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TECHNICAL ARTICLE

Influence of Past Mining on the Quality of Surface Waters at Funtana Raminosa (Sardinia)

Rosa Cidu

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Abstract Cu–Pb deposits at Funtana Raminosa in Central Sardinia were intensively exploited, mostly underground, from 1917 until 1983. Flotation tailings were dumped near the mine plant. A hydrogeochemical survey carried out in 2004 showed that mine drainage collected from several galleries was circumneutral, due to the availability of carbonate minerals that buffer the acidity produced by the oxidation of Fe-bearing sulphides. The mine waters contained higher concentrations of dissolved SO_4, F, Zn, Cd, Pb, Mn, and Mo than was observed in uncontaminated spring and stream waters in the area. Drainage from the oldest flotation tailings showed much lower concentrations of Zn, Cd, and Pb than those generally observed in mine waters. In contrast, drainage from the recent flotation tailings had the highest levels of dissolved SO_4, Zn, and Cd (1,600, 30, and 0.8 mg/L, respectively) when sampled in the dry season; these were two orders of magnitude lower in the rainy season under high flow condition. Pb was $\approx$ 5 μg/L under different flow conditions. Water in the Rio Saraxinus, a stream that drains the entire mining area, had a relatively low level of contamination (170 μg/L Zn, 7 μg/L Cd, and 0.9 μg/L Pb).

Introduction

The potential adverse effects of mine closure were not given proper consideration when mining operations in Sardinia ceased. The hazards posed by mine wastes, and especially the deterioration of water quality in mined areas, are nowadays recognized worldwide (e.g., Peplow and Edmonds 2006). To address stricter environmental regulations and the increased concern of local communities, it is now important to assess the impact of past mining and ore processing on the aquatic system. The derived information should be considered by Regional Authorities prior to remediating abandoned mine areas.

The Funtana Raminosa area is located in Central Sardinia (Fig. 1; Cidu and Mereu 2007). The nearest village Gadoni, located 4 km northwards, has 2,000 inhabitants; local economic activities consist of poor-developed agricultural and farming. Funtana Raminosa has been an important site for copper exploitation, with mines dating back to Nuragic (around 1,500–500 BC), and later, Roman times (Mezzolani and Simoncini 1993). Since 1997, Funtana Raminosa has been part of the Sardinian Geomining Park (*Parco Geominerario Storico e Ambientale della Sardegna*; RAS 1998a). The geological setting consists of Palaeozoic volcano-sedimentary sequences affected by low-grade metamorphic processes, namely metavolcanic rocks, quartzite, meta-sandstone, meta-limestone, and black shale (Carmignani et al. 2001). Hercynian post-orogenic subvolcanic events caused transformations of the country rocks; the main products were quartz-feldspatic hornfels in terrigenous units, and garnet-pyroxene skarn in carbonate sequences; later hydrothermal alteration produced hydrothermalite rocks, mainly consisting of chlorite, epidote, quartz, and calcite (Protano et al. 1996). Small outcrops of Jurassic carbonate rocks and recent sediments occur in the study area. Ore deposits are generally hosted in hydrothermalite rocks, with minor occurrence in skarn (Garbarino et al. 1984; Protano et al. 1996). Veins of Cu–Pb ores were exploited intensively from 1917 to 1983.

R. Cidu (✉)
Department of Earth Sciences, University of Cagliari,
Via Trentino 51, 09127 Cagliari, Italy
e-mail: cidur@unica.it

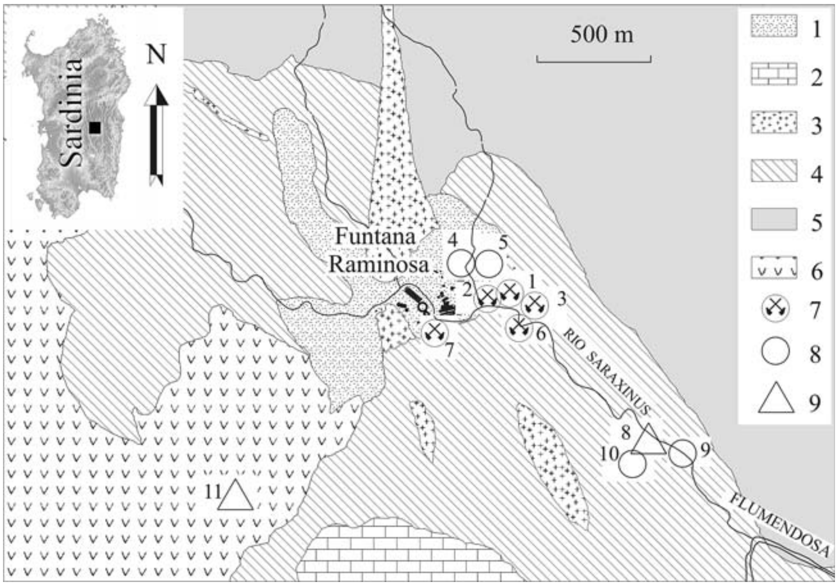

Fig. 1 Schematic geology at Funtana Raminosa and locations of water samples: *1* recent sediments, *2* Jurassic carbonate rocks, *3* subvolcanic rocks (Permo-Trias), *4* Silurian-Devonian black shale and metacarbonate hosting ore-bearing horizon, *5* metasandstone, quartzite, phyllite (Barbagia Metamorphic Complex), *6* middle Ordovician metavolcanic rocks, *7* mine water samples, *8* spring and stream water samples, *9* tailings drainage (Cidu and Mereu 2007)

