The Abandoned Antimony-mines of SE Sardinia: Impact on Surface Waters

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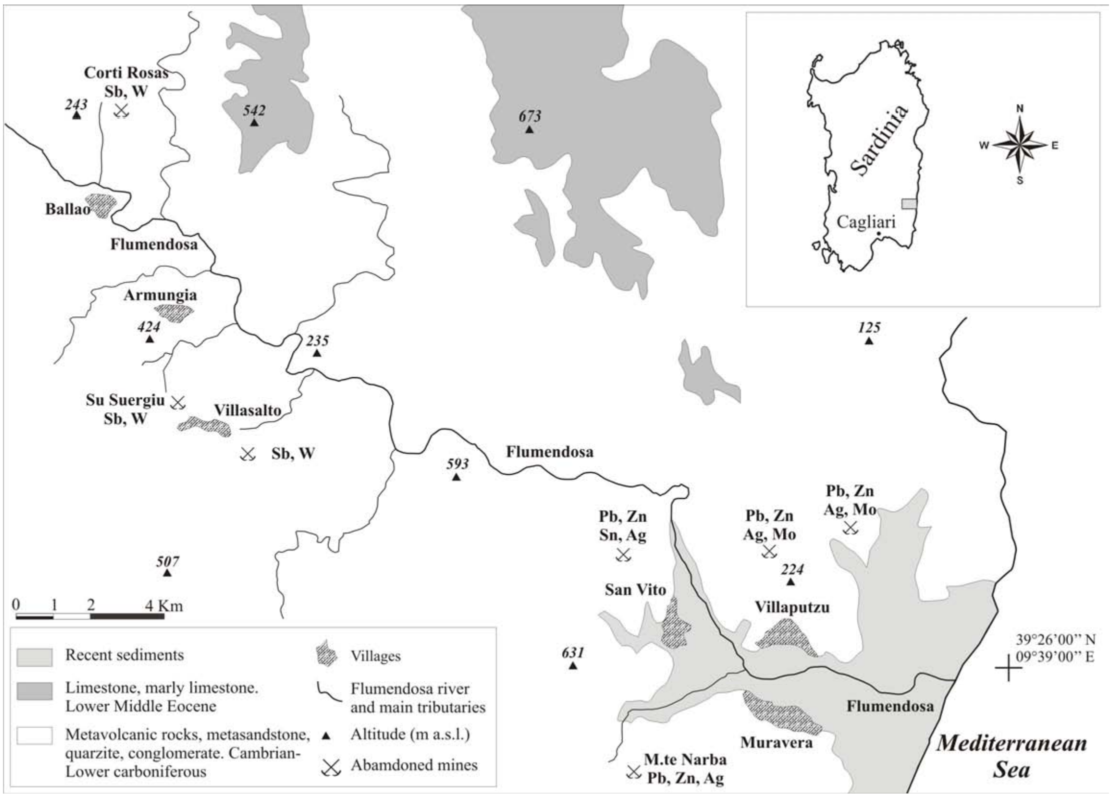
Abstract
This study investigates the impact of abandoned Sb-mines on the Flumendosa River, which is the most important water resource in southern Sardinia. Hydrogeochemical surveys carried out in 2005 and 2006 indicated a significant impact of waters flowing out from adits, slag, tailings and waste materials on surface waters. The contaminated waters show alkaline pH, and high dissolved SO_4, Sb and As (up to 1900, 9.6 and 3.5 mg/L, respectively). Although the flow rates of drainages from the mining area are usually low (in the range of < 0.1 to 1 L/s), the contribution to dissolved concentrations of Sb in the streams downstream of mines is high. Sampling under high flow conditions in the Flumendosa River before the confluence with the contaminated streams showed Sb concentrations below the limits established by the guidelines of World Health Organization for drinking water (i.e. 20 μg/L), while downstream of the confluence dissolved Sb was 32 μg/L. Contamination in the Flumendosa extended 16 km, and attenuation (15 μg/L Sb) was only observed close to the Flumendosa mouth.

