

## Contamination trend at flooded mines: 20 y time-series at Casargiu, Sardinia

Rosa Cidu<sup>1\*</sup>, Franco Frau<sup>1</sup>, Riccardo Petrini<sup>2</sup>

<sup>1</sup>*Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, via Trentino 51, 09127 Cagliari, Italy, cidur@unica.it*

<sup>2</sup>*Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56126 Pisa, Italy*

**Abstract** At Casargiu, Pb-Zn ores were exploited for a century. After mine closure, pumping systems were shut down allowing rebound. First outflow of contaminated water occurred in 1997. This study reports contamination trends based on 26 hydrogeochemical surveys carried out from 1997 to 2016. Results showed contamination peaks at the first flushing. After 20 y, concentrations of Ni and Co showed marked decreases, followed by Mn, sulfate, Pb, Zn and Cd. Although a decrease of contaminants has been occurring, high contamination persists at Casargiu. This suggests the need of remediation actions for preventing dispersion of contaminants downstream of abandoned mines.

**Key words** rebound, mine drainage, sulfate, metals, arsenic

### Introduction

Outflow drainages following rebound at abandoned mines usually cause contamination in the aquatic system downstream of mine (Younger et al. 2005). Contamination peaks are often observed at the first flushing (Nordstrom 2009, Wolkersdorfer 2005), whereas concentrations of contaminants generally decrease with increasing time since rebound (Cidu et al. 2005). However, long-time is usually to be expected for attaining levels of contaminants observed prior to rebound.

This paper is aimed at assessing contamination trends following rebound at the abandoned mine of Casargiu in SW Sardinia (Italy). Results of hydrogeochemical surveys carried out over 20 y are reported. At Casargiu, Pb-Zn sulfide veins were exploited for nearly a century until the 1980's. After the cessation of mining operations, the pumping systems used to dry underground workings were shut down and the mine underwent flooding. Since the first outflow in 1997, the Casargiu drainage has been discharged directly into the Rio Irvi, a tributary of the Rio Piscinas that flows into the Mediterranean Sea, causing the deterioration of aquatic systems.

### Methods

The water flowing out of the Casargiu shaft has been sampled and analyzed 26 times from 1997 to 2016. The main results of surveys carried out prior to the 2016 have been reported in previous studies (Cidu 2011, Cidu and Fanfani 2002, Cidu and Frau 2009, Frau et al. 2015). Temperature, pH, redox potential (Eh, Pt electrode, Orion), dissolved oxygen (DO), electrical conductivity (EC) and  $\text{HCO}_3^-$  were determined on site. Immediately upon collection, the water was filtered through 0.45  $\mu\text{m}$  pore-size Nuclepore polycarbonate filters into pre-cleaned high-density polyethylene bottles. One filtered aliquot was used to analyze the anions by ion chromatography (IC, Dionex). One filtered aliquot was acidified on site with

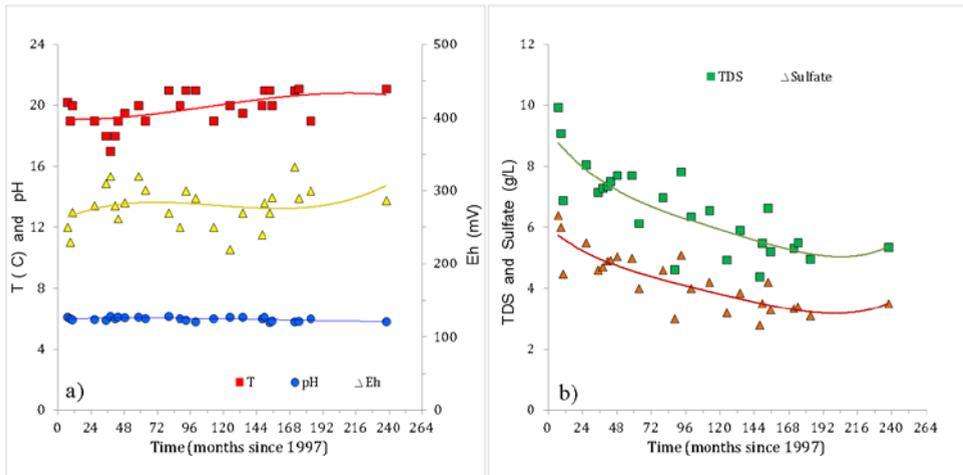
suprapure-grade  $\text{HNO}_3$  for metal analyses by quadrupole inductively coupled plasma–mass spectrometry (ICP-MS, Perkin Elmer) and major cations by inductively coupled plasma–optical emission spectrometry (ICP-OES, ARL Fisons). One filtered aliquot was acidified on site with suprapure-grade HCl for the determination of arsenic by online hydride generation – ICP-MS. In the 2016 survey, the concentration of bivalent iron was determined on site by portable spectrophotometer. Field blank solutions were used for assessing eventual contamination during sampling operations. Certified reference solutions NISTSRM1643a-e were used to evaluate analytical errors that were usually below 10%.