Fig. 2 View of the recent tailings of Taccu Zippiri at Funtana Raminosa in 2004 (photo by L. Mereu)

Elevation of mined areas ranges between 600 and 400 m above sea level (asl). The flotation plant was located at 430 m asl. Mining activities ceased in 1983 and, following a stand-by period, the mine was closed in 1987. Mine waste dumps and flotation tailings were left nearby. The Tialesi tailings were dumped from 1970 to 1980 downstream of the mine plant (close to No. 8 in Fig. 1), at about 400 m asl, while the Taccu Zippiri tailings were dumped in 1982–1983 upstream of the mine plant (close to No. 11 in Fig. 1), at about 700 m asl. Both tailings dumps have lateral drains to minimize surface runoff and are partially covered by vegetation. A view of the Taccu Zippiri tailings is shown in Fig. 2.

The study area has a semi-humid climate, with dry summers and variable rainfall, mostly occurring from November to April. Precipitation and temperature data collected from 1922 to 1992 at stations near the study area are reported in Table 1 (raw data from RAS 1998b); the long-term mean annual precipitation is 790 mm and the mean annual temperature is 14°C.

Springs are scanty and have low flow (<0.5 L/s). The Rio Saraxinus is the only perennial stream in the area; it receives all drainage from the mines and tailings dumps, and is a tributary of the Flumendosa River. The Flumendosa is a significant water resource. In fact, several reservoirs are located in the Flumendosa catchments; they supply water for domestic and agricultural use to a large part of the Southern Sardinia population. This water resource needs to be protected from potential contamination. Therefore, a hydrogeochemical survey was carried out to evaluate the impact of past mining at Funtana Raminosa on the surface waters. To minimize dilution by rainwater, and to better highlight the water-rock interaction processes, the survey was carried out at the end of summer, i.e., when rainfall was very low. However, the limited availability of water at that time only allowed us to collect 11 samples. For a preliminary assessment of the water quality in the area, a large set of major and trace components was determined.

Records on the Composition of Ore and Water

Among a large variety of primary sulphides and oxidized minerals (Stara et al. 1999), including the rare mineral creedite (Frau et al. 1998), the main exploited minerals at Funtana Raminosa were chalcopyrite, galena, and sphalerite. The raw ore was concentrated to give three fractions, respectively, enriched in Cu, Pb, and Zn. The production

Table 1 Mean precipitation (*P*, mm) and temperature (*T*, °C) observed over the period 1922–1992 at stations near Funtana Raminosa (RAS 1998b)

Station	m (asl)	Years	January	February	March	April	May	June	July	August	September	October	November	December	Annual
Laconi *P*	637	67	88	87	78	68	57	21	11	13	42	80	99	107	752
Meana *P*	585	64	95	92	88	82	65	26	10	11	49	93	113	122	846
Seulo *P*	797	70	91	90	74	69	59	28	14	18	49	79	98	117	787
Mean *P*			91	90	80	73	60	25	12	14	47	84	103	116	790
Desulo *T*	920	64	4.9	5.3	7.8	10.2	14.1	18.6	22.3	22.3	19.0	14.1	9.5	6.1	12.8
Meana *T*	585	25	7.4	7.7	9.4	11.7	16.0	20.2	24.2	24.0	20.7	16.4	11.5	8.4	14.8
S. Sofia *T*	825	23	4.6	5.1	6.8	8.5	13.0	17.2	21.0	20.8	17.8	13.7	8.8	5.6	11.9
Villan. *T*	347	37	7.9	8.4	10.1	12.1	15.9	20.1	23.5	23.7	20.8	16.2	12.0	8.9	15.0
Mean *T*			6.2	6.6	8.5	10.6	14.8	19.0	22.7	22.7	19.6	15.1	10.5	7.3	14

Years: number of years available at each station for mean calculation

and composition of ore at Funtana Raminosa for 1979 is reported in Table 2 (Tylecote et al. 1984).

To compare the present water quality in the abandoned mining area with the chemical composition of waters during exploitation, the results of hydrogeochemical surveys carried out in 1979 and 1980 were considered. They comprise data on the chemical composition of waters collected inside the mine, or at outflow of galleries, as well as springs and surface waters circulating in nearby areas; about 100 water samples were collected over an area of 150 km^2 (Bertorino et al. 1981). Previous Funtana Raminosa mine water records during exploitation in 1980 are reported in Table 3. These mine waters were not acidic, and have total dissolved solids (TDS) in the range of 0.19–0.89 g/L. Dissolved SO_4 concentrations increase as salinity increases. Most waters show F concentrations higher than 1 mg/L, while Zn, Cu and Pb were relatively low (other trace metals were not determined).

Methods

Water sampling was carried out in September 2004 under low-flow conditions. Waters sampled out of the mines comprise one spring (No. 5) and three streams (Rio Brebegargiu No. 4, Rio Saraxinus No. 9, Rio Tialesi No. 10); the latter is the only water flowing outside of the mineralized area. Five samples were collected inside the mine galleries (Brebegargiu No. 1, Yvonne No. 6, Ribasso VI No. 7) or at the outflow of adits (S. Eugenio No. 2, Galleria Romana No. 3). Two samples were collected at drainages from flotation tailings: the old ones at Tialesi (No. 8) and the more recent tailings at Taccu Zippiri (No. 11). Tailings drainage No. 11 was sampled again in September 2005 during low-flow condition, and in February 2006 during high flow. The water sample locations are shown in Fig. 1.