Key words: Antimony, abandoned mine, surface water, ground water, mine water, Sardinia

Introduction and study area
Although Sb can be introduced into the environment through natural processes (e.g. soil-rock weathering and volcanic-geothermal activity), anthropogenic activities may represent relevant sources for the release of Sb to the soil and aquatic systems (Filella et al. 2002a). In particular, high levels of Sb contamination have been reported at former mining and smelting sites (e.g. Flynn et al. 2003; Hammel et al. 2000). Data on Sb partition between solid and dissolved phases in natural waters clearly indicate that Sb is present nearly exclusively in the dissolved phase (Filella et al. 2002b). Dissolved Sb is considered of environmental concern because its toxicity is similar to that of As species, with Sb(III) being much more poisonous than Sb(V) (Filella et al. 2002a and references therein).
In SE Sardinia, Sb-W deposits have been exploited at Su Suergiu and Corti Rosas (Figure 1). These ores are hosted in Palaeozoic black schists and metalimestones. The mineralization consists of antimonite, scheelite, arsenopyrite, pyrite and gold, with calcite and quartz in the gangue (Funedda et al. 2005; Marcello et al. 2007). The antimony deposits were underground mined since 1880 with exploitation peaks in the 1920-1930's. The deposit at Su Suergiu was the most important one; here, a foundry was active from 1882 to 1987; after the mine closure in 1960, Sb-ore coming from Turkey and China was processed at Su Suergiu (Mezzolani and Simoncini 2001). Slags and tailings (87%) and waste rocks (13%) were dumped near the mine plant over a surface of 33000 m^2 and are altogether estimated at about 66000 m^3 (R.A.S. 2003). At Corti Rosas, a flotation plant operated from 1940 to 1960; waste rocks (13336 m^3) and flotation tailings (8504 m^3) extend over a surface of 10920 m^2 (R.A.S. 2003).
This study is focused on the impact of the past Sb mining and processing activities on the surface waters in the area. The study area comprises the Su Suergiu and Corti Rosas sites and the lower part of the Flumendosa catchment (Figure 1). This area has a semi-humid climate with 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 (R.A.S. 1998). Due to the low permeability of most outcropping formations, spring waters are scanty and usually have low flow (< 1 L/s). The area is crossed by the Flumendosa River, which is the larger river in Southern Sardinia. 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 strongly depends on rainfall, and may vary by several orders of magnitude in a year. Through some tributaries, the Flumendosa receives untreated drainages from Su Suergiu, Corti Rosas and other abandoned Pb-Zn mines in the area (see Figure 1).

Figure 1 *Map showing the main geological features and the location of abandoned mines in the study area.*



Methods

The analytical dataset considered in this study derives from different sampling campaigns. Surface water (73 samples) from the Flumendosa river and its tributaries, and ground water (22 samples) were collected in April and June 2005, respectively (Cidu et al. 2008); 16 stream and ground water samples from the Su Suergiu area were collected in June 2006. As regards to surface waters, sampling in April 2005 was carried out after heavy rain events and represented high-flow conditions, while sampling in June 2005 and 2006 was done under low-flow conditions.

At the sampling site, the physical-chemical parameters and alkalinity were measured; waters were filtered (0.4 µm pore-size, 47 mm diameter, polycarbonate Nuclepore) into pre-cleaned high-density polyethylene bottles, and acidified with suprapure HNO_3 for metal analyses by quadrupole ICP-MS. An aliquot of filtered sample was acidified with suprapure HCl for the determination of As by on-line hydride generation ICP-MS. Dissolved components refer to concentrations measured in the filtered sample. Analytical errors have been estimated at ≤10% for concentrations >1 µg/L and ≤20% for concentrations in the range of 0.01 to 1 µg/L.

Table 1 *Statistical parameters of pH, TDS, SO_4 and trace elements dissolved in surface, ground and mine waters from SE Sardinia.*

