# Overview of the environmental geochemistry of mining districts in southwestern Sardinia, Italy

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**ABSTRACT:** In southwestern Sardinia the areas around Iglesias and Guspini–Arbus represent the heart of the former mining industry. Lead and zinc ores were extensively exploited from 1850 to 1995. Geochemical studies in these areas have identified the main sources of contamination to be from drainage of flooded mines, mining wastes and tailings abandoned in settling ponds, and exposed ores. The transport of the fine materials eroded from the tailings ponds contributes to spreading pollution over larger areas downstream. Concentrations of Pb, Cd and Zn in the streams draining the mining area (up to 1, 1.7, and 1000 $mg\,l^{-1}$, respectively) are several orders of magnitude higher than those observed in rivers outside the mining areas in Sardinia (Pb: $<0.004\,mg\,l^{-1}$, Cd: $<0.001\,mg\,l^{-1}$, and Zn: $<0.02\,mg\,l^{-1}$), and greatly exceed the Italian drinking water standards (Pb: $0.01\,mg\,l^{-1}$, Cd: $0.005\,mg\,l^{-1}$, and Zn: $3\,mg\,l^{-1}$).

**KEYWORDS:** *hydrogeochemistry, heavy metals, mining, Sardinia*

## INTRODUCTION

Sardinia was the most important Italian mining region in the 19th and 20th centuries. The two main mining districts (Iglesias and Guspini–Arbus) are located in the southwestern part of the island (Fig. 1).

The Iglesias district extends over an area of about 120 $km^2$, from the Mediterranean Sea to approximately 20 km inland. Here, massive sulphide ore bodies and stratabound deposits in Lower Cambrian limestone–dolomite formations (Pillola *et al.* 1998) were exploited by 40 mines over this time period. The mined minerals were sphalerite, galena and pyrite (the last containing up to 1000 ppm arsenic) and sometimes baryte (Boni 1994).

In the Guspini–Arbus district, the hydrothermal or contact-metamorphic vein deposits (Ludwig *et al.* 1989) extend over 12 km. The ore is hosted in Ordovician siliciclastic metasediments (Barca *et al.* 1981) and, subordinately, in Hercynian granite rocks (Secchi *et al.* 1991). From 1848 to 1991, when mining ceased, approximately $3 \times 10^6$ tons of lead and zinc were exploited from the Montevecchio–Ingurtosu mining complex extending underground in a system of overlapping galleries for a length of 100 km horizontally and 600 m vertically. Here, the ore-veins were mainly composed of quartz, galena and sphalerite, with local occurrences of carbonate minerals (siderite, ankerite, dolomite and calcite) especially abundant at Ingurtosu. Pyrite, chalcopyrite, pyrrhotite, arsenopyrite and tetrahedrite are subordinately associated with the ore (Caboi *et al.* 1999, and references therein).

In both these mining districts of southern Sardinia, peaks in Pb–Zn production were reached in the middle of the 20th century. The decline of the mining industry, due to the fall in value of base metals and the increase in labour costs, led to the closure of all base-metal mines during 1970–1995. At that time no adequate closure safety measures were taken because of the economic situation and the lack of an environmental mining policy. The environment in these areas, therefore, has progressively deteriorated. In particular, abandoned flotation mud from settling ponds and wastes from rock dumps (estimated volume: $8 \times 10^6$ $m^3$) remain on site, spread over an overall area of approximately 12 $km^2$. Furthermore, contaminated streams flow out of the adits of mines that were flooded after the dewatering plants were stopped.

In Sardinia, contamination from solid materials abandoned on the ground at the end of the mining activity is enhanced by the climatic peculiarities of the region. Long periods of heat and drought, interrupted by short rainy periods, with occasional storm events, facilitate the weathering process and increase dispersion. Strong western winds blow dust from mine wastes onto the inhabited areas east of the district.

The quality of the water in some aquifers and reservoirs is degraded by underground and/or superficial transport in solution of the contaminants, increasing the deficit between water resources and demand in southwestern Sardinia where approximately 60 000 residents live.

The paper aims to add new data and critically review previous data concerning the contamination of water bodies by abandoned mining activity, and to highlight some hazards that local communities and regional government will have to face in the near future. The focus is upon four identified important contamination sources: a flooded mine contaminating an important aquifer; a dump made up of metallurgic wastes; a discharge from a flooded mine into a small stream; and the leachate from a large abandoned tailings pond.

## METHODOLOGY

At the sampling site, waters were filtered at 0.4 μm and acidified for metal analyses. The pH, redox potential (Eh), temperature,