At the sampling site, temperature, pH by glass electrode, redox potential (Eh) by platinum electrode, electrical conductivity and alkalinity were measured; water samples were filtered (0.45 µm), and an aliquot was acidified to 1% HNO_3 for cation analyses. Anions were determined by ionic chromatography, major cations by ICP-OES and trace elements by ICP-MS (Perkin Elmer Elan5000, REE by ElanDRC). An aliquot of the filtered sample was acidified with HCl for the determination of As and Sb by on-line hydride generation ICP-MS. Dissolved components refer to concentrations measured in the filtered sample. The ionic balance was always less than 5%; both precision and accuracy were estimated at ≤10% by analyses of randomly duplicate samples and standard reference solutions (NIST1643 d, e). Speciation and equilibrium calculations with respect to mineral phases were carried out using the PHREEQC computer program (Parkhurst and Appelo 1999). The saturation index (SI) with respect to a mineral phase is equal to log(IAP/K), where IAP is the ionic

Table 2 Output and composition of ore at Funtana Raminosa for 1979 (Tylecote et al. 1984)

	Tonnes	Cu (%)	Pb (%)	Zn (%)	Ag (%)	Cd (%)	As (%)
Raw ore	44,800	0.76	0.77	2.1	0.00646	–	–
Chalcopyrite	1,022	26.65	5.04	4.43	0.099	–	0.1
Galena	467	2.98	50.31	8.75	0.1454	–	–
Sphalerite	1,567	2.12	0.64	48.4	0.0112	0.97	–
Tailings	41,754	0.05	0.12	0.23	0.00137	–	–

Table 3 Previous records on chemical composition of mine waters at Funtana Raminosa (Bertorino et al. 1981)

No.	*T* (°C)	pH	TDS (g/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Alk (mg/L)	Cl (mg/L)	SO_4 (mg/L)	SiO_2 (mg/L)	*F* (mg/L)	Zn (μg/L)	Cu (μg/L)	Pb (μg/L)
260	17	8.0	0.27	22	4	51	0.8	104	25	48	15.0	3.6	4	0.6	0.2
261	14	7.4	0.49	54	11	35	1.6	140	28	110	9.0	2.1	7	1.3	0.5
353	16	7.9	0.25	32	11	21	2.3	134	21	14	13.8	0.8	28	1.3	1.9
383	15	7.6	0.55	104	16	32	1.6	140	28	211	10.2	2.1	13	0.5	1.2
385	13	7.7	0.28	48	9	18	1.2	110	28	58	9.0	1.1	34	9.5	18
386	14	7.8	0.56	68	15	53	1.6	140	25	235	16.8	1.8	23	1.0	0.5
387	14	7.7	0.89	168	28	81	6.6	92	35	456	14.4	2.7	20	2.5	1.8
388	13	7.8	0.89	156	36	30	7.0	98	28	528	7.2	0.8	3	6.5	8.9
389	14	7.6	0.52	60	18	46	2.7	128	25	226	17.4	1.7	11	0.7	0.9
390	14	7.5	0.23	34	7	16	1.6	73	25	58	10.2	1.5	20	1.1	0.6
391	14	7.8	0.25	30	7	21	2.3	98	21	58	11.4	1.5	8	1.2	0.7
392	15	7.8	0.23	32	6	21	0.8	67	25	62	10.2	2.3	15	1.5	1.0
393	16	8.1	0.30	24	5	51	0.4	85	25	91	13.2	3.8	5	1.1	0.3

activity product in the water, and K is the equilibrium constant at the water temperature.

Results and Discussion

The physical–chemical characters and the major dissolved components in waters sampled at Funtana Raminosa during this study are reported in Table 4. Dissolved minor components are reported in Table 5. Dissolved contents reported for worldwide rivers (Chester 1990) and mean values observed in Sardinian rivers (Cidu and Frau 2007) are also reported in Table 5 for comparison.

Table 4 shows that except for Rio Saraxinus No. 9, the studied waters have low flow. The water temperature reflected the air temperature at the sampling time. The pH was neutral or slightly alkaline (7.1–8.0), which was consistent with the availability of carbonate minerals in the area. The pH values in the mine waters sampled in 2004 were similar to those reported under exploitation (see Table 3). The redox potential values (Eh ranged from 450 to 580 mV) indicated prevalent oxidizing conditions. The

Table 4 Physical and chemical parameters and dissolved major components (mg/L) in waters at Funtana Raminosa

