

Legacy at abandoned mines: impact of mine wastes on surface waters

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ABSTRACT

In the Iglesias district (SW Sardinia, Italy), massive Pb-Zn sulphide deposits, hosted in Lower Cambrian limestone and dolostone, have been exploited intensively from 1870 to 1995.

The cessation of mining left large quantities of tailings and mine waste dumps. Among the tailings, the "Red Muds" derive from electrolytic processing to recover zinc. These materials contain high amounts of iron oxides and metals, such as 8.8 % Zn, 1.1 % Pb, and 0.04 % Cd. Seeps from the "Red Muds" show near-neutral pH and extremely high concentrations of sulphate (8000 mg/l), Mg (1400 mg/l), Zn (580 mg/l), Cd (2.5 mg/l), and Pb (0.4 mg/l). Although the flow rates of tailings drainages are usually very low (< 0.1 l/s), the contribution to dissolved concentrations of SO₄, Zn, Cd, and Pb in the Rio San Giorgio, the main stream that drains the mining district, is very high. At present, the weathering of electrolytic and flotation tailings represents a relevant hazard to the aquatic system in the Iglesias valley.

INTRODUCTION

The Iglesias district has been an important mining area for centuries. Massive sulphide ore bodies and stratabound deposits, hosted in lower Cambrian limestone-dolomite formation (Pillola *et al.*, 1998), have been exploited by some 40 mines spread over about 150 km², an area known as the "Metalliferous Ring". The main exploited minerals were sphalerite, galena, pyrite, and sometimes barite (Boni, 1994).

The Cambrian carbonate formations host important aquifers due to the intense fracturing and karst formation. The occurrence of large quantities of water underground severely hindered exploitation. In order to keep the pits dry, pumping stations were successively installed at the Monteponi mine at increasing depths, down to 200 m below sea level in 1990. The groundwater pumped out of the Monteponi mine was highly saline (Cl up to 12 g/l) due to contamination of sea water; concentration of metals, particularly Pb, Cd and Hg, were also relatively high (Bellè *et al.*, 1996). After closure of mines in the Iglesias district, the pumping system was deactivated in 1997. At the beginning of rebound, an increase in dissolved Zn, Cd, Pb, and Hg was observed under near-neutral pH conditions (Cidu *et al.*, 2001). Following peak concentrations, a marked decrease of Zn, Cd, and Hg, and to a lesser extent Pb, occurred. In 2004, after 7 years of rebound, the dissolved concentrations of these metals at most mine sites were relatively low, but generally higher than values observed in waters draining unmined areas (Cidu *et al.*, 2005).

Although the groundwater quality in flooded mines improved significantly over the last years, the presence of several abandoned open pits, large quantities of tailings, mine waste dumps and flotation ponds spread all over the Iglesias district, still pose a potential hazard to the aquatic system.

The amount of mine wastes in the Iglesias valley is estimated at 3.5 million tons, they cover a surface of about 180,000 m² (Buosi *et al.*, 2001). Among the tailings, the "Red Muds" were dumped during the period 1926 to 1983, and are estimated to amount about 2 million tons. These materials derive from the sulphuric acid attack on the oxidized ore (mainly constituted of smithsonite and goethite) and electrolytic processing to recover zinc. They are very fine (about 62% < 40 µm in size) and contain high amounts of iron oxides (45 % Fe₂O₃) and metals such as 8.8 % Zn, 1.1 % Pb, 0.04 % Cd, and 0.4 % Mn (Buosi *et al.*, 2001). The high Mn content is due to the use of pyrolusite (MnO₂) in the ore processing.

This paper reports the impact of mine wastes and tailings on surface waters in the Iglesias valley. The study area covers about 40 km² southwest of the town of Iglesias (Figure 1). The area has a semi-arid climate, variable rainfall ranging from 400 to 900 mm/y, and long drought periods. The long-term mean of precipitation is 600 mm/y with a mean of 50 rainy days. The mean annual temperature is 17 °C, evapotranspiration about 57 % and runoff 24 % (Civita *et al.*, 1983).

