

## Diel changes in water chemistry in the Baccu Locci stream (Sardinia, Italy) affected by past mining

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**Abstract** Diel variations in dissolved As and Zn concentrations in the Baccu Locci stream (Sardinia, Italy), affected by past mining, were studied. Sorption/desorption to/from streambed material, in particular ferrihydrite, is believed to be the main process controlling the diel cycles of trace elements. Another possible process that deserves an in-depth assessment is co-precipitation of As and Zn with calcite. Both processes should be carefully considered to assess the effectiveness of remediation actions currently in progress at Baccu Locci.

**Key Words** Diel cycle, trace elements, sorption, co-precipitation, Baccu Locci mine, Sardinia

### Introduction

The sulphide deposit of Baccu Locci, located in the Sarrabus-Gerrei mining district (SE Sardinia, Italy), consists of about equal amounts of galena and arsenopyrite. Exploitation for Pb and As (1873–1965) produced serious environmental contamination, principally due to the unwise practice of discharging tailings from the flotation plant, built up in 1949, directly into the Baccu Locci stream (BLs), with consequent dispersion of highly contaminated materials over the whole catchment as far as the coastal plain located about 10 km downstream from the mine. Arsenic represents the most relevant environmental concern because it is released to surface waters up to and over 1 mg/L mainly by desorption from ferrihydrite (HFO) contained in stream sediments/tailings along the course of the BLs (Frau and Ardaù 2003, 2004).

This study aims to investigate diel changes in water chemistry, and especially in trace element concentrations, during base-flow conditions at a specific sampling site in the BLs. The absence of anthropic activities other than past mining, the presence of diffuse contamination and the climatic and hydrologic conditions make the Baccu Locci catchment a good test area for this type of study.

Climatic conditions in the study area are characterized by prolonged dry and warm periods, generally extending from May to September, and relatively short rainy and cold periods, with occasional heavy rain events. Mean annual rainfall is about 750 mm/a. The temperature in summer often reaches and exceeds 35 °C, and seldom drops below zero in winter; the diurnal temperature range may exceed 10 °C, especially in summer. The BLs is characterized by a typical torrential regime, with alternation of long low-flow periods and recurrent, sometimes catastrophic, floods.

### Sampling and Methods

Sampling at a specific site in the BLs was conducted over a 20-hour period from 11:00 am until 7:00 am the next day (July 15–16, 2006; 8 samples). The sampling site, located about 500 m downstream from the flotation plant, was chosen for favourable logistics and narrow flow section (about 1 m) with a rocky bed. The day of sampling was preceded by a long period of drought, as evidenced by the very low stream flow (about 0.2 L/s). No lateral surficial water inflow to the BLs was present in vicinity of the sampling site, and base flow remained unchanged all the time.

Temperature, pH, Eh (redox potential), conductivity and alkalinity were measured at the sampling site. Each water sample was filtered through 0.4 µm pore size into pre-cleaned HDPE bottles. An aliquot of the 0.4 µm filtered sample was filtered again through 0.015 µm. Filtered aliquots were acidified with 1% v/v suprapure HNO<sub>3</sub> for metal analyses by ICP-OES and/or ICP-MS. An aliquot was acidified with 0.2% v/v suprapure HCl for the determination of As by hydride generation ICP-MS. Anion analysis by ion chromatography (IC) was performed on an unacidified filtered aliquot.

Speciation-solubility calculations were performed using the computer program PHREEQC Interactive (version 2.15.0.2697 released on February 5, 2008; Parkhurst and Appelo 1999) with the included thermodynamic database "wateq4f.dat".

**Results and Discussion**

The BLs water composition was dominated by Ca-SO<sub>4</sub>-HCO<sub>3</sub>, with a slightly alkaline pH (7.7–8.1) and a moderately oxidizing Eh (average 0.45 V). Mean salinity was 0.55 g/L. Due to the extreme low-flow conditions during the period of sampling, air temperature (21–31°C) and water temperature (23–34°C) were very similar and closely correlated; the maximum water temperature occurred at 14:00, then a gradual decrease was observed until 7:00 the next day (fig. 1a). Conductivity varied from 816 to 850 µS/cm; a gradual increase occurred from 14:00 until 2:00 (fig. 1a). Values of pH and Eh exhibited opposite trends, with a general pH falling and Eh rising (fig. 1b).

Alkalinity, expressed as mg/L of HCO<sub>3</sub><sup>-</sup>, increased from 123 to 148 mg/L in the 14:00–23:30 hourly span, then remained almost constant until 7:00 the next day (fig. 1c). Alkalinity exhibited strong inverse relations with temperature and pH (R<sup>2</sup> = 0.93 and R<sup>2</sup> = 0.85, respectively), and an equally strong but positive relation with conductivity (R<sup>2</sup> = 0.94). These relations can be mainly explained by the temperature-dependent CO<sub>2</sub> solubility and the biological-induced CO<sub>2</sub> production, both of which are higher during the night. The diel variation for Ca was of only 4 mg/L, with a general increase from 84 to 88 mg/L (fig. 1c). The positive relation between alkalinity and Ca (R<sup>2</sup> = 0.87) might indicate a possible control by calcite. The BLs water was slightly oversaturated with respect to calcite, with the saturation index (SI) decreasing from 0.65 to 0.21 (fig. 1c) because of the pH decrease. Other major dissolved constituents did not show significant diel variations.