No.	Date	Flow	*T*	Eh	pH	Cond	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	F	SiO_2
Spring 5	09.04	0.1	16	470	7.2	0.62	0.43	72	16	35	3.1	143	68	75	0.8	13.5
Streams																
4	09.04	0.01	17	470	8.0	0.63	0.45	82	14	27	2.8	148	36	120	2.0	15.7
9	09.04	100	16	470	8.0	0.63	0.47	80	18	29	2.7	179	45	102	0.8	11.1
10	09.04	0.05	24	450	7.8	0.63	0.55	80	30	24	3.9	326	40	37	0.4	12.4
Mine waters																
1	09.04	0.1	15	470	7.6	0.83	0.57	47	7.8	103	8.6	182	44	160	4.3	13.3
2	09.04	0.33	17	490	8.0	1.08	0.81	150	40	27	3.0	210	41	330	1.7	12.3
3	09.04	0.08	16	510	7.8	1.57	1.23	235	41	54	4.5	99	25	760	2.3	13.0
6	09.04	1	16	490	7.5	0.58	0.43	67	17	30	3.0	145	39	110	1.3	14.0
7	09.04	0.1	18	460	7.8	0.70	0.52	91	15	38	3.6	159	34	170	1.6	11.5
Tailings drainages																
8	09.04	0.1	16	480	7.8	1.01	0.83	150	38	27	2.8	360	39	200	0.5	9.2
11	09.04	0.03	18	580	7.2	2.64	2.34	515	43	44	9.1	104	20	1,590	2.1	15.1
11	09.05	0.04	12	510	7.1	2.53	2.49	600	48	43	10	75	19	1,680	2.7	15.8
11	02.06	2	10	460	7.2	0.17	0.11	12	3.3	14	1.7	25	26	22	0.3	6.4

Flow L/s; *T*: °C; Eh: mV; Cond (electrical conductivity): mS/cm; *TDS* total dissolved solids: g/L

Table 5 Concentrations of minor components (μg/L) dissolved in waters at Funtana Raminosa and mean values in worldwide rivers (WR: Chester 1980) and Sardinian rivers (SR: Cidu and Frau 2007)

No.	Date	Al	B	Li	Rb	Sr	Ba	Mn	Fe	Ni	Cu	Zn	Cd	Pb	Mo	U
Spring 5	09.04	8	21	8.6	1.2	189	14.3	3	29	1.2	3.4	123	2.4	1.1	2.8	0.5
Streams																
4	09.04	29	20	17.5	2.1	241	16.9	6	70	1.4	3.8	141	4.5	4.2	24	1.4
9	09.04	8	24	8.7	2.2	200	42.0	2	8	1.6	6.0	172	6.9	0.9	5.0	1.1
10	09.04	11	34	9.8	4.3	104	10.3	11	44	1.3	2.1	13	0.3	0.6	4.2	1.7
Mine waters																
1	09.04	29	161	58.0	20.6	525	18.0	317	605	1.0	1.8	12	0.2	1.1	148	0.6
2	09.04	15	27	82.0	10.8	610	29.0	4	29	3.5	5.4	396	4.1	1.3	88	18
3	09.04	23	51	109.1	6.2	1,407	21.5	178	54	23	32	4,600	135	7.9	35	13
6	09.04	166	26	17.6	3.3	225	36.5	118	27	5.2	172	944	24	2.3	14	1.0
7	09.04	15	38	22.5	8.7	575	16.4	69	43	1.5	3.8	27	0.9	1.5	16	2.3
Tailings drainages																
8	09.04	9	33	13.2	1.6	324	19.5	5	15	2.4	41	87	1.8	0.7	4.0	1.9
11	09.04	8	69	56.0	19.6	3,000	17.4	71	16	20	13	34,200	850	6.1	6.4	2.6
11	09.05	4	80	45	18.5	2,370	17.7	92	20	11	11	30,000	760	4.6	5.5	2.5
11	02.06	170	15	1.7	1.5	35	6.8	18	250	0.9	5.0	120	1.7	5.0	0.1	0.1
Mean WR		50	18	12	1.5	60	60	8.2	40	0.5	1.5	30	0.02	0.1	0.5	0.2
Mean SR		300	53	5.5	2.6	210	34	44	360	1.8	3.0	186	1.4	9.4	0.7	1.0

conductivity was <0.7 mS/cm in the streams and the sampled spring; it increased in the mine water, with the highest values (>2.5 mS/cm) in tailings drainage No. 11.

Dissolved Mg, Na, and K were generally low, and were not correlated to conductivity. In most samples, dissolved Cl was much lower than HCO_3 and SO_4. Concentrations of Cl appear not to be correlated with those of Na (Fig. 3). The spring and stream waters are found close to the line representing the Na:Cl ratio in seawater (sw in Fig. 3), reflecting the character of the local atmospheric precipitation. Many mine waters and the tailings drainages show molar Na:Cl ratios higher than the value in seawater; this implies an additional source of Na, probably from dissolution of Na-bearing silicate minerals.

Dissolved Ca was the dominant cation, except in water No. 1 where Na prevailed; Ca concentrations increase with increasing conductivity. Figure 4 shows Ca concentrations versus HCO_3. Samples No. 11 and 3 have the highest Ca and lowest HCO_3; the remaining waters are close to the line of molar Ca:HCO_3 = 1:2. This ratio results from calcite dissolution by carbonic acid, as shown in reaction (1):

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-. \tag{1}$$

Figure 5 shows concentrations of SO_4 versus HCO_3, with both anions normalized to the sum of the major anions; it indicates that the spring and stream waters had a dominant bicarbonate component, while some drainage from mines (No. 3) and tailings (No. 11) had a marked sulphate component. Dissolved SO_4 correlated with Ca ($r^2 = 0.98$), and increased with the increase of TDS (Fig. 6). Since Ca was the dominant cation, two groups of waters can be distinguished, namely Ca–HCO_3 at low salinity and Ca–SO_4 at higher salinity. The former group comprises waters related to a circulation in carbonate-bearing formations with a low content of sulphide minerals; the latter consists of waters interacting with sulphide-bearing materials (ore minerals and tailings).