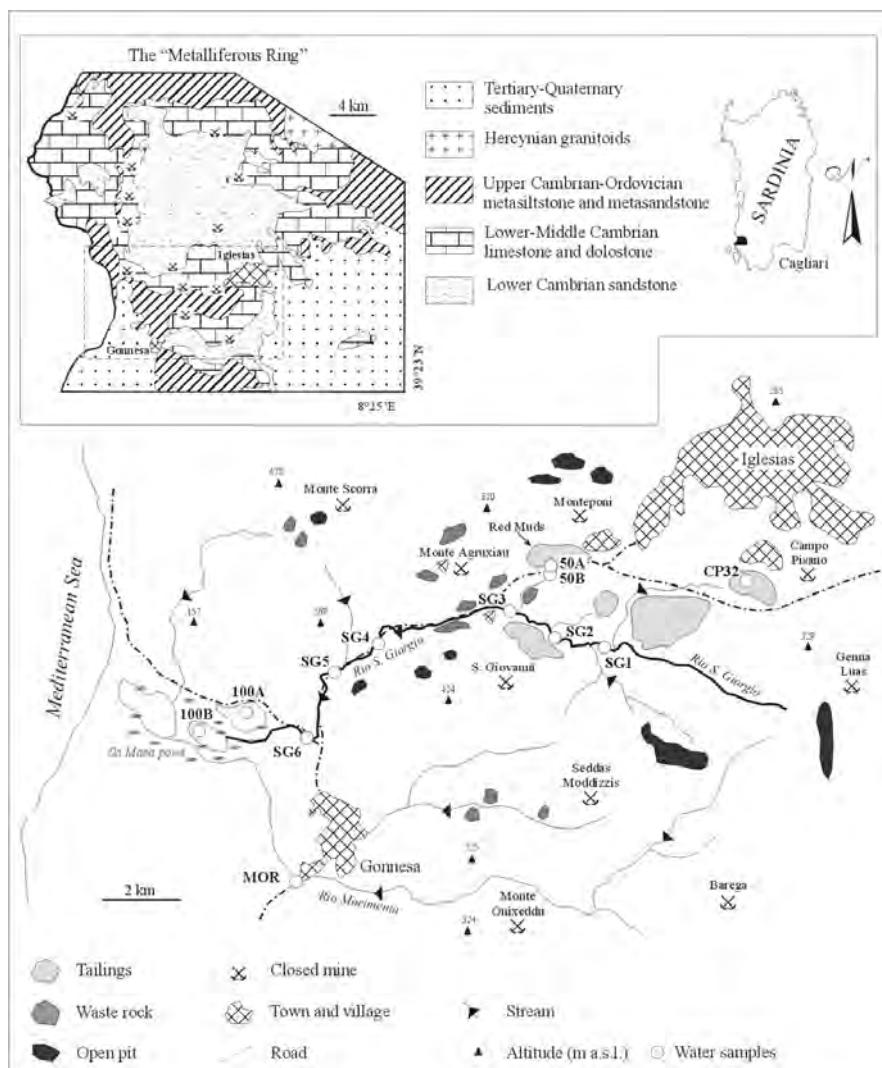
The Rio San Giorgio stream is the only perennial stream of the area, and flows E-W in the structural valley of Iglesias. The Rio Morimenta drains the southern part of the area, but flow in this stream only occurs during the rainy season. Both the Rio S. Giorgio and the Rio Morimenta flow into Sa Masa pond.

