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Technical Article

Temporal Variations in Water Chemistry at Abandoned Underground Mines Hosted in a Carbonate Environment

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Abstract. Closure of Pb-Zn mines in the Iglesias district (SW Sardinia, Italy) caused the cessation of pumping in 1997, and the consequent flooding of underground workings. Deep saline water mixed with the shallow groundwater as the water table rose, increasing salinity. Stratification caused the saline water at depth to settle over a period of three years. At the beginning of rebound, an increase in dissolved Zn, Cd, Pb, and Hg was observed under near-neutral pH conditions. Following peak concentrations, a marked decrease of Zn, Cd, and Hg, and to a lesser extend Pb, occurred. After 7 years of rebound, the concentrations of these metals are relatively low at most mine sites, although the levels are generally still higher than in unmined areas. Nowadays, the highest release of metals to the aquatic system occurs from the weathering of tailings and mine wastes.

Key words: abandoned mines; heavy metals; monitoring; Sardinia; speciation; water chemistry

Introduction

Much progress has been made in assessing the potential environmental impact of mine wastes (Jambor et al. 2003), and mine water management (Younger and Robins 2002), but site-specific characteristics, such as climate, geology, mineralogy, and type of mineral processing (Plumlee 1999; Dold and Fontboté 2001) makes it difficult to transfer the information learned at one mine site to similar sites elsewhere. Within such a context, improving understanding on the temporal evolution of water quality in abandoned mining areas at a local scale becomes important.

In the Iglesias district (SW Sardinia, Italy), massive sulphide ore bodies and stratabound deposits are hosted in Lower Cambrian limestone and dolostone (Pillola et al. 1998, and references therein). The area has a semi-arid climate, rainfall ranging from 400-900 mm/y, with a mean of 50 rainy days, and drought periods usually extending from May to September. The mean annual temperature is 17°C. Evapotranspiration averages about 57%, and runoff 24% (Civita et al. 1983). Surface drainage occurs after heavy rain events. The Rio San Giorgio is the only perennial stream in the study area. The Cambrian carbonate formations host the most important aquifers due to intense fracturing and karstification. Dominant winds in the area blow from the NW and carry sea spray inland.

The Iglesias district (known as the "Metalliferous Ring") covers about 150 km^2 of the Cambrian carbonate formations, extending through the villages of Buggerru, Domusnovas, Iglesias, Gonnesa, and Nebida (Figure 1). The Pb-Zn deposits were intensively exploited from 1870 to 1995. Sulphide minerals mainly consist of sphalerite, galena, and pyrite (Boni et al. 1999), though at some locations, barite is the most prominent mineral. Since 1910, the Monteponi Mine drainage system has allowed exploitation at depth (Figure 1); the water discharges into the sea through the Umberto I drain. Pumping stations were successively installed at increasing depths to lower the water table to 160 m below sea level (Bonato et al. 1992; Bellé and Cherchi 1996). The groundwater pumped out of the Monteponi Mine was highly saline (chloride concentration reached 12 g/L in 1996); this has been attributed to contamination by seawater (Civita et al. 1983; Cidu et al. 2001). Concentrations of metals, particularly Pb, Cd, and Hg, were also relatively high. After closure of mines in the Iglesias district, the pumping systems ceased operation in 1997. The water quality has been monitored prior to and during the mine flooding, since 1996. This paper reports the temporal variations in chemical composition of the mine waters over the seven years of rebound.

Sampling and Methods

Water sampling was initially carried out in July 1996 under dewatering conditions, when the water table at Monteponi was 160 m below sea level. Mine flooding started in January 1997, and sampling was carried out intensively from then until October 1998 when the water table rose up to 7 m below sea level (see Cidu et al. 2001). As flooding progressed, several mines became inaccessible; sampling at the most representative accessible sites continued over 1999-2004. To acquire hydrogeochemical information on the whole mining

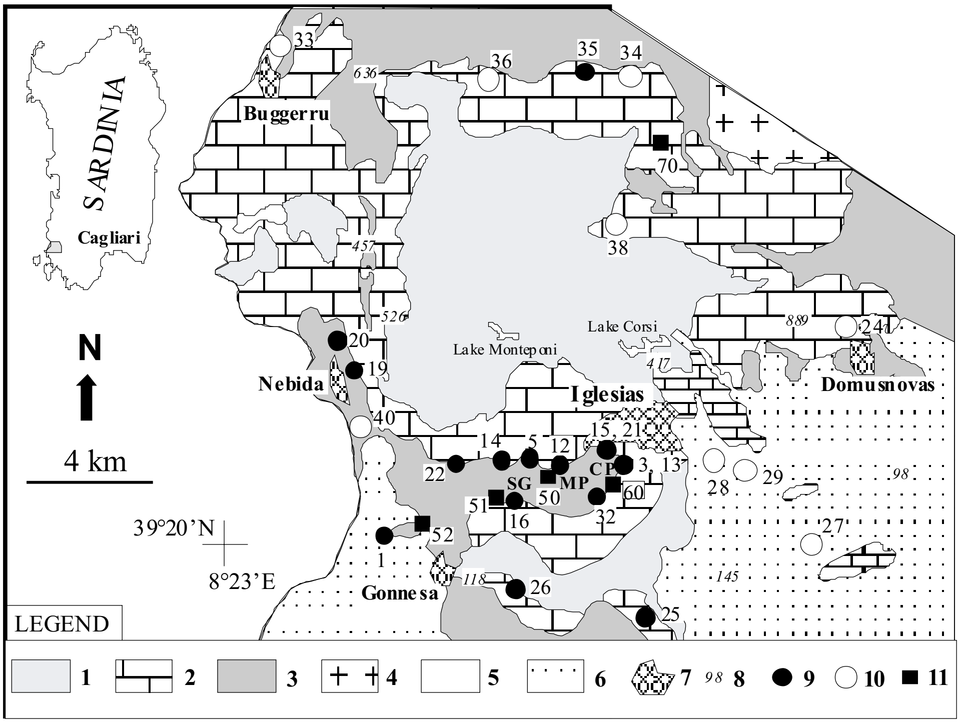

Figure 1. Map showing the geology and location of water samples in the Iglesias district, Sardinia: 1. Lower Cambrian sandstone; 2. Lower Cambrian limestone and dolostone; 3. Ordovician meta-siltstone-sandstone and quartzite; 4. Hercynian granite complex; 5. Porfiroid complex; 6. Tertiary-Quaternary sediments; 7. Town and village; 8. Altitude above sea level (m); 9. Mine water; 10. Water outside of the mines; 11. Tailings and waste dump drainage. CP: Campo Pisano, MP: Monteponi, SG: San Giovanni

district of Iglesias, additional samples were collected in 2002. Sampling sites are shown in Figure 1 and briefly described in Table 1. Most samples were collected inside mines or at adit outflows, and are labelled as *mine waters*. The few water samples collected from tailings and mine-waste dumps are labelled as such. Samples from non-mined sites are labelled as *waters outside mines*.

The sampling procedures and analytical protocols reported in Cidu et al. (2001) were used for the entire monitoring period. At each sampling site, temperature, pH, redox potential (Eh), conductivity, and alkalinity were measured; water samples were filtered (0.4 μm, Nuclepore 111130), and acidified for metal analysis. Anions were determined by ionic chromatography, and cations by ICP-OES and ICP-MS. The ionic balance was always less than ± 5%, suggesting that the analyses are of reasonable quality. Both precision and accuracy were estimated at ± 10% or better, using randomly duplicate samples and standard reference solutions (NIST1643c, d).

Results and Discussion

Water Quality

The chemical composition of water from the Iglesias district during the 1999-2004 monitoring period are reported in Tables 2 and 3. The water samples were all near neutral to slightly alkaline pH (7.1-8.2), reflecting their dominant circulation in carbonate rocks. Most had Eh values >0.4 V, indicating oxidising conditions, due to the relatively fast groundwater circulation through karst features and fractures.