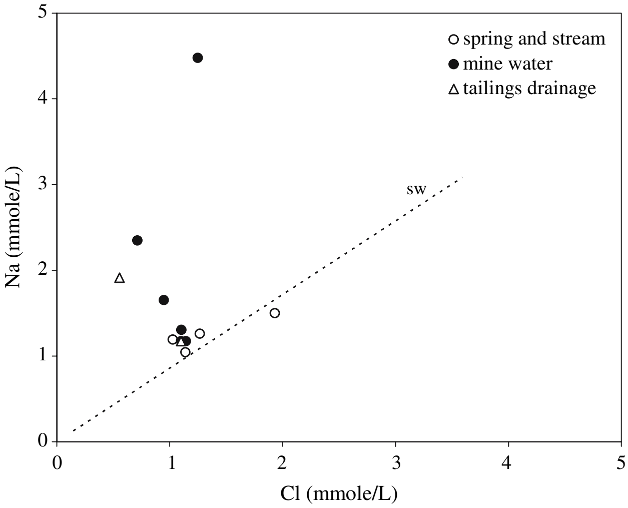

Fig. 3 Dissolved Na concentrations versus Cl in the waters from Funtana Raminosa sampled in September 2004. The *dashed line* indicates the Na:Cl molar ratio in seawater (*sw*)

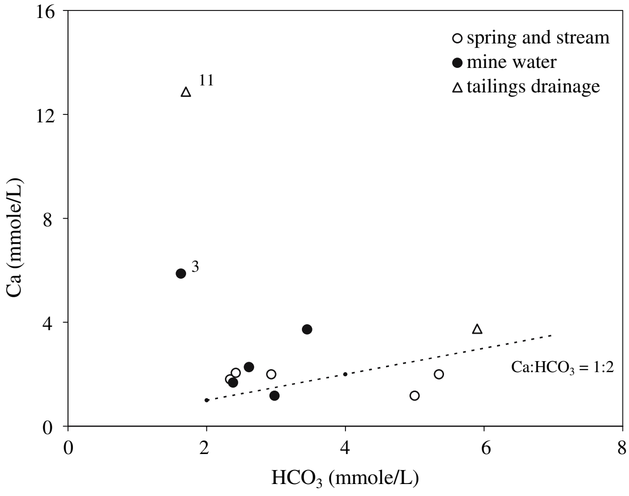

Fig. 4 Dissolved Ca concentrations versus HCO_3 in waters from Funtana Raminosa sampled in September 2004; the *dashed line* indicates calcite dissolution, resulting in a molar ratio of $Ca:HCO_3 = 1:2$

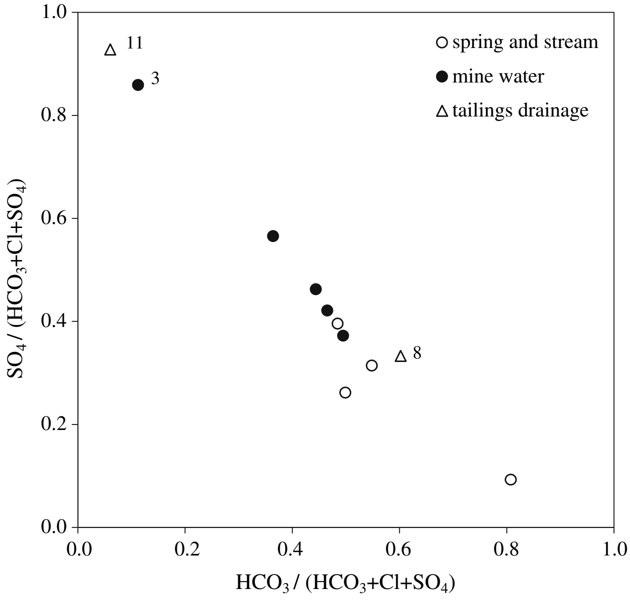

Fig. 5 Dissolved SO_4 versus HCO_3, both normalized to the sum of major anions (sampled in September 2004)

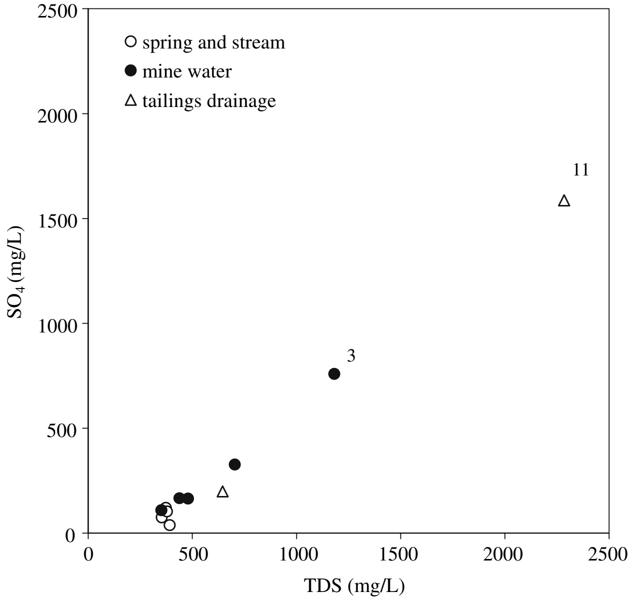

Fig. 6 Dissolved SO_4 versus total dissolved solids (*TDS*) in waters sampled in September 2004