SAMPLING AND ANALYTICAL METHODS

Twelve water samples were collected in June 2004. At that time, all streamlets were dry indicating that the sampling period likely represents low-flow conditions. Sample locations are reported in Figure 1. Samples Nos. 50A and 50B drain the "Red Muds" tailings, the 50A water was collected at the first outflow of the heap and the

50B about 20 m downstream, at the base of the heap. Samples Nos. SG1 to SG6 were collected at the Rio S. Giorgio stream. In particular, sample SG3 was collected after the input of the “Red Muds” seeps, and the sample SG6 about 4 km downstream. Sample MOR was collected in the Rio Morimenta, downstream of the Gonnessa village. Samples 100A and 100B were collected in the Sa Masa pond. Finally, the sample CP32 is a small pond in the flotation tailings of Campo Pisano that forms only after rainy events; it was collected in February 2004. Water samples were filtered in situ through a 0.4 μ m pore-size membrane filter with an all-plastic filtration assembly, and acidified upon filtration for metal analyses. At each sampling site, temperature, pH, alkalinity, redox potential (Eh) and conductivity were measured. The Eh was measured by platinum electrode, and the value corrected against the Zobell’s solution (Nordstrom, 1977). Ammonia and dissolved oxygen concentrations were also measured in the field using titration kits. Anions were determined by ion chromatography (HPLC Dionex DX-120), and cations by ICP-AES (ARL3520) and ICP-MS (ELAN 5000). The ionic balance was always less than \pm 5%, suggesting that the analyses were of reasonably good quality; both precision and accuracy were estimated at \pm 10% or better, using randomly duplicate samples and standard reference solution (NIST1643d).

Figure 1. Schematic geological map with location of the most important dismantled Pb-Zn mines in the “Metalliferous Ring” and map of the Iglesias valley showing the mining works and location of the water samples.



RESULTS AND DISCUSSION

The chemical composition of the waters sampled in the Iglesias valley is reported in Table 1. Some trace components were below the detection limits, and therefore were not reported in Table 1 (i.e. Be < 0.3 µg/l, Cr < 0.9 µg/l, Ag < 1 µg/l, Sb < 0.8 µg/l, Te < 0.1 µg/l, and Bi < 0.3 µg/l).

Sample	T (w) °C	T (a) °C	Flow l/s	pH	Eh mV	O ₂ mg/l	Cond. mS/cm	TDS g/l	Ca	Mg	Na	K	Alk	Cl	SO ₄	PO ₄	F	Br	NO ₃	NO ₂	NH ₄
50A	15	15	0.05	7.0	0.6	nd	5.6	7.6	508	1040	73	49	79	107	5800	nd	0.4	0.6	40	nd	nd
50B	15	15	0.05	6.9	0.6	nd	6.7	10	490	1400	77	54	54	107	7900	nd	0.4	0.6	42	nd	nd
CP32	14	18		7.7	0.4	nd	0.6	0.4	99	21	11	1.8	40	20	265	nd	0.2	<0.2	4.1	nd	nd
SG1	16	20	10	7.6	0.5	2.4	1.5	0.9	126	55	105	8.7	365	128	200	6.6	0.2	0.4	26	7.6	3.5
SG2	20	32	10	8.1	0.5	7.0	1.0	1.0	152	67	119	8.1	344	143	321	<0.1	0.3	0.7	20	2.9	<0.1
SG3	18	27		8.1	0.5	8.8	2.2	1.4	193	89	148	9.5	371	178	535	<0.1	0.7	0.7	4.4	<0.1	<0.1
SG4	21	26	60	8.2	0.5	8.8	2.2	1.3	199	87	152	11	362	197	523	<0.1	0.6	0.7	10	<0.1	0.3
SG5	20	33	20	8.2	0.5	7.4	2.2	1.3	186	86	155	13	353	196	517	<0.1	0.8	0.8	7.3	<0.1	0.3
SG6	20	29	140	8.2	0.5	7.0	2.2	1.3	189	85	148	12	347	198	518	<0.1	0.8	0.8	3.7	<0.1	0.3
MOR	22	25	1	7.9	0.4	8.0	2.8	1.7	272	79	210	11	364	264	719	<0.1	0.3	1.0	31	0.3	0.3
100A	24	28		7.5	0.4	2.8	2.2	1.2	192	86	165	13	354	206	514	<0.1	0.8	0.8	<0.1	<0.1	0.5
100B	18	26	10	7.6	0.5	3.2	2.2	1.3	183	75	174	11	376	218	469	<0.1	0.8	0.8	4.3	1.1	3.5