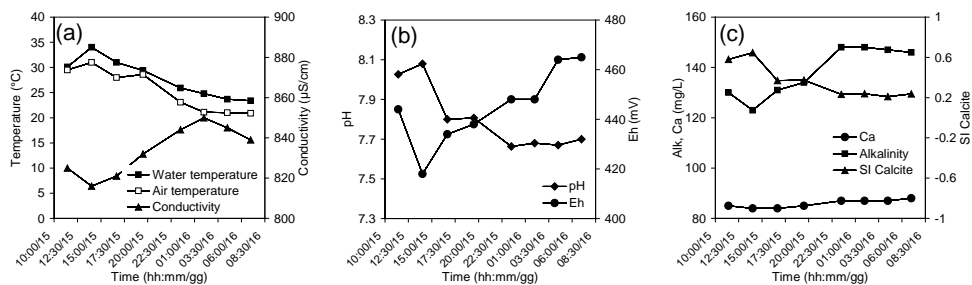
Among trace elements, As and Zn showed the most significant variations. Only data derived from analysis of the 0.4 µm filtered aliquots were used; in fact, significant differences with respect to concentrations determined in the 0.015 µm filtered aliquots were not observed.

The diel variation for As was of about 100 µg/L, with a general increase from 934 to 1030 µg/L throughout the day. Arsenic showed moderate inverse relations with temperature and pH (R<sup>2</sup> = 0.65 and R<sup>2</sup> = 0.70, respectively), and a stronger but positive relation with alkalinity (R<sup>2</sup> = 0.80) (fig. 2a-c). Aqueous As speciation was dominated by HAsO<sub>4</sub><sup>2-</sup>.

The diel variation for Zn was of almost 200 µg/L, with a general increase from 192 to 390 µg/L during the period of sampling. Zinc exhibited strong inverse relations with temperature and pH (R<sup>2</sup> = 0.92 and R<sup>2</sup> = 0.93, respectively), and an equally strong but positive relation with alkalinity (R<sup>2</sup> = 0.96; fig. 2a-c). Other trace elements, such as Mn, Cd and Ni, showed trends similar to Zn, whereas Pb and Cu remained almost unvaried. Aqueous Zn speciation was dominated by Zn<sup>2+</sup> and ZnCO<sub>3</sub><sup>o</sup>.

Solubility calculations with PHREEQC indicate that the BLs water was always strongly undersaturated with respect to the main As- or Zn-bearing secondary minerals occurring in the Baccu Locci area (e.g. bianchite, goslarite, scorodite). Undersaturation in smithsonite ZnCO<sub>3</sub> was less marked but the SI values remained nearly constant, in the range of -1.01 to -1.07. These data suggest that the diel variations for As and Zn can not be explained with precipitation/dissolution of pure As or Zn phases.

Concurrent diel variations in water temperature and dissolved As concentrations showed an ambiguous timing: an initial partial matching was interrupted by a sharp gap in the 19:30–23:30 hourly span, where As increased from 956 to 1030 µg/L, followed by another partial matching (fig. 2a). Sorption of As onto HFO is known to be an exothermic process (Gammons et al. 2007), in-

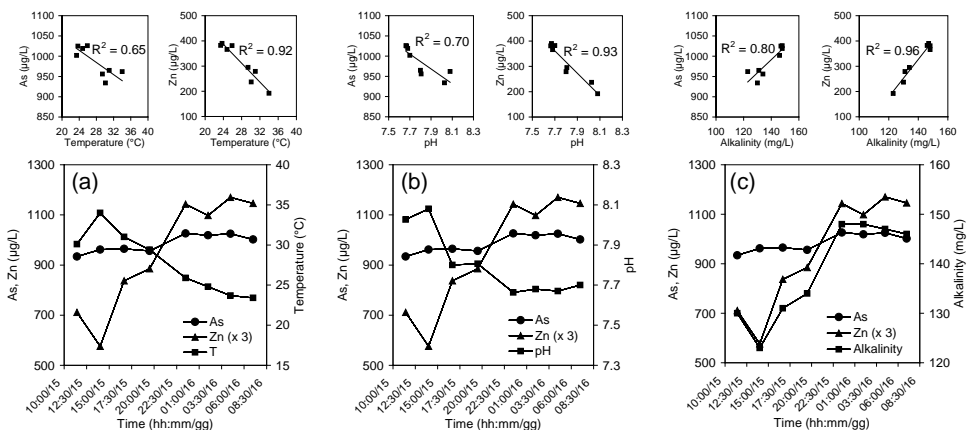


**Figure 1** Diel variation of temperature and conductivity (a), pH and Eh (b), and calcium, alkalinity and saturation index (SI) for calcite (c)