Table 6 reports the SI values with respect to a set of minerals consistent with the ore assemblage and host rocks, namely barite, calcite, chalcedony, fluorite, and gypsum. Data referred to sampling in September 2004 were considered in these calculations. Equilibrium with respect to chalcedony was attained in all waters, which have SiO_2 concentrations in the range of 9–16 mg/L. It was also observed that all waters, even those waters with low HCO_3, were at equilibrium or supersaturated with respect to calcite (Fig. 7a). Equilibrium with respect to gypsum was only attained in the tailings drainage No. 11 (Fig. 7b), which showed the highest concentration in SO_4 when sampling was carried out under low-flow condition (see Table 4). This water, together with mine waters having high SO_4 concentrations, was slightly supersaturated with respect to barite (Fig. 8a). It was observed that dissolved Ba (ranging from 10 to 40 µg/L) increased with increasing SO_4 until supersaturation with respect to barite was reached.

In agreement with previous records (see Table 3), dissolved F concentrations were relatively high, with several waters have F concentrations higher than the limits established by the World Health Organization for drinking water (i.e., $F > 1.5$ mg/L; WHO 2006). Dissolved F concentrations increase as dissolved SO_4 increases; mine waters and tailings drainage No. 11 are either close to equilibrium or slightly supersaturated with respect to fluorite (Table 6; Fig. 8b). The relatively high values of F in these waters are consistent with the occurrence of fluorite in the ore mineral assemblage and host rocks. Previous studies had already showed that dissolved F, combined with dissolved SO_4, was an efficient hydrogeochemical indicator in the prospecting of sulphide deposits hosted in Palaeozoic formations of Central Sardinia (Bertorino et al. 1987).

Considering other analyzed components, NO_3 ranged from 1 to 6 mg/L (not reported in the tables), and did not show large differences among different water samples. Detectable PO_4 (1 mg/L) was only found in mine water No. 1. The low NO_3 and PO_4 contents may indicate that contamination derived from farming and domestic wastes is negligible. Mine waters had the highest values of B, Li,

Table 6 Values of saturation index (SI) with respect to some mineral phases in waters sampled in September 2004

No.	Barite	Calcite	Chalcedony	Fluorite	Gypsum
Spring 5	–0.45	–0.33	–0.01	–1.09	–1.71
Streams					
4	–0.22	0.54	0.07	–0.27	–1.48
9	0.12	0.60	–0.08	–1.07	–1.57
10	–1.04	0.75	–0.12	–1.78	–2.04
Mine waters					
1	–0.05	–0.06	0.01	0.16	–1.58
2	0.24	0.85	–0.06	–0.29	–0.94
3	0.29	0.41	–0.01	0.09	–0.51
6	0.10	–0.07	0.03	–0.71	–1.58
7	–0.17	0.41	–0.10	–0.46	–1.33
Tailings drainages					
8	–0.09	0.89	–0.17	–1.32	–1.14
11	0.24	–0.08	0.04	0.17	–0.06

and Rb (up to 160, 100, and 20 µg/L, respectively). Dissolved Sr ranged from 100 to 3,000 µg/L and correlated with Ca ($r^2 = 0.90$).

Among toxic or harmful elements, dissolved As and Sb were always <0.8 µg/L, with the exception of mine water No. 2 where 1.7 µg/L Sb was detected. Dissolved Co, Cr, and V were mostly below the analytical detection limits (0.5, 3, and 5 µg/L, respectively); Co < 3 µg/L was only detected in water samples No. 3 and 11. Nickel ranged from 1 to 23 µg/L; the highest values were observed in mine water No. 3 and in tailings drainage No. 11 (see Table 5). Mercury was below 0.5 µg/L, except in samples No. 1 and 11 (1.7 and 1.3 µg/L Hg, respectively) sampled in September 2004. The relatively low concentrations of these elements are consistent with their low occurrence in the ore assemblage.

Concentrations of dissolved Y, rare earth elements (REE), and Th in waters from the Funtana Raminosa area are reported in Table 7. Concentrations of these elements in the water are not regulated. Nevertheless, they have been considered in this evaluation of past mining impact on the aquatic system because the REE can be regarded as potentially toxic, due to their geochemical behavior, and because of their rapidly increasing applications (Haxel et al. 2002; Verplanck et al. 2005). Moreover, the REE may occur at high level in different ore deposits (e.g., Leybourne et al. 2000; Merten et al. 2004). The highest concentrations of Y and REE occur in tailings drainage No. 11, while the other samples show much lower concentrations. Figure 9 shows the abundance of each REE in the water normalized to the corresponding value in post-archean average Australian Shale (PAAS; McLennan 1989). The REE patterns are characterized by a more or less marked negative anomaly in Ce. Considering the