	SiO ₂ mg/l	Li	Rb	B	Sr	Ba	Al	V	Fe	Mn	Co	Ni	Cu	Zn	Cd	Tl	Pb	As	Mo	Hg	U
50A	5.1	167	80	73	650	10	5.0	<7	<100	7400	54	79	25	300000	1350	60	307	<0.5	<4	0.7	<1
50B	2.3	168	87	72	580	10	6.0	<7	<100	20000	120	140	33	580000	2500	79	410	<0.5	<4	1.1	<1
CP32	0.5	0.7	0.5	10	50	13	14	<0.7	175	190	1.5	3.9	2.7	3100	41	0.4	120	<0.5	<0.4	nd	<0.1
SG1	14	4.5	6.9	260	180	41	7.0	0.7	25	790	0.6	3.1	2.8	110	0.4	<0.2	1.3	1.4	0.2	<0.8	0.4
SG2	11	7.3	6.9	240	250	35	6.0	0.7	26	38	0.5	3.3	3.5	180	0.7	<0.2	2.5	1.6	0.7	<0.8	0.5
SG3	6.4	16	16	230	290	33	4.0	1.1	40	330	1.2	5.1	4.3	1800	13	2.2	10	1.8	1.1	<0.8	0.5
SG4	7.1	16	18	230	300	34	17	1.2	49	450	1.2	4.7	4.2	1100	4.1	1.6	20	2.8	1.1	<0.8	0.7
SG5	9.2	17	16	230	290	33	11	0.9	20	110	0.7	5.0	5.8	2100	24	2.2	29	3.0	1.5	<0.8	0.9
SG6	9.0	17	16	230	310	39	7.0	1.0	22	150	0.7	4.5	5.2	1900	18	2.0	28	2.9	1.5	<0.8	1.0
MOR	18	130	15	250	910	61	54	2.0	89	48	0.4	6.3	5.0	140	<0.4	1.5	4.5	2.5	1.3	<0.8	16
100A	14	18	13	290	330	25	11	1.1	270	390	0.6	4.0	2.4	390	1.9	<0.2	12	3.5	0.7	<0.8	0.2
100B	10	34	13	320	430	48	19	1.7	300	710	1.6	19	5.3	1700	9.1	1.6	13	4.0	1.4	1.1	2.5

Table 1. Physical-chemical parameters and dissolved components in waters from the Iglesias valley.

The waters show near-neutral to slightly alkaline pH (6.9-8.2), reflecting their dominant interaction with carbonate rocks. The stream waters have dissolved oxygen concentrations mostly in the range of 7.0-8.8 mg/l, and Eh values > 0.4 V, indicating oxidising conditions. Relatively lower dissolved oxygen concentrations were found in the samples collected at Sa Masa pond (100A: 2.8 mg/l and 100B: 3.2 mg/l) and at Rio S. Giorgio (SG1: 2.4 mg/l). At these sites waters run slowly and abundant vegetation was observed.

Figure 2 shows the Piper diagram for the studied waters. Stream waters and the waters collected at Sa Masa ponds show dominant Ca-sulphate composition, except for sample SG1 which has prevalent Ca-bicarbonate composition.