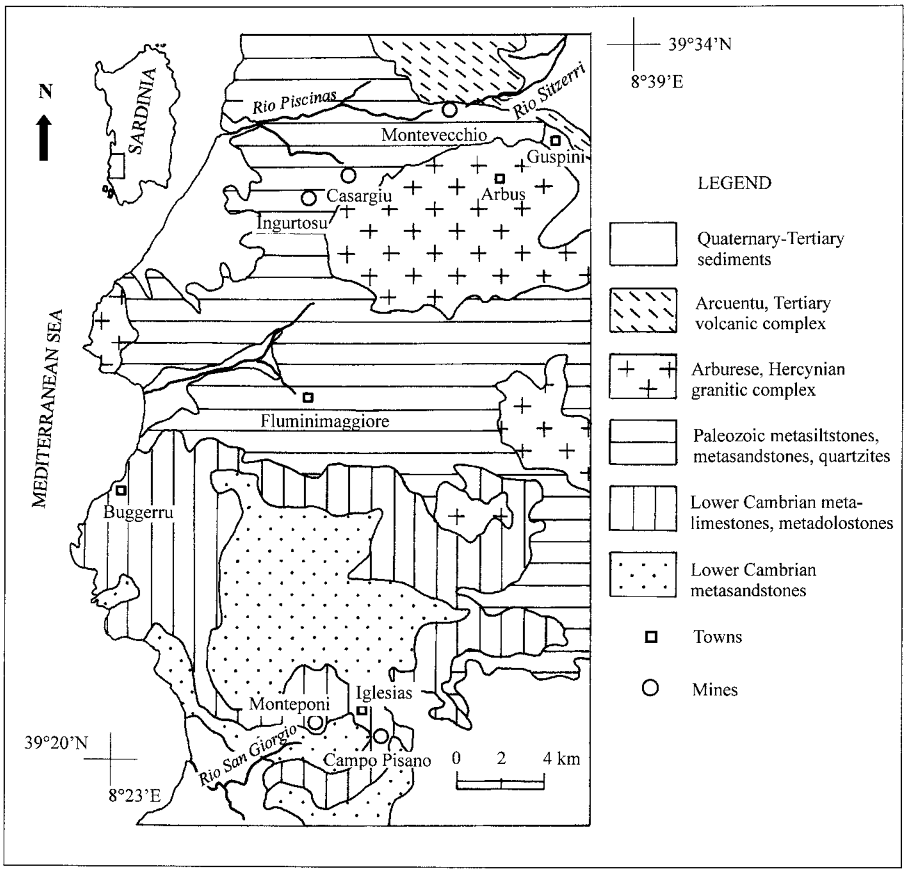

**Fig. 1.** Schematic geological map of southwestern Sardinia, showing the Iglesias and Guspini–Arbus mining districts.

conductivity and alkalinity were measured on site. The Eh was measured by platinum electrode, and the values corrected against the ZoBell's solution (Nordstrom 1977). Major, minor and trace elements in solution were analysed by ionic chromatography, inductively coupled plasma (ICP) atomic emission spectrometry, and ICP mass spectrometry (Cidu 1996).

Since the considered conditions are subject to changes in time and season, hydrogeochemical monitoring programmes, designed specifically for each site, have been carried out at the Department of Earth Sciences, University of Cagliari, since 1992 (details on these ongoing programmes can be found in the quoted references). Surface and groundwater samples from about 90 sites in the Iglesias and Guspini–Arbus mining districts have been investigated. Only selected data on the most representative samples are reported in this paper.

## RESULTS AND DISCUSSION

### Impact of mine flooding at Monteponi

The Monteponi mine is located at the centre of the Iglesias district. Intense fracturing and karstification of the carbonate formations required strenuous efforts to keep the pits dry during exploitation. Here, the underground workings had to be drained at a depth that increased regularly as the mine works got deeper. From 1910, the water collected in the Monteponi mine was discharged into the sea through a partially underground drain, 6 km long. As a result of lowering the water table at Monteponi from 15 to 160 m below sea-level between 1928 and 1990, the quantity of water extracted, as well as the concentrations of $Cl^-$, increased with depth (Fig. 2). The chemical and isotope composition at Monteponi indicated an influx of seawater up to 60% (Cidu *et al.* 2001, and references therein). The water at Monteponi is supposed to have been highly enriched in Zn, Cd and Pb already in the first stages of the mine works, though detailed data for the early years are completely lacking. During 1990–1996, when the mean flow rate to keep the mine dry was $1800\ l\ s^{-1}$, the dissolved content transferred to the sea (in tonnes per year) is calculated to have been approximately: zinc, 100; lead, 5; mercury, 2.7; silver, 2.5; and cadmium, 0.4. Table 1 lists the chemical composition of the water during the last dewatering period (1996) at Monteponi and Campo Pisano. The Campo Pisano mine is located at the periphery of the mining district where the seawater inflow appears to be negligible. In 1996, mining activity at Monteponi was stopped due to high operating costs. In January 1997, the flow rate was gradually reduced and, finally, in July 1997 the pumping system was completely deactivated, so that the Monteponi mine system was flooded. In 1999 the drain connecting the mine level at 8 m above sea-level (asl) to the sea was sealed.

When the deactivation of the pumping system at Monteponi was planned, the main environmental concern of the local authorities was the potential salinization of the peripheral water resources, such as those coming from the Campo Pisano mine, which were used to supply the town of Iglesias. Contamination from metals was underestimated. Scientists, in fact, expected that flooding at Monteponi would have negative effects on the Campo Pisano water, both on account of the dissolution of Zn, Cd and Pb (largely available in the underground workings, now flooded) and the dissolution of Hg and Ag, (which form stable Cl-complexes on mixing with marine water). Indeed, shortly after the beginning of flooding and until the summer of 1998, a moderate salinization effect (doubling of the dissolved amounts of Cl, Na, $SO_4$ and Br) was observed in the water from Campo Pisano. But this increase in salinity was accompanied by a dramatic increase in zinc (from 0.4 to $10\ mg\ l^{-1}$) and