## Results

Under dewatering conditions in 1973 the water pumped out of Casargiu showed 7.5 pH, 1400 mg/L sulfate and high metals: 70 mg/L Zn; 4.6 mg/L Fe; 1.2 mg/L Cd; 0.8 mg/L Pb; 0.5 mg/L Mn (Biddau 1978). In 1997, the first outflow from the flooded mine showed a pH value of 6.0, temperature of 20°C, Eh 0.25 V, 6,400 mg/L sulfate and concentrations of Zn, Cd, Fe and Mn 2 to 3 orders of magnitude higher than those observed in groundwater under dewatering conditions. Results of the hydrogeochemical survey carried out in 2016 are reported in Table 1. The water was slightly acidic and reduced (low Eh and dissolved oxygen), had high total dissolved solids (TDS) and a predominant Zn-sulfate composition. Ferrous iron was about 90% of total iron, which is consistent with the observed reducing condition. Concentrations of sulfate, metals and arsenic were much above the Italian limits established for industrial discharges (GURI 2006).

**Table 1** Physical and chemical characteristics of the Casargiu drainage in 2016.

Flow	T	pH	Eh	DO	EC	TDS	
L/s	°C		V	mg/L	mS/cm	g/L	
24	21	5.8	0.29	<0.2	4.39	5.35	
Zn	Ca	Mg	Na	K	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
630	400	220	70	9	81	133	3500
Fetot	Fe <sup>2+</sup>	Mn	Cd	Pb	Ni	Co	As
mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L
224	202	61	950	550	2400	1400	160



**Figure 1** Plots showing variations of temperature ( $T$ ), pH and Eh values (a) and TDS and sulfate concentrations (b) in the Casargiu drainage.

In the 1997-2016 monitoring period, temperature ( $20 \pm 2$  °C), pH ( $6.0 \pm 0.2$ ) and redox potential ( $280 \pm 40$  mV) values showed relatively low fluctuations (Fig. 1a), regardless the flow values that varied from 20 to 70 L/s. Values of TDS and sulfate concentrations showed decreasing trends versus time (Fig. 1b). Concentrations of Zn, Mn, Ni and Co in the water sampled in 2016 decreased significantly as compared to concentrations observed at the first flushing (Fig. 2a, b, c). Concentrations of Cd, Fe and Pb showed marked fluctuations under the monitoring period (Fig. 2d, e, f), with lower concentrations being observed in general under high flow conditions. Concentrations of As ( $130 \pm 30$  mg/L) showed relatively low fluctuations (Fig. 2f).

Variations of iron over time were not dependent on physical-chemical conditions, nor on concentrations of other major components. It is worth to point out that flooding of the adit area hampered sometimes collecting water at outflow, but some 50 m downwards. In such conditions abundant Fe precipitates were observed in the flooded area. Sorption processes on Fe solid phases may have affected the concentration of other metals, such as Cd that showed a temporal trend (Fig. 2d) similar to the Fe trend (Fig. 2e). Further research is warranted to understand these processes.

## Conclusions

Despite decreasing trends of contaminants, the Casargiu drainage is still heavily contaminated with sulfate, Zn, Cd, Fe, Mn, Pb, Ni, As and Co. Several decades are probably expected before contamination will reach the level observed in the water under dewatering conditions.

Downstream of the mine area, at the Rio Irvi confluence with the Rio Piscinas (about 6 km downstream of Casargiu) the pH decreased below 4 due to abundant iron precipitation, which allowed As to be scavenged from the stream water by precipitation and/or sorption