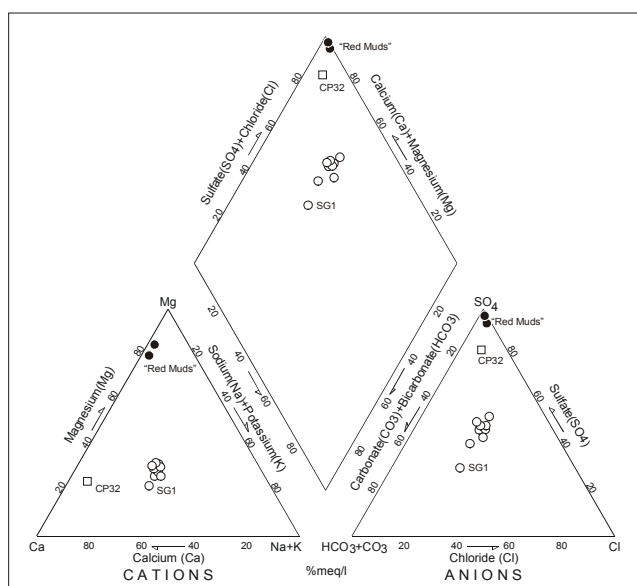


Figure 2. Piper diagram showing the major ionic composition of waters in the Iglesias valley.

These waters have relatively low salinity, total dissolved solids (TDS) are in the range of 0.9 -1.7 g/l. Seeps from the "Red Muds" show a marked Mg-sulphate composition, and have TDS up to 10 g/l. The high SO₄ concentrations in drainages from the "Red Muds" are due to the dissolution of sulphate minerals. In the dry season, secondary sulphate minerals are clearly observed at the surface of the "Red Muds" due to evaporation of seeps; the sulphate derives from the sulphuric

acid used in the processing of the oxidized Zn-ores (mostly smithsonite). The high molar Mg/Ca ratio observed in drainages from the “Red Muds” is likely due to the higher solubility of Mg-sulphate.

Dissolved nitrate occurs in a wide range (<0.1 to 42 mg/l). The highest nitrate concentrations were found in the seeps flowing out of the “Red Muds”, in the Rio S. Giorgio downstream of the Iglesias town (SG1), and in the Rio Morimenta (MOR) downstream of the Gonnese village. The relatively high nitrate concentrations in SG1 are associated with high reduced nitrogen species and high concentrations of PO₄, probably due to uncontrolled urban discharges from Iglesias. Relatively high dissolved concentrations of reduced nitrogen species were also observed at Sa Masa pond (100B).

Results reported in Table 1 show that the seeps from the “Red Muds” (50A and 50B) have extremely high concentrations of Mn, Zn, Cd and Pb, much higher than limits established by Italian regulations for industrial discharges into the aquatic systems and soils (see Table 2). Dissolved Co, Cu, Ni and Tl concentrations in the seeps are also much higher than values found in the surface waters of the investigated area. Dissolved concentrations of sulphate and metals in the “Red Muds” seeps did not decrease over 8 years, being in the same order of magnitude as observed in 1997 (Buosi *et al.*, 2001; Cidu *et al.*, 2005).

It is important to note that the water in the flotation tailings at Campo Pisano (CP32) shows the lowest salinity (0.4 g/l) but high Zn, Cd and Pb (see Table 1). It testifies that the release of metals occurs as soon as rain water comes in contact with these materials.

Elements		W.H.O.		Italy	
		(1)	(2)	(3)	(4)
Cl	mg/l	250	250	–	–
F	mg/l	1.5	1.5	6	1
Na	mg/l	200	200	–	–
NO ₃	mg/l	50	50	–	–
SO ₄	mg/l	250	250	–	500
Al	µg/l	200	200	1000	1000
As	µg/l	10	10	500	50
B	µg/l	500	1000	2000	500
Ba	µg/l	700	–	20000	10000
Cd	µg/l	30	5.0	20	–
Cu	µg/l	2000	1000	100	100
Fe	µg/l	–	200	2000	2000
Hg	µg/l	1	1	5	–
Mn	µg/l	500	50	2000	200
Ni	µg/l	20	20	2000	200
Pb	µg/l	10	10	200	100
Sb	µg/l	50	5.0	–	–
U	µg/l	20	–	–	–
V	µg/l	–	50	–	100
Zn	µg/l	–	–	500	500

(1) = W.H.O. (World Health Organization), 1998. Guidelines for drinking-water quality, 2nd edition.
Addendum to Vol.1, recommendation. (http://www.who.int/water_sanitation_health/GDWQ/Chemicals/).