		Surface water						Ground water						Mine water					
		n	Min	Max	Mean	SD	Median	n	Min	Max	Mean	SD	Median	n	Min	Max	Mean	SD	Median
pH		73	6.5	9.0	7.7	0.4	7.7	22	6.4	8.1	7.2	0.4	7.3	15	7.4	8.4	7.8	0.3	7.9
TDS	g/L	73	0.1	0.7	0.2	0.1	0.2	22	0.1	0.8	0.4	0.2	0.4	15	0.3	3.0	0.9	0.9	0.6
SO_4	mg/L	73	5	160	46	35	32	22	11	236	67	54	48	15	58	1900	453	570	220
Zn	µg/L	73	4	63	15	12	10	22	6	120	37	30	28	15	7	410	89	110	34
Pb	µg/L	71	0.1	22	1.3	3.3	0.4	8	0.2	1.0	0.6	0.3	0.5	15	0.2	36	8	12	1
Cu	µg/L	73	0.7	8.4	2.0	1.6	1.5	22	0.2	47	3	10	1	15	0.8	15	3.5	3.8	2.3
Cd	µg/L	67	0.03	0.6	0.14	0.13	0.08	21	0.06	11	0.8	2.3	0.2	15	0.1	10	2.0	2.7	0.4
As	µg/L	72	0.1	31	2.8	4.9	1.4	22	0.2	75	6.0	17	1.1	15	1.4	3550	280	910	4.8
Sb	µg/L	65	0.1	32	4.3	8.2	0.3	20	0.04	5.8	0.8	1.3	0.4	15	0.3	9600	1100	2700	2
Mo	µg/L	49	0.1	4	0.7	0.7	0.6	15	0.1	2.4	0.9	0.7	0.5	15	0.4	37	8.8	100	5.4
U	µg/L	62	0.01	1.4	0.5	0.4	0.3	22	0.01	2.3	0.5	0.6	0.2	15	0.6	17	3.8	4.4	2.6

n: number of samples above detection limit; SD: standard deviation; TDS: total dissolved solids.

Results

Water samples were grouped in surface waters (Flumendosa river and its tributaries), ground waters, and mine waters (i.e. all drainages at the abandoned mining sites). Table 1 reports a selection of statistical parameters for the different groups of water, i.e. pH, total dissolved solids (TDS), dissolved sulphate and some elements of environmental interest.

All waters have neutral to alkaline pH. In the mine waters, any acidity produced by the oxidation of sulphide minerals has been buffered by the dissolution of carbonate minerals, mainly calcite. The relative abundance of major ions shows large variations among the three groups and within each water group. The main chemical features can be summarized as follows. Surface and ground waters have chemical composition varying from Na-Cl with low total dissolved solids (TDS 0.1-0.5 g/L) to Ca-HCO_3 with TDS in the range of 0.2 to 0.8 g/L. Most of the mine water samples have a distinguished Ca-SO_4 composition with TDS up to 3 g/L.

Dissolved concentrations of toxic or harmful elements vary significantly; mine waters generally show concentrations much higher than those observed in surface and ground waters. In the NW part of the area, the highest concentrations of Sb and As occurred in the waters that drain the Su Suergiu and Corti Rosas mining sites. In the SE part, where Pb-Zn and Mo deposits prevail (see Figure 1), the highest values of dissolved Pb (36 µg/L), Cd (10 µg/L), Zn (400 µg/L) and Mo (37 µg/L) were observed. The median value of dissolved Cu in mine waters was similar to that observed in the surface and ground waters (Table 1), which is consistent with the scarce occurrence of Cu ores in the area.

Figure 2 *Distribution of dissolved Sb in surface, ground and mine waters collected under high flow (A) and low flow (B) conditions.*