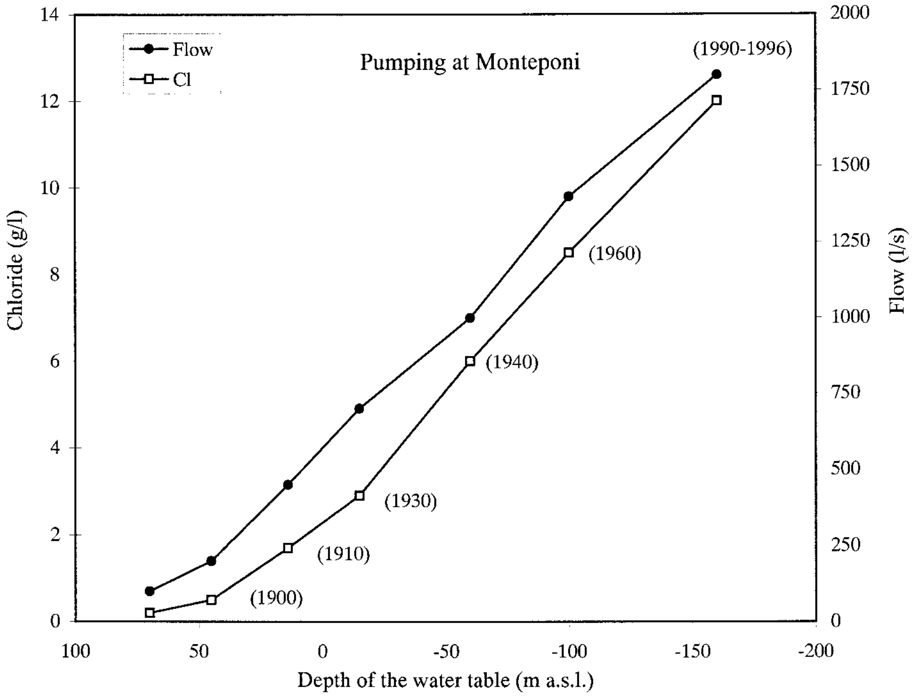

**Fig. 2.** Plot showing the rise of chloride concentrations and flow rates with increasing depth of the water level in the Monteponi mine (years are reported in brackets).

cadmium (from 0.3 to 17 μg $l^{-1}$), and a significant increase in lead (from 7 to 15 μg $l^{-1}$), mercury (from 2 to 10 μg $l^{-1}$) and silver (from 0.05 to 1 μg $l^{-1}$). In February 2000, the water table rose to 20 m asl and a stratification process in the water column appeared to be nearly complete, leaving the saline water at depth. Figure 3a shows the gradual flooding of Campo Pisano mine by saline water when the pumping system at Monteponi was deactivated, and the water stratification that occurred after a short period, leaving fresh water at the surface. Stratification, however, had no effect on the high concentrations of Zn and Cd dissolved at the top of the water column, once the mobility of these elements was enhanced by increased exposure of fine wastes and ore in contact with water (Fig. 3b). On the contrary, the Hg content decreased from 1.9 μg $l^{-1}$ (before flooding) to 1.0 μg $l^{-1}$. Figure 3c shows the reduction of the dissolved concentrations of Pb, Ag and Hg in the shallow water over a relatively short period as a result of water stratification.

It can be inferred from the above that the completion of the water stratification process, combined with a moderate exploitation of the water resource, could keep the shallow water protected from salinization. When $Cl^-$ concentrations are kept low, Hg mobility related to the formation of $[Hg(Cl)_n]^{n-2}$ complexes will be reduced. In contrast, weathering of exposed ores and mine wastes filling up the underground workings will still contaminate the shallow groundwater, and it will take a long time before significant amounts of Zn and Cd can be removed from the waters. However, controlled pumping of shallow groundwater from the Campo Pisano mine could be used for industrial uses in the relatively near future.

## The ‘Red Mud’ case

The Monteponi site is covered by mine wastes and several abandoned flotation ponds are found in the Rio San Giorgio valley (Fig. 1). The ‘Red Mud’ dump is about 40 m high, and extends over about 0.2 $km^2$. The ‘Red Mud’ consists of mine wastes that include the residues from a metallurgical plant for the production of electrolytic zinc from ferruginous calamines (Buosi *et al.* 2001). In this plant Zn-oxidized ore containing 22–26% Zn, prevalently as smithsonite, was chemically dissolved to leave iron oxide tailings (mainly made up of goethite) as a residue. In addition, the ‘Red Mud’ contains abundant gypsum, and it is made up of so fine a material that more than 60% of the grains are smaller than 40 μm in size. This dump marks out the landscape so deeply with its reddish heap supported on its slopes by cane fences, that it has been recognized as a monument of industrial archaeology, and is now subject to preservation regulations.

The Zn-bearing ‘Red Mud’ is the main source of contamination in the Rio San Giorgio valley. The reliability of this statement is evident from Table 2 where two sets of ‘Red Mud’ chemical analyses are reported. The polluting power of the ‘Red Mud’ is confirmed by leaching tests. Buosi *et al.* (2001) indicate high concentrations of toxic metals (Zn: 251 mg $l^{-1}$, Cd: 4.1 mg $l^{-1}$ and Pb: 0.3 mg $l^{-1}$) and sulphate (2800 mg $l^{-1}$) in a leachate at a near-neutral pH; these results agree with those from sequential extraction experiments showing the predominant amounts of Zn, Cd and Pb to be in the soluble or exchangeable fraction (Collu 1998).