(2) = Italian regulations for drinking water (Decreto Legge 2 February 2001 n.31).

(3) = Italian regulations for industrial waste discharge into surface waters (Decreto Legge 11 May 1999 N°152).

(4) = Italian regulations for industrial waste discharge on soils
– = Not regulated

Table 2. World Health Organization (WHO) guidelines for drinking water and Italian regulations for drinking water and industrial discharges.

Figure 3 shows dissolved concentrations of some harmful components in the waters of Rio S. Giorgio, with samples from left to right ordered following the flow direction. The Rio S. Giorgio waters upstream of the “Red Muds” (SG1 and SG2) show relatively low contents of toxic and harmful elements, having concentrations below the limits established by Italian regulations for drinking waters (see Table 2), except for Mn at SG1 (790 µg/l) showing a value 16 times above the limit.

At the SG3 site, downstream the inflow of seeps from the “Red Muds” (see Figure 1), significant increases in dissolved Zn (from 180 to 1800 µg/l), Pb (from 2.5 to 10 µg/l), Cd (from 0.7 to 13 µg/l), and Tl (from <0.2 to 2.2 µg/l) concentrations are observed. Although the flow rates of drainages from the “Red Muds” are very low (usually < 0.1 l/s), their contribution to the dissolved concentrations of Zn, Cd, and Pb in the Rio S. Giorgio is very high. In fact, Cd and Pb concentrations at SG3 reach values above the limits established by Italian regulations for drinking waters. Further downstream, dissolved Zn concentrations in the Rio S. Giorgio do not decrease significantly. Moreover, at SG6, about 4 km downstream of sample SG3, dissolved Cd and Pb concentrations increase (up to 18 and 28 µg/l, respectively). Dissolved Zn, Cd and Pb concentrations persist at relatively high levels in the Rio S. Giorgio due to additional inputs of contaminated waters that drain mining wastes from the mines of S. Giovanni, Monte Agruxiau, and Monte Scorra (see Figure 1).