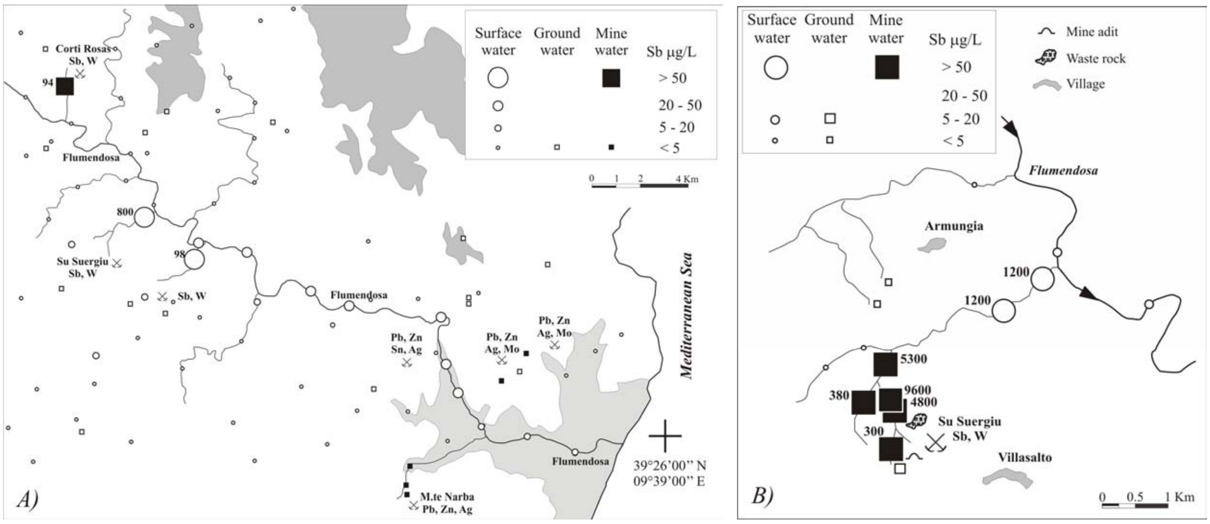


Figure 2 shows the distribution of Sb in the waters sampled under high flow condition in the Flumendosa basin (Figure 2A) and under low flow condition in the Su Suergiu area (Figure 2B). Dissolved Sb concentrations in the stream draining the Su Suergiu area, about 3 km downstream of the mine site, were 800 µg/L (Figure 2A) and 1200 µg/L (Figure 2B), under high (about 200 L/s) and low flow (3 L/s) conditions, respectively. Detailed sampling at Su Suergiu (Figure 2B) showed Sb concentrations in the range of 0.4 to 7 µg/L in waters not interacting with the mineralized rocks and up to 380 µg/L in waters from adits. The highest concentrations of Sb (up to 9600 µg/L) were observed in waters flowing out of the waste materials derived from the ore processing; these waters also showed high concentrations of dissolved As (up to 3500 µg/L). Chemical and mineralogical studies of these materials are in progress; preliminary leaching tests carried out with deionized water (solid to water ratio = 1:20; interaction time of 2 hours) showed that these materials react very fast and the highest release of Sb and As occurs from the foundry slag.

In order to evaluate the risk associated with these contamination sources we must consider that the streams that drain Su Suergiu and Corti Rosas are tributaries of the Flumendosa River which, in the lower course, is a significant resource used to supply water to a fertile plain. Sampling of the Flumendosa River under high flow conditions before the confluence with the contaminated streams

showed Sb concentrations of 4 µg/L, i.e. much lower than the limit established by the World Health Organization guidelines for drinking water (20 µg/L; WHO 2006), while downstream of the confluence dissolved Sb was 32 µg/L; the Flumendosa flow before and after the confluence was about 700 and 900 L/s, respectively. Antimony contamination in the Flumendosa extended some 16 km downstream of the abandoned mines; an attenuation (15 µg/L Sb) was only observed close to the mouth when the flow rose to 3000 L/s. The decrease of dissolved Sb in the Flumendosa near to the mouth might be due to dilution by uncontaminated tributaries; Sb scavenging via fine particles could also explain the observed decrease of Sb in the river water. According to Filella et al. (2002b), Sb removal may occur at low TDS and release at intermediate TDS, with adsorption-desorption reactions probably playing a major role.
Speciation calculation by PHREEQC (Parkhurst and Appelo 1999) indicate that the SbO_3^- is the dominant species in the studied waters, which is consistent with redox potential values indicating oxidizing conditions. However, according to Belzile et al. (2001), reduced Sb species can exist even in oxygen-rich environments since biological activity or kinetic considerations are not included in thermodynamic calculations.

Conclusions

This study showed that the more intensive Sb and As contamination at Su Suergiu comes from the mining, sorting and processing of the ore minerals. These materials are highly contaminated and react fast when water interacts with them. Drainage waters from these materials have high concentrations of Sb and As; they flow directly into streams that flow into the Flumendosa River causing a serious degradation in the water quality, especially after heavy rain events. Su Suergiu and Corti Rosas have been identified as polluted sites by the Regional Government (R.A.S. 2003), and remediation actions to mitigate the environmental risk in the area are expected.

Acknowledgements

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