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Impact on streams and sea water of a near-neutral drainage from a flooded mine in Sardinia, Italy

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Abstract

After mine closure and subsequent shutdown of the dewatering system, groundwater rebound led to drainage outflow from the Casargiu gallery (Montevecchio mine, SW Sardinia, Italy) since 1997. As compared with the first discharge, a very high contamination level still persists after almost 20 years of flushing. Mine drainage (20-70 L s^{-1}; pH 6.0±0.2; Zn-Mg-Ca-SO_4 composition) flows into the Rio Irvi. Abundant precipitation of amorphous Fe(III)-(oxy)hydroxides occurs. Moreover, sulfate-bearing green rust is observed to flocculate in the reach of the Rio Irvi where pH is still circumneutral. Water sampling along this stream shows a pH decrease from 6.0 to 4.0 and a significant removal of Fe (46%) and As (96%), while sulfate, Zn, Mn, Co, Ni and Cd show small variations downstream. Lead is initially adsorbed onto Fe(III)-(oxy)hydroxides, then desorbed as pH drops below 5.4. A conservative estimation of dissolved metals discharged into the Mediterranean Sea is significant (e.g. 900 kg day^{-1} Zn, 1.4 kg day^{-1} Cd, 5 kg day^{-1} Ni).

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1. Introduction

Sardinia is an Italian region with mining activities dating back to pre-Roman times. Peaks in Pb-Zn production were reached in the ‘50s and ‘60s decades of the last century. The decline of the mining industry led to the progressive closure of most mines in the 1970-1990 period. One of the problems associated with mine closure was the shutdown of pumping for dewatering of underground mining works. The consequent rebound of the water table has caused flooding of galleries and interaction of groundwater with exposed mineralization and mining wastes used

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to fill galleries and voids. In some cases the contaminated groundwater has reached the surface through shafts and/or galleries, with deleterious effects on receiving waters.

This study focuses on the Casargiu outflow in the abandoned Montevecchio mine, the most important case of groundwater discharge from a flooded mine in Sardinia (Italy)[1].

2. Study area

The Arburese mining district (SW Sardinia) is mainly composed of the Montevecchio and Ingurtosu mines. Casargiu is a mine yard belonging to the Montevecchio mining system. The hydrothermal sulfide veins (mainly galena and sphalerite) are hosted in Palaeozoic silicate-dominant rocks. Mineralization at Casargiu mainly consists of sphalerite with an ankerite-siderite gangue.

Ore exploitation in the Montevecchio area extended in a system of interconnected galleries at depths down to 600 m below ground level. The mine closure in 1990 led to the shutdown of pumping systems; drainage flowing out of the Casargiu gallery was observed beginning in 1997[2]. The Casargiu drainage flows into the Rio Irvi that after about 6 km merges with the Rio Piscinas, which in turn flows into the Mediterranean Sea after about 2 km. The outflow from the Casargiu gallery represents the main water contribution to the Rio Irvi throughout the year.

3. Sampling and methods

The water flowing out of the Casargiu gallery (CAS1) was collected during 23 surveys carried out from 1997 to 2012. In June 2009 a complete sampling of the Rio Irvi was carried out. The Rio Irvi was mainly fed by the Casargiu drainage (about 50 L s^{-1}). The tributaries of the Rio Irvi were dry, therefore no lateral surface inputs of water to the Rio Irvi downstream of the Casargiu discharge were present. For the analytical methods see the article published[1].

In June 2009 solid precipitates at each sampling site were collected for mineralogical analyses by XRD.

Speciation-solubility calculations were performed using the computer program PHREEQC Interactive with the included thermodynamic database ‘‘wateq4f.dat’’.

4. Results and discussion

4.1. Chemistry of the Casargiu discharge

The first outflow from the Casargiu gallery in 1997 had pH 6.0 and dissolved concentrations of sulfate and metals generally much higher than those observed in 1995 during groundwater rebound (Fig. 1). These dramatic increases can be explained by the flooding of galleries and the consequent interaction of groundwater with sulfides (especially sphalerite) and secondary minerals, including soluble efflorescent salts.