Table 3 reports the dissolved amounts of two seeps at the base of the ‘Red Mud’ heap, and a dissolved amount of the run-off flowing from the dump to the Rio San Giorgio downstream. The range of values observed in Sardinian rivers draining areas away from the mining district is also reported for comparison. Concentrations of $SO_4$, Zn, Cd and Pb in the waters draining the ‘Red Mud’ confirm their polluting power, which was observed in laboratory tests. These concentrations are several orders of magnitude higher than those in uncontaminated rivers, and pose a serious hazard to the quality of the water in Rio San Giorgio. The contamination effects of the fine sediments transported by the dust have not been evaluated but they seem less important than the water contamination.

## Tailings weathering and mine flooding westward of Montevecchio

In the western area of the Guspini–Arbus district, the wastes from several washeries and flotation plants were stored in ponds, whose dams are now nearly completely destroyed.

**Table 1.** *Chemical composition of waters from Monteponi and Campo Pisano in 1996, during the last dewatering period*

| Name | Depth (m) | Flow (l s$^{-1}$) | T (°C) | Eh (mV) | pH | Conductivity (mS cm$^{-1}$) | TDS (g l$^{-1}$) | Ca (mg l$^{-1}$) | Mg (mg l$^{-1}$) | Na (mg l$^{-1}$) | K (mg l$^{-1}$) | Cl (mg l$^{-1}$) | Alk (mg l$^{-1}$) | $SO_4$ (mg l$^{-1}$) | Br (mg l$^{-1}$) | B (μg l$^{-1}$) | Li (μg l$^{-1}$) | Sr (μg l$^{-1}$) | Ba (μg l$^{-1}$) | Zn (μg l$^{-1}$) | Cd (μg l$^{-1}$) | Pb (μg l$^{-1}$) | Ag (μg l$^{-1}$) | Hg (μg l$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Monteponi | −160 | 1800 | 23 | 440 | 7.5 | 32.3 | 20.2 | 530 | 690 | 6200 | 230 | 11 000 | 330 | 1500 | 38 | 1800 | 90 | 3900 | 63 | 1800 | 7 | 88 | 46 | 50 |
| Campo Pisano | −128 | 180 | 20 | 450 | 6.8 | 1.55 | 0.88 | 110 | 69 | 110 | 5.3 | 180 | 430 | 200 | 0.7 | 60 | 6 | 170 | 39 | 440 | 0.4 | 7 | 0.07 | 1.9 |

From Cidu & Fanfani (1998).

TDS, total dissolved solids; Alk, alkalinity as $HCO_3^-$.

