PERGAMON

Applied Geochemistry 16 (2001) 489–502

Applied Geochemistry

www.elsevier.com/locate/apgeochem

Mine closure at Monteponi (Italy): effect of the cessation of dewatering on the quality of shallow groundwater

R. Cidu *, C. Biagini, L. Fanfani, G. La Ruffa [1], I. Marras

Dipartimento Scienze della Terra, via Trentino 51, I-09127 Cagliari, Italy

Received 12 March 2000; accepted 11 April 2000

Editorial handling by W.H. Edmunds

Abstract

At the Monteponi Pb–Zn mine located in south-western Sardinia intensive dewatering has been carried out over about 100 a. A marked increase in the salinity and Hg concentration of deep groundwater occurred as the water table level was lowered from +15 to −160 m a.s.l. over this period. Closure of the mine implied the cessation of the expensive pumping system, and prompted the assessment of the contamination risk for the shallow groundwater system supplying Iglesias town. This study shows that deep water was mixed into the shallow aquifer as the water table level rose. An increase of salinity, mainly due to Na and Cl^-, has been observed in shallow groundwater. The input of Cl^- facilitates the dissolution of Hg. Moreover, the progressive mine flooding is causing an increase of other dissolved metals, mainly due to the weathering of primary sulphides and secondary minerals present in the ore, and remobilization of metals in the mine waste left in the galleries. A stratification process will allow the saline water at depth to settle, and this is expected to occur in a relatively short time (few years). The leaching of metals represents a greater concern for the quality of shallow groundwater, and the time necessary to clean up will be much longer (probably several decades) than that expected for the stratification of the water body. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The final stages of mining exploitation plans typically involve the closure of the mine, implementation of reclamation and environmental requirements associated with the cessation of mining operations, and the liability associated with mine wastes that extend beyond the life of a given project. Within this context, the potential impact of mining works and their cessation on the quality of water resources is a primary concern in local communities. In many mining regions, even in some arid environments, pits may intercept groundwater, and require pumping during exploitation. When mining has ceased, these pits will fill nearly to the historical groundwater level, but the water quality will deteriorate. The chemistry of mine waters has been studied by several authors (e.g. Alpers et al., 1992; Nordstrom et al., 1992; Banks et al., 1997), most of the attention being devoted to acid mine waters, since these usually carry huge amounts of metals, and cause impressive visual impacts (Bowen et al., 1994). However, methods for assessing pit water quality, how it affects the surrounding groundwater, and how long adverse effects will persist are presently not adequate (Miller, 1997).

In Europe, most mines have been closed for economic reasons during the past decades. In the Iglesias district (Sardinia, Italy) the closure of metal mines implied the cessation of the expensive pumping system located at the Monteponi mine. The rise of deep saline waters, consequent to the planned mine flooding, prompted the assessment of the contamination risk for shallow groundwater. Water demand in the area exceeds water reserves, and restrictions on the water supply are frequent, especially during the summer. Therefore, mine

---

* Corresponding author. Tel.: +39-70-67-57-724; fax: +39-70-282-236.

E-mail address: cidur@unica.it (R. Cidu).

[1] Present address: IIRG–CNR, via Alfieri 1, I-56017 San Giuliano, Italy.

0883-2927/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0883-2927(00)00046-9

waters are regarded as an important potential resource. In fact, shallow groundwater from the Campo Pisano mine has been used after mixing with better quality water to supply Iglesias town over recent years. A project for monitoring the water level and some chemical parameters has been carried out by the company (former Miniere Iglesiente S.p.A.) managing the mines. Watering operations at Monteponi started in January 1997, and continued by gradual decrease in flow rate until pumping stopped in July 1997. The objectives of the present study were to investigate the geochemical properties of the mine waters and related ground waters to monitor the water quality prior to and during the mine flooding, and to assess the contamination risk for shallow groundwater.

2. Historical records and hydrology

The Iglesias district is located in south-western Sardinia. The study area extends about 20 km from the Mediterranean sea inland, with maximum elevation of 807 m a.s.l. (Fig. 1). Southern Sardinia has a semi-arid climate, characterised by rainfall in the range of 400–900 mm/a, with a mean of 50 rainy days, and long periods of dry weather. At the Monteponi meteorological station, the long-term mean rainfall is 800 mm/a, mean annual temperature 17°C, evapotranspiration 57%, and runoff 24% (Civita et al., 1983).

The Iglesias district has been an important mining area for centuries. Lead–Zn ores hosted in lower Cambrian limestone-dolomite (the Gonnesa Group; Pillola et al., 1998 and references therein) have been exploited by some 40 mines spread out over about 150 km^2, an area known as the "Metalliferous Ring". Massive sulphide ore bodies and stratabound deposits show variable metal contents from area to area, and mineral assemblages mainly consist of sphalerite, galena and pyrite (the latter containing up to 1000 ppm As and small chalcopyrite inclusions), and more rarely barite (Boni, 1994).

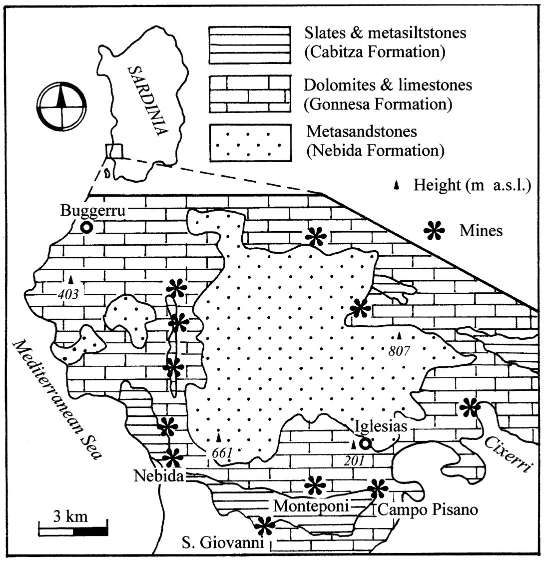

Fig. 1. Schematic geology, and location of the most important Pb–Zn mines in the "Metalliferous Ring" (Iglesiente district, Sardinia).

The Cambrian carbonate formations host important aquifers due to intense fracturing and karstification. The occurrence of large quantities of water underground severely hindered exploitation, and strenuous efforts were made to keep the pits dry. Since 1910 the main drainage system has been located at the Monteponi mine and the water discharged into the sea (at about 6 km distance), through the Umberto I drain (Fig. 2). Pumping stations at increasing depths were successively installed to lower the water table down to 160 m below sea level: in 1928 at −15 m; in 1936 at −60 m; in 1956 at −100 m; in 1990 at −200 m a.s.l. (Bonato et al., 1992; Bellé and Cherchi., 1996). At Monteponi 2.5×10^9 m^3 of water were pumped out from 1890 to 1990 (Bonato et al., 1992). In the period from 1990 to 1996 the mean flow rate was 1800 l/s.

With the increasing quantity of water to be pumped out of mines as exploitation reached lower depths, the effects on the water table extended to a large area westward and southward of Monteponi, and the quality of groundwater drained underwent a marked deterioration, mainly due to the rise in Na and Cl$^-$. Over about 90 a the Cl$^-$ concentration reached 12 g/l (Fig. 3), and Hg rose to 60 μg/l as the water table level fell to 160 m below sea level (Amat et al., 1996; Bellé et al., 1996; Cidu and Fanfani, 1998). Among heavy metals, the presence of Hg is not surprising since this, like Ag, has been at times recovered in addition to the main Pb and Zn products. During the 1906–1918 period, 3522 kg of Hg were produced from the galena processed at Monteponi (Rolandi, 1972).

Hydrological studies in the Iglesiente district showed that the average effective infiltration over the "Metalliferous Ring" was much less (about 50%) than the volume (about 1300 l/s at that time) pumped out of the −100 m level at Monteponi (Civita et al., 1983). The aquifer in the "Metalliferous Ring" is considered to be confined between impermeable beds (Bellé et al., 1996). In particular, the connection with the adjacent Cixerri aquifer, located eastwards of Iglesias (Fig. 1), seems unlikely, since pumping at Monteponi did not influence the water table level in the Cixerri (Bellé et al., 1996). However, the potential infiltration from the Cixerri aquifer has been considered, and estimated at 270 l/s (Amat et al., 1996). This quantity would correspond to 15% of the volume (1800 l/s at that time) pumped out of the −200 m level at Monteponi, not enough to explain the volume deficit between infiltration and pumping.

