals occurs downstream by precipitation of solid phases. In the reach of the Rio Irvi stream (pH 6-7), low crystalline goethite as fresh and more consolidated precipitates, and "green rust" as very thin layers in the ochreous deposits and suspended colloidal particles have been observed.

Despite the load of dissolved contaminants decreases from the mine site downstream, the dispersion of toxic elements extends about 5 km westwards to the Mediterranean Sea. The estimated amount of dissolved metals discharged into the sea is relevant (e.g. 900 kg/day Zn, 1.4 kg/day Cd, 0.8 kg/day Pb).

## 1. INTRODUCTION

Sardinia is an Italian region with relevant mining activities dating back to pre-Roman times. Peaks in Pb-Zn production were reached in the 1950-1960 decades. The decline of mining industry, due to the fall in value of base metals and the increase of labor costs, led to the closure of base-metal mines over the 1970-1990 period. The potential adverse effects of mine closure were not given proper consideration, especially the risk to human health due to the proximity of mining sites to water resources. 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 (WHO, 2006).

In the Arburese mining district (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. Figure 1 shows the location of mines, flotation plants and tailings. 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.

This paper focuses on the impact of mine drainage from the Casargiu shaft (Figure 1) on the water system and its influence on the Mediterranean Sea.

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 rainfall is 500 mm per year, with a mean of 50 rainy days per year; the mean annual temperature is 15°C (RAS, 1998).