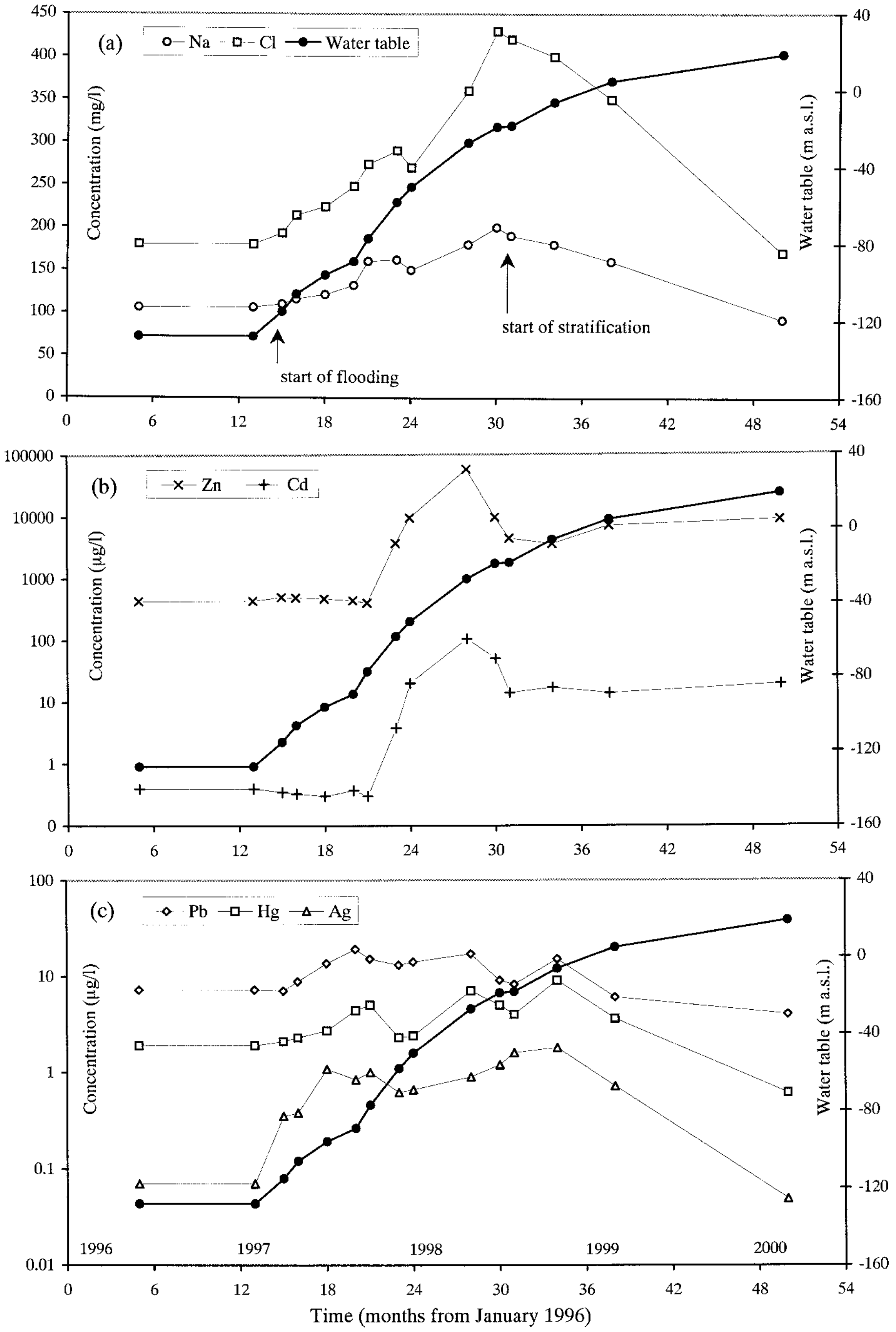

**Fig. 3.** Plots showing the effect of flooding on the water chemistry at Campo Pisano. In 1997, the pumping system at Monteponi was deactivated causing flooding by saline water at Monteponi, in addition to surrounding mines as well. (**a**) After a $Cl^-$ peak the saline water began to deposit at depth. (**b**) In 1998, flooding at the Campo Pisano well caused a dramatic increase in Zn and Cd, still persisting at high concentrations, while (**c**) Pb, Hg and Ag decreased after water stratification.

Figure 4 shows the extension of the area affected by the dispersion of tailings from the main plants (Sanna, Lamarmora, Brassey).

**Table 2.** *Chemical composition of the 'Red Mud' (mean values)*

| | Buosi *et al.* (2001) | Collu (1998) |
|---|---|---|
| $Fe_2O_3$ (%) | 45 | 50 |
| Zn (%) | 8.8 | 8.4 |
| Pb (%) | 1.1 | 0.8 |
| Cd (ppm) | 390 | 260 |
| As (ppm) | 54 | 75 |
| Hg (ppm) | 58 | nd |

nd, not determined.

The tailings initially contained by dams along the streams Rio Naracauli, Rio Irvi and Rio Roia Cani are deeply eroded at present, and most of the material has been transported and deposited along the banks (Fig. 4). The flow of these streams is perennial, though scarce (a few litres per second), except after high run-off storms. Tailings along the Rio Naracauli are highly contaminated and contain average amounts of Pb, Zn and Cd estimated at 1.3%, 1.5% and 84 ppm, respectively, mainly hosted in the finest fractions (Caboi *et al.* 1999). Further studies (Fanfani *et al.* 1997), combining a sequential extraction procedure with mineralogical investigations, indicate approximately ≥75% of Pb and 50% of Cd easily dissolved, Zn largely removed from the primary sulphide and adsorbed onto Fe-oxides, most Pb in the form of anglesite and cerussite, siderite prevalent among the Fe-phases, and S in the form

**Table 3.** *Chemical composition of waters from the 'Red Mud' and Sardinian rivers*

| | Seeps (Buosi *et al.* 2001) | | Run-off (Collu 1998) | Rivers[1] |
|---|---|---|---|---|
| pH | 6.8 | 6.2 | 6.4 | 7.1–8.2 |
| $SO_4$ ($g\,l^{-1}$) | 13 | 18 | 8.5 | 0.01–0.17 |
| Ca ($mg\,l^{-1}$) | 460 | 520 | 420 | 10–110 |
| Mg ($mg\,l^{-1}$) | 2500 | 2600 | 1700 | 5–35 |
| Zn ($mg\,l^{-1}$) | 550 | 7100 | 440 | 0.003–0.02 |
| Cd ($mg\,l^{-1}$) | 2.4 | 23 | 2.7 | <0.001 |
| Pb ($mg\,l^{-1}$) | 0.9 | 1.4 | 0.5 | <0.001–0.003 |

[1] Range of values from 10 major rivers located away from the mining district.

of easily soluble secondary sulphate minerals, as well as metallic sulphides.

Caboi *et al.* (1993, 1995, 1996) reported the main characteristics of the stream waters (Rio Naracauli, Rio Irvi, Rio Piscinas and Rio Roia Cani; see Fig. 4) in this area: the pH is between 7.2 and 7.6, conductivity relatively low ($<1.5\ mS\,cm^{-1}$), sulphate $<500\ mg\,l^{-1}$, Zn up to $100\ mg\,l^{-1}$, Cd between 300 and $1900\ \mu g\,l^{-1}$, Pb between 50 and $1100\ \mu g\,l^{-1}$ and Fe $<90\ \mu g\,l^{-1}$. These data confirm the polluting effect of the abandoned tailings on the water system, notwithstanding the strong buffering effect observed. This buffering capability is related to the occurrence of abundant siderite and other carbonate minerals in association with the sulphide ores in the western part of the mining district.

In the Rio Naracauli, the precipitation of metals is controlled by the equilibria with two solid phases: one with the mineral hydrozincite ($Zn_5(CO_3)_2(OH)_6$ occurring in the upper course, the other with an amorphous Zn–Si–O–H phase observed in the medium course. The precipitation of hydrozincite, restricted to the spring season, has been described as the result of photosynthetic metabolism of a microbial community which shifts the inorganic C species in solution to the carbonate form (Podda *et al.* 2000). The capability of micro-organisms to clean water in a natural environment by immobilizing toxic metals in insoluble compounds may contribute extensively to develop soft technologies in the remediation of mine wastes.

In the western part of the district other sources of heavy metal pollution are represented by water flowing out of several adits and drainage tunnels. This phenomenon had already been identified when the mines were still active, but it became increasingly problematic after the closure, i.e. when the underground workings, no longer drained by pumps, became flooded.