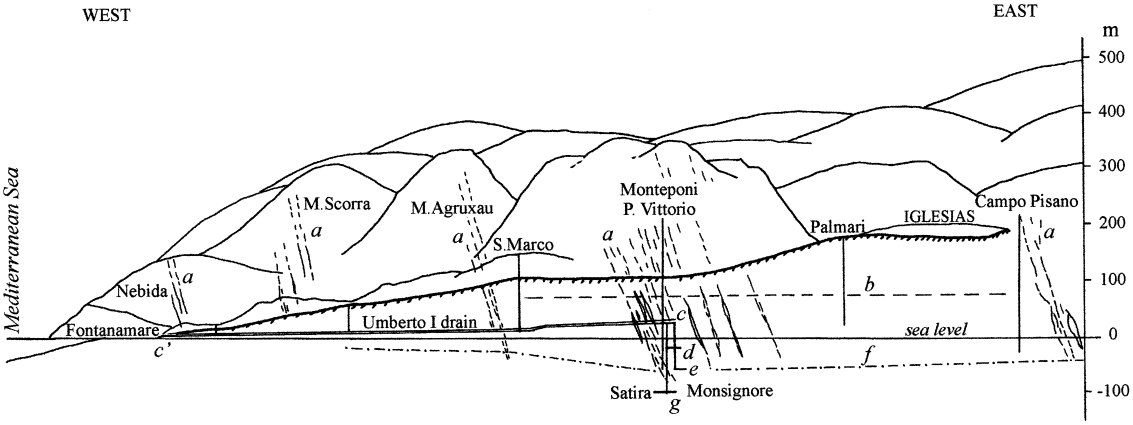

Fig. 2. Schematic view of the mining area close to Iglesias with a W–E profile crossing Monteponi, location of the main shafts, and dewatering system (Società di Monteponi, 1951, modified). (a): Pb–Zn ore; (b) water table level in 1870; (c) Umberto I drain system extending 6 km from Monteponi to the sea; (d) pumping station at-15 m a.s.l.; (e) pumping station at −60 m a.s.l.; (f) water table level in 1950; (g) pumping station at −100 m a.s.l.

Therefore, a deep source of water at Monteponi must be taken into account. The results of structural, remote-sensing, hydrological, and isotopic studies support the hypothesis of contamination of the water system by seawater which infiltrates in deep fractures far from the coast, and rises up due to the intensive pumping at Monteponi (Civita et al., 1983; Bellé et al., 1996).

3. Sampling and methodology

The first sampling was carried out prior to cessation of dewatering operations in July 1996. On the basis of previous records samples from Campo Pisano (No. 3) and San Marco (No. 5) mines are supposed to represent aquifers essentially fed by rainfall, and, therefore, represent the shallow groundwater. Satira (No. 8), and Monsignore (No. 6), both located in the Monteponi mine at −100 m a.s.l. (Fig. 2), and the water pumped out of the S. Giovanni mine (Fig. 1), derive water from aquifers largely fed by deep sources. The water from the Umberto I drain (No. 1), collected at Fontanamare (Fig. 2), is the bulk water pumped off from the Monteponi mine to the sea.

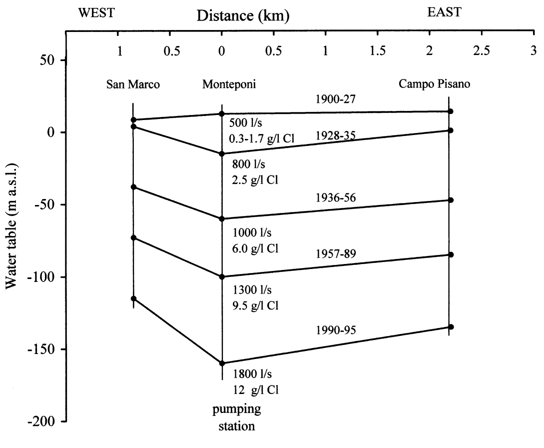

Fig. 3. Lowering of the water table level induced by pumping at Monteponi during the 1900–1995 period. Increasing flow rates at Monteponi over this period and corresponding Cl^- concentrations are shown (data from the former Miniere Iglesiente S.p.A.).

Sampling continued during 1997 and 1998 following the progress of mine flooding, but due to the closure of most mines few sampling sites were accessible. In June 1997 the water table reached a level of −100 m a.s.l. causing flooding of the Satira and Monsignore wells. Afterwards sampling continued at the Pozzo Vittorio well (No. 12), a shaft located in between Satira and Monsignore, and accessible from outside (Fig. 2). A similar situation occurred at the San Marco well, and here sampling continued taking the water directly at the flooding of the San Marco gallery (No. 11). Following the progress of flooding water, samples were also collected at the Campo Pisano gallery (No. 13), Palmari gallery (No. 15), and Monte Agruxau mine (No. 14) (Fig. 2).

Those waters showing relevant stratification due to the high salinity were sampled at about 15 m below the water table level. At the sampling site, temperature, pH, redox potential, conductivity and alkalinity were measured, waters were filtered (0.4 μm, Nuclepore 111130), and acidified for metal analyses. The redox potential (Eh) measured by a Pt electrode was corrected against Zobell's solution (Nordstrom, 1977). Anions were determined by HPLC (DIONEX)®.

Table 1
Chemical composition of waters from Monteponi and surroundings during the 1996–1998 monitoring period

No.	Name	Date	Flow l/s	T °C	Eh mV	pH	Cond mS/cm	TDS[a] g/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	Alk[b] mg/l	SO_4 mg/l	Br mg/l	B µg/l	Li µg/l	Rb µg/l	Sr µg/l	Ba µg/l	Mn µg/l	Zn µg/l	Cd µg/l	Pb µg/l	Ag µg/l	Hg µg/l
Deep mine waters																											
1a[c]	Monteponi	04/06/96	1800	23	440	7.5	32.30	20.2	530	690	6200	225	10700	330	1500	38.1	1750	90	55	3900	63	7	1840	7	88	46	50
1a	Monteponi	11/03/97	1400	21	430	7.6	33.80	21.9	550	720	6070	239	12200	310	1660	40.6	1900	95	60	4400	63	14	1960	7	130	46	38
1a	Monteponi	30/04/97	850	22	410	7.6	35.40	23.1	560	760	6700	252	12900	320	1720	42.5	2080	44	70	4800	62	64	3200	20	210	42	25
1a	Monteponi	05/06/97	100	21	470	8.0	30.00	20.2	480	660	5600	226	11400	340	1600	38.1	1900	96	63	3900	48	128	2400	15	100	23	19
1a	Monteponi	17/06/97	800	23	430	7.4	33.50	20.9	510	690	5900	224	11900	330	1580	41.7	2080	95	64	4000	50	70	4450	22	190	46	29
1a	Monteponi	06/08/97	100	26	440	8.3	32.80	21.3	522	680	6200	220	11800	300	1690	46.0	2080	93	65	3900	50	77	2150	17	60	18	16
1a	Monteponi	11/09/97	100	24	440	8.0	23.50	20.0	480	650	5700	223	11100	300	1700	40.9	2100	91	70	4000	53	72	3900	20	80	32	13
1a	Monteponi	21/11/97	100	19	540	8.0	4.90	2.8	210	119	600	23	1200	310	480	4.9	210	18	14	620	48	126	5000	14	33	1.6	2.2
1a	Monteponi	18/12/97	50	17	400	7.7	4.70	2.7	180	122	610	29	940	290	710	4.3	310	25	13	780	49	420	2250	10	13	0.7	1.1
1a	Monteponi	27/02/98	100	19	410	7.7	22.60	12.4	450	430	3600	137	6450	310	1170	27.6	1000	60	40	2760	39	175	3200	15	92	17	16
1a	Monteponi	17/06/98	100	21	520	7.8	23.00	14.2	500	470	4120	149	7640	310	1170	28.8	1230	77	50	3220	45	143	4100	22	210	12	7
1a	Monteponi	16/10/98	80	18	450	8.0	7.20	4.6	300	200	1010	43	1820	320	1050	5.4	660	31	18	940	26	990	3170	17	100	7.5	10
6b[d]	Monsignore	04/06/96		23	470	7.3	7.10	4.7	480	220	900	47	1480	190	1490	6.7	240	38	15	710	20	210	7400	29	1000	0.1	42
6b	Monsignore	11/03/97		21	410	7.0	32.50	20.4	700	660	5400	220	11100	370	2200	38.6	1790	95	59	3900	38	390	14300	113	2000	12	59
6b	Monsignore	30 /04/97		18	480	7.1	16.70	11.3	800	460	2420	90	4700	320	2620	16.4	570	50	27	1700	21	1470	36000	220	1300	3.9	69
8b	Satira	04/06/96		23	560	7.0	7.00	4.4	340	230	850	33	1630	390	1010	6.2	290	35	11	700	19	200	3900	9	165	7.0	100
8b	Satira	11/03/97		20	450	7.0	11.80	7.0	290	230	1870	66	3780	380	530	13.1	410	35	16	1230	37	13	2000	9	78	26	72
8b	Satira	30/04/97		20	500	7.1	13.20	7.8	300	260	2130	68	4240	380	590	14.5	440	34	18	1400	42	23	1860	9	180	29	28
12b	Pozzo Vittorio	06/08/97		19	470	7.1	27.10	17.2	490	550	4700	170	9500	340	1550	36.2	1650	93	56	3200	80	310	5600	26	140	28	10
12b	Pozzo Vittorio	11/09/97		18	440	7.1	3.70	2.1	190	91	400	16	800	310	450	0.8	129	10	6.8	310	46	300	11400	40	97	2.4	5
12b	Pozzo Vittorio	21/11/97		17	190	7.2	8.60	4.8	230	180	1230	46	2460	350	500	9.9	340	37	21	1120	92	320	5440	15	85	4.1	7
12b	Pozzo Vittorio	18/12/97		22	420	7.2	4.90	2.8	180	110	610	17	1300	350	290	6.3	140	15	10	560	140	100	3900	10	54	7.7	14
12b	Pozzo Vittorio	27/02/98		19	410	7.2	6.20	3.4	260	136	810	25	1480	330	500	5.7	130	14	9.4	520	59	72	8400	17	97	5.3	10
12b	Pozzo Vittorio	17/06/98		17	470	7.3	6.50	3.8	270	140	920	26	1860	350	410	6.7	150	16	9.5	560	52	37	5600	12	71	5.3	7
12b	Pozzo Vittorio	23/10/98		15	500	7.2	6.50	3.9	240	142	890	22	2000	340	370	6.6	140	11	8.4	500	51	38	5600	11	88	5.5	10
16b	S. Giovanni	27/02/98		17	350	7.1	26.30	15.2	540	540	4700	160	7900	310	1200	33.8	1300	70	48	3270	44	42	3550	15	140	24	42
16b	S. Giovanni	03/07/98		18	370	7.2	18.70	11.5	530	510	4600	163	8500	300	1230	27.0	1210	72	50	3270	46	63	4000	18	200	20	11
16b	S. Giovanni	23/10/98		17	400	7.2	27.20	17.3	540	550	4700	167	9800	300	1400	37.0	1370	86	52	3210	43	167	4780	27	200	18	11
Shallow mine waters																											
3b	Campo pisano	04/06/96	180	20	450	6.8	1.55	0.88	105	69	106	5.3	180	430	203	0.7	60	6	2.4	170	39	5	440	0.4	7	0.1	1.9
3b	Campo pisano	11/03/97	180	18	470	7.2	1.64	0.98	112	85	100	5.8	190	420	270	0.7	60	7	2.6	190	40	2	500	0.2	7	0.5	2.1
3b	Campo pisano	30/04/97	180	21	430	7.3	1.69	0.99	110	84	116	5.4	210	430	240	0.8	56	6	2.4	180	37	4	490	0.3	9	0.3	2.3
3b	Campo pisano	17/06/97	180	21	430	7.3	1.71	1.01	116	81	121	5.6	220	420	250	0.8	59	5	2.6	180	37	6	470	0.3	14	1.1	2.7
3b	Campo pisano	06/08/97	180	21	440	7.3	1.77	1.24	120	84	132	5.4	250	430	290	0.9	66	2	2.5	180	35	3	440	0.4	19	0.8	4.4
3b	Campo pisano	11/09/97	60	21	460	7.3	1.94	1.19	126	87	160	6.3	270	440	300	1.1	64	6	2.3	180	22	3	400	0.3	15	1.0	5.0
3b	Campo pisano	21/11/97	60	18	320	7.2	2.13	1.26	135	97	162	6.9	290	380	360	1.2	65	8	6.1	260	30	260	3700	3.8	13	0.6	2.3
3b	Campo pisano	18/12/97	40	25	180	7.1	2.17	1.30	133	95	154	7.7	290	370	420	1.4	70	7	6.0	260	39	290	9500	20	14	0.7	2.4