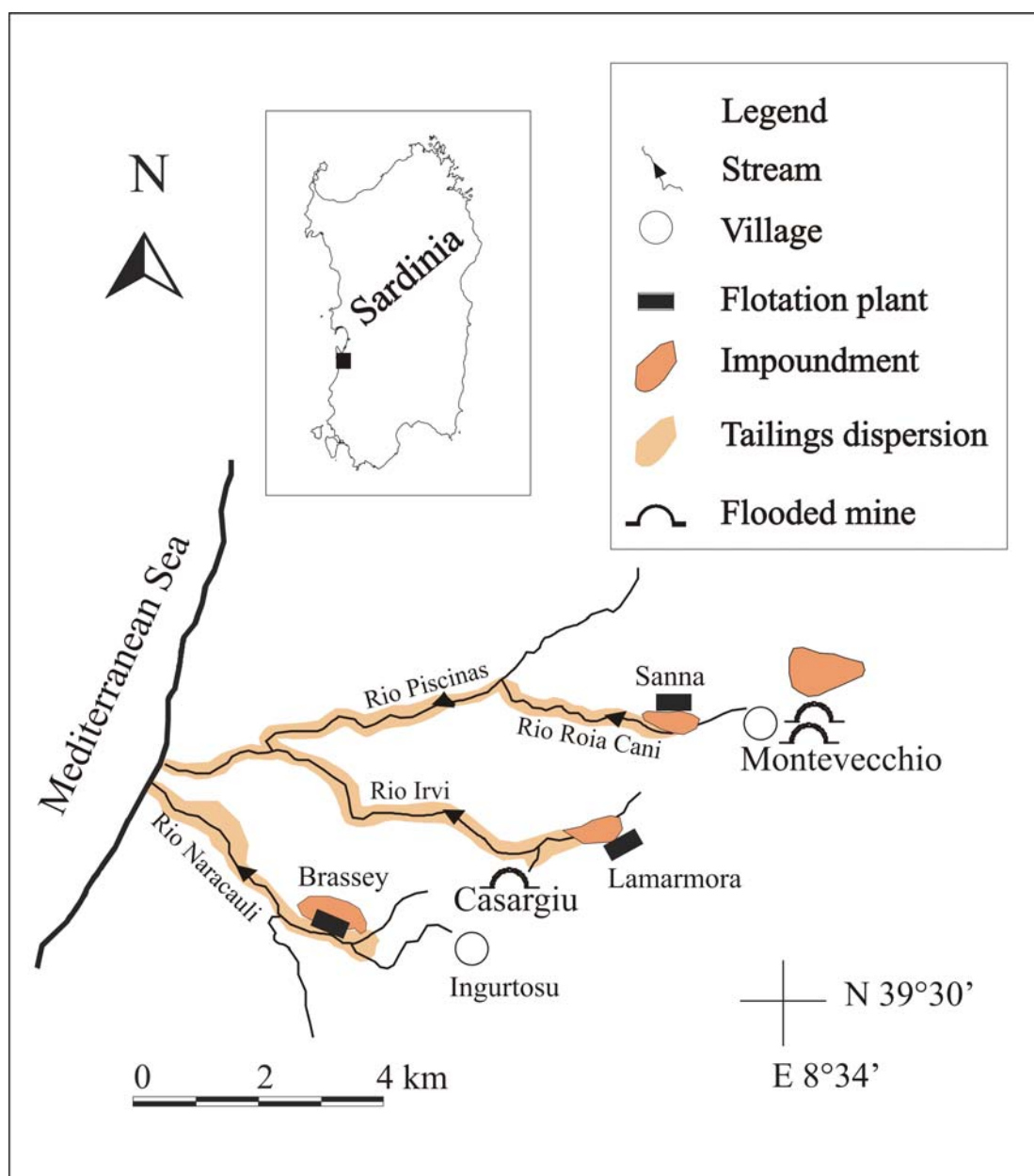


Figure 1. Map showing the Arburese mining district.

## 2. SAMPLING AND METHODS

At Casargiu, sampling and analyses of mine waters and surface waters draining mining sites have been carried out under different seasonal conditions since 1997 till present. At the sampling site, the pH, redox potential (Eh), temperature and alkalinity were measured; waters were filtered through 0.4  $\mu\text{m}$  and 0.01  $\mu\text{m}$  pore-size Nuclepore polycarbonate filters into pre-cleaned high-density polyethylene bottles. Filtered aliquots were acidified on site with suprapure grade  $\text{HNO}_3$  for metal analyses by quadrupole inductively coupled plasma - mass spectrometry (ICP-MS) and major cations by inductively coupled plasma – optical emission spectrometry (ICP-OES). Anions were determined by ion chromatography on a filtered (0.4  $\mu\text{m}$ ), not acidified aliquot. In this paper dissolved concentrations refer to elements determined in the aqueous fraction <0.4  $\mu\text{m}$ .

Preliminary mineralogical analyses by X-ray powder diffraction (XRD) were performed on samples of precipitates collected in the bed of the Rio Irvi stream, as well as on suspended particulate material retained on filters upon water filtration.

### 3. IMPACT OF PAST MINING ON WATER SYSTEMS

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). At Casargiu, in 1973 (i.e. under active mining; Biddau, 1978) the pH was near neutral, concentrations of sulfate and metals were high (see Table 1). The closure of mines implied the shutdown of pumping systems, thereafter waters flowing out of galleries and shafts were observed since 1996 (Cidu and Fanfani, 2002). At the beginning, mine drainages showed dissolved concentrations of sulfate and metals (especially Zn, Mn, and Fe) much higher than those observed under dewatering conditions (Table 1). This 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, and the dissolution of efflorescent salts. Also, mine wastes and flotation tailings have been used to refill the underground workings; the small grain size of these materials has certainly favored water-rock interaction and transport of fine particles.

Table 1. Mine drainage at Casargiu during exploitation and after closure.

	exploitation	closure
date	1973*	1997
pH	7.5	6.0
SO <sub>4</sub> (mg/L)	1400	5000
Zn	70	1000
Cd	1.2	2
Pb	0.8	0.8
Mn	0.5	150
Fe	4.6	230

\* from Biddau (1978)

Results of hydrogeochemical surveys carried out during the period 1996-2009 can be summarized as follows. The flow from the Casargiu shaft varied from 20 to 70 L/s depending on rainfall infiltration. The acidity produced by the oxidation of sulfide minerals is in part buffered by the occurrence of calcite and ankerite. As compared with values recorded at the first stages of rebound, a significant decrease (about 50%) in dissolved sulfate and metal concentrations were observed in 2009 (Figure 2); nevertheless, a very high contamination level still persists after 14 years of flushing.