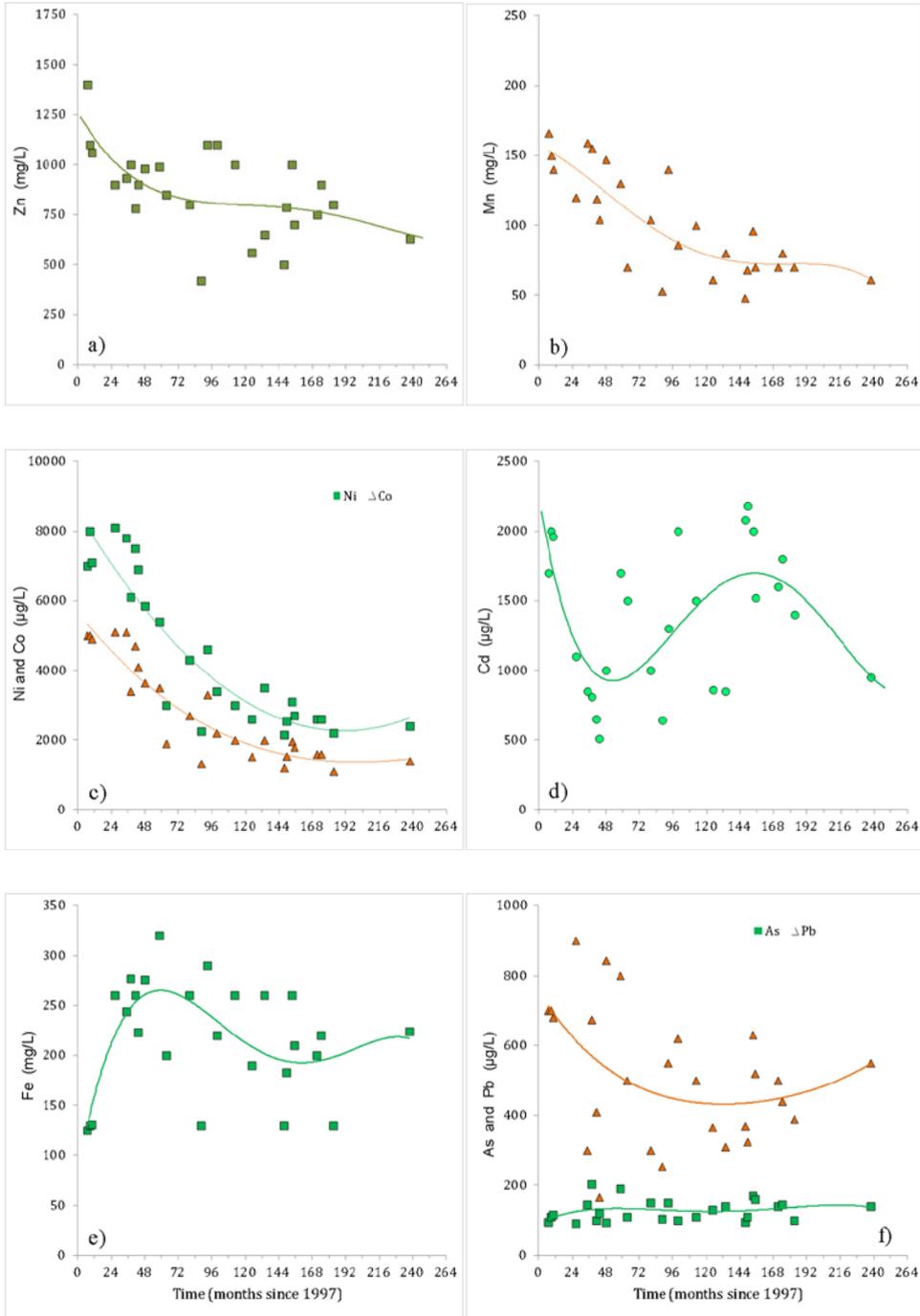


Figure 2 Plots showing trends of contamination in the Casargiu drainage.

processes. On the contrary, the acidic environment favored the persistence of Pb, Cd and Zn in the water. Because the contaminated waters are discharged into the Mediterranean Sea (Fig. 3), with potential adverse effects on biota, remediation actions should be undertaken for the attenuation of environmental risks.



**Figure 3** Google map showing the Rio Piscinas mouth (accessed in March 2017).

### Acknowledgements

The authors thank financial support by the University of Cagliari (CAR Cidu) and the Regione Autonoma della Sardegna (Premio RAS Cidu).

### 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)
- Cidu R (2011) Mobility of aqueous contaminants at abandoned mining sites: insights from case studies in Sardinia with implications for remediation. *Environmental Earth Science* 64:503–512, Online First 2 December 2010, ISSN: 1866-6280, doi: 10.1007/s12665-010-0874-y
- Cidu R, Biddau R, Spano T (2005) Temporal Variations in Water Chemistry at Abandoned Underground Mines Hosted in a Carbonate Environment. *Mine Water and the Environment* 24:77–87
- Cidu R, Fanfani L (2002) Overview of the environmental geochemistry of mining districts in southwestern Sardinia (Italy). *Geochemistry Exploration Environment Analysis, SI Heavy Metals* 2:243–251, ISSN: 14677873, doi: 10.1144/1467-787302-028
- Cidu R, Frau F (2009) Effects of past mining on the quality of water resources in Sardinia. *Proceedings International Mine Water Conference 2009*, pp 903–909, Pretoria, SA
- Frau F, Medas D, Da Pelo S, Wanty RB, Cidu R (2015) Impact on aquatic system and metal discharge to the Mediterranean Sea from a near-neutral zinc-ferrous sulfate mine drainage. *Water Air Soil Pollution*, 226:55 doi: 10.1007/s11270-015-2339-0
- GURI (2006) Decreto legislativo 3 aprile 2006, n. 152 Norme in materia ambientale. *Gazzetta Ufficiale della Repubblica Italiana* n. 88 del 14-4-2006. Istituto Poligrafico dello Stato, Roma (in Italian)
- Nordstrom DK (2009) Acid rock drainage and climate change. *J Geochemical Exploration* 100:97–104, doi:10.1016/j.gexplo.2008.08.002
- Wolkersdorfer C (2005) Mine water tracer tests as a basis for remediation strategies. *Chemie der Erde* 65:65–74, doi:10.1016/j.chemer.2005.06.003
- Younger PL, Coulton RH, Froggatt EC (2005) The contribution of science to risk-based decision-making: lessons from the development of full-scale treatment measures for acidic mine waters at Wheal Jane, UK. *Sci Total Environ* 338:137–154, doi:10.1016/j.scitotenv.2004.09.014