(*continued overpage*)

Table 1 (*continued*)

No.	Name	Date	Flow l/s	T °C	Eh mV	pH	Cond mS/cm	TDS[a] g/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	Alk[b] mg/l	SO_4 mg/l	Br mg/l	B µg/l	Li µg/l	Rb µg/l	Sr µg/l	Ba µg/l	Mn µg/l	Zn µg/l	Cd µg/l	Pb µg/l	Ag µg/l	Hg µg/l
3b	Campo pisano	08/04/98	40	18	220	6.5	2.50	1.85	170	145	188	9.0	360	260	800	1.5	90	7	8.1	240	36	3180	57400	105	15	0.9	5.7
3b	Campo pisano	17/06/98	40	20	250	7.1	2.48	1.51	160	105	199	6.8	430	340	400	1.5	60	7	4.0	220	34	490	9650	50	9	1.2	4.7
3b	Campo pisano	03/07/98	40	20	440	7.2	2.34	1.49	160	102	199	6.8	420	390	410	1.6	59	6	3.6	230	37	140	4400	14	8	1.6	4.0
3b	Campo pisano	16/10/98	30	17	500	7.2	2.47	1.52	160	112	199	6.7	400	390	410	1.6	52	7	3.6	220	31	83	3600	17	11	1.8	10
13d[e]	Campo pisano	21/11/97		19	490	7.2	1.95	1.18	130	83	150	8.9	280	370	310	1.3	57	7	7.8	250	37	17	750	2.1	18	0.6	2.1
13d	Campo pisano	18/12/97		22	370	7.3	1.64	0.97	112	67	122	6.9	233	300	270	1.0	65	5	7.5	200	70	18	450	1.4	39	0.2	1.9
13d	Campo pisano	27/02/98		19	400	7.3	1.63	0.89	107	64	121	6.8	230	280	217	0.9	50	4	5.9	170	52	5	300	0.5	15	0.4	3.1
13d	Campo pisano	17/06/98		16	460	7.4	0.88	0.51	82	43	48	7.0	80	280	110	0.5	20	2	15	93	65	20	92	0.2	17	0.1	0.3
13d	Campo pisano	16/10/98		15	460	7.4	0.86	0.55	77	46	56	3.2	99	330	69	0.4	23	3	5.7	79	87	7	155	0.3	23	0.1	0.3
15d	Palmari	18/12/97		19	350	7.2	1.22	0.65	91	49	80	8.5	130	370	99	0.6	220	4	8.6	130	73	47	400	1.4	38	0.1	0.3
15d	Palmari	27/02/98		17	390	7.1	4.90	2.58	190	116	630	21.6	1170	330	280	4.4	200	12	14	400	160	200	2800	7.8	470	0.3	3.4
15d	Palmari	17/06/98		16	470	7.3	4.47	2.37	170	105	580	23.0	1090	280	250	4.2	310	11	12	380	62	98	1900	4.3	32	1.2	1.2
15d	Palmari	16/10/98		15	450	8.2	1.03	0.58	43	49	84	9.8	121	290	55	0.6	510	3	10	60	78	26	115	0.5	130	< 0.1	1.3
21e[f]	Palmari	17/06/98	0.1	16	440	8.2	1.24	0.78	101	54	102	9.9	133	490	49	0.6	610	3	2.2	117	92	2	150	0.4	42	0.3	10
21e	Palmari	16/10/98	0.2	15	440	8.2	1.14	0.75	96	53	88	9.1	128	470	40	0.5	570	2	2.3	117	97	1	170	0.65	28	0.4	12
5b[d]	San Marco	04/06/96		21	470	7.3	1.45	0.79	87	53	122	5.9	240	370	82	0.9	20	5	2.1	140	71	12	820	2.5	30	0.1	1.0
5b	San Marco	11/03/97		19	460	7.2	1.88	1.02	98	62	180	7.8	390	330	131	1.3	60	7	2.8	180	58	9	750	1.5	50	1.6	10
5b	San Marco	30/04/97		19	440	7.3	2.03	1.10	98	63	190	7.7	400	350	158	1.4	59	6	3.4	180	60	15	1250	2.3	100	0.8	6.6
11d[e]	San Marco	06/08/97		19	480	7.1	2.07	1.21	140	72	190	10.8	360	420	230	1.3	73	6	3.8	190	73	170	12000	49	27	1.2	2.3
11d	San Marco	11/09/97		19	490	7.1	2.40	1.41	150	75	210	13.0	410	390	300	1.6	70	9	7.2	210	58	180	6700	23	24	0.1	0.5
14b[d]	M. Agruxau	21/11/97		18	460	7.3	4.58	2.56	180	106	570	18.0	1220	360	280	5.0	120	12	9.6	470	89	68	4000	4.9	48	3.4	9.1
14b	M. Agruxau	18/12/97		22	420	7.2	4.73	2.73	220	122	600	20.7	1090	350	500	4.8	150	14	13	560	100	220	9600	17	70	3.2	7.3
14b	M. Agruxau	27/02/98		19	420	7.2	4.48	2.53	170	107	640	23.1	1160	350	240	4.6	120	10	6.8	440	64	29	5140	11	50	9.7	23
14b	M. Agruxau	03/07/98		19	470	7.2	2.05	1.02	123	66	210	7.2	450	390	91	1.6	53	5	3.0	160	120	43	1740	2.7	41	1.6	2.7
14b	M. Agruxau	23/10/98		18	520	7.2	2.43	1.40	128	73	250	7.0	600	400	108	2.1	59	2	3.1	170	104	31	1600	2.6	65	1.7	7.7

[a] TDS: total dissolved solids.

[b] Alk: alkalinity reported as HCO_3^-.

[c] Drain.

[d] Well.

[e] Floodings.

[f] Seepage.