Additional contamination in the streams of the area derives from the weathering of mining-derived solid materials abandoned on the ground (Caboi et al., 1993; 1995; 1996; 1999). 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. Further attenuation in the dissolved load of contaminants occurs by precipitation of solid phases. As an example, in the Rio Naracauli (Figure 1) the precipitation of Zn is controlled by the equilibria with hydrozincite  $Zn_5(CO_3)_2(OH)_6$  and an amorphous Zn-Si-O-H phase; the precipitation of hydrozincite has been described as the result of photosynthetic metabolism of a microbial community which shifts the inorganic C species in solution to the carbonate form (Podda et al., 2000).

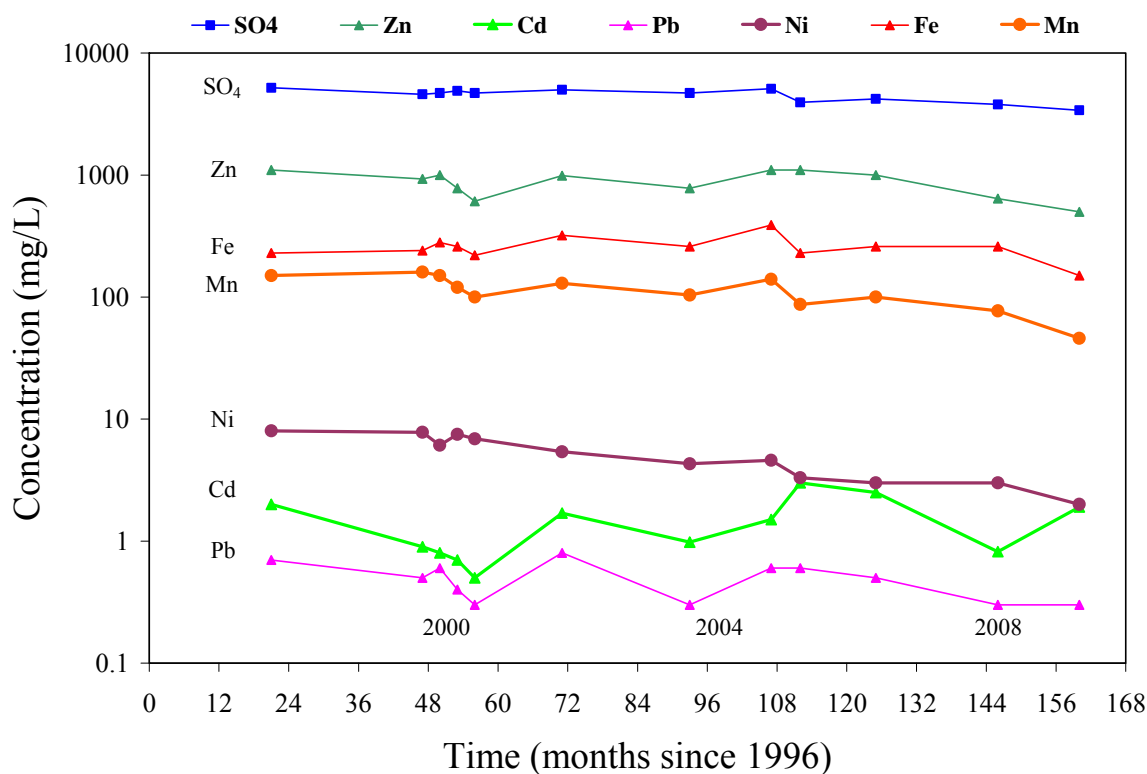


Figure 2. Temporal variations of dissolved sulfate and metals in water flowing out of the Casargiu shaft. The pH values were  $6.0 \pm 0.2$ . As compared to the first stage of rebound, a decrease of about 50% in the dissolved load of sulfate and metals occurred.