Results of hydrogeochemical surveys carried out during the period 1997-2012 can be summarized as follows: (i) the flow from the Casargiu gallery has varied from 20 to 70 L s^{-1} depending on rainfall and rain infiltration; (ii) the values of pH (6.0±0.2) and Eh (0.28±0.05 V) have shown small variations over time; (iii) the acidity produced by the oxidation of sulfide minerals has been buffered by the occurrence of ankerite-siderite gangue in the Casargiu ore; (iv) the dissolved O_2 is very low (≤2 mg L^{-1}) and the dissolved Fe is present as Fe(II) species; (v) a more or less large decrease in sulfate, Zn, Mn, Ni, Co and Pb has been observed with time, while Fe, Cd and As have shown minor variations (Fig. 1). A very high contamination level still persists in the Casargiu drainage water after almost 20 years of flushing from the first outflow.

4.2. Chemistry of the Rio Irvi

The reach of the Rio Irvi extending upstream of the Casargiu discharge is uncontaminated. Waters from the Casargiu gallery and the Rio Irvi downstream are characterized by a Zn-Mg-Ca-SO_4 composition. The variation of pH and Eh with distance from Casargiu shows a non-linear pH decrease from 6.0 to 4.0 coupled with an increasing mirror trend of Eh from 0.3 to 0.5 V (Fig. 2b). As the groundwater flowing out from the Casargiu gallery comes in contact with the atmospheric O_2, Fe(II) oxidizes to Fe(III) and precipitation of Fe(III)-(oxy)hydroxides occurs.

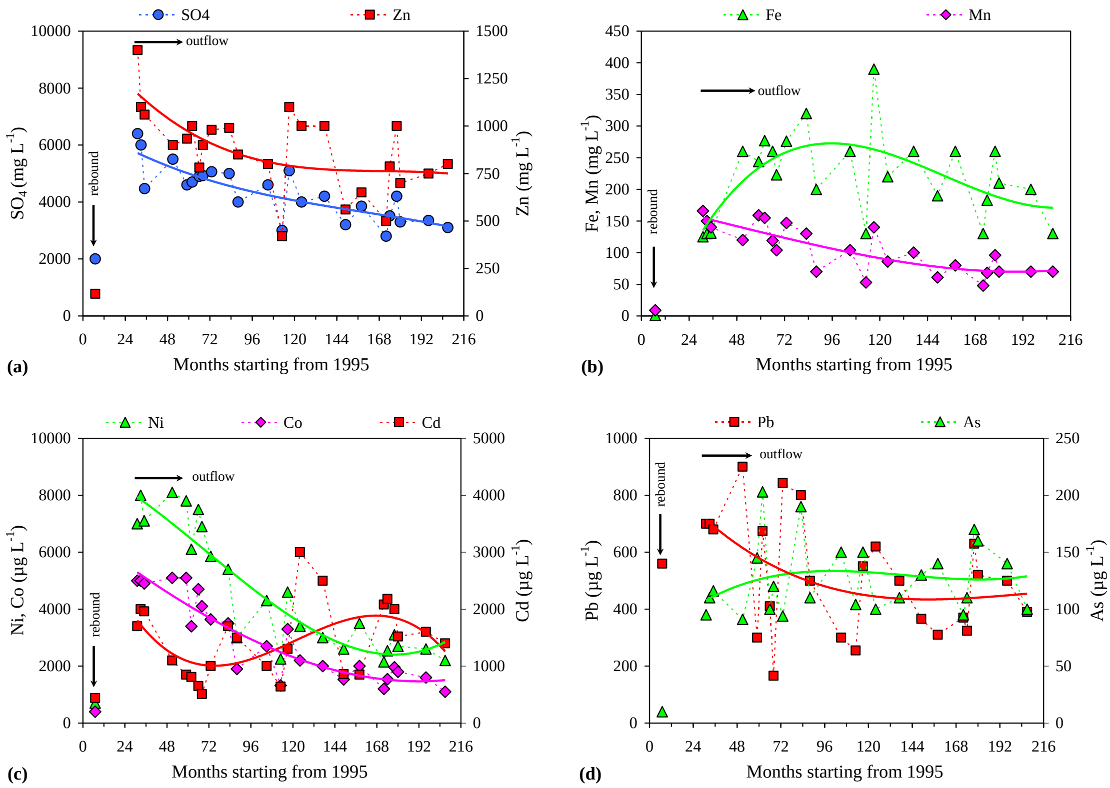

Fig. 1. Temporal changes in water chemistry at the Casargiu mine. A third degree polynomial curve was used to fit the data.

