Antimony contamination of surface water at abandoned Sardinian mine sites

Rosa Cidu, Riccardo Biddau, Elisabetta Dore

Cagliari University, Dipartimento di Scienze Chimiche e Geologiche, via Trentino 51, 09127 Cagliari, Italy, cidur@unica.it

Abstract

The element antimony raises much concern from both toxicological and environmental viewpoints. The World Health Organization has established a guideline value of 20 µg/L Sb for drinking water, while the Italian legislation indicates a lower value (5 µg/L Sb). Antimony is ubiquitously present throughout the environment as a result of both natural and human processes. Particularly high concentrations of Sb may occur in water draining abandoned mining sites and in adjacent soils.

This study is aimed to assess the Sb occurrence, and dispersion in aquatic systems located in the Sarrabus-Gerrei mining district, south-eastern Sardinia (Italy). In this area, Sb ores have been mined till the 1980s. Thereafter, mines were closed and mining residues were abandoned without intervention to mitigate the environmental impact. Surface waters downstream of the mine show high concentrations of Sb (up to 1500 µg/L) and As (up to 230 µg/L). Contamination extends several kilometers downstream of the mine and affects the Flumendosa river, which water is used for irrigation and domestic purposes. Antimony concentrations in the Flumendosa water exceed 5 times the Italian standard for drinking water.

The Regional Government has recently recognized this site as a priority in the remediation plan for contaminated sites. The results derived from this study can give a valuable contribution in the correct management and preservation of aquatic bodies, and also in suggesting the appropriate actions able to mitigate environmental effects in Sb-contaminated aquatic systems.

Keywords: antimony, speciation, mine water, abandoned mine, Sardinia

Introduction

Antimony is present in the aquatic environment either as a result of rock weathering or anthropogenic activities. Antimony is categorized as a non-essential element for plants, animals or humans. High concentrations of Sb are toxic to most organisms. Based on the potentially harmful effects recognized by health authorities, Sb has been listed as a priority pollutant by the US Environmental Protection Agency and the World Health Organization. Toxicological effects of Sb rely on its chemical state and speciation. Some studies mentioned that the inorganic components are more toxic than the organic ones and toxicity of Sb(III) is stronger than that of Sb(V) (Filella et al. 2002; Gebel 1997).

Many factors may impact the Sb mobility in aquatic systems. As for other multivalent elements, the Sb behavior in the environment greatly depends on its oxidation state (Filella et al. 2002). Based on thermodynamic knowledge, in the simple chemical system Sb-H-O under reducing conditions, aqueous Sb may occur as antimonous acid, $Sb(OH)_3$, and the products of its protonation and deprotonation reactions, $Sb(OH)_2^+$ and $Sb(OH)_4^-$, respectively. Under oxidizing conditions, aqueous Sb occurs as antimonic acid and related species, namely the dissociation product $Sb(OH)_6^-$ and several polymeric species. Thermodynamically unstable Sb(III) has been detected in oxigenated waters, and oxidized species in anoxic waters have been also reported, suggesting that redox kinetics may play a significant role in defining the impact and fate of Sb in the environment (Filella and May 2003).

The determination of antimony in natural waters is often problematic as typical concentrations are usually <1 μg/L in unpolluted waters, but concentrations up to mg/L level may occur near anthropogenic sources. Total concentration data are not sufficient to assess Sb environmental behavior because mobility, bioavailability and toxicity of this element depend on its chemical speciation. With antimony increasingly recognized as an inorganic contaminant, investigations aimed to better understand factors affecting the Sb transport and fate in aquatic systems are required. This study is aimed to investigate the occurrence and speciation of Sb in waters impacted by past Sb mining and processing activities.

Study area

The study area comprises the Su Suergiu mine site and the Rio Ciurixeda catchment (SE Sardinia, Italy). At Su Suergiu, Sb-W deposits were mined underground since 1880, with exploitation peaks in the 1920-1930's. The mineralization is hosted in Paleozoic black schists and metalimestones, and consists of antimonite, scheelite, arsenopyrite, pyrite and gold, with calcite and quartz in the gangue (Funedda et al 2005). At Su Suergiu, a foundry was active since 1882 to 1987. After the mine closure in 1960, Sb-ore coming from Turkey and China was processed. Slag and tailings (87% of dumped materials) and waste rocks (13%) were dumped nearby the mine plant over a surface of 33,000 m^2 (Figure 1). Mining residues are altogether estimated at about 66,000 m^3 (RAS 2003).

Climate in the study area is semi-humid, characterized by dry summer and rainfall variable from year to year, mostly occurring from October to April. Data collected from 1955 to 1992 at stations located in the area show mean annual precipitation of 670 mm and mean annual temperature of 16.2 °C (RAS 1998). Spring waters are scanty and usually have low flow (<0.1 L/s). The main river is the Flumendosa. In the area under study, only a few tributaries are large streams (flow > 100 L/s) while the other ones are intermittent streams; their flow may vary several orders of magnitude in a year depending on rainfall. The Rio Ciurixeda stream receives the untreated drainage from the Su Suergiu mine, it flows directly in the Flumendosa River, which supplies water for agricultural and domestic uses.