Mine drainages from Casargiu flow into the Rio Irvi stream (Figure 1). Abundant precipitation of solid phases occurs downstream from the Casargiu outflow. Preliminary sampling and XRD analysis of these precipitates showed the presence of low crystalline goethite as fresh and more consolidated precipitates (Figure 3). Interestingly, “green rust” has been observed in the field and identified by XRD (Figure 3); it occurs as very thin (2-3 mm) layers just below the surface of the ochreous deposits, and as suspended colloidal particles especially in the reach of the Rio Irvi stream (about 500 m downstream from the Casargiu outflow) where the high concentration of ferrous iron is evidenced by the green color taken from stream water. Green rusts are mixed ferrous/ferric layered double hydroxides with various anions (e.g. chloride, sulfate, carbonate) and water molecules occupying the interlayer between the iron-hydroxide layers (Bearcock et al., 2006). They typically form under weakly acidic to alkaline conditions in suboxic environments and when exposed to oxic conditions rapidly transform (within minutes) to various iron (oxyhydr)oxides. At Casargiu, the occurrence of green rust has been demonstrated by analyzing the suspended colloidal material retained on  $0.4 \mu\text{m}$  filter upon water filtration. Although this material showed a color change from dark-green to dark-orange during the short period of storage (less than 24 hours) before analysis, its typical layered structure was preserved as testified by its XRD pattern (Figure 3) that clearly shows peaks ( $2\theta^\circ = 8.12$ ,  $d_{001} = 10.88 \text{ \AA}$ ;  $2\theta^\circ = 16.36$ ,  $d_{002} = 5.42 \text{ \AA}$ ;  $2\theta^\circ = 24.53$ ,  $d_{003} = 3.63 \text{ \AA}$ ) representing reflections from the basal plane of the sulfate form of green rust.

These solid phases potentially act as a temporal sink for dissolved contaminants because they may undergo dissolution in the next rain event and/or be affected by various processes (e.g. oxidation/reduction, sorption/desorption) linked to changes in geochemical conditions. Although the load of dissolved sulfate and iron significantly decreases from the Casargiu mine downstream, high dissolved concentrations of Zn, Ni, Cd and Pb persist in the Rio Irvi. The dispersion of these metals extends about 5 km westwards till to the Mediterranean Sea. In contrast to what observed in the nearby Rio Naracauli stream under near neutral conditions (Podda et al., 2000), Zn precipitates in the Rio Irvi have been not observed because the precipitation of iron gradually produces acidity (pH about 4 at the last sampling point downstream), i.e. environmental conditions that allow Zn, Ni, Cd and Pb to remain into solution.