Figure 2 shows the Piper diagram (Hitchon et al. 1999) for the studied waters. Water outside of the mines is dominantly Ca-Mg bicarbonate, with relatively low salinity and total dissolved solids (TDS) in the range of 0.3-0.6 g/L, except for sample No. 40, which measured 1.3 g/L TDS (see Table 3). Chloride and SO_4 dominate in mine waters that have TDS in the range of 0.9-6 g/L. Sulphate is the dominant anion in water flowing out of tailings and mine wastes.

Figure 3 shows Cl concentrations versus SO_4. Chloride enrichment is associated with a relative enrichment in Br, Na, and Mg, and increased concentrations of B, Sr, Li, Rb, and U (Tables 2 and 3). Previous studies have demonstrated the contamination of the water system by seawater due to the intensive pumping at Monteponi (Civita et al. 1983, Cidu et al. 2001); some mine waters reflect this, aligning with the Cl:SO_4 ratio observed in seawater. The enrichment in SO_4 observed in most mine waters and in the waters draining tailings and mine waste dumps derives from sulphide oxidation.

Table 1. Description of water samples collected in the Iglesiente district, Sardinia

No.	Location	Description and Use
	Waters Outside Mines	
24A	Domusnovas	Spring at San Giovanni caves, sampling at outflow. Domestic use
24B	Domusnovas	≈ 500 m downstream of 24A
27	Villamassargia	Caputacquas spring, sampling at ESAF plant. Domestic use
28	Iglesias	Monte Figu 2 well. Industrial use
29	Iglesias	Monte Figu 1 well. Industrial use
33	Buggerru	San Salvatore spring sampled at overflow. Domestic use
34	Fluminimaggiore	Pubusinu spring sampled at overflow. Domestic use
36	Fluminimaggiore	Su Mannau spring sampled at overflow. Domestic use
38	San Benedetto	Angiueddu spring. Domestic use
40	Nebida	Spring on Funtanamare-Nebida road
	Mine Waters	
1	Umberto I	Outflow from the Monteponi-Funtanamare gallery
3	Campo Pisano	Pozzo Campo Pisano, sampling at the basin tube. Industrial use
13	Campo Pisano	Flooding in the Campo Pisano mine
23	Campo Pisano	Seep in the Campo Pisano mine
5	San Marco	Pozzo Sonda shaft
12	Monteponi	Pozzo Vittorio shaft
12A	Monteponi	Pozzo Sella shaft
14	Monte Agruxau	Pozzo Vittoria shaft
15	Palmari	Water table at 5 m above sea level in 1999, flooded in 2000
21	Palmari	Seep at 10 m above sea level, flooded in 2000
16	S. Giovanni	Pozzo Carolina shaft
16A	S. Giovanni	Flooding at Seddas Moddizzis ramp
19	Nebida	Pozzo Santa Margherita shaft
20	Masua	Pozzo Calligaris shaft
22	Gran Sorgente	Outflow from a mine crevasse, flooded in 2000
25	Barega	Flooding at level Barega
26	Monte Onixeddu	Flooding at level Monte Onixeddu
32	Hubert Cabitza	Pozzo Hubert Cabitza shaft
35	Gutturu Pala	Outflow from the main adit
	Tailings and Waste Dump Drainages	
50A	Red Muds	Seep
50B	Red Muds	About 20 m downstream of sample 50A
51	San Giorgio	Rio San Giorgio stream at Bindua
52	San Giorgio	Rio San Giorgio stream about 3 km downstream of sample 51
60	Campo Pisano	Pond extending about 5000 m^2 on the flotation tailings
70	Arenas	Drainage at base of waste dump at Punta Pilocca

Calcium concentrations are correlated with Mg (Figure 4) ($R^2 = 0.84$). Most waters are aligned at molar Ca/Mg = 1, indicating a prevalent circulation in dolomite formations. Enrichment in Mg occurs in the mine waters mixed with the marine-derived water. The high Mg in the Red Muds tailings is due to the use of Mg in the ore processing.

Some chemical components show relatively small variations among samples and over time. The mean concentrations of SiO_2 and Al are 9 mg/L ($\sigma = 2.4$) and 12 μg/L ($\sigma = 7.8$), respectively. The amount of dissolved Ba is controlled by equilibrium with barite ($BaSO_4$); all of the studied waters show a barite saturation index in the range of 0.1 to 0.5. Concentrations of dissolved Ni, Cu, As, and Sb in waters outside and inside of the mines are well below the limits established by Italian regulations for drinking water (see Table 4).

Water samples from outside of the mines are mostly from the northern and eastern part of the area, and are not influenced by past pumping at Monteponi. They are derived from infiltration of rain and surface water and their enrichment in Ca reflects their interaction with the carbonate formations. Many of these sources are used for drinking water in the area (see Table 1).

The increase in Ni (up to 18 μg/L), Cu (up to 18 μg/L), and Co (up to 3.8 μg/L), observed in some mine waters are associated with relatively high Fe (up to 3500 μg/L), and Mn (up to 1240 μg/L). These concentrations are associated with an increase in total suspended solids, and occurred when flooding invaded the underground galleries refilled with mine waste materials. The highest concentrations of Ni, Co, Cu, and Mn occur in seeps flowing from the Red Muds tailings.

Influence of Mine Flooding on the Quality of Groundwater

The temporal variations of dissolved SO_4, Cl, Na and Mg in waters at the Monteponi (Pozzo Vittorio No. 12), S. Giovanni (No. 16), Monte Agruxau (No. 14) and Campo Pisano (No. 3) mines are shown in Figure 5. Data from before 1999 are taken from Cidu et al. (2001).

At the beginning of flooding in January 1997, the highest seawater contribution occurred at the Monteponi (10 g/L Cl) and S.Giovanni (8 g/L Cl) mines, both of which were highly influenced by past pumping, and to a lesser extent at Monte Agruxau (1.2 g/L Cl). Groundwater at the Campo Pisano mine showed a negligible seawater contribution (0.2 g/L Cl), and was employed for domestic use during periods of drought. In 1997, i.e. during the first year of rebound, the water table rose from 160 m to 50 m below sea level in the Monteponi mine, but small variations in the chemical

Table 2. Characteristics of and dissolved components in mine water from the Iglesiente district, Sardinia