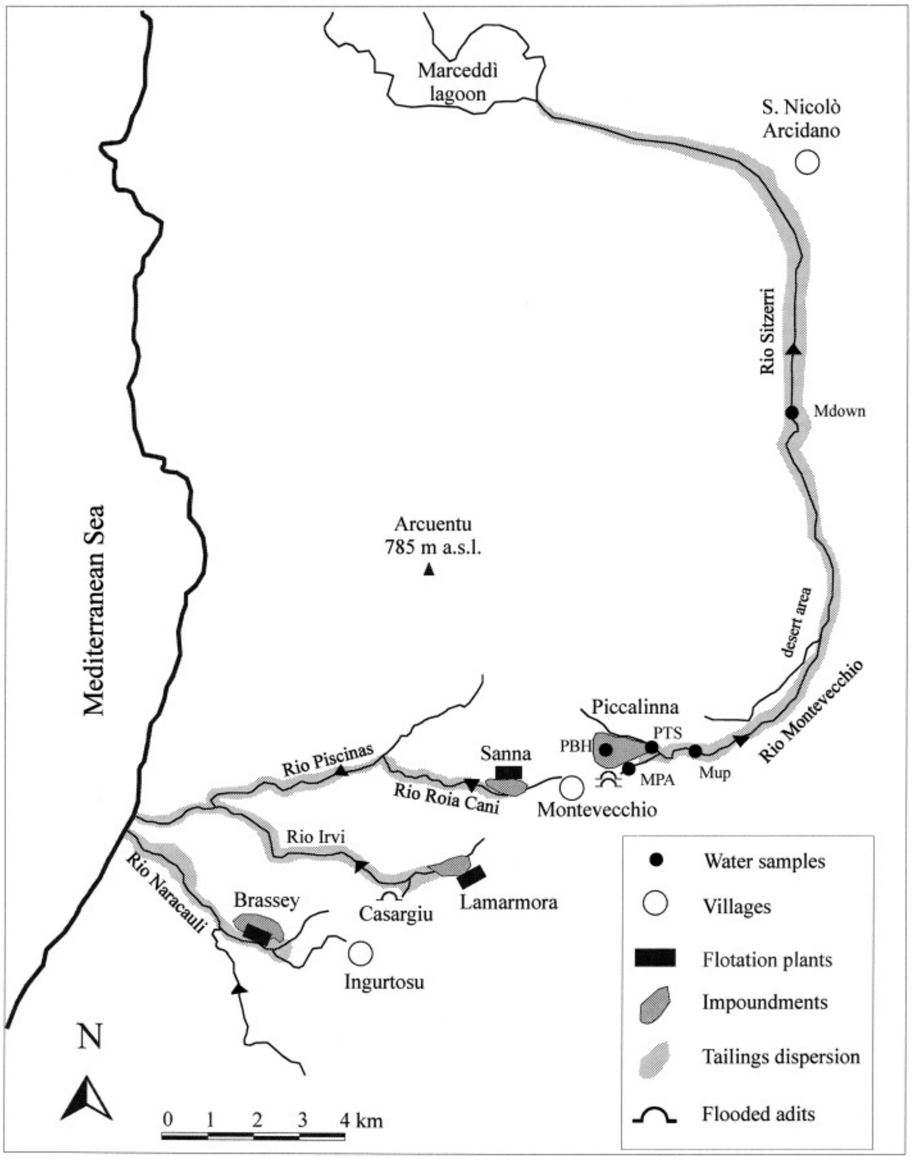

**Fig. 4.** Map showing the dispersion of tailings in the Guspini–Arbus mining district.

**Table 4.** *Chemical composition of drainage from the Casargiu shaft (Fanfani* et al. *2001) and standards for drinking water*

| Date | Mar. 1999 | Nov. 1999 | Feb. 2000 | June 2000 | Aug. 2000 | Nov. 2001[1] | Drinking water[2] |
|---|---|---|---|---|---|---|---|
| pH | 6.0 | 6.0 | 6.2 | 6.0 | 6.1 | 6.1 | |
| $SO_4$ (mg $l^{-1}$) | 6400 | 4600 | 4700 | 4900 | 4700 | 5000 | 250 |
| Ca (mg $l^{-1}$) | 470 | 490 | 450 | 520 | 510 | 460 | |
| Mg (mg $l^{-1}$) | 530 | 390 | 320 | 410 | 420 | 410 | |
| Fe (mg $l^{-1}$) | 260 | 240 | 280 | 260 | 220 | 320 | 0.2 |
| Zn (mg $l^{-1}$) | 340 | 930 | 1000 | 780 | 610 | 990 | 3 |
| Cd (mg $l^{-1}$) | 1.1 | 0.9 | 0.8 | 0.7 | 0.5 | 1.7 | 0.005 |
| Pb (mg $l^{-1}$) | 1.0 | 0.3 | 0.7 | 0.4 | 0.2 | 0.8 | 0.01 |
| Ni (mg $l^{-1}$) | 8.1 | 7.8 | 6.1 | 7.5 | 6.9 | 5.4 | 0.02 |
| Co (mg $l^{-1}$) | 5.1 | 5.1 | 3.4 | 4.7 | 4.1 | 3.5 | |
| Mn (mg $l^{-1}$) | 36 | 160 | 150 | 120 | 100 | 130 | 0.05 |
| Cu (μg $l^{-1}$) | nd | <80 | 4 | 1 | 4 | 5 | 1000 |
| As (μg $l^{-1}$) | 91 | 150 | 200 | 47 | nd | 200 | 10 |
| Hg (μg $l^{-1}$) | 7 | 4 | 1 | <0.5 | 2 | <0.5 | 1 |
| Tl (μg $l^{-1}$) | 13 | 8 | 10 | <3 | 7 | 13 | |

nd, not determined.

