

Arsenic contamination in the Baccu Locci mine watershed (Sardinia, Italy) after remediation

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Abstract The old Pb-As Baccu Locci mine represents the first and only case of mine site remediation in Sardinia, Italy. This paper reports preliminary results on the level of contamination in the Baccu Locci stream after remediation. In particular, distribution of dissolved As has not substantially changed compared to pre-remediation situation, showing an increasing trend along the stream and a concentration of about 400 µg/L at a distance of 5 km from the mine. Future monitoring of the Baccu Locci system will provide fundamental information on the effectiveness of remediation measures adopted and their applicability to other mine sites in Sardinia.

Keywords Baccu Locci mine (Sardinia, Italy), arsenic contamination, remediation, environmental issues

Introduction

The sulfide deposit of Baccu Locci is located in south-east Sardinia, Italy. The extraction of galena [PbS] and arsenopyrite [FeAsS] for about a century (1873–1965) has left a significant environmental legacy, especially due to the unwise practice of discharging tailings from the flotation plant directly into the Baccu Locci stream (BLs), which drains the homonymous mine area, with consequent accumulation and wide scattering of highly contaminated materials over the whole watershed (Fig. 1) as far as the coastal plain located about 10 km downstream from the mine. The BLs is characterized by a typical torrential regime with alternation of low-flow periods, even in fall-winter, and recurrent, sometimes catastrophic, floods.

Arsenic represents the most relevant environmental concern in the Baccu Locci watershed, with concentrations in surface waters up to and sometimes over 1 mg/L (Frau and Ardau 2003; Frau *et al.* 2009, 2012). Previous studies (Frau and Ardau 2003, 2004; Frau *et al.* 2005, 2009), conducted before remediation, pointed

out that waste-rock dumps and flotation tailings represent point and widespread contamination sources, respectively. The waste-rock dumps are located in the upper BLs course, where also the mining works occur; the flota-



Fig. 1 Reddish-brown stain left by tailings on the rocks in the Baccu Locci stream at a height of about 1 meter from the bed, testifying that the tailings slurry discharged from the flotation plant for about 15 years (1949–1965) filled completely the watercourse even during drought periods.

tion tailings are scattered in the medium-lower BLs valley and mostly represent a “hidden” contamination source because they are mixed with and buried under stream sediments. Arsenic is released to surface waters mainly by desorption from two-line ferrihydrite (HFO) contained in stream sediments/tailings along the medium-lower course of the BLs (Frau *et al.* 2008, 2010).

Remediation actions started in August 2008 and concluded in February 2012 with an all-in cost of 5.1 million euros. They were conducted according to regional guidelines (RAS 2009) and mainly consisted in: 1) creation of a “Storage Site” (Fig. 2), where materials from different waste-rock dumps and several tailings piles occurring along the BLs (Fig. 3) were placed; 2) permanent on-site safety measures on three waste-rock dumps; 3) treatment of leachate from the Storage Site and acidic water

from the S. Riccardo adit (see Fig. 4) by passive adsorbent systems.

In previous studies, a prolonged persistence of As contamination was hypothesized (Frau and Ardaù 2003) and the expected positive effects of remediation measures were evaluated at least as uncertain (Frau 2009), especially with regard to As contamination. For these reasons, this paper reports the first results on the BLs water chemistry after completion of remediation in order to immediately follow the geochemical evolution of the Baccu Locci system and understand how it will react with time to the remediation actions conducted.

Sampling and methods

The map of the BLs watershed (Fig. 4) shows the location of sampling stations, waste-rock dumps subjected to permanent on-site safety