creasing as temperature decreases and decreasing as temperature increases. The moderate relation between As and temperature suggests the potential influence of additional factors. The nearly concurrent opposite timing between pH and As (fig. 2b) is not consistent with a pH-dependent sorption/desorption mechanism since a decrease in pH should be associated with either a decrease or an invariance in dissolved As concentration depending on position of the pH edge as a function of the As(V)/ferrihydrite ratio (Dixit and Hering 2003). On the contrary, concurrent diel variations in alkalinity and As showed a good match (fig. 2c) that is consistent with the known displacement action of aqueous carbonate species on As(V) sorbed onto ferrihydrite (Appelo et al. 2002, Frau et al. 2008).

Concurrent diel variations in water temperature and dissolved Zn showed a marked opposite timing. In particular, the sharp increase in temperature from 30 to 34 °C at 14:00 was simultaneous with the sharp decrease in Zn concentration from 237 to 192 µg/L (fig. 2a). This strong relation is consistent with sorption of cations onto HFO that is known to be an endothermic process (Gammons et al. 2005), increasing as temperature increases and decreasing as temperature decreases. Also pH exhibited a nearly concurrent opposite timing with Zn (fig. 2b) that is consistent with pH-dependent sorption/desorption of metals onto/from HFO. However, the slightly alkaline pH values and the small range of diel pH variation suggest a limited influence of pH on Zn. The strong positive relation between alkalinity and Zn (fig. 2c) might be incidental because the alkalinity variation was mainly responding to CO<sub>2</sub> solubility/production via temperature/biological activity.

An alternative explanation for the observed variations in pH, temperature, alkalinity, Ca, Zn, Mn, Cd, Ni and As, also considering the invariance of Pb, might be the precipitation of calcite. At higher pH during the warmer afternoon hours calcite precipitation would be more pronounced, at lower pH during the night calcite precipitation would slow down or stop. Co-precipitation with calcite would account for trace metal variations. In fact, Zn, Mn, Cd and Ni may easily enter the calcite lattice in substitution of Ca (Rimstidt et al. 1998), while As in the form of oxyanion may replace CO<sub>3</sub><sup>2-</sup> (Alexandratos et al. 2007). However, the degree of oversaturation with respect to calcite in the BLs water (maximum SI = 0.65 at 14:00; fig. 1c) was probably not sufficient to promote calcite precipitation with incorporation of trace elements. Moreover, micro-analysis of the streambed materials has never shown the presence of calcite (Frau and Arda 2004, Frau et al. 2008), although more detailed and finalized analyses on suspended solids and mineral and biological materials coating the streambed would be needed.



**Figure 2** Diel variation of dissolved arsenic and zinc with temperature (a), pH (b), and alkalinity (c). Zinc concentration is multiplied by three. Above each plot are shown the linear relations of arsenic and zinc with the corresponding parameter (temperature, pH and alkalinity) with indication of the R<sup>2</sup> value

## Conclusions

Diel variations of As and Zn in the BLs were related to sorption/desorption to/from streambed material containing ferrihydrite (HFO). Diel As variation was affected by the dual action of temperature and competitive effect of aqueous carbonate species, whereas diel Zn variation was mainly affected by temperature. Co-precipitation of As and Zn with calcite is also another possible mechanism that deserves to be taken into account and further investigated.

Trace element concentrations in streams impacted by mining activity are generally used to (i) establish baseline environmental conditions, (ii) identify the location of point and diffuse sources of contamination, and (iii) plan remediation actions to eliminate or attenuate contamination. However, if the observed differences in the degree of contamination between successive sampling sites along the stream are not only the result of actual inputs/trends but also an artifact of sampling time, all interpretations could be partially invalidated, especially in the presence of wide diel variations in trace element concentrations. Therefore, a particular sampling strategy should be adopted involving at least two sampling teams in two sufficiently distant sampling sites to conduct a perfectly synchronized sampling for at least 48 consecutive hours. This strategy should make it possible to distinguish a change in concentration due to the diurnal cycle from a change in concentration due to other mechanisms, as well as to determine whether the magnitude of the diurnal cycle is constant along the stream.

Remediation actions are currently in progress at Bacchu Locci: 1) creation of a “Collection Site” where the material from different mining dumps and several tailings piles occurring along the BLs will be placed; 2) securing of the three largest waste-rock dumps; 3) treatment of leachates from the “Collection Site” and of acidic water from an adit by a passive adsorbent system.

To avoid misleading evaluations, it is important that diel cycles of trace elements be taken into account when the effects of remediation currently in progress at Bacchu Locci will be monitored.

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