Water chemistry changes along the Rio Irvi show small to moderate decreases of sulfate, Zn, Mn, Cd, Ni and Co from the Casargiu outflow to the last sampling point at a distance of 6 km, while Fe exhibits a strong decrease (about 50% of the initial concentration) due to Fe(III)-(oxy)hydroxides precipitation (Fig. 2a). Lead exhibits a distribution consistent with adsorption/desorption onto/from Fe(III)-(oxy)hydroxides, with an initially strong decrease as pH increases and a subsequent strong increase as pH drops below 5.4. Also As shows a distribution linked to sorption by Fe(III)-(oxy)hydroxides, but since As remains adsorbed at acidic pH[3,4], it is removed almost totally (Fig. 2b).

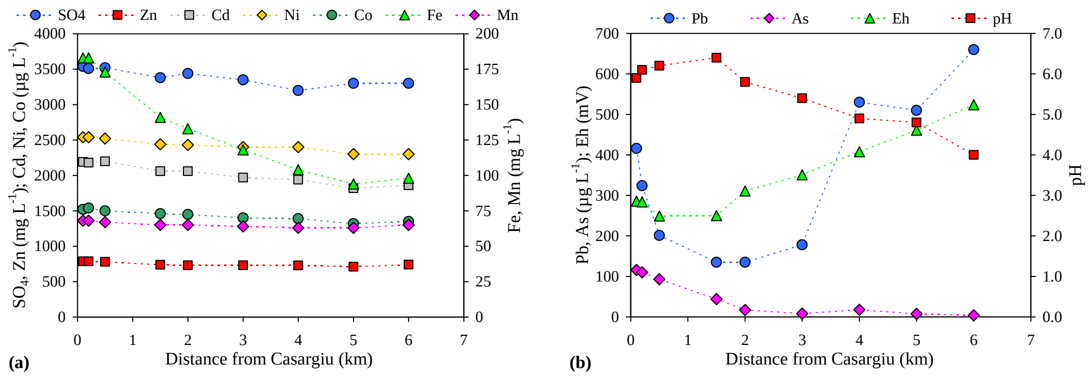

Fig. 2. Chemistry changes along the Rio Irvi.

4.3. Mineralogy of precipitates

At the Casargiu outflow and along the Rio Irvi ochreous precipitates can be observed; however, only flocculation of a peculiar green phase occurs in the reach of the Rio Irvi where pH is still circumneutral. XRD analysis of these precipitates have shown the presence of amorphous Fe(III)-(oxy)hydroxides and sulfate-bearing green rust (Fig. 3). The green rust is a mixed Fe(II)/Fe(III) layered double hydroxide forming under weakly acidic to alkaline conditions in sub-oxic environment. Being an unstable phase under atmospheric conditions, there is no persistent accumulation of green rust in the Rio Irvi streambed, even where stream water is clearly oversaturated with respect to green rust.

Fig. 3. Ochreous precipitate (left) and green rust flocculation (right) in the Rio Irvi.

4.4. Metal load to the Mediterranean Sea

Assuming the lowest flow measured in the Rio Irvi in 2008 (20 L s^{-1}) as the mean annual flow, the amount of metals discharged in the year 2008 into the Mediterranean Sea was estimated at 328, 1.8, 0.5 and 0.3 tons of Zn, Ni, Cd and Pb. Compared to the global flux of dissolved metals from uncontaminated rivers to the oceans[5], a conservative estimation of the contribution of Zn from the Casargiu mine drainage to the sea would correspond to 1.4% of the global riverine annual flux of dissolved Zn.

5. Conclusions

This study shows that drainages from flooded mines are significant mining-related sources of contamination. In particular, near-neutral drainages may be highly contaminated and represent a major risk to the hydrographic system, heavily modifying water chemistry and composition of stream sediments. The geochemical-mineralogical processes described in this study can help remediate the contaminated drainage at Casargiu before discharge into the Rio Irvi.

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