No.	Name	Date	Flow L/s	T °C	Eh mV	pH	Cond mS/cm	TDS	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Cl mg/L	Alk mg/L	SO_4 mg/L	SiO_2 mg/L	Br mg/L	NO_3 mg/L
1 j	Umberto I	Feb 99	70	10	490	7.7	3.90	2.90	254	142	520	23	860	348	900	9.3	3.1	4
1 j	Umberto I	Feb 00	1	15	440	7.5	2.40	1.70	160	98	250	18	382	296	639	8.1	1.4	6
1 j	Umberto I	Mar 02	1	17	480	7.2	2.75	1.83	201	114	241	20	350	306	737	8.8	1.2	3
1 j	Umberto I	June 03	0.1	18	490	7.2	2.00	1.55	190	96	180	14	339	330	560	10.1	0.9	2
1 j	Umberto I	Nov 03	1	18	450	7.4	2.12	1.45	155	81	182	14	354	360	475	8.6	1.2	26
1 j	Umberto I	Feb 04	1	16	510	7.4	1.57	0.97	97	59	154	9	258	220	280	7.8	0.9	4
3 k	C. Pisano	Feb 99	40	18	460	7.4	2.25	1.53	172	112	168	7.2	354	360	475	8.6	1.2	26
3 k	C. Pisano	Feb 00	60	18	473	7.2	1.46	0.91	103	69	92	7.0	168	382	231	8.6	0.6	47
3 k	C. Pisano	Mar 02	50	17	505	7.2	1.52	0.82	113	69	94	8.6	145	391	186	9.5	0.5	45
3 k	C. Pisano	Sept 03	60	18	420	7.3	1.02	0.75	96	58	91	7.2	177	427	100	8.7	0.5	54
3 k	C. Pisano	Jan 04	50	16	530	7.3	1.27	0.71	106	59	90	1.7	165	360	95	9.4	0.6	58
13 f	C. Pisano	Feb 99		17	440	7.4	0.99	0.63	86	51	63	4.6	117	390	84	12.4	0.4	35
13 f	C. Pisano	Feb 00		18	464	7.4	1.20	0.69	80	51	84	7.7	142	410	47	16.1	0.4	57
23 g	C. Pisano	Feb 00	0.1	19	448	7.3	1.17	0.66	88	48	81	6.7	123	459	30	9.0	0.3	45
5 k	S. Marco	Feb 00		17	427	7.8	1.64	0.93	73	46	170	30	384	171	123	10.6	1.4	14
5 k	S. Marco	Mar 02		18	502	7.4	1.35	0.71	83	50	102	7.1	172	325	90	8.9	0.6	37
12 k	Montep.	Feb 99		17	470	7.2	6.26	3.91	255	150	930	22	199	342	360	9.2	5.8	8
12 k	Montep.	Feb 00		17	442	7.4	1.88	1.14	117	65	180	11	357	374	167	12.5	1.3	44
12 k	Montep.	Mar 02		16	545	7.3	1.27	0.70	87	51	89	7.1	155	359	83	8.9	0.6	44
12A	Montep.	Sept 03	60	17	290	7.5	1.30	0.71	83	50	98	6.2	214	323	90	8.0	0.5	26
12A	Montep.	Jan 04		16	490	7.5	1.15	0.63	82	48	85	5.3	170	276	94	8.0	0.7	19
14 k	M. Agruxau	Feb 99		19	420	7.1	2.83	1.61	146	83	338	9.7	694	360	144	12.7	2.5	10
14 k	M. Agruxau	Feb 00		18	445	7.3	3.25	1.90	140	83	433	15	888	375	137	11.0	2.7	14
14 k	M. Agruxau	Mar 02		18	497	7.2	1.86	0.95	100	61	132	7.0	353	384	77	11.3	1.3	13
14 k	M. Agruxau	Jan 04		16	580	7.2	1.75	0.92	105	61	155	5.1	327	380	69	12.1	1.1	11
15 f	Palmari	Feb 99		14	420	7.7	1.04	0.66	62	50	92	11	145	291	90	9.2	0.4	62
15 f	Palmari	Feb 00		16	442	7.4	1.15	0.78	90	42	119	7.4	173	379	77	7.3	0.6	75
21 g	Palmari	Feb 99	0.1	15	440	8.2	1.06	0.74	91	54	88	8.4	137	520	36	8.8	0.4	72
16 k	S. Giovanni	Feb 99		14	300	7.2	8.20	6.08	470	220	130	47	277	171	115	5.9	9.0	4
16 k	S. Giovanni	Feb 00		18	448	7.3	3.80	2.35	154	97	550	19	111	378	200	9.6	3.5	21
16 k	S. Giovanni	Mar 02		17	520	7.2	2.97	1.76	145	83	400	15	740	365	250	10.8	2.7	22
16 k	S. Giovanni	Jan 04		16	530	7.4	1.89	1.19	142	76	168	8	336	340	285	8.4	1.2	24
16A	S. Giovanni	Mar 02		17	483	7.2	2.03	1.27	135	82	200	9.3	353	375	270	8.9	1.2	23
16A	S. Giovanni	Jan 04		16	500	7.2	1.61	1.07	128	79	136	6.7	253	370	273	8.6	0.9	32
19 k	Nebida	Feb 99		17	440	7.4	1.87	1.13	100	64	200	6.8	441	293	150	10.4	1.5	12
19 k	Nebida	Feb 00		17	456	7.5	1.85	1.13	107	60	205	8.5	421	273	173	9.1	1.4	13
19 k	Nebida	Mar 02		18	470	7.4	2.07	1.09	107	60	201	9.3	413	270	150	9	1.5	9
19 k	Nebida	Feb 04		17	500	7.5	1.86	1.09	113	59	195	7.5	423	260	158	8.4	1.4	10
19A	Nebida	Feb 04	<0.01	14	550	8.3	1.04	0.68	92	46	108	3.9	200	290	71	9.1	0.7	1
20 k	Masua	Feb 99		15	440	7.6	1.15	0.77	93	40	100	6.9	180	230	200	5.9	0.6	31
20 k	Masua	Feb 00		15	440	7.7	1.36	0.86	97	42	125	8.5	227	210	225	9.0	0.7	22
20 k	Masua	Mar 02		14	477	7.4	1.53	0.83	107	43	126	8.6	210	250	190	7.5	0.7	15
20 k	Masua	Feb 04		14	500	7.6	1.32	0.82	124	42	104	9.2	193	230	230	7.0	0.7	16
22 e	G. Sorgente	Feb 99	50	15	460	7.4	2.95	1.69	140	84	353	9.7	748	390	150	11.7	2.6	9
25 f	Barega	Feb 00		16	438	7.3	1.51	0.94	108	66	113	6.6	222	440	92	15.0	0.9	105
26 f	M. Onixeddu	Feb 00		14	188	7.7	2.52	1.44	29	73	410	8.6	682	344	62	3.0	2.5	1
32 k	H. Cabitza	Mar 02		17	451	7.3	1.79	1.06	120	81	126	8.1	196	390	280	9.4	0.7	38
32 k	H. Cabitza	Feb 04		17	500	7.2	1.82	1.20	146	95	138	8.3	234	370	390	8.5	0.8	40
35 j	G. Pala	Mar 02	1	16	479	8.1	0.78	0.45	86	28	45	1.8	75	317	44	6.3	0.3	3
35 j	G. Pala	Feb 04	5	12	480	8.3	0.77	0.40	23	29	45	2.3	83	314	50	7.2	0.3	2