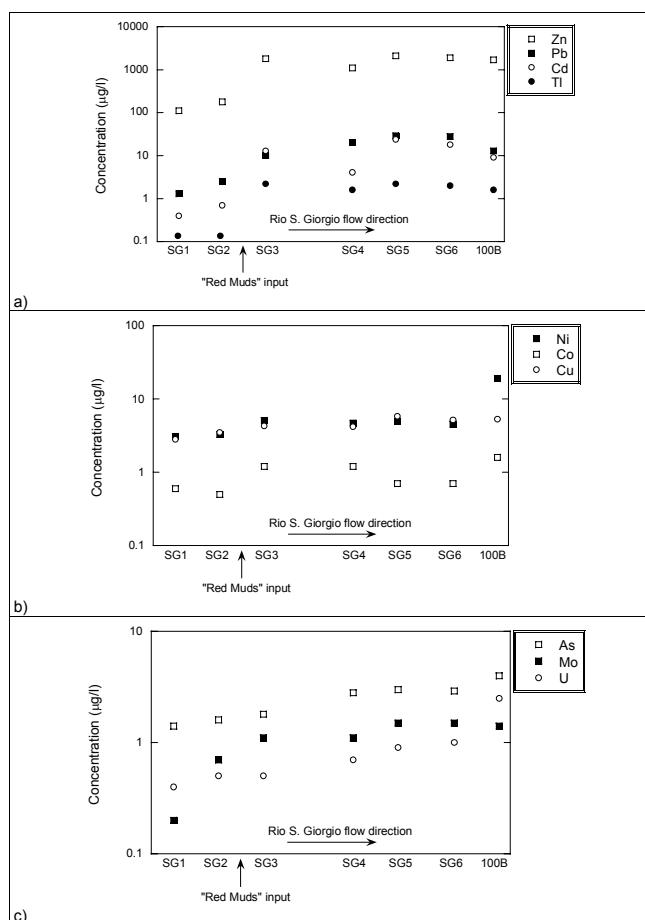


Figure 3. Concentrations of Zn, Pb, Cd and TI (a); Ni, Co and Cu (b); and As, Mo and U (c) in the Rio S. Giorgio.

Figure 3b shows the concentrations of Ni, Co and Cu in the Rio S. Giorgio waters. Although the concentrations of Ni, Co and Cu measured at the seep from the “Red Muds” are at least one order of magnitude higher than those observed in the sample SG1, their impact on the Rio S. Giorgio appears to be negligible. In fact, dissolved concentrations at SG3 after the input from the “Red Muds” are only slightly higher than those observed at SG1 and SG2 located upstream of the “Red Muds”. This behaviour is probably due to the relatively low mobility of Ni, Co and Cu in alkaline environments (Smith & Huyck, 1999). At low concentrations, these elements are mostly present as bivalent cations and are easily adsorbed onto solid phases.

Arsenic, Mo, and U, are below the detection limits in seeps from the “Red Muds”, and < 5 µg/l in the Rio S. Giorgio. The lowest Mo and U values occur at SG1 and 100A where the lowest dissolved oxygen was determined. These elements are generally present as oxoanions in oxidized environments. The concentrations of As, Mo, and U slightly increase along the Rio S. Giorgio stream up to the Sa Masa pond (Figure 3c). The highest concentration of U (16 µg/l) was found in the Rio Morimenta (MOR). At this site, relatively high concentrations of SO₄, NO₃, SiO₂, Li and Sr were also observed (see Table 1), probably related to uncontrolled discharge from the Gonnese village.

At Sa Masa pond, different concentrations in trace metals were observed between samples 100A and 100B (see Table 1). At the 100A sampling point, the very low flow rate, the presence of organic matter in decomposition, and low dissolved oxygen point to more reducing conditions as compared to the 100B site. This might explain the lower concentrations of elements, such as U, Hg and Mo; their mobility is favoured at oxidizing conditions. The higher concentrations of elements such as Zn, Cd, and TI observed at 100B as compared with those at 100A are due to the inflow of Rio S. Giorgio.

CONCLUSIONS

This study describes the geochemical characteristics of surface waters interacting with mine wastes in the Iglesias valley, where massive Pb-Zn sulphide deposits and oxidized ore have been mined extensively for 100 years.

The “Red Muds”, made up of wastes derived from electrolytic processing of oxidized Zn-ore, appear to be the main source of contamination in the study area. Rain water interacting with these materials carries very high concentrations of sulphate and dissolved metals, especially Zn, Cd, Pb and Mn. Drainages from the “Red Muds” flow into the Rio San Giorgio degrading the quality of surface water in the valley. The dispersion of toxic elements, particularly Zn, Pb and Cd, is traceable up to several kilometres downstream of the pollution source. The weathering of flotation tailings and mine waste dumps spread over a large area contributes to maintain relatively high concentrations of dissolved metals in the Rio S. Giorgio till its inflow into Sa Masa marsh.

The “Red Muds” have recently been qualified as an industrial archaeology site subject to regulation for their preservation. Nevertheless, reclamation of the mining wastes is urgently called in order to contain the progressive contamination of water and soil in the plain. It appears that an adequate treatment of the seeps from the “Red Muds” would reduce significantly the dissolved amount of toxic components in the Rio San Giorgio.

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