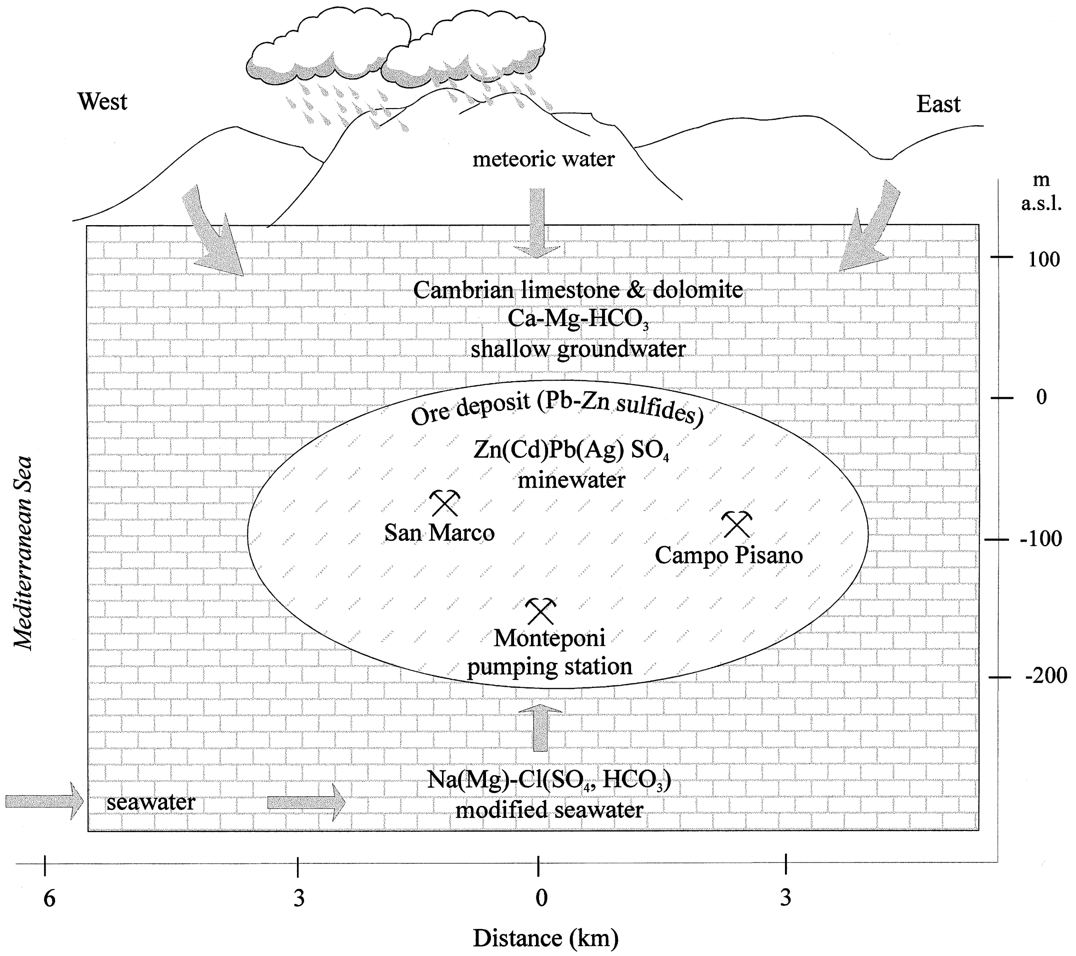

Fig. 4. Scheme of water mixing in the Iglesiente district during exploitation. Meteoric water interacting with carbonate rocks yields Ca–Mg–HCO_3 water; oxidation of sulphide minerals introduces SO_4 and metals into mine water; seawater infiltration, due to intensive pumping at Monteponi, gives rise to saline water.

Metals were determined by atomic absorption spectroscopy (GFAAS, PE ZEEMAN-3030®), inductively coupled plasma optical emission spectroscopy (ICP-OES, ARL-3520®) and inductively coupled plasma mass spectrometry (ICP–MS, ELAN-5000®); while Hg, As and Sb were determined by ICP–MS after flow injection Hg-vapour or hydride generation (Cidu, 1998). The detection limit for chemical components was calculated at 5 times the standard deviation of blank solutions. The accuracy was evaluated using standard reference materials (NIST 1643c,d, and NRC CASS-3). Both precision and accuracy were estimated at ±8 and ±17%, or better, at the mg/l and μg/l concentrations respectively.

The $^{18}O/^{16}O$ and D/H ratios were determined by mass spectrometry at the International Institute of Geothermal Research (IIRG, Pisa), and results are expressed in delta-notation and referred to the V-SMOW standard. Precision has been estimated at ±0.2‰ and ±1.3‰ for $\delta^{18}O$ and δD, respectively.

In this paper, the terms "dissolved" and "in solution" refer to components present in the fraction below 0.4 μm. Speciation and equilibrium calculations were carried out using the WATEQP (Appelo, 1988) computer program. The ionic balance calculated by WATEQP was always less than±1%. The saturation index (SI) with respect to a mineral phase is defined as $\log(IAP/K)$, where IAP is the ionic activity product and K the thermodynamic constant of equilibrium for a given temperature.

4. Results and discussion

Selected data for the most representative samples considered in this study are given in Table 1. The pH is near-neutral or slightly alkaline, as expected in a carbonate environment. The redox potential shows oxidising to transitional conditions, indicating an oxygenated environment and a relatively fast water circulation. The temperature of the deep groundwater at Monteponi is slightly influenced by seasonal variations.

With regard to chemical components not reported in the table, the amount of SiO_2 was in the range of 9–15 mg/l, and the Al concentration during monitoring was nearly constant at about 20 µg/l in most samples. Although the mineral deposits in the Iglesias district are dominated by Pb and Zn ores, other elements present as minor components (e.g. Ag, Cd, Hg) or impurities and considered important in the evaluation of water quality have been determined. The concentrations of Cu, Ni, and Co were in the range of 1–30, 1–10, and 0.2–2 µg/l, respectively, while As and Sb were usually close to or slightly above the detection limit of 0.3 µg/l. Occasional higher concentrations of Ni (70 µg/l), Co (30 µg/l), Sb (16 µg/l), and As (5 µg/l) have been observed in waters still turbid after the 0.4 µm filtration. Those waters with high suspended matter also showed high concentrations of Mn and Zn (e.g. sample No. 3 on 08/04/98, Table 1), and Fe up to 30 mg/l, probably present as <0.4 µm colloidal particles.

4.1. Geochemical features during exploitation

A scheme of the water circulation under dewatering conditions in the Iglesias district is shown in Fig. 4. This scheme shows that the "Metalliferous Ring" receives water contributions differing in quality. A relatively small quantity derives from rainfall (about 800 mm/a) and shows low salinity (<1 g/l) waters, and Ca–Mg–HCO_3 as the main chemical composition. Waters showing these characteristics have been observed in springs flowing out of the Cambrian carbonate formations in neighbouring areas to the east and north of Iglesias, which were not affected by the pumping system at Monteponi (Bertorino et al., 1981). The shallow mine waters roughly preserve these characteristics: Campo Pisano (No. 3) and San Marco (No. 5) waters show low total dissolved solids (TDS <1 g/l), Ca–Mg–HCO_3 composition, with Ca/Mg molar ratios close to 1 due to interaction with dolomite formations (Fig. 5a). Equilibrium with respect to calcite and dolomite is also attained in the less saline samples. However, in addition to the interaction of rain water with the carbonate rocks leading to the main chemical characteristics mentioned above, the interaction of water with the ore deposits brings sulphate and metals, mainly Zn and Pb (Fig. 5b), into solution, through oxidation of sulphide minerals, and remobilization of metals present in secondary minerals.

The waters pumped off from the deepest levels at Monteponi (No. 1) and San Giovanni (No. 16) mines show high salinity (>15 g/l), a dominant sodium chloride composition, and Ca/Mg molar ratios $<<1$ (Fig. 5a) indicating sources other than rainfall. Previous studies have already demonstrated the contamination of the water system by seawater due to the intensive pumping at Monteponi (Civita et al., 1983).

4.2. Mixing processes

Mixing of shallow groundwater with the deep saline water (e.g. sample Nos 6, 8, 12) is marked by increasing TDS, decreasing Ca/Mg molar ratios, Na–Cl dominant character, and higher concentrations of B, Li, Rb and Sr. The Na/Cl and Br/Cl molar ratios are close to values observed in seawater; and Cl, Na, K, Br, B, Li, Rb and Sr show high correlation coefficients with each other supporting an origin from a diluted, modified seawater.

The isotopic data reported in Table 2 show values ranging from −6.47 to −2.02 and −39.4 to −10.8‰ for ^{18}O and ^{2}H, respectively. The enrichment in heavy isotopes is coupled with an increase in Cl^- from 0.13 to

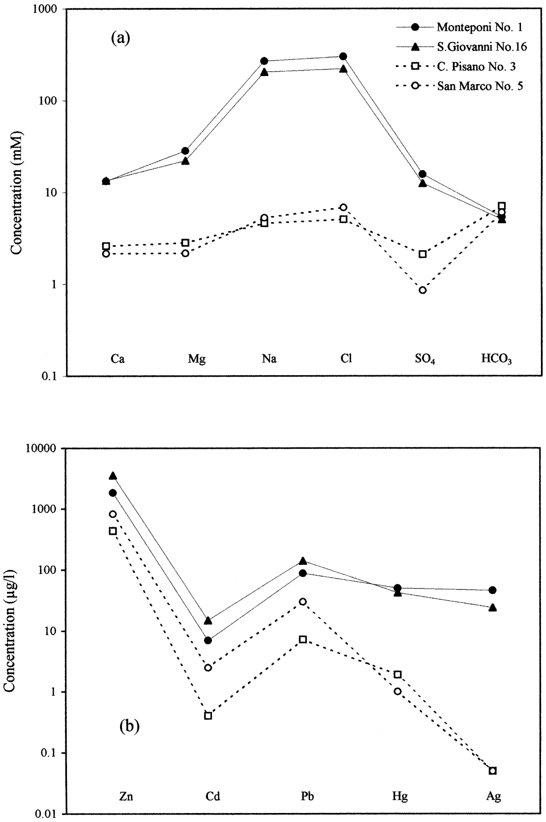

Fig. 5. Main chemical composition (a) and concentration of trace metals (b) in mine waters under dewatering conditions (sampling on July 1996).