e: spring; f: flooding; g: seep; j: adit; k: shaft; nd: not determined

Table 2. Continued

No.	Date	Al µg/L	B µg/L	Li µg/L	Rb µg/L	Sr µg/L	Ba µg/L	Zn µg/L	Cd µg/L	Pb µg/L	Hg µg/L	Ag µg/L	Mn µg/L	Fe µg/L	Ni µg/L	Co µg/L	Cu µg/L	As µg/L	Sb µg/L	U µg/L
1 j	Feb 99	5	330	20	7.8	559	21	2100	7.5	13	1.0	0.50	600	40	7	1.1	5	<0.5	<0.8	1.85
1 j	Feb 00	8	300	15	6,7	335	22	411	7.2	3	0.5	0.08	667	12	3	1.2	2	<0.5	<0.6	1.93
1 j	Mar 02	25	285	15	7.1	335	24	560	16	7	0.4	0.15	1000	32	4	1.8	3	<0.5	<0.5	2.05
1 j	June 03	10	290	14	9.2	344	28	940	15	5	2.2	<0.5	940	30	3	1.6	1	<0.5	<0.5	2.09
1 j	Nov 03	7	270	14	6.9	300	26	490	12	3	1.4	<0.5	740	10	3	1.1	3	<0.5	<0.5	1.53
1 j	Feb 04	3	150	11	4.9	220	29	315	7	4	1.1	<0.3	235	10	2	0.4	2	<0.5	<0.5	1.01
3 k	Feb 99	6	46	6	4.8	201	29	7060	14	6	3.6	0.72	290	268	8	2.0	4	<0.3	<0.8	0.6
3 k	Feb 00	20	110	4	4.0	141	71	8780	19	4	0.6	0.05	351	550	10	3.8	2	<0.2	<0.6	0.4
3 k	Mar 02	2	85	3	2.9	130	43	1400	2.4	6	0.3	0.15	31	210	2.8	0.2	1	<0.5	<0.5	0.4
3 k	Sept 03	2	84	3	2.8	143	75	506	0.8	9	1.4	0.34	9	60	2	0.2	3	<0.5	<0.5	0.5
3 k	Jan 04	4	108	4	3.2	140	80	460	0.7	9	1.2	0.35	12	10	2	0.2	3	<0.5	<0.5	0.5
13 f	Feb 99	14	30	2	7.0	99	93	200	0.3	8	0.3	<0.1	11	38	2	0.2	3	<0.5	<0.8	0.28
13 f	Feb 00	16	255	2	3.2	107	99	248	0.5	12	1.2	0.20	11	18	2	0.3	2	1.2	<0.6	0.31
23 g	Feb 00	13	423	2	1.5	94	162	85	0.2	58	3.3	0.35	0.6	9	1.8	0.3	1	<0.5	<0.6	0.31
5 k	Feb 00	15	34	14	50	130	90	118	0.4	5	3.5	<0.05	28	65	1.7	0.1	1	<0.5	<0.6	0.30
5 k	Mar 02	14	78	4	3.1	112	69	420	0.6	28	0.9	0.3	3	24	1.5	0.1	1	<0.5	<0.5	0.40
12 k	Feb 99	18	115	13	8.2	485	47	4660	11	51	7.0	5.5	40	83	9	0.6	10	<0.5	<0.8	0.45
12 k	Feb 00	15	106	7	5.0	172	49	1780	2.5	63	0.9	0.13	12	10	3	0.2	2	<0.5	<0.6	0.48
12 k	Mar 02	15	86	3	3.1	109	73	600	1.2	44	0.5	0.12	6	34	2	0.1	2	<0.5	0.4	0.40
12A k	Sept 03	17	57	5	3.8	120	64	700	1.4	36	1.1	0.14	14	900	2	0.2	3	<0.5	0.4	0.39
12A k	Jan 04	16	50	5	3.4	110	59	570	1.6	42	0.5	<0.3	15	190	2	<0.3	4	<0.5	<0.5	0.37
14 k	Feb 99	26	62	7	4.1	210	84	1800	2.5	45	7.0	3.2	39	130	5.7	0.4	10	<0.5	<0.8	0.45
14 k	Feb 00	16	100	8	4.7	233	75	1423	2.0	64	9.7	6.1	8	22	2.7	0.2	2	<0.5	<0.6	0.53
14 k	Mar 02	23	53	4	2.3	116	71	1110	1.3	49	2.9	1.8	8	27	2.1	0.2	3	<0.5	<0.5	0.42
14 k	Jan 04	8	55	5	2.4	120	80	1200	1.1	57	3.0	2.0	8	67	1.8	<0.3	3	<0.5	<0.5	0.46
15 f	Feb 99	10	400	3	14	85	56	215	0.3	10	<0.5	<0.1	15	52	2.7	0.3	6	<0.5	<0.8	0.19
15 f	Feb 00	66	44	6	3.9	156	134	1200	0.7	87	1.7	0.06	52	379	18	0.5	18	<0.5	<0.6	0.26
21 g	Feb 99	6	530	2	1.8	97	100	92	0.4	14	5.9	0.27	0.6	8	2.4	0.3	2	<0.5	<0.8	0.13
16 k	Feb 99	7	240	30	29	822	49	3300	22	350	1.5	0.38	540	3000	17	3.8	10	<0.5	3.7	0.87
16 k	Feb 00	28	114	10	6.3	318	59	1890	3.1	71	11	7.0	9	30	3.8	0.3	2	<0.5	<2	0.60
16 k	Mar 02	24	89	7	6.4	208	42	3200	8.2	64	1.3	1.0	13	45	7.8	1.2	4	<0.5	1	0.66
16 k	Jan 04	3	70	7	6.0	180	30	3700	9.1	79	1.6	0.44	8	14	8.9	1.0	9	<0.5	0.8	0.94
16A f	Mar 02	21	72	6	3.2	173	35	2500	5.0	29	0.9	0.47	6	18	4.2	0.3	3	<0.5	<0.5	0.69
16A f	Jan 04	5	75	5	2.9	160	35	2900	6.4	37	1.5	<0.3	7	14	3.3	<0.3	2	<0.5	<0.5	0.65
19 k	Feb 99	9	68	6	3.1	190	50	1000	2.2	26	<0.7	0.24	7.2	29	2.8	0.1	4	<0.5	<0.8	0.6
19 k	Feb 00	22	64	7	3.5	199	48	1390	3.3	50	0.9	0.20	6.6	23	2.3	0.1	2	<0.5	<0.6	0.7
19 k	Mar 02	23	68	6	3.6	190	43	1510	3.7	61	<0.5	0.36	5.9	34	2.7	0.2	4	<0.5	<0.5	0.70
19 k	Feb 04	2	67	7	3.8	200	39	1500	3.7	56	1.8	0.40	3.9	22	2.2	<0.3	4	<0.5	<0.5	0.67
19A g	Feb 04	15	50	9	2.9	150	40	300	2.0	22	nd	<0.3	8.8	50	1.9	<0.3	7	nd	nd	1.35
20 k	Feb 99	8	73	7	3.6	143	27	1470	11	56	<0.7	<0.1	3	13	2.1	0.1	4	<0.5	<0.8	0.32
20 k	Feb 00	13	84	9	4.3	165	28	1520	9.7	65	1.3	0.14	9	15	1.7	0.1	2	<0.5	<0.6	0.29
20 k	Mar 02	15	97	7	3.8	150	29	1800	8.2	79	<0.5	0.16	5.6	22	1.9	0.1	2	<0.5	<0.5	0.41
20 k	Feb 04	7	100	10	5.8	180	31	2050	9.1	98	1.4	<0.3	8.7	42	2.3	<0.3	4	<0.5	<0.5	0.56
22 e	Feb 99	3	60	6	3.6	207	76	1890	2.5	29	7.3	3.1	15.4	9	3.5	0.2	3	<0.5	<0.8	0.45
25 f	Feb 00	10	72	5	3.6	638	204	185	0.2	21	6.4	0.11	6.4	25	4.0	0.2	5	0.6	5.4	0.66
26 f	Feb 00	64	95	21	2.5	101	228	390	0.9	93	3.1	0.07	1244	3500	10.4	2.9	16	0.7	1.5	0.10
32 k	Mar 02	20	75	4	2.5	137	40	570	0.7	30	1.8	0.44	6.7	90	2.7	0.3	2	<0.5	<0.5	0.5
32 k	Feb 04	4	80	6	3.2	160	38	650	0.6	25	2.2	0.43	5	15	2.3	0.3	3	<0.5	<0.5	0.7
35 j	Mar 02	6	31	1	0.7	76	100	830	0.7	9.6	0.3	<0.05	1.8	2	1.8	<0.2	6	<0.5	<0.4	0.3
35 j	Feb 04	23	39	2	0.9	88	102	990	1.1	17	<0.5	<0.3	2	10	1.2	<0.3	2	<0.5	<0.5	0.4

c: well; d: stream; e: spring; f: flooding; g: seep; h: pond; j: adit; k: shaft; nd: not determined

composition were observed in waters at Pozzo Vittorio, S.Giovanni, and Monte Agruxau (Figure 5a-c). In contrast, Cl, SO_4, Na, and Mg in the Campo Pisano water increased significantly from June 1997 to October 1998 (Figure 5d), due to mixing of the shallow groundwater with saline water from below. In February, 1999, the concentrations in Cl, SO_4, Na, and Mg started to decrease, while alkalinity was nearly constant. Figure 6 shows the concentrations of dissolved major components in the Campo Pisano water sampled at the surface of the water table, and at 20 m below the water table surface. A stratification process showing less saline water at the surface can be observed. In February 2000, after three years of flooding, the water table at the Monteponi, S.Giovanni, Monte Agruxau and Campo Pisano mines rose to about 20 m above sea level, and the seawater contribution decreased significantly at all sites.

Figure 7 shows dissolved nitrate in some mine waters during the monitoring period. Following flooding, an increase in NO_3 concentrations was observed at all sites. In particular, at Campo Pisano, NO_3 reached concentrations above the limit (50 mg/L) established by Italian regulations for drinking water. The highest NO_3 concentrations (up to 105 mg/L) were found in mine waters at Barega (No. 25) and Palmari (No. 15) in 2000 (see Table 2). Waters outside of the mines show nitrate in the range of 1−14 mg/L. A similar range is also observed in water draining tailings and waste dumps, with the exception of water flowing out of the Red Muds, which contain 40 mg/L NO_3. More investigation is needed to understand the source of nitrate and its temporal variations; however, based on the available data, it seems that the high dissolved NO_3 in mine waters might be related to the past exploitation processes, such as the use of explosives and wood in mining workings.