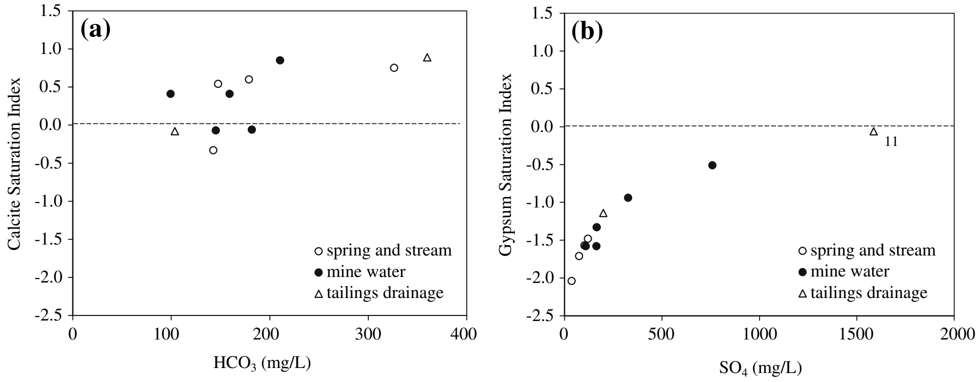

Fig. 7 Values of calcite saturation index versus HCO_3 concentrations (**a**) and gypsum saturation index versus SO_4 (**b**) in waters from Funtana Raminosa; *dashed lines* indicate equilibrium

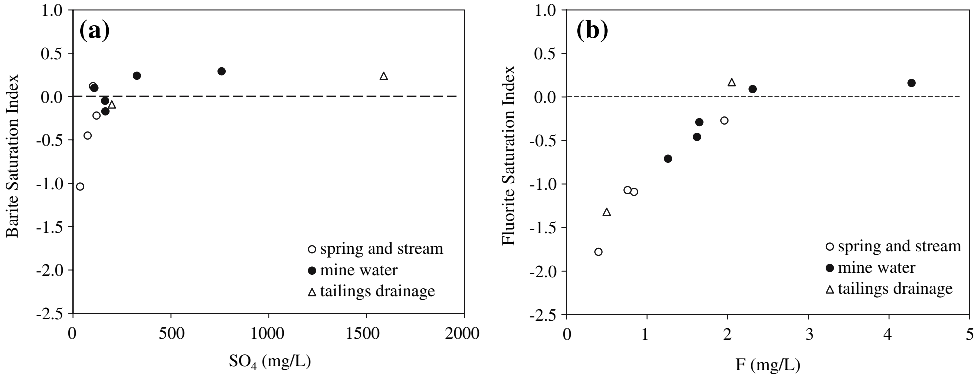

Fig. 8 Values of barite saturation index versus SO_4 concentrations (**a**) and fluorite saturation index versus *F* (**b**) in waters from Funtana Raminosa; dashed lines indicate equilibrium

oxidizing conditions of these waters, dissolved Ce has presumably been oxidized to Ce^{4+} and consequently precipitated as the CeO$_2$ solid phase. In tailings No. 11, the negative Ce anomaly in 2006 under high flow condition is less marked than that observed in 2004 and 2005 under low flow. This might result from an increase of Ce hosted in very fine particles (i.e., a <0.4 μm pore-size filter was used in this study), which are more abundant at high flow, as testified by the significant increase in Al and Fe observed in 2006 (see Table 5). A positive anomaly in Eu occurs in many waters; it may be due to dissolution of Eu-enriched minerals, such as Ca-feldspar, calcite, and sulphides (Lee et al. 2003; Leybourne et al. 2000).

To better assess the environmental impact of past mining activities, the pre-mining conditions in the area need to be considered. Unfortunately, the pristine aqueous concentrations at Funtana Raminosa are unknown. Among the water samples considered in this study, the Rio Tialesi stream No. 10 showed the lowest concentrations in Zn, Cd, and Pb. Other trace metals were lower than, or close to, the mean value reported for worldwide rivers and Sardinian rivers; only dissolved Mo was significantly higher. Considering that this water does not drain the mineralized area, and taking into account the low value of dissolved SO$_4$, the metal concentrations observed in water No. 10 probably represent the background values in the area surrounding the Funtana Raminosa mineral deposit. Dissolved Zn, Cd, and Pb in spring No. 5 and streams No. 4 and 9 were much higher than observed in water No. 10. Although these samples do not flow out of mines and flotation tailings, they seem to reflect a circulation in the mineralized area.

Concentrations of many metals in the mine waters were much higher than those observed in water No. 10, which is assumed to represent the local background. However, most metals showed large variations under similar pH and Eh conditions. For example, the highest concentrations of Fe, Mn, and Mo were observed in mine water No. 1; the highest Cu and REE occurred in No. 6; dissolved Zn and Cd were higher in No. 3; dissolved U was highest in No. 2 and 3. While concentrations of several metals varied by several orders of magnitude, the distribution of aqueous species did not vary significantly among the mine waters, as well as with respect to the other samples. For example, the species Cd^{2+}, Cu(OH)$_2^0$, Pb(CO$_3$)^0, Zn^{2+} and Zn(CO$_3$)^0 were always dominant, with SO$_4$-complexes (≤30%) only increasing in the high-SO$_4$ waters. The differences in metal content observed in the mine waters indicate different flow paths into the underground workings, and probably reflect the discontinuity in the ore-bearing vein system, and the large variations that occur in the ore minerals (Stara et al. 1999).