12.9 g/l and suggests that addition of marine water to the local groundwater may account for the variations observed. In Fig. 6 the correlation between local groundwater of meteoric origin and seawater are shown separately for H and O stable isotopes (a) and for Cl and ^{18}O contents (b). In Fig. 6 (a) it may be seen that all the water samples deviate in different proportions from the local meteoric water line (Caboi et al., 1993), and lie on a mixing line.

Considering that the two end-members of the mixing process are represented by seawater (SW), with an isotopic composition of 0.6 and 4.0‰ for ^{18}O and ^{2}H respectively, and a Cl content of 20 g/l, and by a freshwater (FW) of meteoric origin, with $\delta^{18}O = -6.3‰$, $\delta D = -38.0‰$ and Cl = 0.13 g/l, the definition of the different mixtures (Mix) can be obtained by the application of the mass balance equations:

Table 2
Values of Cl, δD, and $\delta^{18}O$ during the March 1997 to February 1998 monitoring period

Name	No.	Date	Cl g/l	δD‰ vs. V-SMOW	δ¹⁸O‰ vs. V-SMOW
Monteponi	1(a)	11.03.97	12.2	−12.2	−2.23
Monteponi	1(a)	30.04.97	12.9	−12.3	−2.02
Monteponi	1(a)	05.06.97	11.4	−11.8	−2.03
Monteponi	1(a)	17.06.97	11.9	−10.8	−2.23
Monteponi	1(a)	06.08.97	11.8	−11.1	−2.11
Monteponi	1(a)	11.09.97	11.1	−12.5	−2.40
Monteponi	1(a)	21.11.97	1.2	−36.0	−5.99
Monteponi	1(a)	18.12.97	0.94	−31.9	−5.13
Monteponi	1(a)	27.02.98	6.5	−19.0	−5.53
Monsignore	6(b)	11.03.97	11.1	−13.2	−2.66
Monsignore	6(b)	30.04.97	4.7	−25.0	−4.41
Satira	8(b)	11.03.97	3.8	−30.7	−5.28
Satira	8(b)	30.04.97	4.2	−29.5	−5.19
PozzoVittorio	12(b)	06.08.97	9.5	−16.3	−3.02
PozzoVittorio	12(b)	11.09.97	0.8	−36.6	−6.23
PozzoVittorio	12(b)	18.12.97	1.3	−36.3	−6.21
PozzoVittorio	12(b)	21.11.97	2.5	−36.3	−6.11
PozzoVittorio	12(b)	27.02.98	1.5	−33.5	−6.00
S.Giovanni	16(b)	27.02.98	7.9	−17.1	−3.27
Campo Pisano	3(b)	11.03.97	0.19	−36.8	−6.22
Campo Pisano	3(b)	30.04.97	0.21	−37.2	−6.23
Campo Pisano	3(b)	17.06.97	0.22	−37.6	−6.15
Campo Pisano	3(b)	06.08.97	0.25	−37.3	−6.18
Campo Pisano	3(b)	11.09.97	0.27	−36.2	−6.16
Campo Pisano	3(b)	21.11.97	0.29	−38.3	−6.29
Campo Pisano	3(b)	18.12.97	0.29	−37.9	−6.17
Campo Pisano	3(b)	08.04.98	0.36	−34.8	−6.18
Campo Pisano	13(d)	21.11.97	0.28	−37.1	−6.12
Campo Pisano	13(d)	18.12.97	0.23	−37.3	−6.02
Campo Pisano	13(d)	27.02.98	0.23	−34.5	−6.04
San Marco	4(b)	30.04.97	0.3	−37.2	−6.43
San Marco	4(b)	11.09.97	0.48	−37.3	−6.36
San Marco	5(b)	11.03.97	0.39	−38.1	−6.40
San Marco	5(b)	30.04.97	0.40	−39.4	−6.47
San Marco	11(d)	06.08.97	0.36	−37.3	−6.23
San Marco	11(d)	11.09.97	0.41	−36.6	−6.24
Palmari	15(d)	18.12.97	0.13	−37.9	−6.32
M. Agruxau	14(b)	21.11.97	1.2	−36.9	−6.32
M. Agruxau	14(b)	18.12.97	1.1	−36.4	−6.38
M. Agruxau	14(b)	27.02.98	1.2	−34.4	−6.31

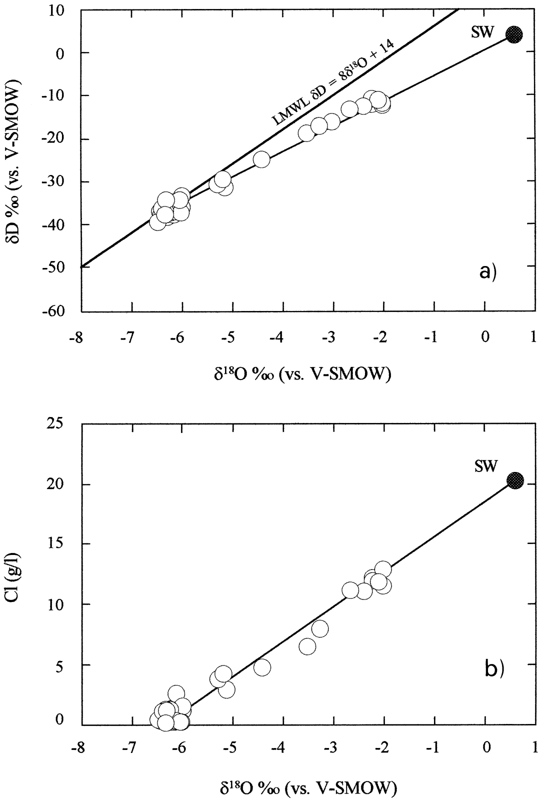

Fig. 6. Plot of δD‰ versus $\delta^{18}O$‰ (a), and C^- concentration versus $\delta^{18}O$‰ (b), indicating a mixing process between local groundwater and seawater (SW). LMWL: local meteoric water line (Caboi et al., 1993).

Table 3
Evaluation of the marine component (%) in waters from Monteponi using the mass balance Eqs. (1)–(3)

	Cl (g/l)	δ¹⁸O ‰	δD ‰
No. 1 (30.04.97)	12.9	−2.02	−12.3
	64%	62%	61%
No. 1 (27.02.98)	7.64	−3.53	−19.0
	38%	40%	45%
No.6 (30.04.97)	4.7	−4.41	−25.0
	23%	27%	31%
No. 8 (11.03.97)	3.78	−5.28	−30.7
	18%	15%	17%
SW[a]	20	0.6	4.0
FW[b]	0.13	−6.3	−38.0

[a] SW: seawater.

[b] FW: freshwater.

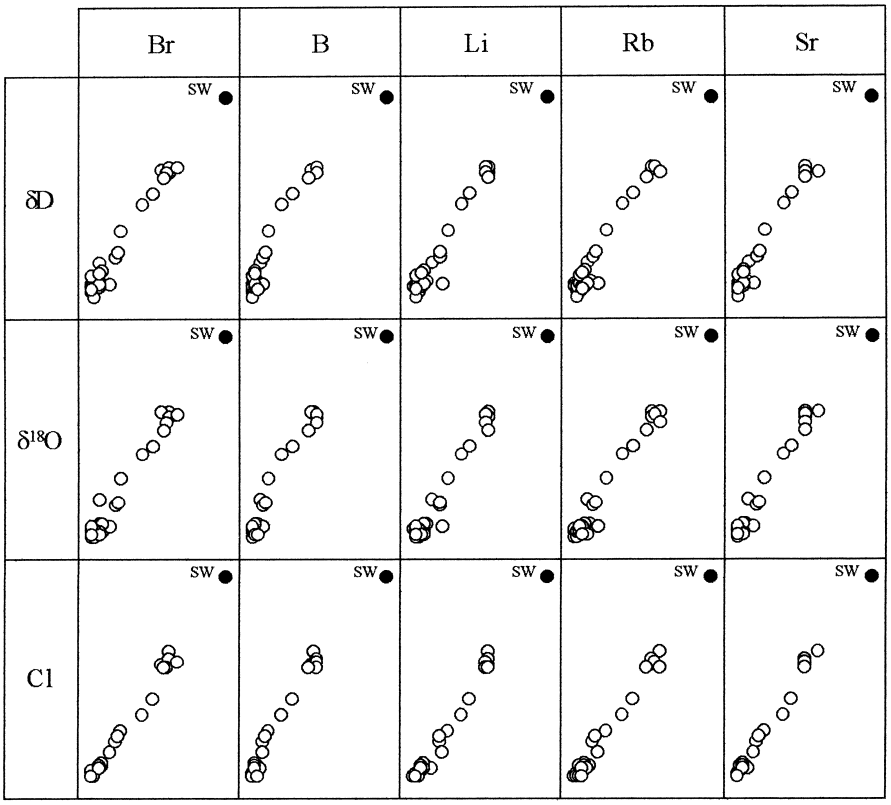

Fig. 7. Scatterplot matrix of correlation showing a mixing process between local groundwater and seawater (SW).

$$x\delta^{18}O_{SW} + (1 - x)\,\delta^{18}O_{FW} = \delta^{18}O_{Mix} \quad (1)$$

$$x\delta D_{SW} + (1 - x)\,\delta D_{FW} = \delta D_{Mix} \quad (2)$$

$$xCl_{SW} + (1 - x)\,Cl_{FW} = Cl_{Mix} \quad (3)$$

Table 3 summarises some results obtained applying Eqs. (1)–(3) to some waters from Monteponi assuming hypothetical mixtures of seawater and the local freshwater (such as the shallow groundwater at Palmari, No. 15 sampled on 18/12/97, derived from infiltration of surface water only, and showing the same isotopic composition of the FW). The values obtained using the 3 different parameters are in good agreement, both for samples with high and low seawater contributions. The observed discrepancies may be overcome by taking into account the variability of the FW composition.