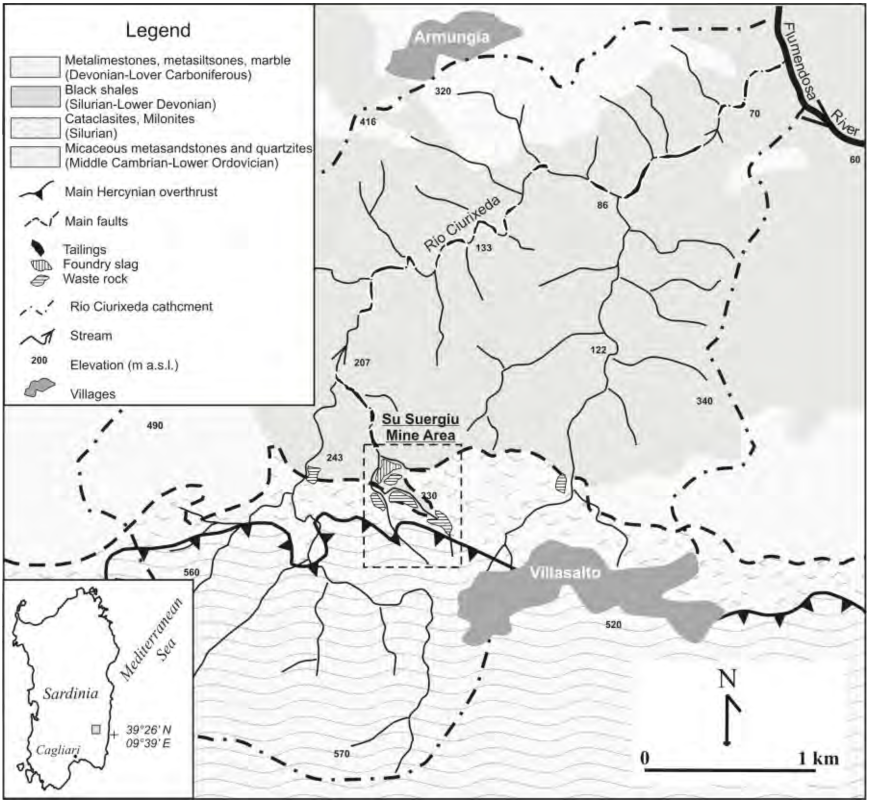

Figure 1 *Map showing geological features of the Su Suergiu mine area and the Rio Ciurixeda catchment.*

Methods

For this study, 16 water samples were collected in May 2012 under low-flow conditions. They consist of springs and surface waters located out of the mine area, mine drainages, water draining the slag materials, and surface waters located downstream of the slag drainage.

At the sampling site, the physical–chemical parameters and alkalinity (titration with HCl 0.01 N and methyl orange indicator) were measured; water was filtered (0.45 μm pore-size, Nuclepore polycarbonate) into pre-cleaned high-density PE bottles, and acidified with supra pure HNO_3 (1%, v/v) for metal analysis by quadrupole ICP–MS (Perkin Elmer DRC-e) using Rh as internal standard. An aliquot of water was filtered and stabilized with HNO_3 (1%, v/v) and (L^+) tartaric acid (0,2%, v/v) for Sb(III) analysis. The concentrations of Sb(III) were measured by adsorptive stripping voltametry (ASV) at the hanging mercury drop electrode (HMDE) in 0.6 mol/L HCl supra pure. Voltametric measurements were done on a Metrohm 797 VA Computrace using the method developed by Metrohm

(Application Bulletin 74/3e; www.metrohm.com). Antimony(V) was calculated by subtracting Sb(III) from total Sb concentration measured by ICP-MS.

Results

Results on previous surveys carried out in 2005 and 2006 can be summarized as follows (Cidu 2011). Dissolved Sb concentrations in the Rio Ciurixeda stream draining the Su Suergiu area, about 3 km downstream of the mine site, were 800 µg/L and 1200 µg/L, under high (about 200 L/s) and low (3 L/s) flow conditions, respectively. Detailed sampling at Su Suergiu showed Sb concentrations in the range of 0.4–7 µg/L in waters not interacting with the mineralization, and up to 380 µg/L in water flowing from adits. The highest concentrations of dissolved Sb (up to 9600 µg/L) and As (up to 3500 µg/L) were observed in waters flowing out of the slag materials derived from the processing of Sb-ores. The Flumendosa River water sampled upstream of the contaminated tributary showed 4 µg/L Sb and 2 µg/L As, i.e. values below the limits established by the World Health Organization guidelines for drinking water (20 µg/L Sb and 10 µg/L As; WHO 2006), while downstream of the Rio Ciurixeda confluence dissolved Sb was 32 µg/L and As 7 µg/L. Antimony contamination in the Flumendosa water extended some 16 km downstream from the abandoned mines, and was observed to attenuate (about 15 µg/L Sb) only at the mouth (Cidu et al 2008a, b).