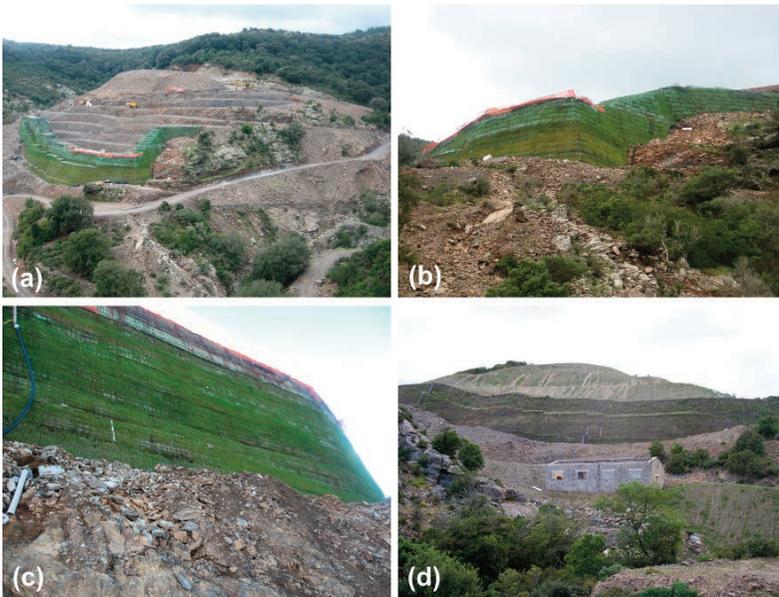


Fig. 2 Some views of the Storage Site in February 2010 during its construction (a), (b) and (c), and in May 2012 after completion of remediation (d). The perimeter retaining wall is about 12 meters high.

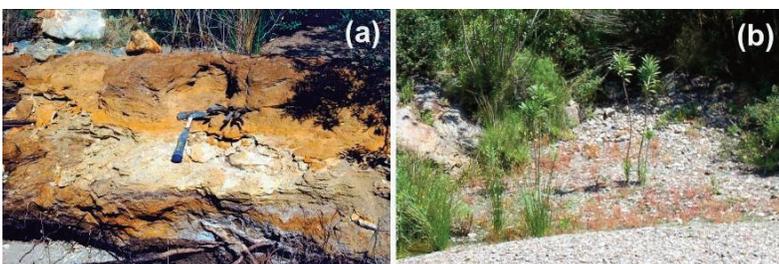


Fig. 3 One of the sites along the Baccu Locci stream where the tailings deposits were more visible, photographed in January 2001 before remediation (a) and in May 2012 after remediation (b).

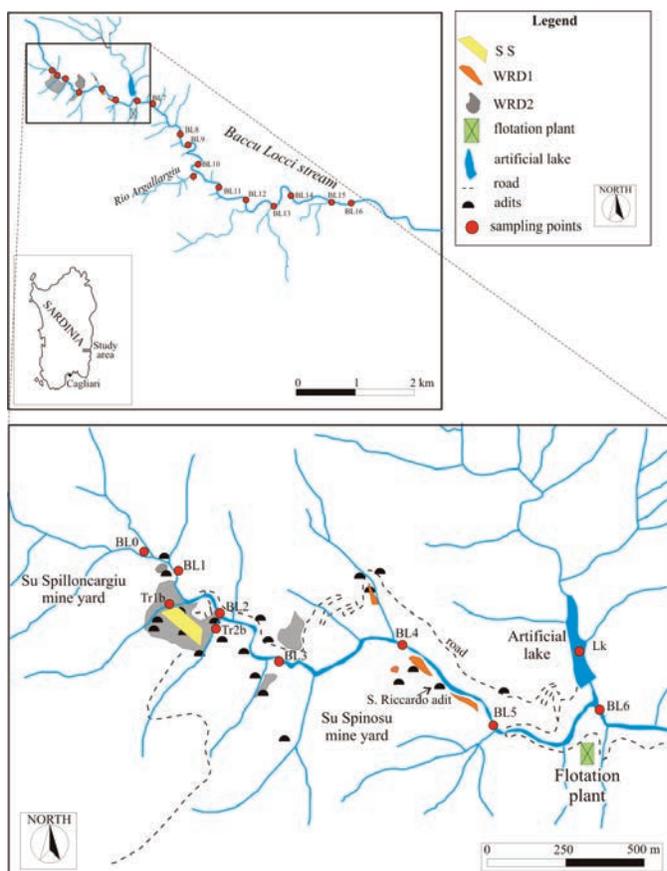


Fig. 4 Schematic map of the Baccu Locci stream watershed showing the location of sampling stations (BL0-BL14, Tr1b, Tr2b, Lk), waste-rock dumps left in place (WRD1) and removed (WRD2), and the Storage Site (SS). The stations BL6, BL15 and BL16 were not sampled in May 2012.

measures and those removed, and the Storage Site. The BLs was sampled in May 2012 at 14 different points from BL0, located upstream of the mine area, to BL14. The BLs was in a period of low flow; most of tributaries were dry (only the tributaries Tr1 and Tr2 were sampled), and the BLs water flow occurred in the hyporheic zone in some stretches and definitively downstream of the BL14 sampling station (Fig. 5). However, some water from the artificial lake (see Fig. 4) overflowed the dam and flowed into the BLs.