Figures 8a-d show the behaviour of Pb, Zn, Cd, and Hg in some mine waters during the monitoring period. On the basis of speciation computation, Pb is preferentially complexed by the CO_3^{2-} ligand (mainly as $PbCO_3^0$ species), the free ion being usually <15% of the total concentration. The Pb speciation does not change significantly due to flooded or dewatered conditions, or at low or high TDS. Zinc, like Pb, was present in solution mainly as $ZnCO_3^0$ under dewatered conditions and during the first year of flooding, but free ions became increasingly important

Table 3. Characteristics of and dissolved components in water from outside the mines and from tailings and waste dumps in the Iglesiente district, Sardinia

No.	Name	Date	Flow L/s	T °C	Eh mV	pH	Cond mS/c	TDS g/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/	Cl mg/L	Alk mg/	SO_4 mg/L	SiO_2 mg/L	Br mg/	NO_3 mg/L
Water Samples from Outside of the Mines																		
24A e	Domusnovas	Feb 00	2	15	472	7.5	0.54	0.31	68	12	33	2.4	57	224	22	7.0	0.2	2
24A e	Domusnovas	Mar 02	10	16	483	7.5	0.57	0.29	61	11	30	1.8	53	193	23	7.6	0.2	2
24A e	Domusnovas	Feb 04	30	14	480	7.6	0.51	0.30	68	11	30	1.9	54	200	24	6.9	0.2	1
24B d	Domusnovas	June 03	0.5	25	425	7.7	0.61	0.33	56	13	42	2.5	81	173	34	10.8	0.2	1
27 e	Villamass.	Feb 00	20	22	415	7.4	1.11	0.63	99	36	76	3.5	142	401	46	18.6	0.5	10
28 c	Iglesias	Feb 00		17	467	7.2	1.00	0.56	76	43	63	6.6	108	366	56	12.3	0.5	14
29 c	Iglesias	Feb 00		16	427	7.4	0.94	0.53	72	41	61	5.4	105	366	46	11.4	0.4	10
33 e	Buggerru	Mar 02	20	21	811	7.3	0.92	0.47	85	25	58	2.3	102	303	32	8.2	0.4	4
33 e	Buggerru	Feb 04	>20	20	520	7.5	0.82	0.47	85	24	61	2.8	108	292	40	8.1	0.4	4
34 e	Fluminimag.	Mar 02	100	15	493	7.5	0.53	0.32	78	12	30	1.6	45	235	22	7.1	0.2	3
34 e	Fluminimag.	Feb 04	100	15	500	7.5	0.52	0.32	72	13	29	2	49	216	37	8.8	0.2	2
36 e	Fluminimag.	Mar 02	10	14	472	8.0	0.69	0.35	60	22	42	2	65	252	21	7.9	0.2	5
36 e	Fluminimag.	Feb 04	>10	14	480	8.0	0.59	0.34	62	21	40	2.2	71	235	22	8.9	0.2	5
38 e	S. Benedetto	Mar 02	1	16	506	7.8	0.57	0.28	42	21	33	1.5	52	196	14	8	0.2	13
40 e	Nebida	Feb 04	0.01	13	480	8.1	2.06	1.25	120	96	220	3.7	438	500	110	8.7	1.4	10
Tailings and Waste Dump Drainages																		
50 g	Red Muds	Mar 97	0.1	12		6.6	9.4	10.9	420	1700	70	56	140	35	8600	4.6	0.7	45
50A g	Red Muds	Feb 04	0.05	15	600	7.0	5.58	7.62	508	1040	73	49	107	79	5800	5.1	nd	40
50B g	Red Muds	Feb 04	0.05	15	600	6.9	6.69	10.0	490	1400	77	54	107	54	7900	2.3	nd	42
51 d	Rio S. Giorgio	Mar 02	5	16	505	7.9	1.99	1.36	180	84	131	18	197	312	590	2.8	0.7	2
51 d	Rio S. Giorgio	June 03	0.1	23	454	8.1	2.23	1.50	208	97	158	11	225	463	558	7.5	1.0	2
51 d	Rio S. Giorgio	Nov 03	10	12	460	8.0	1.58	1.05	153	65	92	12	142	244	454	10.1	0.5	8
51 d	Rio S. Giorgio	Feb 04	50	9	480	8.1	1.87	1.35	189	83	137	14	197	284	580	9.7	0.7	11
52 d	Rio S. Giorgio	Mar 02	5	17	491	8.0	2.06	1.36	178	82	150	18	210	290	565	7.1	0.8	5
52 d	Rio S. Giorgio	Jan 03	50	11	489	7.9	1.13	0.75	104	46	77	8	112	183	305	7.9	0.4	8
52 d	Rio S. Giorgio	Feb 04	60	11	500	8.3	1.72	1.24	178	78	120	13	168	270	540	8.7	0.6	11
60 h	Campo Pisano	Feb 04		14	500	7.7	0.62	0.44	99	21	11	2	19	40.3	265	0.45	<0.2	4
70 g	Arenas	Mar 02	1	13	507	7.8	2.53	1.76	123	40	376	24	36	150	1080	6.4	0.1	2

c: well; d: stream; e: spring; f: flooding; g: seep; h: pond; j: adit; k: shaft; nd: not determined

Table 3. Continued

No.	Date	Al µg/L	B µg/L	Li µg/L	Rb µg/L	Sr µg/L	Ba µg/L	Zn µg/L	Cd µg/L	Pb µg/	Hg µg/L	Ag µg/L	Mn µg/L	Fe µg/L	Ni µg/L	Co µg/L	Cu µg/L	As µg/L	Sb µg/L	U µg/L
Water Samples from Outside of the Mines																				
24A e	Feb 00	30	21	2	1.0	69	78	208	2.5	11	0.7	0.05	1.4	17	1.1	0.1	1	0.5	<0.6	0.58
24A e	Mar 02	14	23	2	1.0	60	67	220	1.9	9	<0.5	0.15	8.6	21	1.3	0.1	2	<0.5	<0.5	0.59
24A e	Feb 04	3	26	2	1.0	66	68	200	2.7	8	0.6	<0.3	3.8	10	1.0	<0.3	1	<0.5	<0.5	0.60
24B d	June 03	4	33	5	2.3	98	122	1030	21	42	0.7	<0.1	35	13	2.2	0.1	3	<0.5	<0.5	0.32
27 e	Feb 00	2	58	9	3.2	172	163	117	0.4	2	3.0	0.16	2.7	12	0.8	0.1	1	<0.5	<0.6	0.73
28 c	Feb 00	2	57	5	4.3	125	59	1690	0.8	40	1.0	<0.07	18	11	9.5	1.7	2	<0.5	9.3	0.93
29 c	Feb 00	1	46	4	3.8	134	70	1230	0.7	20	0.5	<0.07	15	15	8.1	0.9	1	<0.5	6.1	0.91
33 e	Mar 02	9	40	2	0.77	100	150	350	0.7	21	0.4	0.28	1.8	10	1.2	<0.2	12	0.82	<0.5	0.38
33 e	Feb 04	3.6	56	3	1.06	115	130	470	1.6	27	<0.5	0.47	2	10	1	<0.3	1	<0.5	<0.5	0.51
34 e	Mar 02	23	20	2	0.89	60	125	250	0.8	22	0.4	0.11	8.0	40	1.2	<0.2	3	<0.5	<0.5	0.59
34 e	Feb 04	5.9	25	3	1.6	65	120	350	1.7	19	<0.5	<0.3	2.0	10	1	<0.3	2	<0.5	<0.5	0.58
36 e	Mar 02	9.6	28	2	0.88	136	50	86	0.2	2	0.3	<0.05	4.0	4	0.99	<0.2	2	<0.5	<0.5	0.18
36 e	Feb 04	2.1	34	3	0.95	140	55	148	0.5	6	1.4	<0.3	2.0	10	0.72	<0.3	<0.5	<0.5	<0.5	0.19
38 e	Mar 02	3	21	1	1.0	110	17	13	0.1	1	0.4	<0.05	0.5	2	0.44	<0.2	1	<0.5	<0.5	0.06
40 e	Feb 04	1.9	120	13	2.3	200	70	125	0.1	3	0.8	<0.3	2	10	1.6	<0.3	1	<0.5	<0.5	1.21
Tailings and Waste Dump Drainages																				
50 g	Mar 97	5	70	162	98	750	9	4400	270	480	0.5	<0.2	2600	<100	150	25	24	<0.1	<0.6	<0.5
50A g	Feb 04	5	73	167	80	650	10	3000	135	307	0.7	<3	7400	<100	79	54	25	<0.5	<0.5	<1
50B g	Feb 04	6	72	168	87	580	10	5800	250	410	1.1	<3	2000	<100	140	120	33	<0.5	<0.5	<1
51 d	Mar 02	22	278	13	18	252	27	2050	16	67	<0.5	0.081	78	40	4.3	0.7	5	1.5	0.7	0.57
51 d	June 03	10	318	15	15	303	29	2960	17	13	2.5	<0.1	330	34	4.9	1.4	4	<0.5	<0.5	0.66
51 d	Nov 03	16	170	12	14	230	23	2930	24	20	<0.5	<0.1	160	70	3.6	0.9	6	<0.5	<0.5	0.33
51 d	Feb 04	4.7	175	17	19	260	25	2600	21	20	1.0	<0.3	190	30	3.5	1.0	4	<0.5	<0.5	0.63
52 d	Mar 02	5	270	11	14	240	22	1300	14	16	<0.5	<0.08	24	12	3.1	0.4	4	1.9	1	0.61
52 d	Jan 03	28	116	8	8	160	33	2100	15	34	2.1	0.04	65	66	2.2	0.5	5	1.1	<1	0.36
52 d	Feb 04	6	170	16	16	250	31	2500	19	19	0.7	<0.3	100	12	3.2	0.6	5	0.7	<0.5	0.76
60 h	Feb 04	14	10	1	0.48	50	13	3050	41	120	nd	<0.3	190	176	3.9	1.5	3	<0.5	<0.5	<0.1
70 g	Mar 02	12	20	8	15	130	10	1400	24	30	0.5	<0.05	10	10	8.3	1.1	3	1.3	<0.4	0.21