From the application of the previous mass balance equations, it emerges that the mine waters are involved in mixing processes with seawater contributions ranging from 1 to 64%. In particular, the water samples from the Umberto I drain (No. 1), arising from the deepest

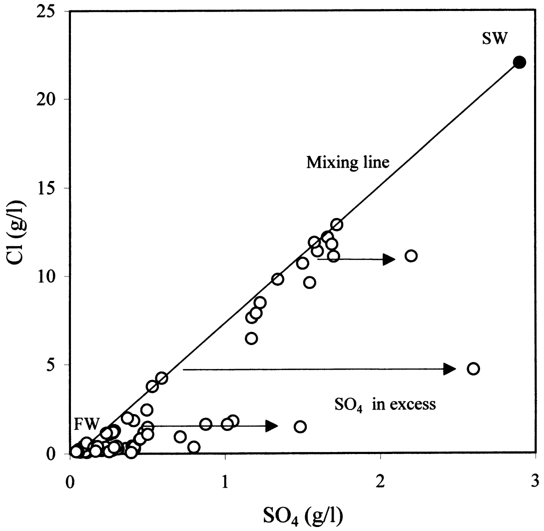

Fig. 8. Chloride versus SO_4 concentration showing a mixing process between freshwater (FW) and seawater (SW) and the SO_4 in excess derived from the weathering of sulphide minerals.

levels of the Monteponi mine, show the highest enrichments in heavy isotopes and Cl^- concentrations, denoting the maximum contribution of water of marine origin. On the other hand, water samples from Campo Pisano and San Marco display the lowest departures from the local meteoric water line. Very similar conclusions may be derived from the inspection of Fig. 6(b), where the Cl^- concentrations are considered. Furthermore, the occurrence of mixing processes seems to be confirmed by the positive correlation existing between different parameters such as the following components: D, ^{18}O, Cl, Br, B, Li, Rb and Sr, as reported in the scatterplot matrix of Fig. 7. Each column and row is scaled exactly as it is in the plot so that the points fill each frame, and for each scatterplot the end-members are represented by the seawater (SW) and the local groundwater (FW).

When the variations in SO_4 in the water samples are taken into account, the interactions between seawater and freshwater appear to be more complex than a simple two-members mixing mechanism. Indeed, SO_4 concentrations in many samples are higher than expected from a dilution process involving seawater. Fig. 8, where SO_4 is correlated with Cl^- ions, discriminates between waters subjected to a single mixing process and waters which contain an excess of SO_4 ions. The low to moderate salinity waters generally show the higher SO_4 in excess. The additional SO_4 content, with respect to that derived from seawater, is likely to be due to the oxidation of sulphides in the ore deposit or the mineralised waste material released in time at depth, and this may occur either in the shallow groundwater or the deep water. The same process also brings metals such as Zn, Cd, Pb, Ag, and Hg into solution (see Fig. 5b). However, the concentration of Zn, Cd and Pb in those waters is much lower than that usually observed in acid mine drainage derived from the leaching of Pb-Zn ores; in contrast, the

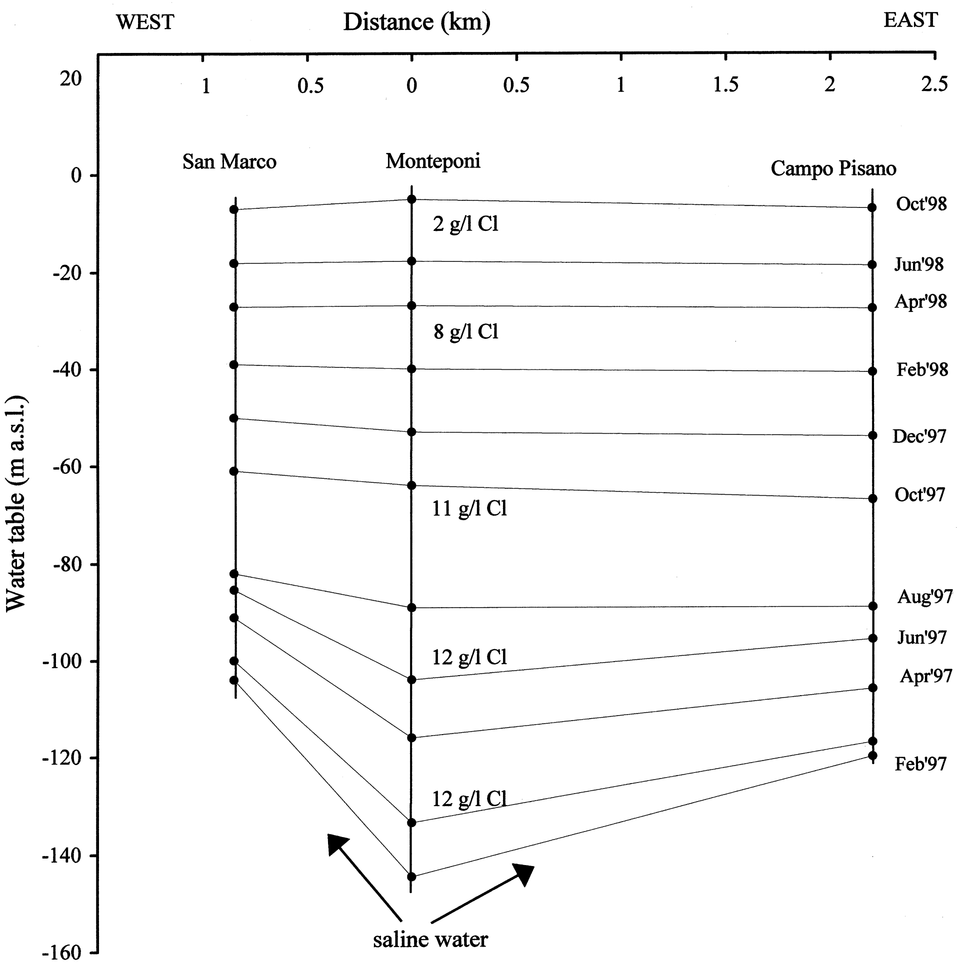

Fig. 9. Water table level during flooding at Monteponi and surroundings (data from the former Miniere Iglesiente S.p.A.).

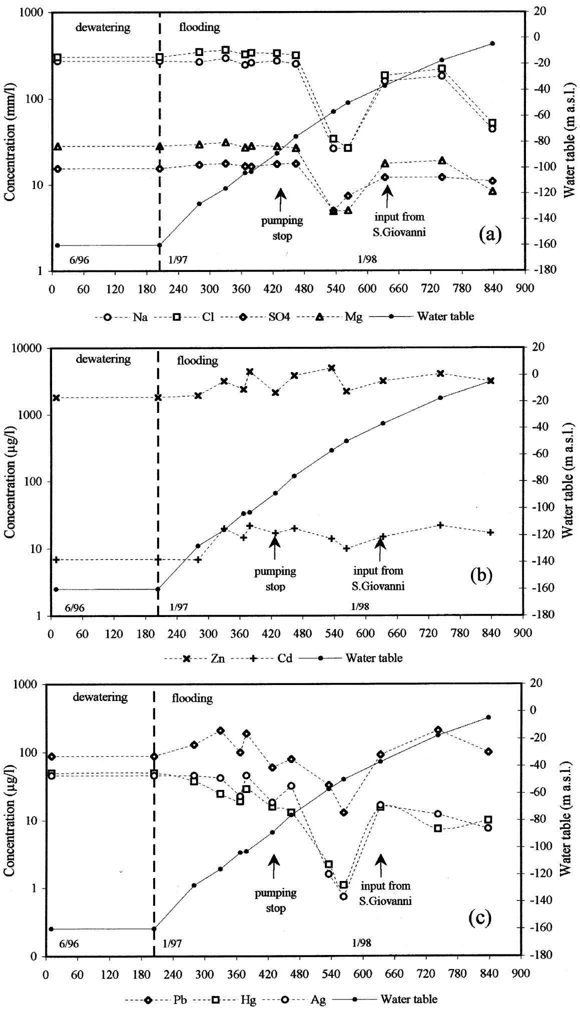

Fig. 10. Concentrations of Na, Mg, Cl and SO_4 (a), Zn and Cd (b), and Pb, Hg and Ag (c) in waters from the Umberto I drain during water table rise at Monteponi. The flow rate of 1800 l/s was gradually decreased starting on January 1997, until pumping stopped on July 1997. Saline waters from S Giovanni were temporary discharged at the drain from February to June 1998.

near-neutral to alkaline environment at Monteponi favours the mobility of Hg in the groundwater (Tunell, 1970).