[1] This study.

[2] Maximum concentration according to Italian regulations (Gazzetta Ufficiale della Republica Italiana 2001).

Indeed, the material used to refill the pits, as their exploitation came to an end, is made up of economically unsuitable fine wastes or gangue extremely hazardous on account of oxidation of the iron and sulphur in the sulphides.

Since the potential contamination associated with the outflow of water from the abandoned mines was not considered carefully at closure, no strategy was prepared to reduce the possible impact on the environment. In 1998, a large amount of water (25 l $s^{-1}$) with a pH of about 6 started to flow out of the Casargiu shaft in the southwestern part of the area (Fig. 2), as soon as the natural recharge flooded a large extent of the underground workings. The deposition of a red mud into the bed of a stream, dry during part of the year, has reached as far as the sea, degrading a unique landscape of dunes and Mediterranean vegetation. Table 4 reports the chemistry of the water flowing out of the Casargiu shaft compared to the drinking water standards according to Italian regulations. On the basis of data collected in 1999 (less than 2 years after the water appeared at the mine surface), the quantity of dissolved metals flowing into the sea was estimated (in tonnes per year) at: Zn, 30; Ni, 0.24; Co, 0.15; Cd, 0.025; and Pb, 0.001. Data collected up to November 2001 confirm the previously observed level of dissolved metals and indicate that a significant washing of the flooded underground workings has not yet occurred.

## Tailings weathering and mine drainage eastward of Montevecchio

In the eastern part of the Guspini district the chemical and mineralogical composition of mined ore does not largely differ from that in the western part, but the less abundant carbonate minerals associated with the ore decrease the buffering capability of the geological environment and increase contamination hazards. Two different sources of contamination affect the plain below: the flow (1.5 l $s^{-1}$) from an adit of the Piccalinna mine, which collects the drainage from underground workings, and the seep (<0.3 l $s^{-1}$) emerging at the base of the Piccalinna tailings impoundment. In a few hundred metres both flows mix with other relatively uncontaminated streams at the base of the hill to originate the Rio Montevecchio–Sitzerri (Fig. 4).

The Piccalinna tailings impoundment is the largest flotation tailings in this area. Here, from 1940 tailings from everywhere in the mining district were stored over those previously deposited from the local mine. The last dam has guaranteed a relatively safe containment of the tailings (about $5 \times 10^6$ $m^3$ in volume) in the pond since mining activity was stopped in 1991. The Piccalinna pond prevalently contains flotation tailings with a grain size smaller than 63 μm. The average metal contents in the Piccalinna tailings are 7.2% Fe, 0.4% Zn, 0.2% Pb, 170 ppm As, 140 ppm Cu, 29 ppm Ni, 27 ppm Cd and 15 ppm Co; *c.* 80% of Pb and 60% of Zn are easily soluble when subjected to a sequential extraction procedure (Da Pelo 1998). The seep from the pond and the flow from the mine adit are the main water suppliers to the Rio Montevecchio–Sitzerri during the dry season; however, their contribution to the pollution of the stream is relevant all the year round.

A further important source of polluted material with a relevant impact on the water quality of the Rio Montevecchio–Sitzerri catchment consists of fine tailings sediments deposited along the stream at different times and, especially after a heavy rainstorm which partially destroyed an old dam in 1936. A few kilometres downstream from the abandoned pond, these sediments have created a desert covered by a thick layer of tailings; in areas further downstream the transported tailings are mixed with the original soil. These reworked materials, when chemically investigated, reveal metal contents higher than those observed in the tailings which are still deposited in the pond, probably indicating a different chemical composition in the old tailings. However, no remarkable difference is observed in the sequential extraction experiments on these sediments and soils when compared with those on the tailings, indicating that the polluting power is the same as in the tailings.

Table 5 lists the chemical data of the water flowing from the Piccalinna mine adit (PMA) and the Piccalinna tailings seep (PTS), the water in the upper Montevecchio stream (Mup) close to the output of the mining area after PMA and PTS mix with two streamlets from relatively uncontaminated areas, and the water about 6 km downstream (Mdown) where the stream is not far from flowing into the Marceddì lagoon. All data are referred to the summer, when the run-off effect is at a minimum (Da Pelo 1998). The chemical composition of the water collected from two boreholes (PBH4 and PBH5) in the Piccalinna impoundment are also reported (Table 5); their listed values are the average of samples collected at different depths, but without significant chemical differences. The water trapped in the tailings (PBH4 and PBH5) shows a near-neutral pH, reducing conditions and relatively high concentrations of metals