c: well; d: stream; e: spring; f: flooding; g: seep; h: pond; j: adit; k: shaft; nd: not determined

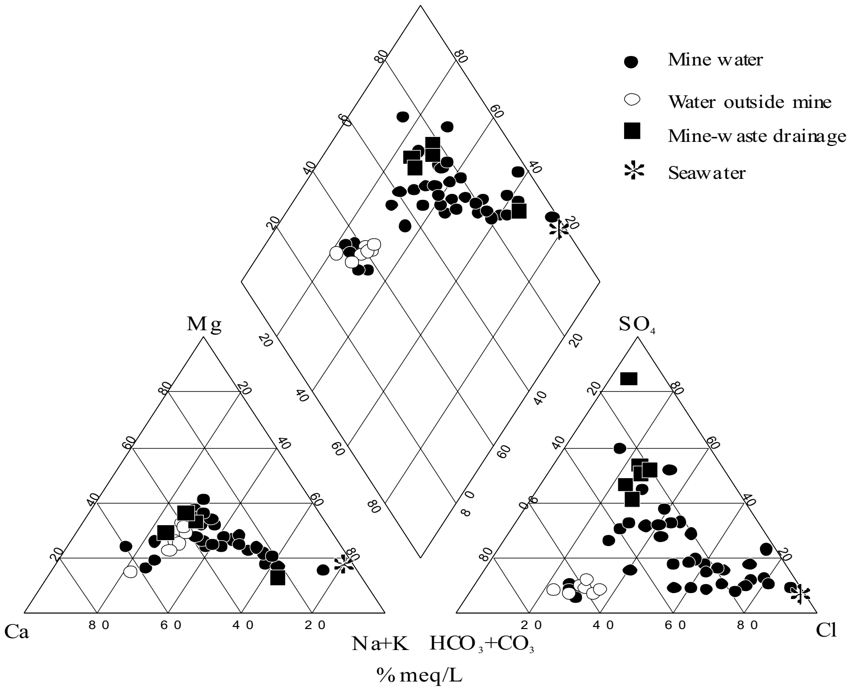

Figure 2. Piper diagram showing the major ionic composition of waters in the Iglesias district

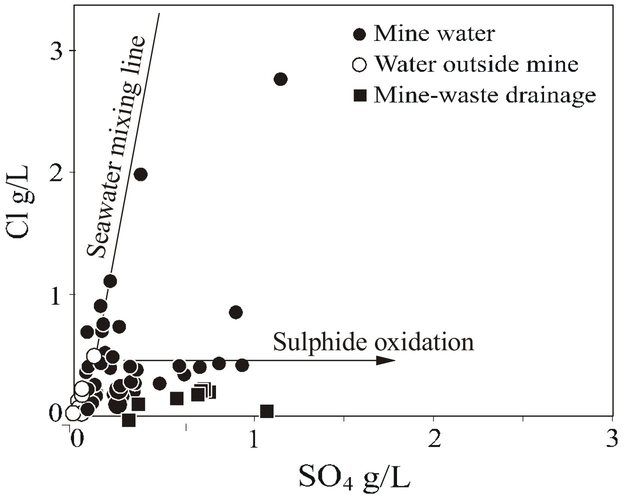

Figure 3. Chloride versus sulphate concentrations in waters in the Iglesias district.

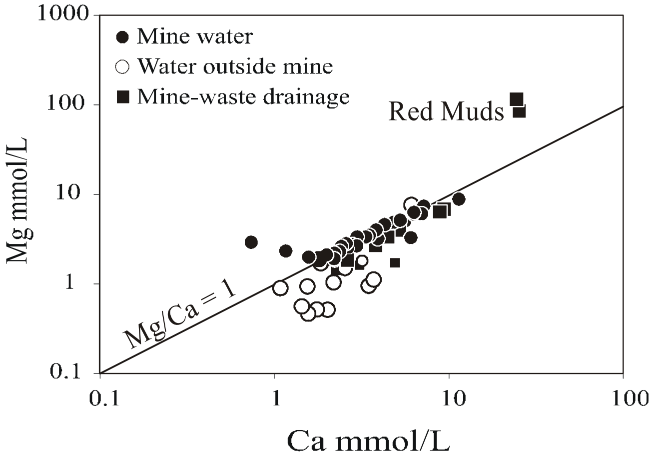

Figure 4. Magnesium versus calcium concentrations in waters in the Iglesias district