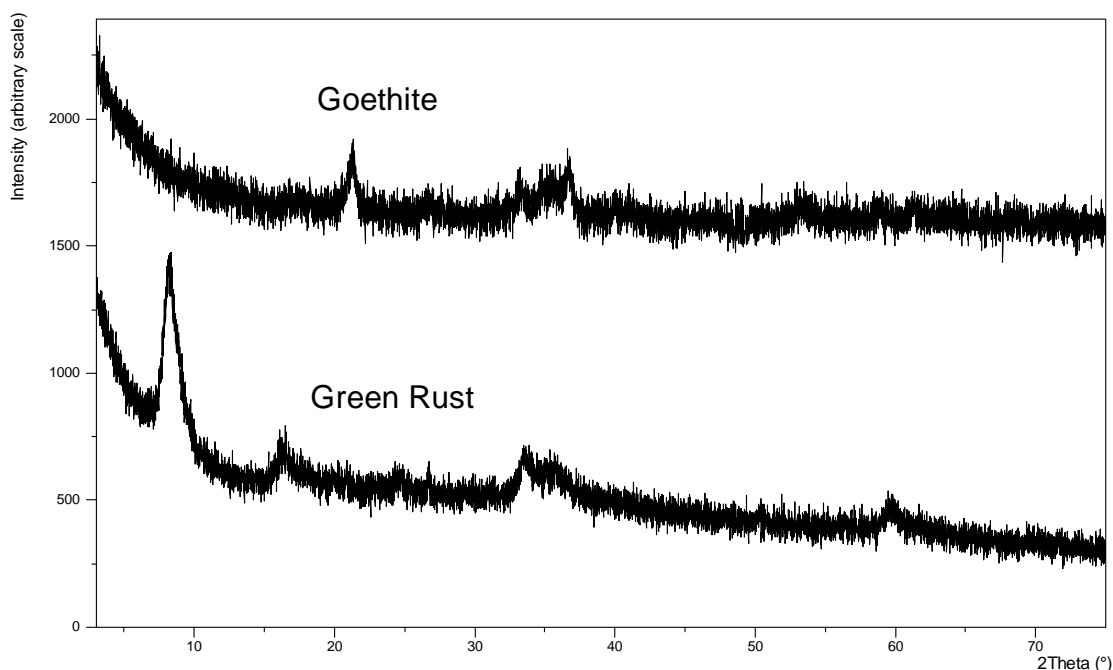


Figure 3. XRD patterns of solid phases collected in the Rio Irvi stream downstream from the Casargiu outflow. Moderately consolidated, ochreous precipitate consisting of low crystalline goethite (upper pattern); suspended colloidal, dark-green material retained on 0.4  $\mu\text{m}$  filter consisting of sulfate-bearing “green rust”.

Table 2. Estimated amount of metals discharged daily from the Rio Irvi into the sea.

source recipient	Casargiu Mediterranean Sea	
	February 2008	April 2009
date	February 2008	April 2009
flow (L/s)	20	70
Zn (kg/day)	900	2400
Cd	1.4	8
Pb	0.8	1.8
Ni	5	6

The estimated amount of dissolved metals discharged daily from the Rio Irvi into the sea is reported in Table 2. These calculations derive from dissolved concentrations measured in the Rio Irvi water collected about 1 km upstream of its mouth. Assuming a mean annual flow of 20 L/s in the stream, the amount of metals discharged in the year 2008 into the Mediterranean Sea is estimated at 328, 1.8, 0.5 and 0.3 tons of Zn, Ni, Cd and Pb, respectively. Considering the global flux estimation of Gaillardet et al. (2003), the contribution of Zn from the Casargiu mine drainage to the sea would correspond to 1.4% of the global riverine annual flux of Zn.

#### 4. CONCLUSIONS

The (hydro)geochemical approach appeared to be a valuable tool for the understanding of contamination processes occurring at abandoned mining sites. This study shows that drainages from flooded mines are relevant mining-related sources of contamination in Sardinia. The water flowing out of the Casargiu shaft is near neutral (pH in the range of 5.9 to 6.2) but has very high concentrations of sulfate and metals. As compared with values recorded at the first stages of rebound at Casargiu, a significant decrease (about 50%) in sulfate and metal concentrations was observed in 2009; nevertheless, a very high contamination level still persists at this site after 14 years of flushing.

The major risks to the water systems are associated with the direct discharge of contaminated waters into the aquatic recipients located downstream of the mine site. Mine drainages from Casargiu (20-70 L/s) flow into the Rio Irvi stream. A significant decrease in dissolved iron and sulfate occurs downstream by precipitation of solid phases. In the reach of the Rio Irvi stream, low crystalline goethite and “green rust” deposits have been observed. The precipitation of iron gradually decreases pH to about 4.0 and also allows the removal of arsenic from solution. In contrast, Zn and Cd concentrations in the Rio Irvi decrease only 10-15% with respect to the Casargiu source. Therefore, relevant amounts of Zn and Cd, together with Pb and Ni, are discharged into the Mediterranean Sea.

This study suggests that the extremely contaminated drainage at Casargiu should be “cleaned” before discharge, and the solid residues derived by the treatment plant should be properly disposed. A treatment plant recently built up by the Regional Government is expected to start operation in the near future. Monitoring of the treated effluent is recommended to verify the efficiency of that plant.

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