**Table 5.** *Chemical composition of waters from the eastern area of Montevecchio*

| | PMA | PTS | Mup | Mdown | PBH4 | PBH5 | Drinking water[1] |
|---|---|---|---|---|---|---|---|
| Date | 28.07.97 | 28.07.97 | 28.07.97 | 28.07.97 | 09.02.98 | 09.02.98 | |
| pH | 3.9 | 2.7 | 3.3 | 5.1 | 6.3 | 6.6 | |
| Eh (V) | 0.57 | 0.66 | 0.59 | 0.47 | 0.20 | 0.22 | |
| TDS ($g\,l^{-1}$) | 4.1 | 8.3 | 3.7 | 5.4 | 3.6 | 4.5 | |
| Ca ($mg\,l^{-1}$) | 200 | 440 | 300 | 420 | 560 | 520 | |
| Mg ($mg\,l^{-1}$) | 76 | 700 | 190 | 280 | 200 | 350 | |
| Cl ($mg\,l^{-1}$) | 59 | 55 | 87 | 150 | 75 | 75 | |
| $HCO_3$ ($mg\,l^{-1}$) | — | — | — | 26 | 82 | 96 | |
| $SO_4$ ($mg\,l^{-1}$) | 2600 | 6000 | 2500 | 3600 | 2400 | 3100 | 250 |
| $SiO_2$ ($mg\,l^{-1}$) | 29 | 21 | 33 | 50 | 44 | 42 | |
| Fe ($mg\,l^{-1}$) | 73 | 80 | 38 | 0.1 | 75 | 140 | 0.2 |
| Mn ($mg\,l^{-1}$) | 38 | 480 | 95 | 140 | 18 | 64 | |
| Zn ($mg\,l^{-1}$) | 980 | 440 | 370 | 610 | 27 | 30 | 3 |
| Cd ($\mu g\,l^{-1}$) | 6200 | 730 | 1500 | 2700 | 54 | 50 | 5 |
| Pb ($\mu g\,l^{-1}$) | 1900 | 1200 | 1700 | 2100 | 360 | 590 | 10 |
| Cu ($\mu g\,l^{-1}$) | 1700 | 630 | 260 | 430 | 38 | 23 | 1000 |
| Ni ($\mu g\,l^{-1}$) | 970 | 2200 | 1100 | 1600 | 1000 | 730 | 20 |
| Co ($\mu g\,l^{-1}$) | 610 | 1800 | 600 | 920 | 350 | 1300 | |

PMA, Piccalinna mine adit; PTS, Piccalinna tailings seep; Mup, Montevecchio upstream; Mdown, Montevecchio downsteam; PBH, boreholes in the Piccalinna tailings pond, average values from different depths.

From Da Pelo (1998).

[1] Maximum concentration according to Italian regulations (Gazzetta Ufficiale della Republica Italiana 2001).

and sulphate. The outflow from the tailings (PTS) causes rapid oxidation (Eh = 0.5) and acidification (pH = 3.3) of the trapped water in the pond (Eh = 0.2 and pH > 6). This fast process related to the oxidation of $Fe^{2+}$ and subsequent precipitation of $Fe^{3+}$ into oxy-hydroxide forms is accompanied by a significant increase in the dissolution of Zn, Cd, Pb and S (as $SO_4$) hosted in the sulphide minerals. The low dissolved amount of carbonate minerals is unable to buffer the system. Calcium concentration is controlled by the gypsum solubility equilibrium before and after the oxidation and acidification processes. The Mup chemical data reflect the mixing of contaminated flows and uncontaminated streams. Here, the adsorption of the upstream dissolved metals onto ferric compounds affects Cu, Ni and Co much more extensively than Zn, Cd and Pb.

An unusual increase in contamination is observed further downstream (Mdown). Indeed, the increase in pH is not accompanied by a decrease in pollution by any contaminant considered, except iron. In fact, in the downstream valley the polluted soils and sediments act as a diffuse source of additional contamination. A dilution effect is observed when uncontaminated tributaries flow into the Rio Sitzerri, but high concentrations of Zn ($23\,mg\,l^{-1}$) and Cd ($100\,\mu g\,l^{-1}$) persist as far as the Marceddì lagoon (Caboi *et al.* 1996).

## CONCLUSIONS

A review of chemical data collected from samples of water, tailings and sediments in the southwest of Sardinia leads to the following conclusions on the contamination derived from the cessation of mining activity.

- A deterioration in the quality of the shallow groundwater has been observed at Campo Pisano due to the flooding of mines in the Monteponi area; the high concentration of Zn and Cd will compromise the domestic use of this resource, at least in the near future.
- In the same area, the coastal marsh downstream from Rio San Giorgio is exposed to chemical contamination mainly from the seep and run-off from the ‘Red Mud’ dump prevalently made up of wastes from the electrolytic plant. A general reclamation of the dump is urgently called for in order to minimize the progressive contamination of the plain downstream. Reprocessing the entire waste deposit may be the best solution, but presently this seems unrealistic considering the laws protecting the deposit as an industrial archaeological site. Immediate mitigation proposals include the reduction of dusts, the partial rain-proofing of the heap and the treatment of any drainage flowing out from the mine wastes (Buosi *et al.* 2001).
- The western area of Montevecchio–Ingurtosu is affected by long-standing contamination from abandoned tailings and recent contamination from the water flowing out of the flooded mines. This phenomenon has a strong impact on the environment, since the washing time is expected to be long according to available early data. Though the area is scarcely inhabited, its high landscape value urgently requires mitigation of the contaminating effects.
- In the eastern part of Montevecchio the seep from the abandoned tailings pond of Piccalinna and the outflow from the mine adit are the main causes of contamination of the valley downstream; reworked contaminated sediments and soils contribute to keep contamination levels high far away from the mine. Reclamation of the area is strongly recommended to protect agriculture in the valley and fishery in the lagoon.

In all the above cases, specific remediation techniques must be applied depending on the nature of the sources and targets. A limitation of the use of some environmental resources may also be suggested.

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