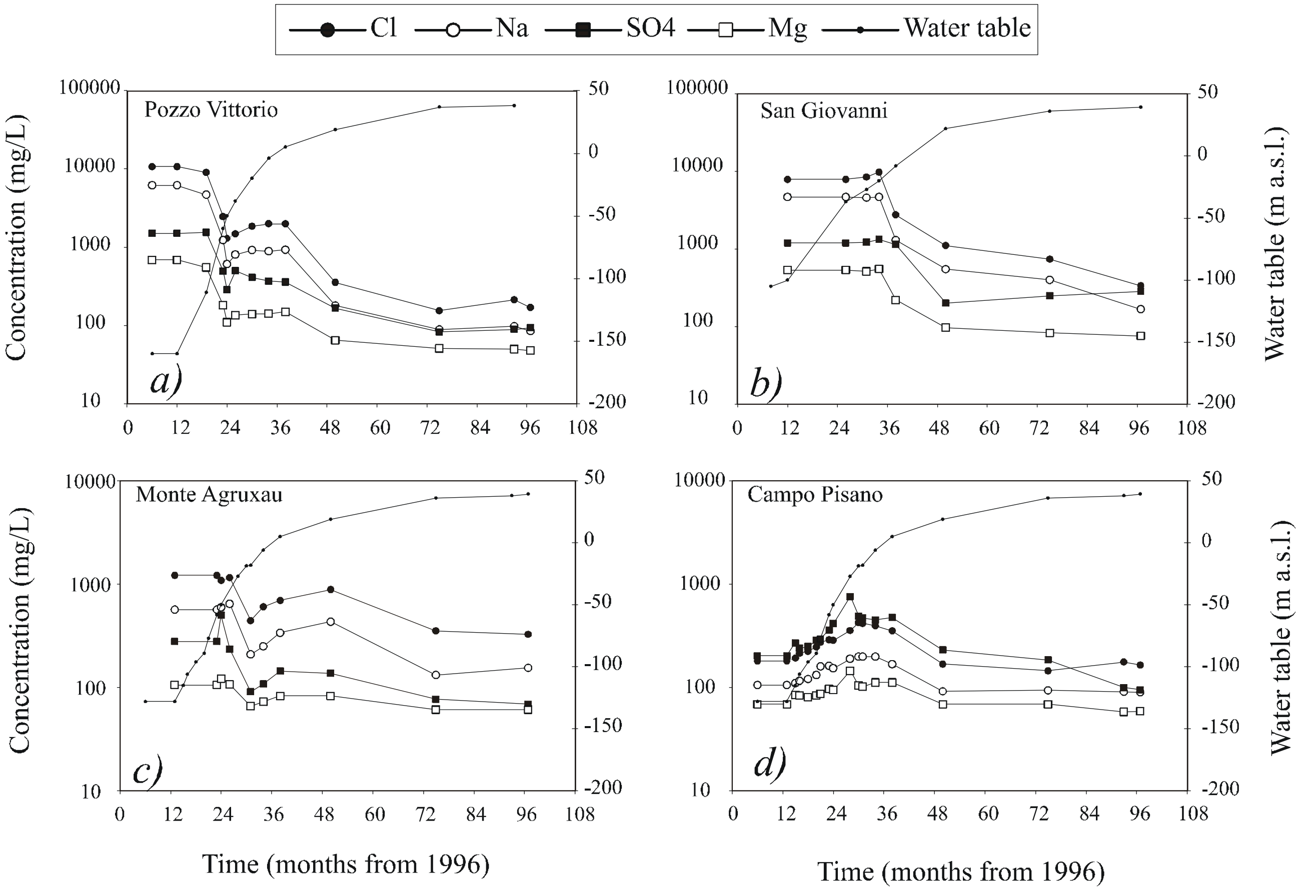

Figure 5. Concentrations of Na, Mg, Cl, and SO_4 in waters from the Pozzo Vittorio at Monteponi (a), Pozzo Carolina at S Giovanni (b), Pozzo Santa Margherita at Monte Agruxau (c) and Pozzo 2 at Campo Pisano (d) from 1996 to 2004

(up to 55%) as the flooding progressed. In the chloride rich waters ($Cl > 0.1$ M), under dewatered conditions and at the first stage of flooding, the $CdCl^+$ and $CdCl_2^0$ species represent about 80% of the total cadmium, while at Cl concentration < 0.009 M and low TDS conditions, cadmium is mostly present as Cd^{2+}, the $CdCO_3^0$ species being prevalent at $pH > 8$ only. The $HgCl_n^{2-n}$ complexes dominate the speciation of mercury; the $Hg(OH)_2^0$ species is only important at Cl concentration < 0.005 M and $pH > 8$. Indeed, the increase in Hg concentrations at Campo Pisano (Figure 8d) is closely associated with an increase in chloride and the decrease in Hg concentrations at Pozzo Vittorio, S. Giovanni, and Monte Agruxau (Figures 8a-c) is closely associated with a decrease in chloride.

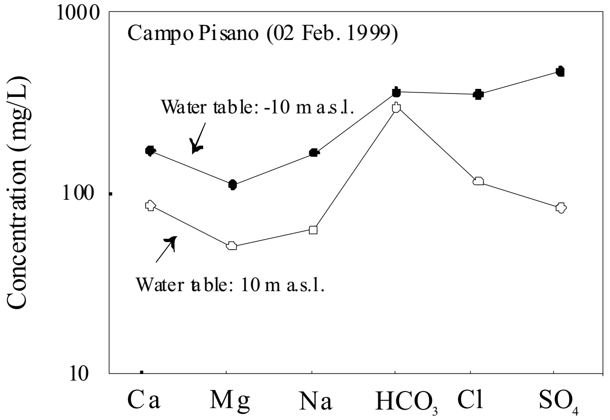

Figure 6. Concentrations of main ions at the water table surface (white circle) and at 20 m below the water table surface (black circle) in the Campo Pisano mine (sampled February 1999)

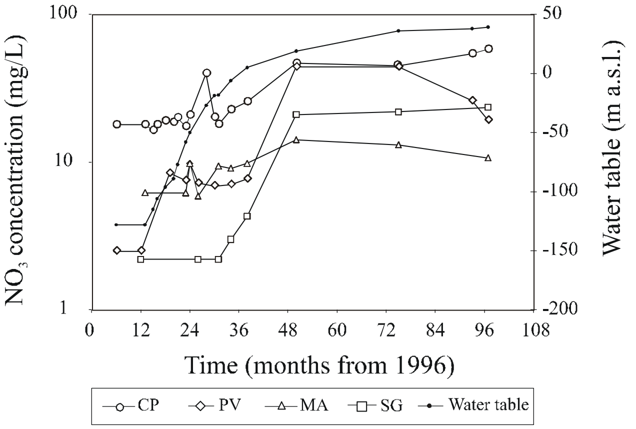

Figure 7. Dissolved nitrate in mine waters, from 1996 to 2004, and variation in the water table level; CP: Campo Pisano, PV: Pozzo Vittorio, MA: Monte Agruxau, SG: San Giovanni