Table 1 reports mean and range values of pH, electrical conductivity, and concentrations of some dissolved elements in waters from the study area. Hydrogeochemical surveys carried out in May 2012 showed results similar to those derived from previous surveys carried out under low flow conditions, therefore they were not distinguished. All waters show redox potential values (0.4±0.1 V, not shown) indicating oxidizing conditions. Local spring and stream waters collected out of the mine area show slightly alkaline pH, relatively low conductivity and sulfate concentration (Table 1). Mean values of As and Sb in these waters are similar to those observed in Sardinian streams and rivers (Cidu and Frau 2009).

In mine drainage located upstream of the slag heap EC increases, especially due to the increase in sulfate and calcium, mean As is similar to springs and streams, but mean concentration of Sb (420 µg/L) is much higher than in local groundwater (Table 1).

Water samples interacting with slag materials are characterized by extreme concentrations of Sb (mean: 9200 µg/L), and also As (mean: 2200 µg/L), clearly indicating that slag materials are the main source of contamination at Su Suergiu. The highest concentrations were observed when the water was collected under very low (<0.1 L/s) flow conditions. Water in the Rio Ciurixeda is affected by the confluence of the slag drainage. Despite the flow of water interacting with slag being usually low (<1 L/s), the Rio Ciurixeda shows elevated concentrations of Sb, while most of As appears removed from solution. The Sb dispersion extends to the Flumendosa river downstream of the Rio Ciurixeda confluence (Table 1).

Table 1 *Mean (in bold) and range (in italics) values of pH, electrical conductivity (EC) and selected components in waters from the Su Suergiu area; n = number of water samples; data refer to water samples filtered through 0.4 µm pore-size filters and surveys carried out in 2005, 2006 and 2012.*

Description	**pH**	**EC mS/cm**	**Ca^{2+} mg/L**	**Cl^- mg/L**	**SO_4^{2-} mg/L**	**As(tot) µg/L**	**Sb(tot) µg/L**
Spring water out of mine (n=11)	**7.3**	**0.46**	**39**	**58**	**50**	**1.2**	**1.6**
	6.9-7.6	*0.4-1.0*	*20-100*	*40-100*	*24-200*	*0.2-2.8*	*0.3-4.2*
Stream water out of mine (n=18)	**7.8**	**0.59**	**67**	**54**	**80**	**1.8**	**2.6**
	6.9-8.2	*0.3-1.1*	*30-170*	*34-75*	*30-300*	*0.4-9.5*	*0.4-7.4*
Mine drainage upstream of slag (n=8)	**7.5**	**1.36**	**240**	**59**	**610**	**2.5**	**418**
	7-7.8	*0.5-3.2*	*42-560*	*46-89*	*120-1900*	*0.5-7.9*	*99-850*
Slag drainage (n=10)	**7.9**	**1.94**	**330**	**56**	**910**	**2150**	**9200**
	7.2-8.4	*1.5-2.8*	*240-450*	*45-67*	*660-1500*	*300-5900*	*4500-15000*
Rio Ciurixeda (n=6)	**8.0**	**0.97**	**147**	**71**	**230**	**93**	**1300**
	7.9-8.3	*0.8-1.1*	*120-170*	*60-81*	*160-300*	*53-230*	*800-1500*
Flumendosa downstream of Rio Ciurixeda (n=5)	**8.0**	**0.66**	**69**	**62**	**84**	**7.1**	**33**
	7.3-8.3	*0.6-0.8*	*58-84*	*53-74*	*76-110*	*4-13*	*29-40*

Regarding the speciation analyses, results show that Sb(V) is the predominant form, while Sb(III) is a minor constituent in the aquatic environment at Su Suergiu. The highest concentration of Sb(III), i.e. 120 µg/l, was observed in water draining the slag materials, and corresponded to about 1% of total dissolved antimony. These results might explain the large dispersion of Sb several kilometers downstream of the contamination source. In fact, it has been observed that Sb(III) species is preferably sorbed to particulate matter in the surface water (Wu et al 2011). Slightly alkaline condition in the Su Suergiu waters favoring the permanence of Sb(V) in solution can explain the large spatial distribution of the Sb contamination.

Conclusions

Results of this study demonstrate that the major process controlling antimony contamination in the study area is the Sb release from slag materials abandoned at Su Suergiu mine. Drainage from the slag affects the Flumendosa river several kilometers downstream of the mine area. Therefore, remediation actions should be addressed to avoid the contact of water with the slag materials and to reduce erosion of the slag heap.

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