Concentrations of toxic elements in drainage from the oldest tailings (sample No. 8) were relatively low, i.e., Cd, Pb, Hg, As, Ni, and Cr were all below the guidelines established by the World Health Organization for drinking water (WHO 2006). Taking into account the significant levels of Pb and Zn left in tailings (see Table 2), the Tialesi tailings, dumped since 1970, appear to have sufficiently recovered to minimize the release of potential contaminants to the aquatic system. In contrast, very high concentrations of Zn, Cd, and REE were observed in the drainage from the more recent Taccu Zippiri tailings (No.

Table 7 Concentrations of Y, REE (La–Lu), and Th (ng/L) dissolved in waters at Funtana Raminosa

No.	Date	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th
Spring 5	09.04	68	26	31	5	16	3	4	4	1	3	1	3	<1	2	<1	<1
Streams																	
4	09.04	56	45	58	9	32	9	4	7	1.3	5	1	3	<1	2	<1	2
9	09.04	62	35	14	6	29	8	11	7	2	6	1	4	<1	3	<1	<1
10	09.04	35	68	110	19	25	2	4	6	1	3	0.4	2	<1	2	<1	<1
Mine waters																	
1	09.04	37	51	85	10	32	6	4	7	1.5	5	1	2	<1	1	<1	5
2	09.04	55	24	17	4	15	5	5	4	1	4	1	2	<1	2	<1	<1
3	09.04	127	77	63	13	45	9	6	11	2	9	2	5	<1	4	1	4
6	09.04	270	360	440	75	300	55	23	66	7	44	8	21	2	18	3	<1
7	09.04	60	430	900	90	180	9	6	30	2	6	1	3	<1	2	<1	<1
Tailings drainages																	
8	09.04	100	75	34	13	52	8	6	9	2	9	1.9	4	<1	4	<1	<1
11	09.04	1,290	5,800	300	400	1,300	170	41	260	30	110	22	53	4	24	3	3
11	09.05	1,100	5,200	230	350	1,100	140	35	220	23	100	20	42	3	20	3	<1
11	02.06	550	710	1,200	220	940	200	44	180	26	120	23	58	7	40	7.4	36

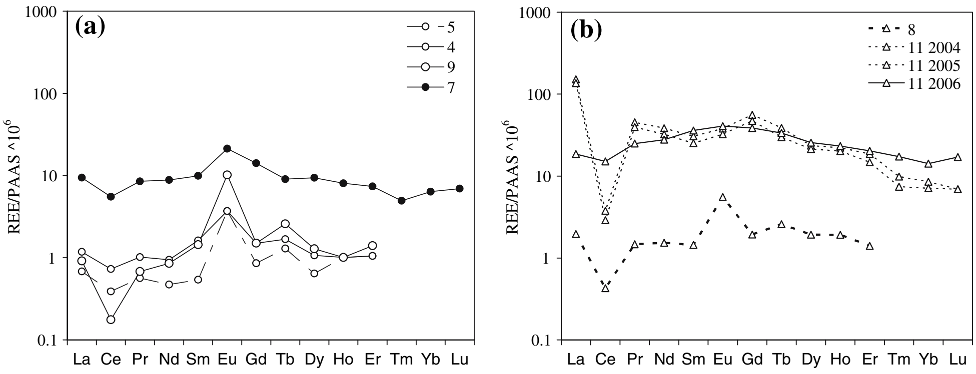

Fig. 9 Dissolved REE concentrations normalized to corresponding values in post-archean average Australian Shale (*PAAS*) in spring, streams and mine waters (**a**) and tailings drainages (**b**) at Funtana Raminosa

11). The release of metals, especially Zn and Cd, from these tailings was higher under low-flow conditions; the sample collected in February 2006 during the rainy season showed much lower SO_4 (Table 4), as well as Zn and Cd (Table 5), though dissolved Pb and many REE were similar to concentrations observed at low-flow. Table 5 shows that dissolved Mo in waters draining the flotation tailings was much lower than values measured in the mine waters. This is consistent with the ore processing used at Funtana Raminosa, where Mo was recovered in the mineral concentrates.

The Rio Saraxinus stream (sample No. 9) receives all drainage from the Funtana Raminosa mines and tailings, and can be used to estimate the influence of past mining on the local surface waters. At the time of sampling, i.e., under low-flow conditions, the concentrations of Zn and Pb in the Rio Saraxinus water were relatively low (170 and 0.9 μg/L, respectively), while dissolved Cd was 7 μg/L.

Conclusions

This study showed that drainage from abandoned mines and flotation tailings at Funtana Raminosa are sources of environmental contamination. High concentrations of SO_4, F, and metals occur, though the pH is neutral to slightly alkaline. The pH, concentrations of major components, and F in the mine waters sampled in 2004 were similar to values reported for mine waters sampled in 1980 during exploitation, except that some samples had much higher levels of Zn and Cu. The recent flotation tailings showed the highest potential for the release of metals, especially Zn and Cd, to the aquatic system. The contaminated waters flow into the Rio Saraxinus, which was sampled about 1 km downstream of the mining area, before its confluence with the Flumendosa River, which is a relevant water resource for the population of southern Sardinia. The water in Rio Saraxinus showed a relatively low level of contamination under low flow conditions. However, more data are necessary to better evaluate the dispersion of contaminants at Funtana Raminosa and the overall impact of past mining on the environment. In particular, detailed hydrogeochemical surveys should be carried out under different seasonal conditions.

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