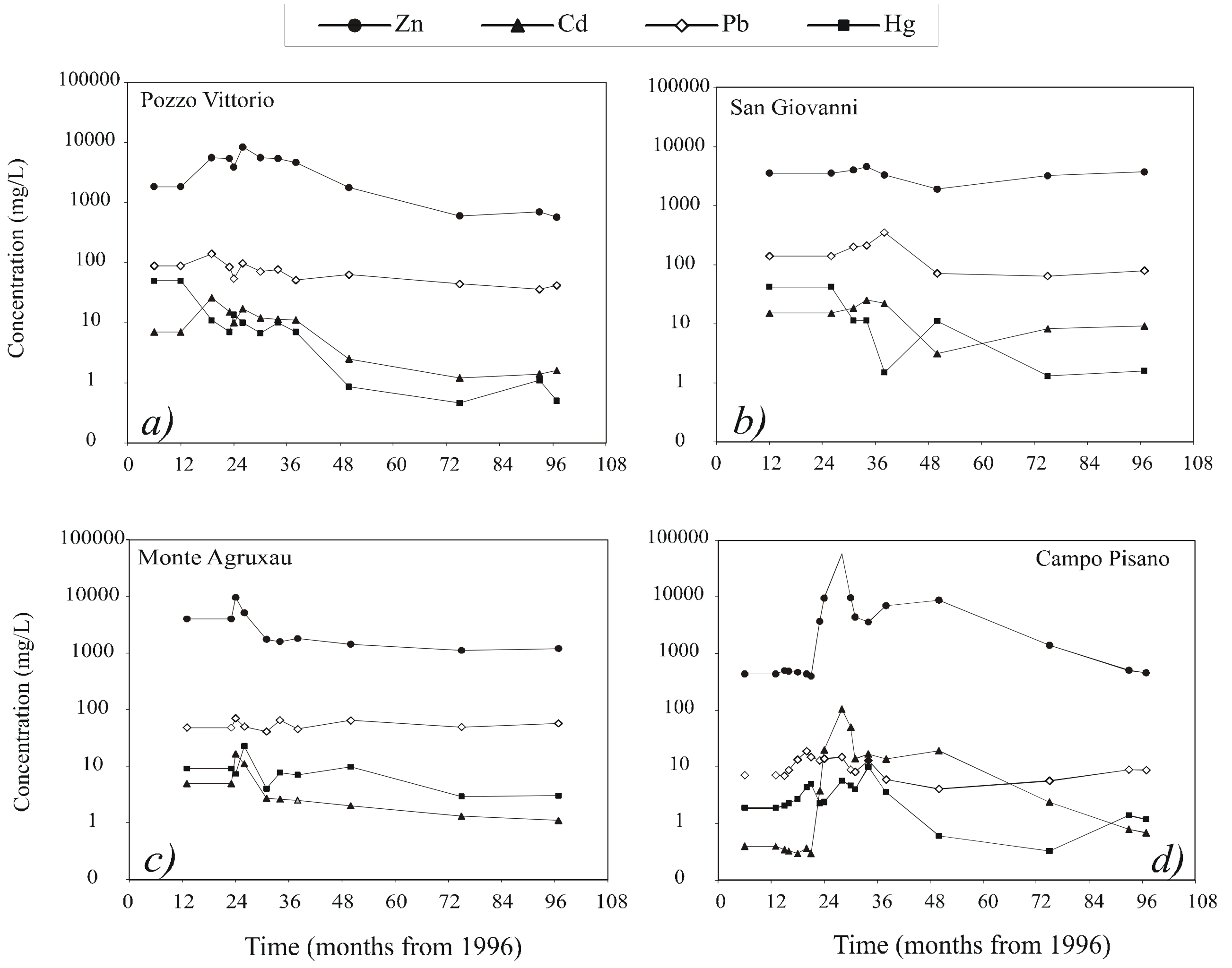

Figure 8. Concentrations of Zn, Cd, Pb and Hg in waters from (a) the Pozzo Vittorio at Monteponi, (b)Pozzo Carolina at S. Giovanni, (c) Pozzo Santa Margherita at Monte Agruxau, and (d) Pozzo 2 at Campo Pisano from 1996 to 2004

Table 4. World Health Organization (WHO) guidelines for drinking water (WHO 1998) and Italian regulations for drinking water, mineral water, and industrial discharges (1-4)

	WHO	Italy			
		(1)	(2)	(3)	(4)
Cl, mg/L	250	250	-	-	-
F, mg/L	1.5	1.5	5.0	6	1
Na, mg/L	200	200	-	-	-
NO_3, mg/L	50	50	45	-	-
SO_4, mg/L	250	250	-	-	500
Al, µg/L	200	200	-	1000	1000
As, µg/L	10	10	10	500	50
B, µg/L	500	1000	5000	2000	500
Ba, µg/L	700	-	1000	20000	10000
Cd, µg/L	30	5.0	3.0	20	-
Cu, µg/L	2000	1000	1000	100	100
Fe, µg/L	-	200	-	2000	2000
Hg, µg/L	1	1	1	5	-
Mn, µg/L	500	50	500	2000	200
Ni, µg/L	20	20	20	2000	200
Pb, µg/L	10	10	10	200	100
Sb, µg/L	50	5.0	5.0	-	-
U, µg/L	20	-	-	-	-
V, µg/L	-	50	-	-	100
Zn, µg/L	-	-	-	500	500

(1) Italian regulations for drinking water (Decreto Legge 2 Feb 2001 N° 31); (2) Italian regulations for bottled mineral water (Decreto Ministeriale 29 Dec 2003); (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 (Decreto Legge 11 May 1999 N° 152); - Not regulated

During the first stage of flooding, dissolved concentrations in Zn, Cd, and Pb did not markedly vary in the water samples from Pozzo Vittorio, S. Giovanni, and Monte Agruxau (Figures 8a-c). At Campo Pisano, a dramatic increase in Zn and Cd was observed as the water table rose to 60 m below sea level in 1998 (Figure 8d). This level corresponded with the Campo Pisano well being flooded. This initiated an increase in suspended matter, and higher levels of dissolved Zn, Cd, Fe, and Mn; these metals are thought to be partially associated with the fine material, with particle size < 0.4 µm.

Compared to the first stages of flooding, a significant decrease in Zn, Cd, Pb, and Hg was observed in all mine waters in February 2004 after seven years of rebound. Relatively high levels of Pb (10-100 µg/L) and Hg (1 to 3 µg/L) are still present.

Influence of Tailings and Mine Wastes on the Aquatic System

The cessation of mining left large quantities of tailings and mine waste dumps. These materials release high amounts of sulphate and metals to the aquatic system. This process seems to occur during a short (a few days) period of water-sediment interaction, as indicated by water sample No. 60, which is from a pond that forms in the flotation tailings at Campo Pisano soon after rainy periods. This water shows low salinity (TDS 0.4 g/L), but elevated sulphate and relatively high Zn, Cd, and Pb.

Among the residues of mining, it must be noted that the Red Muds tailings derive from electrolytic processing to recover zinc. They are very fine grained and contain high amounts of iron oxides (45% Fe_2O_3) and metals such as 8.8% Zn, 1.1% Pb, and 0.04% Cd (Buosi et al. 2001). The Red Muds have recently been qualified as an industrial archaeology site subject to regulation for their preservation. Seeps from the Red Muds show extremely high concentrations of sulphate, Mg, Zn, Cd, and Pb. Their concentrations are much higher than limits established by Italian regulations for industrial discharges into the aquatic system (see Table 4). The pH is near neutral. Dissolved components in February 2004 have values similar to those observed in 1999 (see Table 2), and their impact can be observed by comparing samples 50A and 50B. The 50A water was collected at the first outflow of the heap, and 50B about 20 m downstream, at the base of the heap. A marked increase in TDS, SO_4, Mg, Zn, Cd, Pb, and other metals can be observed in the 50B water. At the 50B sampling site, a whitish, soft and unconsolidated mud occurs. Mineralogical, chemical, and microscopic studies of this solid phase are in progress. According to preliminary X-Ray diffraction (XRD), the precipitate is mainly composed of zinc sulphate, and subordinately of manganese oxide. The XRD spectra also showed significant background noise, likely due to the presence of organic matter. Some toxic or harmful elements, such as Pb (up to 100 mg/kg), Cd (up to 30 mg/kg), Ni (up to 20 mg/kg), Cu (up to 80 mg/kg), and Co (up to 10 mg/kg) appear to be associated (adsorbed and/or co-precipitated) with the solid phase.

The Rio San Giorgio is the main stream that drains the Iglesias mining district. Sample No. 51 was collected after input from the Red Muds seeps. Although the flow rates of tailings drainage are usually very low (≤ 0.1 L/s), the contribution to the concentrations of SO_4, Zn, Cd, and Pb is very high (see Table 2). A small decrease in dissolved chemical components is observed in sample No. 52, collected about 3 km downstream of sample No. 51.

Conclusions

This study shows that salinisation occurred in shallow mine waters due to the rise of deep saline water, and consequent mixing. At Campo Pisano, the peak in salinity was observed in October 1998. Salinity decreased after three years of rebound when stratification caused the saline water to settle at depth.

Increasing concentrations of Zn, Cd, and Pb were observed as flooding progressed. This increase was due to the interaction of water with the ore minerals and with the mine waste accumulated in the pits during the long period of exploitation. The amount and composition of mine wastes present in the flooded galleries of the Iglesiente district is unknown, and therefore the time required for flushing can hardly be estimated. However, the carbonate environment should favour the attenuation of heavy metals in the flooded mines.

About 40 mines have operated in the Iglesias district. This makes it difficult to distinguish waters circulating in mining areas from waters not affected by past mining. Nevertheless, the dissolved Zn, Cd, Pb, and Hg observed in waters sampled outside of the mined areas probably approximate the pre-mining background conditions. In 2004, after seven years of rebound, a significant decrease in dissolved Zn, Cd, Pb, and Hg has been observed in all mine waters, and the concentrations of these metals are approaching the values observed in water sampled outside of the mined area.

At present, the weathering of electrolytic and flotation tailings and waste dumps represents the most significant hazard to the aquatic system in the Iglesiente district.

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