Temperature, pH, Eh, conductivity and alkalinity were measured at the sampling stations. Each water sample was filtered through 0.45 μm pore-size polypropylene filter into pre-cleaned high density polyethylene bottles. Filtered aliquots were acidified on site with 1% v/v suprapure HNO_3 for analyses of major elements by ICP-OES, and minor and trace elements by ICP-MS. A filtered aliquot was acidified on site with 0.2% v/v suprapure HCl for



Fig. 5 The last sampling station BL14 in the Baccu Locci stream in May 2012, downstream of which the water flow definitively occurred in the hyporheic zone.

the determination of As by on-line hydride generation ICP-MS. Major anions were determined by ion chromatography on filtered, unacidified aliquots. Estimated error of analytical data was <5 % for major components and <10 % for minor and trace elements.

Results and discussion

The BLs water is neutral to slightly alkaline (pH 7.2-8.0), oxidizing (Eh 0.44-0.52 V) and with low total dissolved solids (TDS 0.29-0.50 g/L). Major chemistry is dominated by Ca-Mg-HCO₃ or Ca-Mg-SO₄ composition. The chemical changes in the BLs water over a distance of about 7 km (Fig. 6) show strong similarities with pre-remediation samplings (Frau and Ardau 2003). Calcium, sulfate and TDS increase as soon as the BLs enters the mine area (BL0-BL3 stretch), a dilution occurs between BL3 and BL4 due to mixing with a tributary (not sampled), then bicarbonate rapidly becomes the dominant anion upon mixing with water from the lake (BL5-BL7 stretch) and this composition persists until the last sampling station, although with a progressive decrease of calcium, bicarbonate and TDS probably due to hyporheic flow from other tributaries.

Also trace elements distribution along the BLs shows strong similarity with pre-remediation samplings, in particular with low flow conditions (Frau and Ardau 2003). The metals

Zn, Cd, Cu, Ni and Pb rapidly increase in the first km (BL0-BL3 stretch), then they decrease to very low concentrations (not shown).

Contrary to metals, the distribution of As along the BLs is characterized by a peculiar trend, with a gradual increase up to the maximum concentration of about 750 µg/L at BL10 (Fig. 7). Two drastic, significant decreases can be observed in the BL3-BL4 and BL10-BL11 stretches; the first one is probably due to both mixing with a tributary (not sampled) and co-precipitation/sorption with amorphous/low-crystallinity phases; the second one is due to hyporheic flow from the tributary Rio Argalargiu (just 10 µg/L As, when it was possible to sample it; Frau and Ardau 2003). Anyway, the dissolved concentration of As remains very high up to the last sampling station (about 400 µg/L at BL14).

Compared to previous samplings conducted in February 2000 (low flow conditions similar to those in May 2012) and January 2001 (flow higher than in May 2012; Frau and Ardau 2003), As generally exhibits higher concentrations, especially at BL2 and in the BL4-BL10 stretch (Fig. 8 and Fig. 9).

The behavior of As mainly depends on the peculiar feature of the widespread contamination source, represented by the flotation tailings, and its solid speciation. Although the visible tailings piles outcropping on the stream

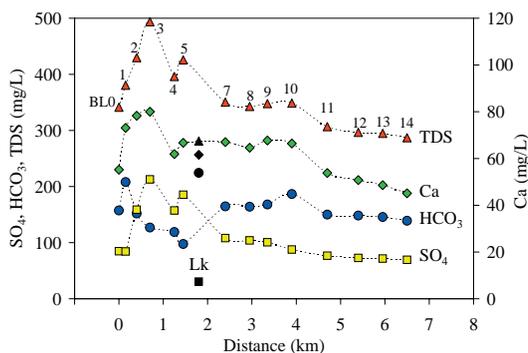


Fig. 6 Major chemistry changes in the Baccu Locci stream (May 2012) over a distance of about 7 km; solid black symbols refer to lake water.

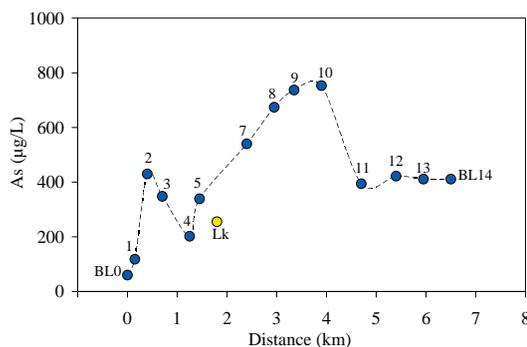


Fig. 7 Arsenic distribution in the Baccu Locci stream in May 2012 over a distance of about 7 km.