4.3. Influence of the mine flooding on shallow groundwater

The aim of gradual flooding the Monteponi mine was to avoid mixing of the deep saline water with the fresh shallow water at Campo Pisano whose water, adequately mixed with uncontaminated water, has been supplied to the town of Iglesias. Concerning this objective it can be observed that during the first sampling campaign in 1996 about 1800 l/s were pumped off Monteponi to keep the water table level at 160 m below sea level. Starting in January 1997 the flow rate has been gradually reduced, and pumping finally stopped in July 1997. During a period of 22 months (January 1997–October 1998) the water table level rose about 150 m to reach the −7 m a.s.l., and the cone of depression gradually disappeared (Fig. 9). When the chemical composition of waters during the flooding is compared with that during dewatering (Table 1), a general increase in TDS is observed with the rise of the water table. In particular, during the first 6 months of flooding the input of deep water was more significant at sampling sites located at depth in the Monteponi mine (Monsignore No. 6, Satira No. 8), than at the peripheral sites of Campo Pisano (No. 3) and San Marco (No. 5).

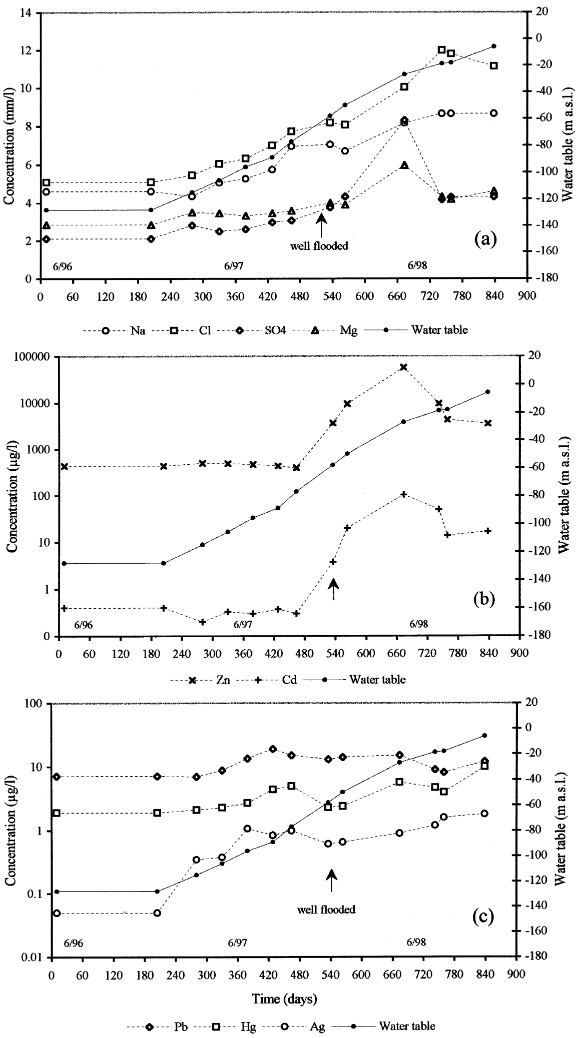

Fig. 11. Concentration of Na, Mg, Cl and SO_4 (a), Zn and Cd (b), and Pb, Hg and Ag (c) during water table rise at Campo Pisano.

The progress of flooding implied significant modifications at most sites, however, the Umberto I drain (Monteponi No. 1) and the water pumped out of the

Campo Pisano mine (No. 3) can be considered as representative of the deep and shallow groundwater, respectively. Since these samples were always accessible during flooding, a good set of data is available to follow the chemical evolution of the aquifer as the water table rises.

The main chemical composition at the Umberto I drain (Fig. 10a) changes little with time until the deep waters from Monteponi are discharged. A marked decrease of Cl, Na, Mg and SO$_4$ has been observed only when shallow mine waters arrived at the drain after pumping was stopped, while a rapid increase has again been observed when the deep water from the San Giovanni mine was temporarily discharged into the drain. The concentrations of Br, B, Sr, Li, and Rb show a behaviour similar to that of Cl and Na (see Table 1), while the amount of Ba in solution is controlled by the equilibrium with respect to barite (all the studied waters show the saturation index of barite in the range of 0.1–0.5). The concentrations of Zn and Cd (Fig. 10b) do not follow those of the main components since these metals are present either in the deep or the shallow mine waters. In contrast, Pb, Hg and Ag (Fig. 10c) show a behaviour similar to the main components since, as described below, their concentration is partially dependent on the increasing concentration of suitable ligands which influences their solubility.

The main chemical composition at Campo Pisano (Fig. 11a) shows a continuous increase of Cl, Na, Mg and SO$_4$ with the rise in the water table, indicating a mixing process with the deep saline water. An increase of metals has been also observed as the water table rises (Fig. 11b, c). It must be pointed out that when the water table reached a level of 60 m below sea level this corresponded with the Campo Pisano well being flooded, and the water was then pumped directly from the floodwater, instead of at the well. This initiated an increase of the matter in suspension, and a marked increase in Zn and Cd concentrations, as well as Fe and Mn; these metals are thought to be partially associated with the fine material in particles of size <0.4 μm.

The amount of organic matter was not determined in any water sample, but is estimated to be very low in this environment, and unlikely to affect metal speciation. On the basis of speciation computation, trace metals are mostly present in solution as inorganic complexes, the free ion being usually $<15\%$ of the total concentration. The speciation of each metal does not significantly change over 22 months under flooding conditions with respect to that observed under dewatering conditions. In particular, Zn and Pb are preferentially complexed by the CO_3^{2-} ligand (mainly as $PbCO_3^0$ and $ZnCO_3^0$), either at low or high TDS conditions, while the $CdCl^+$ and $CdCl_2^0$ species represent about 80% of total Cd.

It is well known that the presence of humic acids and the transformation of Hg^{2+} to CH_3 Hg enhances the mobility of Hg through the environment (Mason et al., 1994; Melamed et al., 1997). The methylation process seems not favoured in coastal environments, due to the high concentration of SO$_4$ which influences various microbial processes (Kannan and Falandysz, 1998). However, organic species of Hg have been sought in the waters from Monteponi, San Giovanni and Campo Pisano by Amat et al. (1996), but Hg-organic species were not detected, and therefore inorganic species should be dominant. As expected from the stability constants of complexes (Turner et al., 1981), Hg speciation is dominated by Hg-Cl complexes. The $HgCl_2^0$ species prevails at a Cl concentration <0.1 M, $HgCl_4^{-2}$ increases as chloride increases and becomes dominant at $Cl>0.3$ M, while $HgCl_3^-$ is about constant at $Cl>0.1$ M (Fig. 12a). The $Hg(OH)_2^0$ species is only important at Cl concentration <0.005 M and pH >8; such conditions are sometimes observed in mine seepage (e.g. sample No. 21, Table 1). The distribution of the Hg-species is independent of the total concentration of Hg in the range of values observed in the studied waters. The Hg–Cl complexes are very stable, allowing Hg transport over several kilometres distance to the sea, and persist in the tap water supplied to Iglesias after the water treatment used for domestic use. The behaviour of Ag is

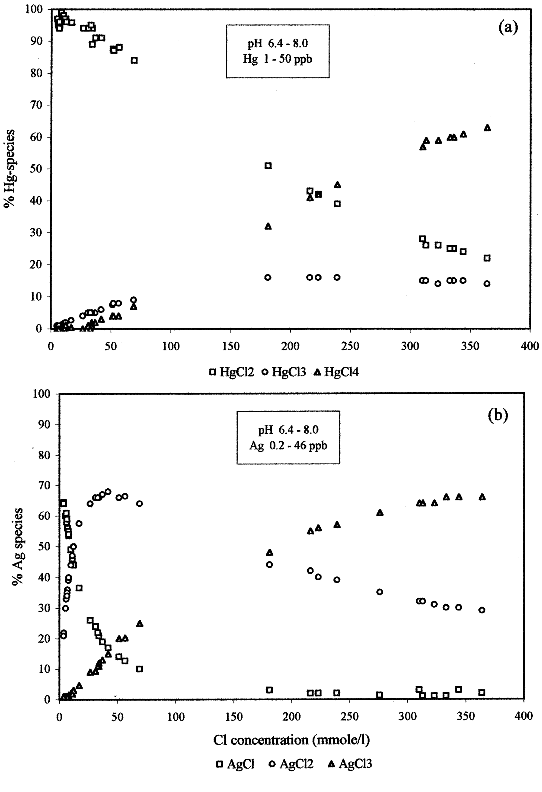

Fig. 12. Distribution of Hg (a) and Ag (b) species in the studied waters.

similar to that of Hg; in fact the increasing Cl concentration allows more Cl-ions to be incorporated in the complex: at Cl < 0.1 M the $AgCl^0$ and $AgCl_2^-$ complexes prevail, while at increasing Cl^- the $AgCl_3^{2-}$ complex is dominant (Fig. 12b).

5. Conclusions

This study shows that the mine closure at Monteponi implies a contamination risk for the groundwater system used for public supplies in the area. In fact it is observed that a salinisation process is occurring in the shallow mine waters due to the rise of the deep saline water and the consequent mixing. At Campo Pisano (No. 3) the TDS by October 1998 was 1.5 g/l, with an increase of 73% with respect to the value observed in June 1996 under dewatering conditions, and sampling sites at San Marco show similar behaviour. The salinisation will decrease and be negligible only after a stratification process occurs, and stabilisation should be expected in a relatively short time (probably a few years). The long periods of dry weather during 1997 and 1998 allowed little infiltration of freshwater into the aquifer, and up to the last sampling date in October 1998 did not favour the anticipated dilution and stratification processes.