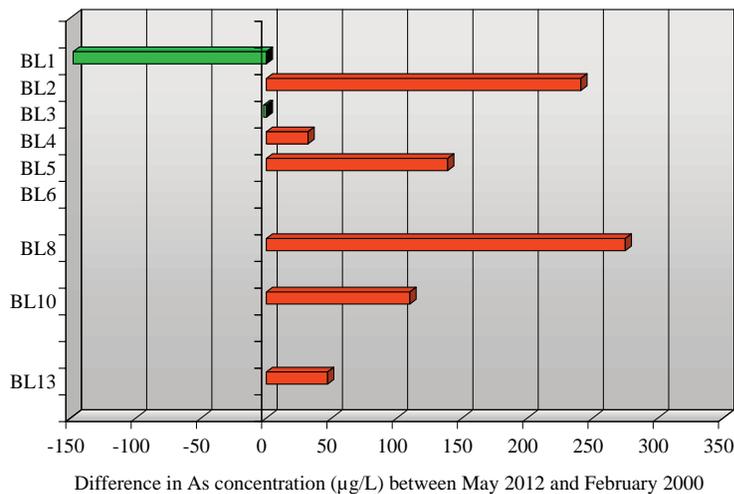


Fig. 8 Difference in As concentration along the Baccu Locci stream between May 2012 and February 2000.

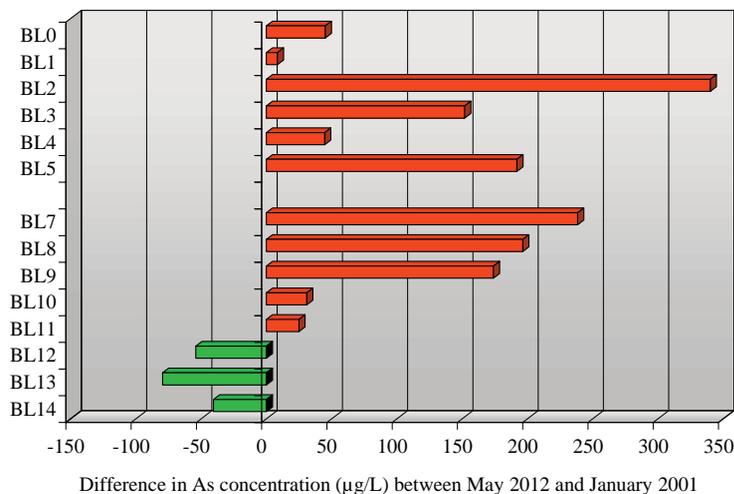


Fig. 9 Difference in As concentration along the Baccu Locci stream between May 2012 and January 2001.

banks have been removed according to the remediation measures adopted, they probably represented a small fraction of the total amount of tailings discharged into the BLs, scattered downstream, mixed with and buried under stream sediments down to at least 3 m deep. This widespread contamination source can not be completely removed and will probably continue to release As for a long time. In fact, the solid speciation of As in flotation tailings/stream sediments in the medium-lower BLs valley is dominated by arsenical ferrihydrite (HFO), and previous studies (Frau *et al.* 2008, 2010) have demonstrated that desorption of As from HFO in the Baccu Locci system is favored under neutral or slightly alkaline pH conditions and by the competitive effect of bi-

carbonate. Contrary to As, Pb is not released from the widespread contamination source in the medium-lower BLs valley because its solid speciation is dominated by plumbojarosite $[\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}]$ that is practically insoluble under the above-mentioned geochemical conditions (Frau *et al.* 2009), and therefore Pb is not at present an environmental concern.

Conclusions

Based on data currently available, the potential positive effects of remediation on water contamination in the Baccu Locci mine watershed are not yet visible. These first results are probably influenced by the short period of time elapsed from completion of remediation, and by climatic conditions, in particular rainfall

and duration of dry and wet periods that can be highly variable in Sardinia, especially affecting a mountain stream like the BLs. Therefore, a prolonged monitoring for several years will be necessary in order to assess the real efficacy of remediation measures. However, post-remediation distribution of As in the BLs shows a trend very similar to pre-remediation conditions. Moreover, the in-depth knowledge of the mineralogical and geochemical processes responsible for contamination in the Baccu Locci system leads to hypothesize probable limited, beneficial effects of remediation on As contamination.

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