The increasing concentration of metals with the progress of flooding is due to the interaction of water with the ore deposit, together with mine waste accumulated in the pits during the long period of exploitation, and represents the most important, and long-term hazard for groundwater quality. In particular, the concentration of Hg in the studied waters is linked to the availability of leachable Hg, and to conditions which favour its aqueous transport, such as Cl^- addition by forming Hg–Cl complexes. The decreasing flow rate in water circulation at depth with the reduction and successive cessation of pumping can explain the decrease of Hg content at sampling sites in the Monteponi and San Giovanni mines, while the input of Cl-rich waters can explain the enrichment of Hg with salinity at Campo Pisano and San Marco. In low salinity, shallow groundwater, Hg dissolution is favoured at alkaline pH by forming Hg-OH complexes.

It is well known that goldmining activity results in severe direct Hg contamination of aquatic ecosystems and harmful effects on humans (Porcella et al., 1997), especially at the local scale (Roulet et al., 1999), but the risk of Hg pollution in mining areas other than Au mines needs to be assessed. This study shows that abandoned mines close to coastal areas must be considered as a great concern, especially when Hg is present as a minor component in the ore. Moreover, ongoing studies in an abandoned mining area in Tuscany (Caboi et al., 1998) also reported Hg contamination in shallow groundwater interacting with Hg deposits hosted in carbonate rocks, located close to the coast, due to the input of seawater induced by seasonal over-pumping.

The amount of mine wastes present in the flooded galleries of the Iglesiente district is considered to be high, but the exact extent is unknown, especially the quantity and composition of materials related to the ancient mine works and processing, and therefore the time required for flushing is difficult to estimate. The temporal evolution of polluted discharges from abandoned mines in the UK has been investigated by Chen et al. (1997) and Younger (1997), and the depletion of metals acquired during the water table rebound is expected over a period of 10–40 a. The different geology, ore composition, and climatic condition in Sardinia, as compared to areas investigated in the UK, does not allow the estimated period to be extrapolated. However, with all probability, the time necessary to clean up will be much longer than that expected to be necessary for the stratification process.

Acknowledgements

This study was partially supported by funds from the Ministero dell'Università e della Ricerca Scientifica & Tecnologica, and the Consiglio Nazionale delle Ricerche. The authors wish to thank the former Miniere Iglesiente S.p.A. for the hydrologic data, and assistance during sampling. The manuscript benefited from the review of W.M. Edmunds and P.L. Younger.

References

Alpers, C.N., Nordstrom, D.K., Burchard, J.M., 1992. Compilation and interpretation of water-quality and discharge data for acidic mine waters at Iron Mountain, Shasta County, California, 1940–1991. USGS Water Resour. Inv. Rep. 91-4160, pp. 173.

Amat, P., Contini, E., Enne, R., Garbarino, C., Sarritzu, R., Tocco, S. et al., 1996. Il ciclo del mercurio nel sistema idraulico carsico associato alle mineralizzazioni piombo-zincifere della sinclinale di Iglesias: proposta di un modello e sue implicazioni. Mem. Associazione Mineraria Sarda, pp. 69–85.

Appelo, C.A.J., 1988. WATEQP — a computer program for equilibrium calculations of water analyses. Institute of Earth Sciences, Free University of Amsterdam.

Banks, D., Younger, P.L., Arnesen, R.T., Iversen, E.R., Banks, S.B., 1997. Mine-water chemistry: the good, the bad and the ugly. Environm. Geol. 32, 157–174.

Bellè, O., Cherchi, F., 1996. Il bacino idrogeologico dell'Anello Metallifero. Mem. Associazione Mineraria Sarda, pp. 51–66.

Bellè, O., Cherchi, F., Salvadori, I., 1996. The aquifer of the Cambrian carbonate basin in the Iglesiente district and the mining industry, mutual effects. In: Proceedings of the 1st Internat. Conference on The Impact of Industry on Groundwater Resources Cernobbio, Como, Italy, 22–24 May 1996, 295–305.

Bertorino, G., Caboi, R., Caredda, A.M., Cidu, R., Fanfani, L., Sitzia, R., Zanzari, A.R., Zuoldas, P., 1981. Le manifestazioni termali del Sulcis (Sardegna sud-occidentale). Periodico Mineralogia 50, 233–255.

Bonato, M., Congiu, M., Fioravanti, E., Lipari, D., 1992. L'impianto di eduzione -200 di Monteponi. Boll. Ass. Min. Subalpina 29, 313–321.

Boni, M., 1994. Ores in southwestern Sardinia. Mem. Descr. Carta Geol. d'Italia XLVIII, 155–184.

Bowen, G., Dussek, C., Hamilton, R.M., 1994. Groundwater pollution resulting from the abandonment of Wheal Jane Mine in Cornwall. In Proceedings of the 3rd Conference on Groundwater Pollution, London, 16–17 March 1994. IBC Technical Services, London.

Caboi, R., Cidu, R., Cristini, A., Fanfani, L., Rundeddu, L., Zuddas, P. et al., 1998. Water quality emergency and territory stresses in a hydrogeochemical study at M.te Argentario. In: Proc. Water in the Mediterranean Area, Chia, Cagliari, pp. WQ-P1.

Caboi, R., Cidu, R., Fanfani, L., Zuddas, P., Zanzari, A.R., 1993. Geochemistry of the high-$P\mathrm{CO}_2$ waters in Logudoro, Sardinia, Italy. Appl. Geochem 8, 153–160.

Chen, M., Soulsby, C., Younger, P.L., 1997. Predicting water quality impacts from future minewater outflows in an urbanized Scottish catchment. In: Chilton, J. (Ed.), Groundwater in the Urban Environment: Probl. Proc. and Manag. Balkema, Rotterdam, pp. 383–388.

Cidu, R., 1998. Determination of inorganic contaminants in water. In: Marini, L., Ottonello, G. (Eds.), Proc. Rome Seminar on Environmental geochemistry. Pacini, Pisa, pp. 162–168.

Cidu, R., Fanfani, L., 1998. Influence of mine watering on groundwater quality at Monteponi, Sardinia, Italy. In: Arehart, G.B., Hulston, J.R. (Eds.), Proc. Water-Rock Interaction 9. Balkema, Rotterdam, pp. 969–972.

Civita, M., Cocozza, T., Forti, P., Perna, G., Turi, B., 1983. Idrogeologia del bacino minerario dell'Iglesiente (Sardegna sud occidentale). Mem. Ist. It. Speleologia, Ser. II 2, 7–137.

Kannan, K., Falandysz, J., 1998. Speciation and concentrations of mercury in certain coastal marine sediments. Water, Air, Soil Poll. 103, 129–136.

Mason, R.P., Fitzgerald, W.F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. Geochim. Cosmochim. Acta 58, 3191–3198.

Melamed, R., Villas Boas, R.C., Goncalves, G.O., Paiva, E.C., 1997. Mechanisms of physico-chemical interaction of mercury with river sediments from a gold mining region in Brazil: relative mobility of mercury species. J. Geochem. Expl. 58, 119–124.

Miller, G.C., 1997. The environmental issues in mining. In: Marcus, J. (Ed.), Mining Environmental Handbook: effects of mining on the environment and American environmental controls on mining. Imperial College Press, London, pp. 725–726.

Nordstrom, D.K., 1977. Thermochemical redox equilibria of ZoBell's solution. Geochim. Cosmochim. Acta 41, 1835–1841.

Nordstrom, D.K., McHutt, R.H., Puigdomenech, I., Smellie, J.A.T., Wolf, M., 1992. Ground water chemistry and geochemical modelling of water-rock interactions at the Osamu Utsumi mine and the Morro do Ferro analogue study sites, Pocos de Caldas, Minas Gerais, Brazil. J. Geochem. Explor. 45, 249–287.

Pillola, G.L., Leone, F., Loi, A., 1998. The Cambrian and Early Ordovician of SW Sardinia. Giornale di Geologia, S.I. 60, 25–38.

Porcella, D.B., Ramel, C., Jernelov, A., 1997. Global mercury pollution and the role of gold mining: an overview. Water Air Soil Poll. 97, 205–217.

Rolandi, G., 1972. La metallurgia in Sardegna. L'Industria Mineraria Ser. II XXIII, 17–22.

Roulet, M., Lucotte, M., Farella, N., Serique, G., Coelho, H., Sousa Passos, C.J. et al., 1999. Effects of recent human colonization on the presence of mercury in Amazonian ecosystems. Water, Air, Soil Poll. 112, 297–313.

Società di Monteponi (Ed.), 1951. Società di Monteponi: centenario 1850–1950. Tipografia Vincenzo Bona, Torino.

Tunell, G., 1970. Solubilities of compounds that control concentrations of mercury in natural waters. In: Wedepohl, K.H. (Ed.), Handbook of Geochemistry. Springer-Verlag, Berlin, pp. 80-H-1-5.

Turner, D.R., Whitfield, M., Dickson, A.G., 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta 45, 855–881.

Younger, P.L., 1997. The longevity of minewater pollution: a basis for decision-making. Sc. Tot. Environm. 194/195, 457–466.